In Their Element: A Deep Dive into Green Chemistry

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Abstract:

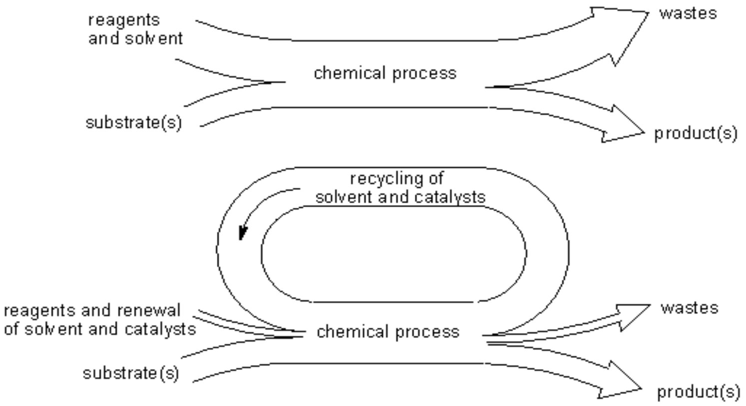
Green Chemistry is a relatively new emerging field that has received widespread interest in the past decade due to its ability to harness chemical innovation to meet environmental and economic goals simultaneously. This project covers the concepts of design and the scientific philosophy of Green Chemistry with some of the finest works done in the field illustrated as examples. Green Chemistry has a framework of a cohesive set of Twelve Principles, which have been systematically surveyed in this review. The timeline of Green Chemistry from its origin to its present state and future trends has also been discussed in this project.

Introduction

Green Chemistry, or Sustainable Chemistry, is the invention, design, and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances.

It is the design, manufacture, and use of environmentally benign chemical products and processes that prevent pollution, minimize or eliminate the use and generation of hazardous waste, and reduce risk to human health and the environment.

The ideology of Green Chemistry calls for the development of new chemical reactivities and reaction conditions that can potentially provide benefits for chemical syntheses in terms of resource efficiency, energy efficiency, product selectivity, operational simplicity, and health and environmental safety.



Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal. It discusses the engineering concept of pollution prevention and zero waste at both laboratory and industrial scales. It encourages the use of economical and eco-compatible techniques that not only improve the yield but also bring down the cost of disposal of wastes at the end of a chemical process.

History of Green Chemistry

In the glorious days of the 1950s and 1960s, chemists envisioned chemistry as the solution to a host of society's needs. They created many of the things we use today and take for granted. The chemical industry grew by leaps and bounds up to the 1980s, however, by the end of the decade, the world saw an increase in resource depletion and chemical pollution.

There was a grand challenge facing government, industry, and academia in the relationship of our technological society to the environment – reinventing the use of materials. Addressing this challenge required grounding in the insights, desires, and uncertainties of an interdisciplinary group of stakeholders.

Input from state and private research investment organizations, policy makers and risk managers, business leaders and consumers, and the scientists, designers, and engineers that serve these interests were all engaged. Therefore, the approach to risk management of materials/chemicals was articulated as intervention approaches intended to reduce exposure of materials that are hazardous to health and the environment.

In 1990, the Pollution Prevention Act encouraged a new tact-elimination of hazards at the source and green chemistry was developed as a response to this. The United States' Act established source reduction as the highest priority in solving eco-problems and this signaled a move away from the "command and control" or "end of pipe" response and towards pollution prevention, that is focused on preventing waste from being formed in the first place, as a more effective strategy.

It was recognized that a variety of disciplines needed to be involved in source reduction and thus, recognition extended to chemists, the designers of molecular structures and transformations. In 1991, the Office of Pollution Prevention and Toxics in the U.S. Environmental Protection Agency (EPA) launched the first research initiative of the Green Chemistry Program, the Alternative Synthetic Pathways.

Foundational work in chemistry and engineering at the National Science Foundation's program on Environmentally Benign Syntheses and Processes was launched in 1992, and formed a partnership with EPA that same year. In 1993, the EPA program officially adopted the name "U.S. Green Chemistry Program".

Both Italy and the United Kingdom also joined this movement. In Italy, a multi-university consortium (INCA) featured research on green chemistry as one of its central themes. Researchers at the University of York contributed to the establishment of the Green Chemistry Network within the Royal Society of Chemistry (RSC).

During the last half of the decade, Japan organized the Green and Sustainable Chemistry Network (GSCN), with an emphasis on promoting research and development on green and sustainable chemistry.

The 12 Principles of Green Chemistry were published in 1998, providing the new field with a clear set of guidelines for further development. The first books, papers, and symposia on the subject of green chemistry were introduced and the inaugural edition of the journal 'Green Chemistry', sponsored by the RSC, appeared in 1999.

And thereafter, there was no looking back. The development of green chemistry has been one of the most important new aspects of chemistry ever since.

Principles of Green Chemistry

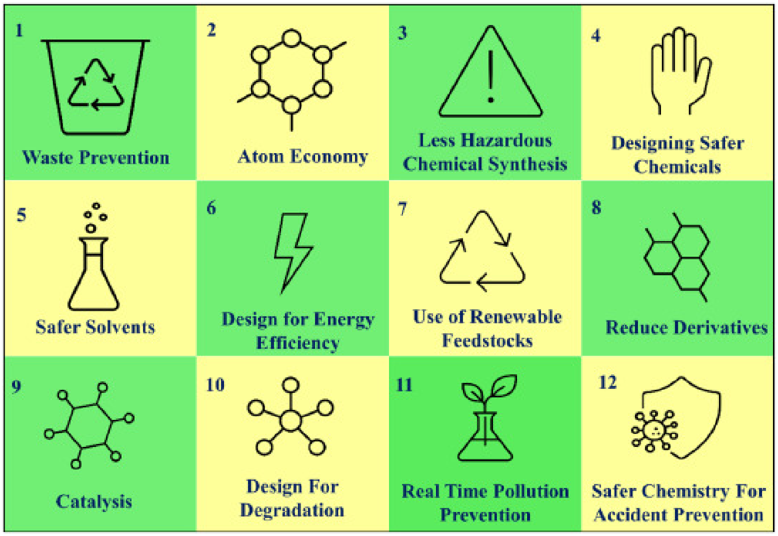
Paul Anastas, then director of the Green Chemistry Program at the US EPA, and John C. Warner published a set of 12 principles to guide the practice of green chemistry in 1998. The twelve principles have been distilled from a diverse set of practices and emerging research.

They address a range of ways to lower the environmental and health impacts of chemical production and also indicate research priorities for the development of green chemistry technologies. They can be viewed as imperatives or directives that address concepts such as:

a. the design of processes to maximize the amount of raw material that ends up in the product;

b. the use of renewable material feedstocks and energy sources;
c. the use of safe, environmentally benign substances, including solvents, whenever possible;
d. the design of energy efficient processes;
e. avoiding the production of waste, which is viewed as the ideal form of waste management

The 12 principles include:



1. Waste Prevention:

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

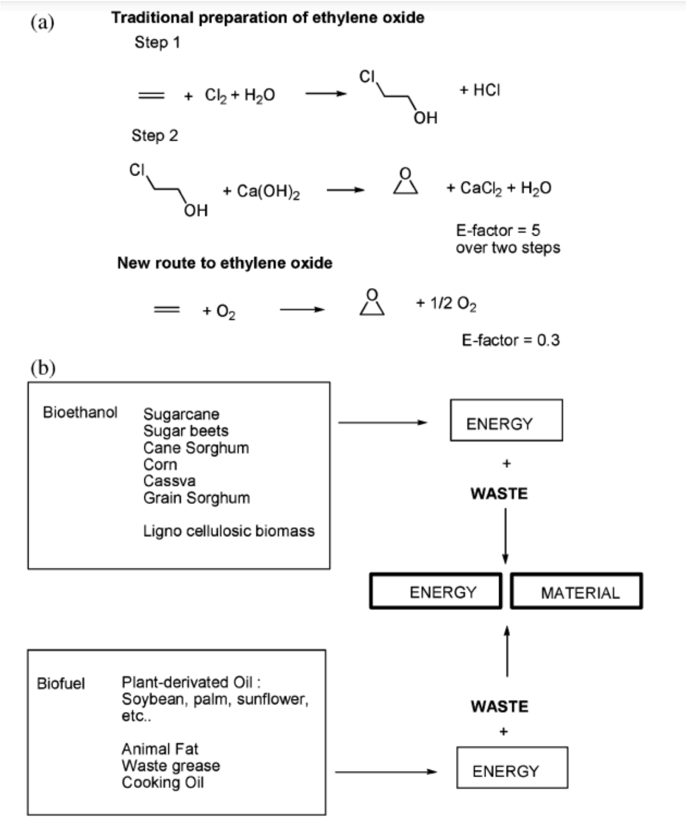
The old adage: "An ounce of prevention is worth a pound of cure" applies here. It is better to prevent the formation of waste rather than to clean it up after the fact. The generation of any material that does not have realized value or the loss of unutilized energy can be considered a waste.

As mentioned above, waste can take many forms and may impact the environment differently depending on its nature, its toxicity, its quantity, or the way it is released. When large portions of the initial raw materials used in a process are lost because of the original design of the process itself then it will inexorably generate waste which is by definition undesirable.

In 1992, the concept of what is now widely accepted as the E-Factor, or Environmental Impact Factor, was introduced by Roger Sheldon. This metric helps to quantify the amount of waste generated per kilogram of product. It is a means to assess the "environmental acceptability" of a manufacturing process.

$$\text{E-Factor} = \frac{Mass\ of\ Wastes}{Mass\ of\ Products} \text{ or } \text{E-Factor} = \frac{Mass\ of\ Raw\ Materials - Mass\ of\ Products}{Mass\ of\ Products}$$

The environmental factor which has been adopted by many in the chemical industry underscores how inefficient certain industrial processes have been and opened the door to creative solutions. One well-known example is the early synthesis of ethylene oxide which was prepared through a chlorohydrin intermediate.



The E-Factor for the entire synthesis as stated above was equal to 5. For each kilogram of product, 5 Kg of waste were to be disposed of. This does not take into consideration the waste water contaminated by chlorine by-products. When the synthesis was modified to use molecular oxygen, thus removing the need for chlorine, the E-Factor dropped to 0.3 Kg of waste. The new process was generating more than 16 times less waste than the original one, eliminating the formation of waste water as well.

When byproducts cannot be avoided, other innovative solutions should be considered and a productive one is to seek an industrial ecology approach where waste can become a new raw material with significant value for another process as it re-enters the life-cycle. This approach is currently being applied to the production of biofuel..

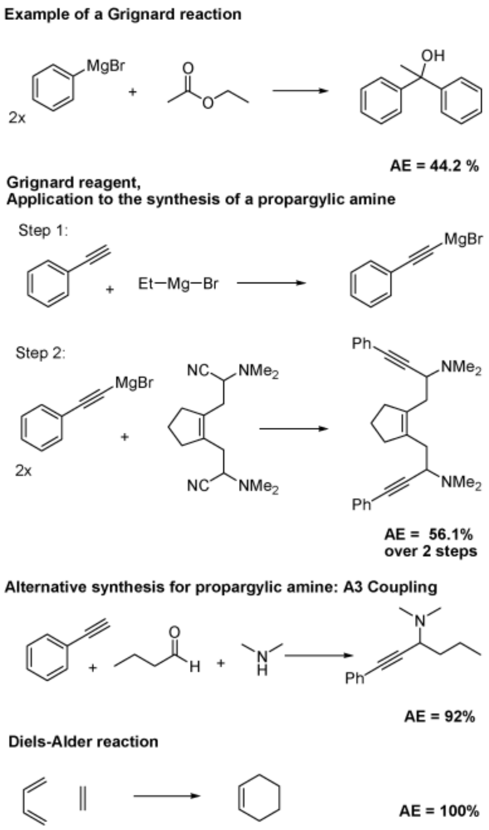
2. Atom Economy

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

In 1990, Barry Trost introduced the concept of synthetic efficiency called Atom Economy (AE) or Atom Efficiency. It refers to the concept of maximizing the use of raw materials so that the final product contains the maximum number of atoms from the reactants. The ideal reaction would incorporate all of the atoms of the reactants. The AE is measured as the ratio of the molecular weight of the desired product over the molecular weights of all reactants used in the reaction. It is a theoretical value meant to quickly assess how efficient a reaction will be.

$$\text{AE} = \frac{Molecular\ Weight\ of\ Desired\ Products}{Molecular\ Weight\ of\ Reagents\ Used}$$

$$\text{AE}\,\% = \frac{Molecular\ Weight\ of\ Desired\ Products}{Molecular\ Weight\ of\ Reagents\ Used} \times 100$$



To illustrate this concept, a few examples such as the Grignard reaction, A3 coupling and the Diels–Alder reaction are presented below. The Grignard reaction, which received the recognition of the scientific community for its importance in organic synthesis, is unfortunately a relatively poor atom economical reaction due to the use of a stoichiometric amount of metal reactant and the necessity to prepare the Grignard reagent separately.

The figure presents a typical Grignard reaction and an application of the Grignard reagent to build a propargylic amine type structure. The values of the AE respectively are 44 and 56% which reflect a loss of half of the raw material. A solution in respect to the last example was proposed by C.J. Li *et al.* in

2002 through the A3 coupling (Alkyne, Aldehyde and Amine). This one-step multicomponent coupling reaction is more efficient and conserves atoms since 92% of the original atoms used are found in the final product.

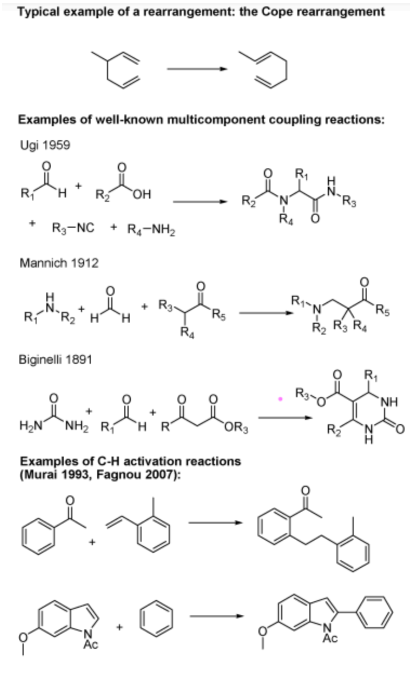
The Diels–Alder reaction is also an excellent example of an atom-economical reaction. Its AE is equal to 100% since all atoms from the reactants are incorporated into the final product. Diels–Alder type reactions belong to the category of cycloaddition which is among the greenest types of reactions in traditional chemistry.

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.

When one looks solely at the product of a chemical transformation, what is often seen is the proverbial "tip of the iceberg". In a multistep reaction sequence, or sometimes even a single step process, "hidden" in its synthetic history often lurk quite hazardous and toxic reagents.

Manufacturing and engineering procedures ensure that contamination from these processes do not appear in the final product. But the process itself still presents a number of hazards. Redesigning existing transformations to incorporate less hazardous materials is at the heart of Green Chemistry.



As illustrated in the figure, the synthetic toolbox of organic chemists has been improved by a significant amount of innovative work. Many of the new reactions that have been developed in the past decade add to the already existing green reactions that were discovered during the past century. Reactions based on cycloaddition, rearrangement, or multicomponent coupling reactions were already known and constitute one category of efficient reactions.

Cascade or tandem reactions, C–H activation, metathesis, and enzymatic reactions, are rather new approaches and illustrate strong examples of cleaner, more efficient synthetic tools available to organic chemists.

C–H activation is a relatively new area of chemistry which holds great promise for the future. In traditional coupling reactions, activated carbon–halogen bonds are usually used because of their high reactivity. Since halogenated molecules are rarely natural, it implies additional steps to produce the precursor. The replacement of traditional coupling reactions with C–H activation eliminates the need for halogenated precursors and therefore the halogenated waste byproduct generated.

Two famous examples of C–H activation were published in 1993 by Murai and in 2007 by Fagnou. In the first case, Murai employed a ruthenium catalyst to couple the inactivated substrates acetophenone and 2-methylstyrene. This work was one of the first examples of C–H activation and represents a milestone in the field. In the second case, Fagnou and Stuart coupled two aromatic compounds selectively without the need for any activating or directing groups. Those examples demonstrate the power of C–H activation in advancing Green Chemistry.

4. Designing Safer Chemicals

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

In contrast to Principle 3, which is concerned with synthetic methods, Principle 4 focuses on products. Highly reactive chemicals are often used by chemists to manufacture products because they are quite valuable at affecting molecular transformations. However, they are also more likely to react with unintended biological targets, human and ecological, resulting in unwanted adverse effects.

Minimizing toxicity, while simultaneously maintaining function and efficacy, may be one of the most challenging aspects of designing safer products and processes. Achieving this goal requires an understanding of not only chemistry but also of the principles of toxicology and environmental science. Without understanding this fundamental structure hazard relationship, even the most skilled molecular magician enters the challenge lacking a complete toolkit.

Mastering the art and science of toxicology requires innovative approaches to chemical characterization that state that hazard is a design flaw and must be addressed at the genesis of molecular design. The intrinsic hazard of elements and molecules is a fundamental chemical property that must be characterized, evaluated and managed as part of a systems-based strategy for chemical design.

Work by Ariëns in 1984 and by Garrett and Devito in 1996 showed that designing safer chemicals is not only highly needed for the advancement of Green Chemistry, but is also possible. In recent decades, there has been a significant amount of work in the field of toxicology that has moved it from being a descriptive science to one that has a large mechanistic component, and even more recently progressively towards the incorporation of an in-silico component.

Because of that transition, it has been possible to create correlations, equations, and models that relate structure, properties, and function. These approaches provide the basis for the work being pursued in the development of a comprehensive design strategy. For instance the existing understanding of medicinal chemistry can already help establish some ground rules for designing less toxic chemicals via incorporation of specific design features that block their access into humans and many animals.

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.

Solvents are perhaps the most active area of Green Chemistry research. They represent an important challenge for Green Chemistry because they often account for the vast majority of mass wasted in syntheses and processes. Moreover, many conventional solvents are toxic, flammable, and/or corrosive. Their volatility and solubility have contributed to air, water and land pollution, have increased the risk of workers' exposure, and have led to serious accidents.

Recovery and reuse, when possible, is often associated with energy-intensive distillation and sometimes cross contamination. In an effort to address all those shortcomings, chemists started a search for safer solutions. Solventless systems, water, supercritical fluids (SCF) and more recently ionic liquids are some examples of those new "green" answers.

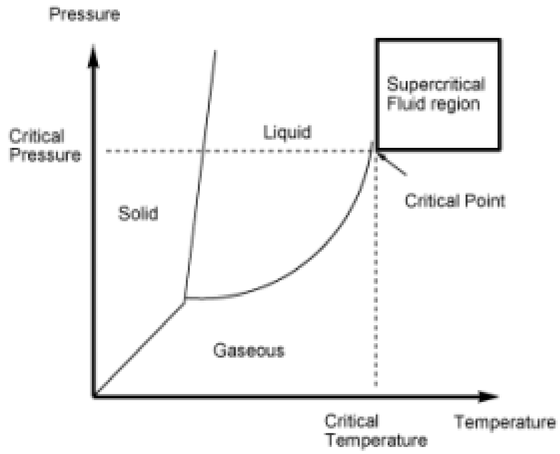
Where possible, the ideal situation would be to not use any solvent because the decision to include an auxiliary always implies efforts and energy to remove it from a designated system. Efforts have therefore been devoted to developing solventless systems. This idea was reinforced by the finding that solvents account for most of the industrial waste.

Depending on the physical properties of the reagents used or the desired outcome of the transformation, the approach often requires a new or redesigned chemistry to allow the reaction to proceed without the original solvent. Water is the most abundant molecule on the planet and is sometimes referred to as a benign "universal solvent". Being able to run a reaction in or on water therefore has significant advantages.

Water is safe and does not pose any hazards. It can be a useful solvent for large scale process chemistry. The properties of water have even led to improved reaction rates through the hydrophobic effect and easier separation since a lot of organic substances do not dissolve in water.

The case of an improved Diels–Alder reaction in water is one of the useful examples illustrating the advantages of water as a solvent. One drawback which may slow down industrial applications and has yet to be addressed is the risk of water contamination that can be very energy intensive to clean.

SCF are another alternative to traditional organic solvents and have been extensively studied in the past decades. They are substances which have been simultaneously heated and compressed above their critical points. Common SCF are generated from water, carbon dioxide, methane, methanol, ethanol or acetone. Carbon dioxide is one of the most widely used SCF. The resulting supercritical CO_2 (or $scCO_2$) has proven to be a versatile solvent, safe and easy to handle, as demonstrated by the work of Poliakoff,



Pressure–temperature phase diagram showing the supercritical region.

Leitner, Jessop, DeSimone, and others. What makes SCF so attractive in general and particularly $scCO_2$ is the change of state that occurs when cooling down the vessel or reducing the pressure.

Above critical points, CO_2 will be a liquid in which reactions can be performed and below, it will be a gas. Degassing the system allows the complete removal of the solvent. $ScCO_2$ has found a wide range of industrial applications with the most famous being the decaffeination of green coffee beans and the replacement of perchloroethylene in dry cleaning. Supercritical fluids have proven to be one valuable alternative to traditional solvents.

Another example of greener solvents would be ionic liquids pioneered in modern times by Seddon. As their name highlights, ionic liquids, or sometimes called room temperature ionic liquids, are liquid salts at room temperature. They have virtually no vapor pressure and very low flammability. What was discovered recently by Jessop *et al.* is a "switchable" ionic liquid.

A "smart-obedient solvent" generated in situ just like the liquid $scCO_2$. Addition of pressurized carbon dioxide into an organic mixture transforms it into an ionic liquid, generating a safer solvent in situ. Releasing the pressure reverses the phenomenon and the ionic liquid is retransformed into the original mixture, thus completely removing the solvent and eliminating tedious purification and extraction steps.

This last example is a good illustration of one of chemistry's major challenges: separation. Apart from certain solventless systems, the new improved green solvents remain auxiliaries and therefore must be isolated from the desired product. If their use cannot be avoided then the issue of separation must be taken into consideration when choosing the appropriate solvent.

6. Design for Energy Efficiency

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.

Rising concerns over the depletion of petroleum feedstocks and the increase in energy consumption have pushed the development of more energy efficient processes and for the search for renewable energies; non-depleting resources in a time frame relevant to human scale.

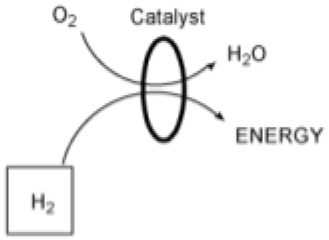
As mentioned in the first section (first principle), unutilized energy may also be considered a waste. The design of chemical reactions or systems that do not require intensive energy use is highly desirable. Reducing the energy barrier of a chemical reaction or choosing appropriate reactants so that the transformation may proceed at room temperature is one example of what chemists can do to reduce energetic requirements, with all the direct and indirect benefits associated with it.

Increasing the energy efficiency of a chemical system is merely one part of the solution. Alternative energies are also needed. Several of those renewable energies have been identified in biofuels production, solar power (thermal and photovoltaic), wind power, hydro power, geothermal energy, and hydrogen fuel cells.

Once again, green chemists have an important role to play in this new challenge as they have the ability to design both energy efficient transformations and materials or chemical systems that can be used to harvest some of those renewable natural energies. Solar energy, the primary sustainable energy source on earth, is one of those alternatives to petroleum. Considerable efforts have been dedicated to understand and design chemical systems that can convert solar radiations into voltaic energy.

Organic, inorganic and hybrid solar cells have received interest although more focus has been placed on organic solar cells because of their higher efficiency. The principle of those cells relies on the ability of the material used to absorb photonic energy from solar radiations. The absorption leads to the formation of excited states that can be relayed and generate electric current.

Building materials and polymers that can efficiently transform light into current remain a challenge and are key to the success of this approach. Proton Exchange Membrane (PEM) fuel cells using hydrogen and oxygen gasses could also provide another solution to the upcoming increase in energy demand.



General concept of a hydrogen fuel cell.

PEM fuel cells have generated research interest, especially in the past decade with the development of increasingly efficient catalysts such as nanoparticles or even hydrogenase enzymes. An important consideration in this approach is the hazard of handling hydrogen gas, which is highly flammable and explosive.

7. Use of Renewable Feedstocks

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

It has been estimated that the vast majority of our manufacturing products are derived from petroleum feedstock or natural gas. The depletion of those resources will touch many aspects of our consumer life and our economy. Turning towards renewable feedstocks both for material and fuel has now become more urgent.

The major renewable feedstock on the planet both for material and energy is biomass, the material available from living organisms. This includes wood, crops, agricultural residues, food, etc. Examples of renewable material include cellulose, lignin, suberin and other wood compounds, polyhydroxyalkanoates, lactic acid, chitin, starch, glycerol and oil.

Lignin, for instance, is a major waste of the pulp and paper industry. It has been burned on the production site to provide energy for many years. In recent years it has found new applications as, for example, dispersants, additives, and raw materials for the production of chemicals such as vanillin, DMSO or humic acid.

Chitin is another abundant natural polymer that constitutes the exoskeleton of arthropods (e.g. crustaceans). It is a major byproduct of the seafood industry and can be transformed into chitosan by deacetylation.

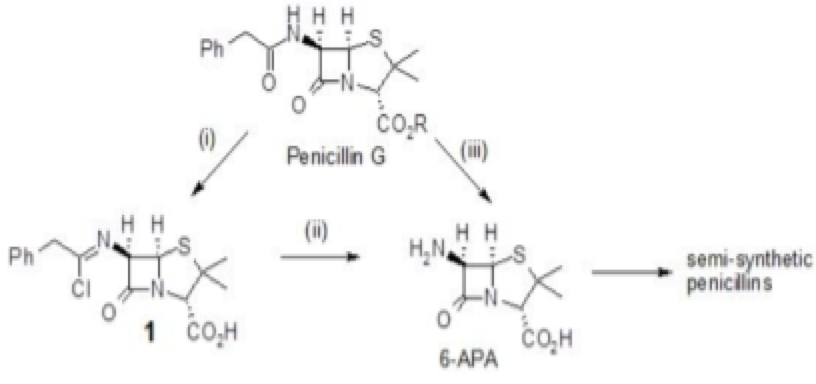
Numerous applications of chitosan have been described from water purification, biomedical applications and other industrial uses. Reusing this waste of the bio-industries should provide a large amount of raw materials to replace the current petroleum feedstocks.

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.

One of the key principles of green chemistry is to reduce the use of derivatives and protecting groups in the synthesis of target molecules. One of the best ways of doing this is the use of enzymes. Enzymes are so specific that they can often react with one site of the molecule and leave the rest of the molecule alone and hence protecting groups are often not required.

A great example of the use of enzymes to avoid protecting groups and clean up processes is the industrial synthesis of semi-synthetic antibiotics such as ampicillin and amoxicillin.



Industrial synthesis of penicillin

(i) TMSCl then PCl_5, $PhNMe_2$, CH_2Cl_2, -40°C (ii) n-BuOH, -40°C, then H_2O, 0°C (iii) Pen-acylase, water

In the first industrial synthesis, Penicillin G (R=H) is first protected as its silyl ester [R = Si(Me)3] and then reacted with phosphorus pentachloride at -40 °C to form the chlorimidate 1. Subsequent hydrolysis gives the desired 6-APA from which semi-synthetic penicillins are manufactured. This synthesis has been largely replaced by a newer enzymatic process using pen-acylase. This synthesis occurs in water at just above room temperature. The new synthesis has many advantages from a green perspective, one of which is that the silyl protecting group is not required.

More than 10,000 metric tons of 6-APA is made every year and much of it by the greener enzymatic process which is a fantastic example of Green Chemistry making a real difference.

9. Catalysis

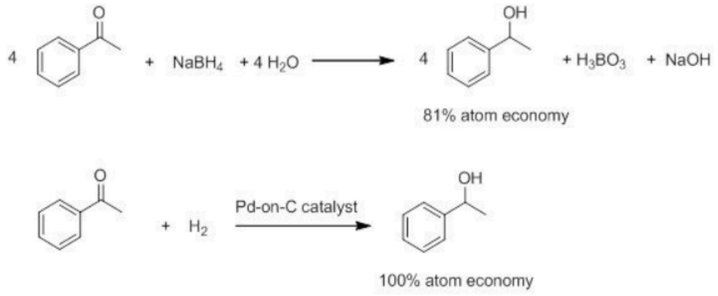
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

In many cases, the formation of waste is linked to the traditional use of a stoichiometric amount of reagents. Switching from stoichiometric methodologies to catalytic processes is perceived as one major way to improve the efficiency of the synthetic toolbox.

Catalytic processes involve catalysts ie. substances that change the velocity of a reaction without itself being changed in the process. They lower the activation energy of the reaction but in doing so it is not consumed. This means that in principle at least, they can be used in small amounts and be recycled indefinitely, without generating any waste.

Catalysis can improve the efficiency of a reaction by lowering the energy input required, by avoiding the use of stoichiometric amounts of reagents, and by greater product selectivity. This implies less energy, less feedstock and less waste. Moreover, it often opens the door to innovative chemical reactions and brings unconventional solutions to traditional chemical challenges.

Oxidation and reduction reactions illustrate this concept. For example, the reduction of a ketone to the corresponding secondary alcohol using sodium borohydride or molecular hydrogen as the reductant. Reduction with the former has an atom economy of 81% while reduction with the latter is 100% atom economic, that is everything ends up in the product and, in principle, there is no waste. Unfortunately, hydrogen does not react with ketones to any extent under normal conditions. For this, we need a catalyst such as palladium-on-charcoal.



Atom Economy Reaction with Catalyst

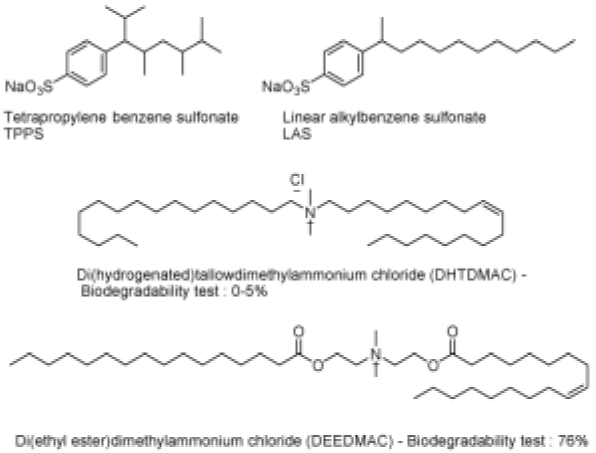
Beyond efficiency, catalysis can also allow for otherwise unfavorable reactions to be realized. This was the case for the metathesis reaction and the development of the Grubbs catalyst. The environmental benefit of this innovation was very important. Biocatalysis is yet another example of “green” chemistry as it is a biomimetic approach relying on natural or modified enzymes.

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.

The problem of persistence has been known for a long time and became apparent in the early stages of industrial development. In the 1950s for instance, tetrapropylene alkylbenzene sulfonate (TPPS) was used as a surfactant for laundry detergents and accumulated into the water supply due to an incomplete degradation.

The situation was so critical that there were examples where "water tended to foam when coming out of the tap". The public outcry prompted the industry to seek an immediate solution and it was found that replacing the methyl branched chain of TPPS by a linear carbon chain reduces the biopersistence.



Integrating biodegradability in the design of surfactants.

Designing biodegradable materials and chemicals, however, is not a simple task. Certain chemical structures such as halogenated moieties, branched chains, quaternary carbons, tertiary amines, and certain heterocycles may possess enhanced persistence and are avoided. On the other hand, integrating functional groups such as esters or amides which are recognized by ubiquitous enzymes may help the design of environmentally degradable products.

Some tools have emerged following decades of data collection. Prediction methods that can guide the design of molecular architecture expected to degrade include rules of thumb linking structural features to degradability or persistence, databases of existing knowledge, models that evaluate biodegradability or PBT attributes, and experimental testing. All of these tools can be adapted to individual chemical sectors and specific objectives.

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.

Real-time feedback is essential in proper functioning chemical processes. It is the goal of green analytical chemistry to measure chemicals without generating waste.

Most chemists are familiar with laboratory analysis from their undergraduate training. But analysis can also be performed in-line, on-line, or at-line in a chemical plant, a subdiscipline known as process analytical chemistry. Such analysis can detect changes in process temperature or pH prior to a reaction going out of control, poisoning of catalysts and other deleterious events before a major incident occurs.

Green analytical chemistry can be defined as the use of analytical procedures that generate less waste and are safer to human health and the environment. This definition includes both aspects of "live" monitoring of a chemical transformation and the environmental shortcomings associated with traditional analysis.

While the traditional roles of analytical chemistry also advance green chemistry goals, the effective application of green process analytical chemistry directly contributes to the safe and efficient operation of chemical plants worldwide.

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 12th green chemistry principle is known as the "Safety Principle" and deals with the control of recognized hazards to achieve an acceptable level of risk. It may be the most overlooked of the twelve principles, yet it is the logical outcome of many of the other principles.

Dangerous substances and processes have multiplied in our working environment. According to the "Chemical accident prevention and the clean air act amendments of 1990," preventing accidents starts by identifying and assessing the hazards. All types of hazards whether it is toxicity, physical hazards such as explosivity or flammability, and global hazards should be addressed in the design of chemicals and processes in order to prevent accidents such as Bhopal or the Love Canal incident.

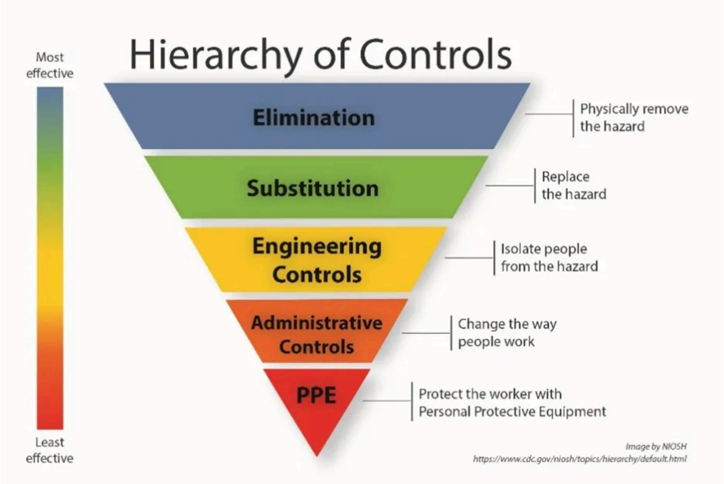


Image by NIOSH
https://www.cdc.gov/niosh/topics/hierarchy/default.html

These past accidents should be a strong reminder to the scientific community that many chemicals we still use present serious hazards and should be replaced by safer alternatives to prevent accidents wherever possible.

While materials and processes that are safer for the environment also are likely to be safer for the general public, another population that benefits from green chemistry and is not often mentioned is workers. The manufacturing or laboratory worker is often the first in-line person to benefit from hazard reductions.

Green Chemistry in the Current

Since its inception, the concepts and practice of green chemistry has grown into a significant internationally engaged focus area within chemistry aimed at meeting the “triple bottom line”—sustainability in economic, social, and environmental performance.

The green chemistry approach seeks to redesign the materials that make up the basis of our society and our economy—including the materials that generate, store, and transport our energy—in ways that are benign for humans and the environment and possess intrinsic sustainability. It strives to achieve sustainability at the molecular level.

Because of this goal, it is not surprising it has been applied to all industry sectors. From aerospace, automobile, cosmetic, electronics, energy, household products, pharmaceutical, to agriculture, there are hundreds of examples of successful applications of award winning, economically competitive green chemistry technologies.

Here are some of the examples illustrated:

1. From Research to Practice:

The 2005 Nobel Prize in chemistry was awarded for the discovery of a catalytic chemical process called ‘metathesis’ – which has broad applicability in the chemical industry. It uses significantly less energy and has the potential to reduce greenhouse gas emissions for many key processes. The process is stable at normal temperatures and pressures. It can be used in combination with greener solvents, and is likely to produce less hazardous waste.

In 2012, Elevance Renewable Sciences won the US Presidential Green Chemistry Challenge Award by using metathesis to break down natural oils and recombine the fragments into high-performance chemicals. The company makes specialty chemicals for many uses, such as highly concentrated cold-water detergents that provide better cleaning with reduced energy costs.

2. Computer Chips:

To manufacture computer chips, many chemicals, large amounts of water, and energy are required. In a study conducted in 2003, the industrial estimate of chemicals and fossil fuels required to make a computer chip was a 630:1 ratio! Compare that to the 2:1 ratio for the manufacture of an automobile.

Scientists at the Los Alamos National Laboratory have developed a process that uses supercritical carbon dioxide in one of the steps of chip preparation, and it significantly reduces the quantities of chemicals, energy, and water needed to produce chips.

Meanwhile, Richard Wool, former director of the Affordable Composites from Renewable Sources (ACRES) program at the University of Delaware, found a way to use chicken feathers to make computer chips. The protein, keratin, in the feathers was used to make a fiber form that is both light and tough enough to withstand mechanical and thermal stresses. The result is a feather-based printed circuit board that actually works at twice the speed of traditional circuit boards.

3. Medicine:

The pharmaceutical industry is continually seeking ways to develop medicines with less harmful side-effects and using processes that produce less toxic waste.

Merck and Codexis developed a second-generation green synthesis of sitagliptin, the active ingredient in Januvia, a treatment for type 2 diabetes. This collaboration led to an enzymatic process that reduces waste, improves yield and safety, and eliminates the need for a metal catalyst. Early research suggests that the new biocatalysts will be useful in manufacturing other drugs as well.

Simvastatin, the leading prescription for treating high cholesterol, follows a traditional multistep manufacturing method that uses large amounts of hazardous reagents and produces a large amount of toxic waste in the process. Professor Yi Tang, of the University of California, created a synthesis using an engineered enzyme and a low-cost feedstock. Codexis, a biocatalysis company, optimized both the enzyme and the chemical process. The result greatly reduces hazard and waste, is cost-effective, and meets the needs of customers.

4. Biodegradable Plastics:

Several companies have been working to develop plastics that are made from renewable, biodegradable sources.

NatureWorks of Minnetonka, Minnesota, makes food containers from a polymer called polylactic acid branded as Ingeo. The scientists at NatureWorks discovered a method where microorganisms convert cornstarch into a resin that is just as strong as the rigid

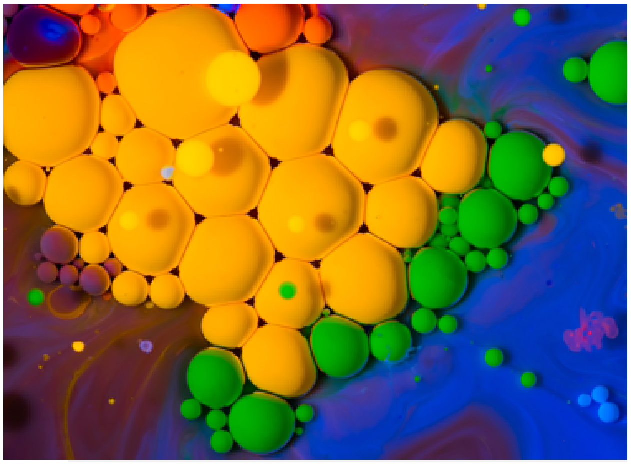
petroleum-based plastic currently used for containers such as water bottles and yogurt pots. The company is working toward sourcing the raw material from agricultural waste.

BASF developed a compostable polyester film called "Ecoflex". They are making and marketing fully biodegradable bags, made of this film along with cassava starch and calcium carbonate. Certified by the Biodegradable Products Institute, the bags completely disintegrate into water, CO_2, and biomass in industrial composting systems. The bags are tear-resistant, puncture-resistant, waterproof, printable and elastic. Using these bags in the place of conventional plastic bags, kitchen and yard waste will quickly degrade in municipal composting systems.

5. Paints:

Oil-based "alkyd" paints give off large amounts of volatile organic compounds (VOCs). These volatile compounds evaporate from the paint as it dries and cures and many have one or more environmental impacts.

Procter & Gamble and Cook Composites and Polymers created a mixture of soya oil and sugar that replaces fossil-fuel-derived paint resins and solvents, cutting hazardous volatiles by 50 percent. Chempol MPS paint formulations use these biobased oils to replace petroleum-based solvents and create paint that is safer to use and produces less toxic waste.



Sherwin-Williams developed water-based acrylic alkyd paints with low VOCs that can be made from recycled soda bottle plastic (PET), acrylics, and soybean oil. These paints combine the performance benefits of alkyds and low VOC content of acrylics. In 2010, Sherwin-Williams manufactured enough of these new paints to eliminate over 800,000 pounds, or 362,874 kgs, of VOCs.

Future of Green Chemistry

The accomplishments in the field of Green Chemistry thus far are impressive due to the scientists in academia, industry, and research institutes around the world. However, many challenges still lie ahead in the development of Green Chemistry.

These future challenges are as diverse as the scientific imagination and address the broadest issues of sustainability. Because of this breadth, these challenges are being pursued for reasons ranging from economic to scientific and the solutions will be found not only in the discipline of chemistry but at its interfaces with engineering, physics, and biology. We can broadly split the challenges into research challenges, implementation challenges and education challenges.

1. Research Challenges:

The challenges to research in achieving green chemistry principles are numerous, and a detailed discussion of each is not possible. Some notable research challenges include:

a. Multi-functional catalysts

Catalysis has made significant progress during the past two decades. However, even today, most catalysts are designed to act on one transformation only and little is known about multi-functional catalysts, defined as the ability of one catalytic system to act on a series of transformations. If the same catalyst could be used for various independent reactions or achieve an entire synthesis in one pot, it will bring chemistry to a new level as more complex molecules could be made with higher material and energy efficiency.

b. Mastering weak forces for synthesis and properties

Non-covalent and weak-force interactions are likely to play an increasingly important role in the future of chemistry. Imparting properties through weak-forces and guiding synthetic pathways in the same manner while minimizing the amount of bond breaking and bond forming can result in significant advantages. These include reducing the amount of energy needed, suppressing the amount of waste, and an increase in efficiencies. Mastering the weak forces in the same way that the field of chemistry has mastered covalent forces holds great potential to help in reaching sustainability at the molecular level.

c. Integrative systems thinking

The traditional approach to scientific investigation has been largely based on the reductionist approach. This approach has brought about a depth of understanding and discovery that have made the things of modern life – from communication to transportation to medicine – possible. It has also resulted in tremendous unintended and unforeseen consequences that have had a damaging impact on humans and the environment. By thinking in terms of systems, Green Chemistry can pursue significant innovations while avoiding unintended results. Coupling reductive and integrated thinking can result in truly transformative innovations.

2. Implementation Challenges

The discovery of more environmentally benign technologies at the research stage does not guarantee that they will be adopted on an industrial scale. A number of barriers hinder the adoption of newer technologies that prevent pollution. Adoption of environmentally benign processes may be facilitated by the following:

- Flexibility in regulations.
- Tax incentives for implementing cleaner technologies.
- Research programs to facilitate technology transfer among academic institutions, government, and industry.
- Patent life extensions for cleaner process optimization.

3. Education Challenges

Students at all levels need to be introduced to the philosophy and practice of green chemistry. Educators need appropriate tools, training, and materials to effectively integrate green chemistry into their teaching and research. Important steps have to be taken to advance green chemistry within the curriculum. Some steps could include the following:

- Development and utilization of practical laboratory experiments to illustrate green chemistry principles.
- Addition of balanced green chemistry equations in organic textbooks and replacement of “yield” with “atom economy”.
- Introduction of the basic concepts of chemical toxicology and the molecular basis of hazard.
- Incorporation of green chemistry topics into existing chemistry courses and certification exams.

Conclusion

For generations, molecular scientists have invented the molecules, materials, and manufacturing processes that have allowed economic and societal development. Green Chemistry is ensuring that all of this creative ability present in the long tradition of chemistry is practiced in a way that it doesn't negatively impact people and the planet. In doing so, Green Chemistry has shown that innovations can be economically more profitable and more environmentally benign at the same time.

Despite the impressive amount of work already done by Green Chemists around the world, the achievements of the past pale by comparison to the power and potential of the field. There will come a day when the 12 Principles of Green Chemistry are simply incorporated as an integral part of everyday chemistry and innovations brought about by chemistry go beyond our imaginations.

Green chemistry is, by definition, a continuously-evolving frontier and will always continue to be one.

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