

**Green chemistry: fundamental principles and application for sustainable development: a review**

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ABSTRACT

“Green Chemistry” is the universally accepted term to describe the movement towards more environmentally acceptable chemical processes and products. Green chemistry, as the name implies, is part of the “greening” of corporate practices that has monoliths like Wal-Mart Stores, Inc., touting “earth-friendly” products. Over the course of the past decade, green chemistry has demonstrated how fundamental scientific methodologies can protect human health and the environment in an economically beneficial manner. In the words of Paul Anastas, who introduced the term ‘green chemistry’ in 1991, “It’s more effective, it’s more efficient, it’s more elegant, and it’s simply better chemistry”. Significant progress is being made in several key research areas, such as catalysis, the design of safer chemicals and environmentally benign solvents, and the development of renewable feed stocks. It is an approach to product manufacturing that seeks to reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and application of chemical products. The concept of green chemistry incorporates a new approach to the synthesis, processing and application of chemical substances in such manner as to reduce threats to health and environment. Current and future chemists are being trained to design products and processes with an increased awareness for environmental impact. This article presents applications of green chemistry in everyday life.

Key words: Green Chemistry, Sustainability, Hazardous chemicals, Health

INTRODUCTION:

The term “green chemistry,” also known as clean chemistry or benign and sustainable chemistry, refers to the design of chemicals and formulation of processes that reduce the risk to humans and minimize environment pollution. The goal of green chemistry solutions is to lessen or eliminate hazardous impacts of chemicals over a chemical product’s life-cycle. “Green Chemistry” is the universally accepted term to describe the movement towards more environmentally acceptable chemical processes and products (1). It encompasses education, research, and commercial application across the entire supply chain for chemicals (2). Green Chemistry can be achieved by applying environmentally friendly technologies – some old and some new (3). While Green Chemistry is widely accepted as an essential development in the way that we practice chemistry, and is vital to sustainable development, its application is fragmented and represents only a small fraction of actual chemistry. It is also important to realize that Green Chemistry is not something that is only taken seriously in the developed

countries. Some of the pioneering research in the area in the 1980s was indeed carried out in developed countries including the UK, France, and Japan, but by the time the United States Environmental Protection Agency (US EPA) coined the term “Green Chemistry” in the 1990s, there were good examples of relevant research and some industrial application in many other countries including India and China (4). 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.

The Americans launched the high profile Presidential Green Chemistry Awards in the mid-1990s and effectively disclosed some excellent case studies covering products and processes (5).

In 1996 the working party on green chemistry was created, acting within the framework of International Union of Pure and Applied 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 technologies. The first conference highlighting green chemistry was held in Washington in 1997. Since that time other scientific conferences have been soon held on a regular basis. The first book and journals on the subject of green chemistry were introduced in 1990, including the *Journal of Clean Processes and Green Chemistry*, sponsored by the Royal Society of Chemistry. The concept of green chemistry incorporates a new approach (6-11) to the synthesis, processing and application of chemical substances in such manner as to reduce threats to health and environment.

The 12 Principles of Green Chemistry were proposed by Anastas and Warner(12) and published in 1998, by 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*.

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. 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"(13).

Basic Principles of Green Chemistry:

1. Prevention

It is 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 Synthesis:

Whenever 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 affect their desired function while minimizing toxicity.

5. Safer Solvents and Auxiliary:

The use of auxiliary substances should be made unnecessary wherever possible.

6. Design for Energy Efficiency:

Energy requirements of chemical processes should be recognized for their environmental and at low temperature and pressure.

7. Use of Renewable Feedstocks:

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

8. Reduce Derivatives:

Unnecessary derivatization (use of blocking groups, protection, deprotection) should be avoided whenever possible.

9. Catalysis:

Catalytic reagents (as selective as possible) are superior 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.

Green Chemistry has been promoted worldwide by an increasing but still small number of dedicated individuals and through the activities of some key organizations. These include the Green Chemistry Network (GCN; established in the UK in 1998 and now with about one thousand members worldwide) (14) Green Chemistry Networks or other focal points for national or regional activities exist in other countries including Italy, Japan, Greece and Portugal and new ones appear every year. The GCN was established to help promote and encourage the application of Green Chemistry in all areas where chemistry plays a significant role. (Fig. 1.)

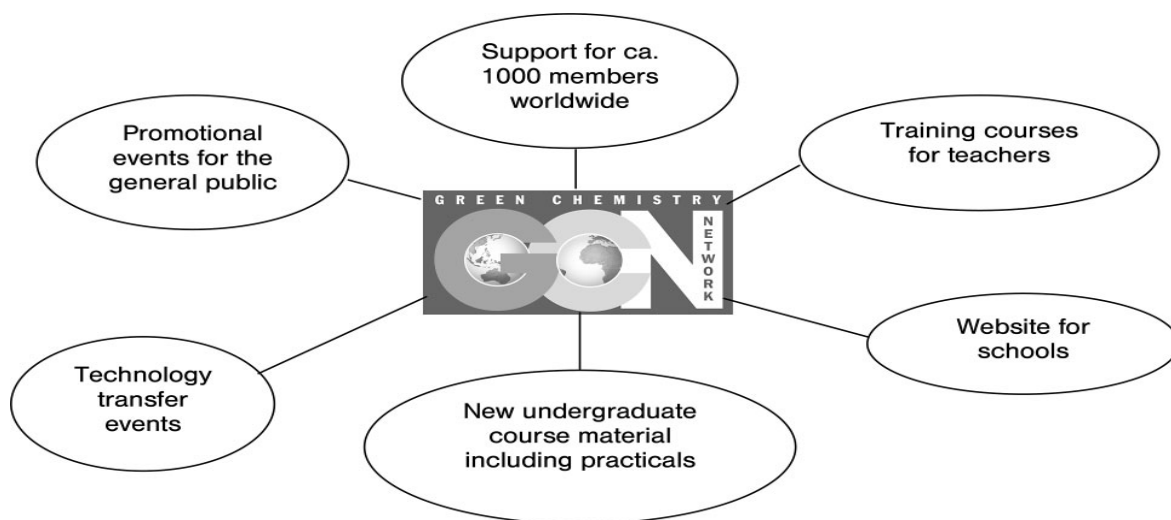


Figure 1: green chemistry plays a significant role.

Applications of Green Chemistry:

1. Green Chemistry in Polymer Chemistry:

In the polymer area, there is also increasing interest in green chemistry. This is evident by many recent symposia organized on this topic at national ACS meetings. In our view, developments in green polymer chemistry can be roughly grouped into the following eight related themes. These eight themes also agree well with most of the themes described in recent articles and books on green chemistry (15-18).

- 1) Greener catalysts (e.g., biocatalysts such as enzymes and whole cells)
- 2) Diverse feedstock base (especially agricultural products and bio based building blocks)
- 3) Degradable polymers and waste minimization
- 4) Recycling of polymer products and catalysts (e.g., biological recycling)
- 5) Energy generation or minimization of use
- 6) Optimal molecular design and activity
- 7) Benign solvents (e.g., water, ionic liquids, or reactions without solvents)
- 8) Improved syntheses and processes (e.g., atom economy, reaction Efficiency, toxicity reduction)

2. Green Chemistry in Nanotechnology (19):

Nanotechnology is an emerging field. It is an interdisciplinary science whose potential has been widely touted for well over a decade. Despite significant private and public investment, progress moving nanomaterials from the laboratory to industrial production has been slow and difficult. Two challenges that have slowed development have been the poor understanding of the new hazards introduced by nanotechnology and lack of

appropriate policies to manage any new risks. Scientists, engineers and entrepreneurs, however, continue to move forward, grappling with challenges that range from the technical to the regulatory and everywhere in between. Just as the concepts of nanoscale invention have required new insights from scientists, they are also demanding new approaches to managing, producing, funding and deploying novel technologies into the larger chemical sector. In this case, there is an unusual opportunity to use science, engineering and policy knowledge to design novel products that are benign as possible to human and environment health. Recognition of this opportunity has led to the development of the “green nanoscience” concept

The project on emerging nanotechnologies at the Wood row Wilson International center for scholars launched a green nano program on Feb 2006. This initiative aims to advance the development of clean technologies of using nanotechnology to minimize potential environmental and human health risk associated with the manufacture and the use of nanotechnology products in general to apply a nano to solve legacy environmental problems and to encourage the replacement of existing products with a new nano products that are more environmentally friendly throughout their life cycle.

3. Green Chemistry in Education (20):

The idea of including Green Chemistry in chemistry education was first put forward in 1994. A complete course was described shortly thereafter (Collins, 1995). Few Green chemistry textbooks have also been published (Ahluwalia and Kidwai, 2003). Graduates, post graduates, teachers and researchers will find these books of immense use. Both Environmental Protection Agency

(EPA) and American Chemical Agency (ACS) have recognized the importance of bringing Green Chemistry to the class room and the laboratory

Several green chemistry activities were designed and incorporated throughout the one year organic chemistry curriculum (both lecture and lab). All activities are based on the twelve principles of green chemistry. Existing

organic reactions at Chandler-Gilbert Community College (CGCC) were replaced with greener alternatives in the form of greener reagents, greener solvents, and greener methodologies. As a result of this endeavor, the generation of hazardous waste has been entirely eliminated. The green lab experiments performed during 2006–2007 academic year are listed in Table 1.

Table 1: Green Laboratory Experiments

Green Reaction	What was green in this Experiment?	Green Chemistry principle utilized
1. Diels-Alder Reaction at 0°C	Low temperature 0° to room temperature	1, 6, 12
Reaction 'on water'	Safer solvent system (water)	1, 5, 12
3. Synthesis of Cyclohexene from Cyclohexanol	Solvent less condition	1, 5, 9, 12
4. Bromination Reactions	Bromine generated in situ; very low temperature conditions	1,3, 6, 10, 12
5. Acetylation of Ferrocene	Solvent less condition; reaction performed under ambient conditions	1, 5, 6, 12
6. Iodination of Vanillin	Natural sources as starting material	1, 7, 12
7. Grignard Synthesis at low temperature	Very mild conditions	1, 6, 12
8. Grignard Reaction in water	Safer solvent conditions	1, 5, 6, 12
9. Green Oxidation	Greener oxidation conditions; water as the solvent; low temperature reactions	1, 5, 6, 8,10,12
10. Combinatorial Synthesis	Single step reaction to produce many products	2, 4, 6, 8

Student involvement in Green Chemistry principles and practices is essential to the integration the environmentally benign technologies in academia and industry. Suggestions for these activities include:

1. Hosting a Green Chemistry speaker
2. Organizing an interdisciplinary Green Chemistry workshop on campus
3. Working with a local company on a Green Chemistry project
4. Developing a Green Chemistry activity with a local school
5. Converting a current laboratory experiment into a greener one
6. Organizing a Green Chemistry poster sessions on campus
7. Distributing a Green Chemistry Newsletter to the local community
8. Designing a green Chemistry web page

4. Green Chemistry in Agriculture (21):

Green chemistry and sustainable agriculture are both revolutionary fields with significant overlap, though the connections are not fully developed nor appreciated. Sustainable agriculture encompasses a wide variety of farming techniques and practitioners. Broadly speaking sustainable agriculture seeks to achieve three goals: farm profitability; community prosperity; and environmental stewardship. The latter includes: protecting and improving soil quality, reducing dependence on non-renewable resources, such as fuel, synthetic fertilizers and pesticides and minimizing adverse impacts on safety,

wildlife, water quality, and other environmental resources.

Green chemistry and sustainable agriculture are inherently intertwined; farmers need green chemists to make safe agricultural chemical inputs. Green chemists need farmers practicing sustainable agriculture to provide truly “green” bio-based raw materials to process into new products.

Biopesticides are a set of tools and applications that will help our farmer’s transition away from highly toxic conventional chemical pesticides into an era of truly sustainable agriculture. Of course biopesticides are only a

part of a larger solution; sustainable agriculture is a broad and deep field. But helping farmers move from their current chemical dependency to organic agriculture and beyond requires tools for the transition and tools for a new era. Biopesticides can and will play a significant role in this process.

5. Green chemistry in engineering:

In fact —Green Engineering is the process and design of products aiming to conserve natural resources leading to sustainability goals. Also, green engineering aims to reduce the impact of processes and products to the natural environment. The term —green engineering is applied to a variety of products, like houses, vehicles, consumer products (materials, electrical and electronic equipment) and devices that requires engineering technologies in the construction or making. Green engineers can now graduate from various university engineering departments in developed industrialized countries. Other engineering graduates can have special training on various fields, attending special classes to understand how materials and other components can be made in an environmentally-friendly way. For example, engineers and architects concerned with home design may learn about the latest building materials and techniques. Green engineering and design is nowadays an important additional qualification for every aspect of engineering.

Green engineering concentrates on how to promote sustainability through science and technology. Green engineers are engaged in designing new materials, products, processes and systems. There are many good examples of electrical machines and electronic products that have end-of-life design features so that can be disassembled into components, recycled, or reused with maintenance and easy repair. Xerox printers are designed so that after their commercial use, can be converted and be remanufactured. Various other big industrial companies have introduced green engineering design features in their products for easy repairs, recyclability or reuse after maintenance ((AT&T, General Electric, IBM, Procter & Gable, Whirlpool, etc).(22-24)

In the last decade there is a major shift in the way industrial manufacturers have changed the design of their products in order to reduce the end-of-life burdens to the environment. The **Product Life Cycle** (PLC) analysis has become a standard method following the various stages of a product's life. From starting materials, manufacture and final disposition the life of a product is analysed quantitatively from its environmental impact and natural resources use. It is represented with a cycle: Design—Manufacturing—Distribution—Customer—End-of-Life.

Many software programmes have been developed recently dealing with PLC. The PLC is associated with engineering tasks, materials and energy, but also can involve marketing activities and new product development. (25-26) **Figure 2**



6. Green Chemistry in Pharmaceutical industry:

Chemistry is an integral part of our pharmaceutical business. Green chemistry is understood to be superior innovative chemistry that is cost effective and has minimal impact on the environment.

Over the past decade, the pharmaceutical industry has been moving toward the application of green chemistry principles, mainly by introducing new production and analytical technologies, using greener solvents and emphasizing enzymatic chemistry.

Green chemistry focuses on making industrial chemistry safer, cleaner and more energy efficient while generating economic benefits. This concept is driven by efficiency combined with environmental responsibility to offer enhanced chemical process economics.

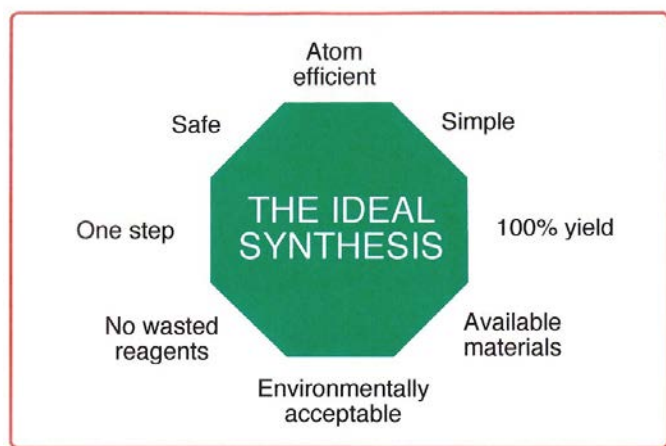
To decrease the environmental footprint and costs associated with the production of dopedogrel hydrogen sulfate (trade name Plavix® or Iscover®), Sanofi set up an ongoing green chemistry project that has led to improved synthetic pathways, increased yields and smaller quantities of solvents in the manufacturing process. These important improvements meet the expectations of both internal and external stakeholders. The discovery of green and sustainable synthesis methodologies is a long-term endeavor. Today, collaborations between academia and pharmaceutical companies provide an opportunity to develop green, safe and more effective processes to deliver medicines for the 21st century.

New Challenges of Green Chemistry:

The challenge for chemists and others is to develop new products, processes and services that achieve the societal, economic and environmental benefits that are now required. This requires a

new approach which sets out to reduce the materials and energy intensity of chemical processes and products, minimize or eliminate the dispersion of harmful chemicals in the environment, maximize the use of renewable resources and extend the durability and recyclability of products—in a way which increases industrial competitiveness. Some of the challenges for chemists include the discovery and development of new synthetic pathways using alternative feedstocks or more selective chemistry, identifying alternative reaction conditions and solvents for improved selectivity and energy minimization and designing less toxic and inherently safer chemicals.

In chemical synthesis, the ideal will be a combination of a number of environmental, health and safety, and economic targets (Fig. 3).



To help illustrate the many challenges ahead and the opportunities for new greener chemistry, two very broadly based generic areas of chemistry can be at least superficially examined in terms of their scope, the environmental unacceptability and poor atom economics of typical processes, and the goals and possible approaches of green chemistry. The emphasis will be on batch type processes involving liquid phase reactions as practiced by fine, specialty chemical and chemical intermediate manufacturers around the world.

Acid catalyzed reactions:

Acid catalysis is the most widely used type of catalysis with applications in all sectors of the chemical, pharmaceutical and allied industries, although the largest scale use is in the petrochemical industries where the processes are largely quite efficient and the use of solid acids is well established.(27)

Traditionally most liquid phase organic reactions have been catalyzed by strong Brønsted acids such as H_2SO_4 and HF and by soluble Lewis acids such as $AlCl_3$ and BF_3 . These acids have many important advantages—they are cheap, readily available and very active. Unfortunately, they also suffer from some serious disadvantages, which are becoming increasingly prominent in these environmentally conscious days—they are difficult to separate from the organic products and their use leads to large volumes of hazardous waste.

Uses of Green Chemistry in daily life

1 Dry Cleaning of Cloths:

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 1999 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(28) has also evolved a metal cleaning system that uses CO_2 and a surfactant thereby eliminating the need of halogenated solvents(29).

2. Versatile Bleaching Agents:

It is common knowledge that paper is manufactured from wood (which contains about 70% polysaccharides and about 30% lignin). 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). By this process about 80-90% of lignin is decomposed. The remaining lignin was so far removed through reaction with chlorine gas (Cl_2). The use of chlorine removes all the lignin (to give good quality white paper) but causes environmental problems. Chlorine also reacts with aromatic rings of the lignin to produce dioxins, such as 2,3,4-tetrachlorodioxin and chlorinated furans. These compounds are potential carcinogens and cause other health problems.

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. 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. A versatile agent has been developed by Terrence Collins of Camegie Mellon University. It involves the use of H_2O_2 as a bleaching agent in the presence of some activators

known as TAML activators¹⁰ that as catalysts which promote the conversion of H₂O₂ into hydroxyl radicals that are involved in oxidation (bleaching). The catalytic of TAML activators allow H₂O₂ 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.(30)

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. The present practice is to use Al-salt to treat such water. 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. Flocculants with slurries were prepared by mixing measured amount of clay and water. 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. 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. The study establishes the powder's potential as an economic flocculants with performance close more established flocculants such as K₂SO₄Al₂(SO₄)₃.24H₂O (potash alum).

CONCLUSION:

"Green chemistry offers many promises, including substantial reductions in the environmental footprint of many chemical processes, improvements in the health and safety of those exposed to chemicals, and enhanced security at facilities with hazardous materials." Green chemistry technologies can contribute to a sustainable economy, relieving the economic pressures on state and local governments, improving the profitability of businesses using safer materials, providing job opportunities, and protecting human health and the environment. Employing the twelve principles of Green Chemistry, biopesticides could provide a new generation of agricultural pest management products that are sustainable both from an environmental and health perspective.

Furthermore, the success of green chemistry depends on the training and education of a new generation of

chemists. Students at all levels have to be introduced to the philosophy and practice of green chemistry. Most importantly we need the relevant scientific, engineering, educational and other communities to work together for sustainable future through Green Chemistry. Great efforts are still undertaken to design an ideal process that start from non-polluting materials.

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