ENVIRONMENTAL AND SOCIO-ECONOMIC IMPACTS OF GREEN CHEMISTRY-A REVIEW

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ABSTRACT

In some industrial chemical processes, not only waste products but also the reagents used for the production may cause a threat to the environment, society and economy. 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 aims at designing of products and processes that reduce or eliminate the use and generation of hazardous substances. It targets pollution at the design stage, before it even begins. The Principles of Green Chemistry can be viewed as imperatives or directives that address alternative starting and target materials, alternative reagents and solvents, catalysts, and improved processes and process control. The present review describes environmental and socio-economic impacts of twelve principles of green chemistry with detail illustrations taking different case studies including US Presidential Green Chemistry Challenge Awards for each guideline. In addition, it summarizes barriers to implementation of the twelve principles of green chemistry and how to overcome the barriers.


INTRODUCTION

In some industrial chemical processes, not only waste products but also the reagents used for the production may cause a threat to the environment. The risk of exposure to hazardous chemical compounds is limited in daily work by protective equipment such as goggles,
breathing apparatus, face-guard masks, etc. According to the principles of green chemistry, a threat can be eliminated in a simpler way, by applying safe raw materials for production process.

Green chemistry is the —design of products and processes that reduce or eliminate the use and generation of hazardous substances. It is a pro-active approach to pollution prevention. It targets pollution at the design stage, before it even begins. 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. These principles can motivate chemistry at all levels: research, education and public perception. The first principle describes the basic idea of green chemistry in protecting the environment from pollution. The remaining principles are focused on atom economy, toxicity, solvent and other media using consumption of energy, application of raw materials from renewable sources and degradation of chemical products to simple, nontoxic substances that are friendly for the environment.

The Principles of Green Chemistry have been distilled from a diverse set of practices and emerging research. They can be viewed as imperatives or directives that address alternative starting and target materials, alternative reagents and solvents, catalysts, and improved processes and process control. In the following briefs of each principle a representative case study is summarized that illustrates an individual principle particularly well. It is acknowledged that each case typically adheres to more than one principle.

The present review describes environmental and socio-economic impacts of twelve principles of green chemistry with detail illustrations taking different case studies including US Presidential Green Chemistry Challenge Awards for each guideline. In addition, it summarizes barriers to implementation of the twelve principles of green chemistry and how to overcome the barriers.

**Principle 1: Waste Prevention**

It is better to prevent waste than to treat or clean up waste after it is formed. This means prevention is better than cure. Ones waste is formed it has impact on the soil, water and living things which live in these environmental media. The waste formed incurs cost of treatment which leads to economic loss. The same waste has health hazard on society which uses the product of that polluted environment. As a result, waste avoidance is the
best option for environmental friendliness, social soundness and economic feasibility using different technology, procedures and methods.

**Case Study 1:** In 1990 the company BHC after prolonged research on the subject discovered a new synthetic route for Ibuprofen with only three steps and increased efficiency.\(^1\) The atoms of the starting chemicals are incorporated into the products of the reactions and waste is minimized. In both synthetic routes the starting chemical is 2-methylpropylbenzene. The innovation in the new method was in the second step. A catalyst of Nickel (Raney nickel) was used thus decreasing substantially the steps of the synthesis (Fig.1.) In the old synthetic route, each step had a yield of 90% so that the final product came to be 40% yield compared to the starting chemical. This resulted in the increased production of by-products as waste. The drug was produced annually (only in Great Britain) in 3,000 tones and we understand that substantial amounts of chemicals were lost as waste. Energy also was lost by the low efficiency of the reaction method. In the —greener—method of three steps the final yield is 77%, whereas the Raney nickel catalyst can be recycled and reused. In the old synthetic route, the AlCl₃ used as a catalyst had to be thrown away as waste. The energy requirements of the second method were much lower than the first. Thus the case draws attention to the significant opportunity for preventing waste as a means of increasing profit margin in these growth areas of the chemical sector (Fig.1.).

![Fig.1. The two synthetic routes of Ibuprofen.](image-url)
Principle 2: Atom economy
Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. This principle gets into the actual chemistry of how products are made. It states that it is best to use all the atoms in a process. And, those atoms that are not used end up as waste. It is a simple measure of the amount of waste in a process or is a measure of the efficiency of a reaction. Chemists have traditionally measured the efficiency of a reaction by determination of the percentage yield (% yield) of the reaction. However the % yield deals with only the amount of the desired product(s) that is isolated (relative to the limiting reagent) and does not consider the efficiency of the reaction relative to (waste) byproducts that are formed. The concept of Atom Economy extends the consideration of the efficiency of a reaction to take into account all the atoms.

The atom economy of the reaction can be determined using the following equation
\[
\% A.E = \frac{\text{mass of desired product}}{\text{mass of desired product} + \text{mass of waste products}} \times 100
\]
\[
= \frac{\text{mass of desired products}}{\text{total mass of all reactants}} \times 100
\]

Carbon efficiency is a simplified formula developed at GlaxoSmithKline (GSK). Carbon efficiency (%)
\[
= \frac{\text{amount of carbon in product}}{\text{total carbon present in reactants}} \times 100
\]

This metric is a good simplification for use in the pharmaceutical industry as it takes into account the stoichiometry of reactants and products. Furthermore, this metric is of interest to the pharmaceutical industry where development of carbon skeletons is key to their work.

Environmental (E) factor
A final way to measure the efficiency of a reaction is using the E-factor. It can be calculated using the following equation.

\[
\text{E-factor} = \frac{\text{total waste (kg)}}{\text{product (kg)}}
\]

Case Study 1: Two different organic chemists use Flexsys NASH reaction to synthesize the same product using two different reaction steps. Which chemist followed better steps to get environmentally friendly, socially sound and economically feasible desired product?
Asnake

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Reaction 1

![Chemical Reaction Diagram]

**Fig. 2. Flexsys NASH reaction 1.**

<table>
<thead>
<tr>
<th>Table 1: The calculation of the Atom Economy of Flexsys NASH reaction 1.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reagent formula</strong></td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>1 C₆H₆</td>
</tr>
<tr>
<td>2Cl₂</td>
</tr>
<tr>
<td>3 HNO₃</td>
</tr>
<tr>
<td>4 C₂H₂N₂</td>
</tr>
<tr>
<td>5 K₂CO₃</td>
</tr>
<tr>
<td>6 H₂</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
</tr>
</tbody>
</table>

The Atom Economy of the reaction is equal to the weight of utilized atoms divided by the weight of all reagents used.

i. Atom Economy (%) = \(\frac{161}{432} \times 100 = 37\%\)

ii. Carbon efficiency (%) = \(\frac{144}{168} \times 100 = 86\%\)

iii. E-factor = total waste (kg) / product (kg) = \(248 \times 10^{-3} \text{kg/mol} / 161 \times 10^{-3} \text{kg/mol} = 1.54:1\)

This calculation demonstrates clearly the problems associated with the current chemistry.

The atom economy shows only 37% of the atoms of the reactants in the final product. The E-factor, confirms waste to product ratio is 1.54:1 showing that more waste is in the environment polluting the environmental media. This incurs cost for treatment (economic loss) and has a health hazard (social issue) (Table 1, reaction 1). The carbon efficiency is good as 86% of carbon is utilized. None of Cl₂ is incorporated in the final yield. It may deplete our ozone layer which blankets us from cancer causing radiations. In addition, there are unsafe acid HNO₃ and salt in environment K₂CO₃. The acid can make the soil acidic and pollute aquatic environment killing aquatic flora and fauna.
A similar calculation of the Atom Economy of the Flexsys NASH reaction is based on the overall reaction shown in Table 2.

Table 2: The data for the reagents and substrates labeled in red are shown in the table below.

<table>
<thead>
<tr>
<th>Reagent Formula</th>
<th>Reagent FW</th>
<th>Utilized Atoms</th>
<th>Wt</th>
<th>Unutilized Atoms</th>
<th>Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₆</td>
<td>78</td>
<td>6 C, 4 H</td>
<td>76</td>
<td>2 H</td>
<td>2</td>
</tr>
<tr>
<td>HNO₃</td>
<td>63</td>
<td>1 N</td>
<td>14</td>
<td>1 H, 3 O</td>
<td>49</td>
</tr>
<tr>
<td>C₆H₇N</td>
<td>93</td>
<td>6 C, 6 H, N</td>
<td>92</td>
<td>1 H</td>
<td>1</td>
</tr>
<tr>
<td>H₂</td>
<td>2</td>
<td>2 H</td>
<td>2</td>
<td>--</td>
<td>0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>236</td>
<td>12C,12H,2N</td>
<td>184</td>
<td>4H,3O</td>
<td>52</td>
</tr>
</tbody>
</table>

The Atom Economy of the Flexsys NASH reaction is given by
i. % Atom Economy = 184/236 x 100 = 78%
ii. Carbon efficiency (%) = 144/144*100=100%
iii. E-factor = total waste (kg) / product (kg) = 52*10⁻³ kg/mol / 184*10⁻³ kg/mol = 0.282.

The atom economy shows and represents a two-fold improvement over the traditional chemistry. The E-factor, confirms waste to product ratio is 0.282 showing that lesser waste is in the environment polluting the environmental media to a lesser extent when compared with reaction 1. This incurs minimum cost for treatment and has a little health hazard (Table 2, reaction 2). The carbon efficiency is higher as 100% of carbon is utilized and no contribution to global warming. None of Cl₂ is incorporated in the reactant. No contribution to ozone layer depletion which blankets us from cancer causing radiations. In addition, there are not unsafe acid HNO₃ as it is for parts of its N is utilized and no salt in environment K₂CO₃.
Principle 3: Less Hazardous Chemical Synthesis
Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment. This principle is focused on how we make molecules and materials. The goal is to reduce the hazard of the chemicals that are used to make a product (the reagents).

Case Study: Large amounts of adipic acid [HOOC(CHCOOH)] are used each year for the production of nylon, polyurethanes, lubricants and plasticizers. Benzene—a compound with convinced carcinogenic properties—is a standard substrate for the production of this acid. Chemists from State University of Michigan developed green synthesis of adipic acid using a less toxic substrate. Furthermore, the natural source of this raw material—glucose is almost inexhaustible. The glucose can be converted into adipic acid by an enzyme discovered in genetically modified bacteria such a manner of production of this acid guards the workers and the environment from exposure to hazardous chemical compounds.

In the past, the industrial production of Adipic acid used benzene as a starting material. Benzene is one of the basic chemicals for industrial reactions and a solvent. It is known that derives mainly from the refining processes of the petrochemical industry. Benzene is also known for its carcinogenic properties (it causes leukemia to highly exposed workers). Afterwards the starting material became cyclohexanone or a mixture of cyclohexanone and cyclohexanol. For the oxidation process it was used nitric acid, producing toxic fumes of nitric oxides, NOx, which are also contributors to the greenhouse effect and the destruction of the ozone layer in the stratosphere.

It was inevitable that the method had to be changed again with more environmentally benign reactions.

Finally, chemical engineers and synthetic organic chemists researched for alternatives. The —greener—method of adipic acid uses a new generation of catalysts. The starting chemical is cyclohexene and its oxidations performed by 30% hydrogen peroxide (H₂O₂). The catalyst is dissolved in a special organic solvent (Aliquat 336). The catalyst is a salt of the metal Tungsten(W). In the second method W salts are used which can be recycled. [Aliquat 336 (Stark's catalyst) is a mixture of octyl C8 and decyl C10 chains with C predominating. It is a quaternary ammonium salt used as a phase transfer catalyst and metal extraction reagent able to dissolve metal complexes].
Although the oxidation with H$_2$O$_2$ is very effective and environmentally benign, scientists improved the reaction with new metal catalysts. They are using Was oxpoeroxo Tungten complexes and Molybdnenium. With starting material cyclohexene or 1, 2-cyclohexanediol the yield is 45-86%.

Other scientists promoted the biocatalytic method of synthetic adipic acid from D-glucose. It is achieved with genetically transgenic bacteria Klebsiella pneumoniae, a non-toxic strain of Escherichia coli, (Enterobacteriaceae). The scientist who researched and applied the new biocatalytic synthesis of adipic acid was awarded the —Presidential Green Chemistry Challenge Awards Program in 1998 in the USA.

**Principle 4: Safer Chemicals Synthesis**

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. This principle is aimed at designing products that are safe, non-toxic and efficacious.

The World Wildlife Foundation (WWF) currently has a campaign to phase out the use of antifouling agents on ships. Large ships traditionally have used chemicals called organotin compounds to prevent accumulation of barnacles and marine plants which increase frictional resistance (drag) of foul ed ship hulls, structural deterioration (corrosion) of engineered materials, restricted flow through foul edaquaculture cage
netting, mechanical blockage of intake and outfall pipes, losses in heat-transfer efficiency of marine cooling systems, increased costs for maintaining all of the above.

**Case Study 1:** Organotin compounds—such as TBT—are considered being amongst the most toxic chemicals ever released into the marine environment. Even when present in the marine environment at very low concentrations, they have been shown to produce demonstrable negative impacts upon marine life. \(^3\) Organotin compounds particularly tributyl tin oxide (TBTO), are very effective as antifoulants and have been the antifoulant of choice for many years.

![Fig.5. Chemical Structure of Trybutyltin Oxide (TBTO).](image)

Although organotin compounds are effective antifoulants and have saved the shipping industry billions of dollars by reducing fuel consumption and reducing dry dock time, in the 1980's it was recognized that TBTO and other organotin antifoulants have relatively long half-lives in the environment (half-life of TBTO in seawater is > 6 months). Thus significant concentrations of these compounds can be found in ocean sediments as well as the water, and they tend to bioconcentrate in marine organisms. As a result of bio-concentration it is not uncommon for the concentration of TBTO in marine organisms to be \(10^4\) times greater than in the surrounding water.

Not only are organotins persistent pollutants, but they are also chronically toxic to marine life at high levels and may enter the food chain. It has been shown in particular that TBTO causes deformations in the thickness of oyster shells, sex changes in whelks and imposex in snails. In addition, the immune systems in dolphins, fish and other marine organisms may be compromised as a result of the bio-concentration of organotin compounds. Because of these environmental problems and concerns, organotin antifoulants are being phased out globally, with the IMO (International Maritime
Organization) in the process of banning the application of organotins as antifouling agents as of January 1, 2003. Japan has already banned the use of organotin antifoulants and in the United States the use of tributyltin in antifoulants has been severely restricted by the Organotin Antifouling Paint Control Act of 1988 (OAPCA).

Rohm and Haas has developed a non-toxic alternative, replacing the Organotin compounds with a product called Sea-Nine, a Green Chemistry Challenge Award winner in 1996. This product degrades quickly in the environment and does not bioaccumulate. It also has no chronic toxicity to the surrounding marine life. This antifoulant is which less harmful to the environment but with the same efficacy as organotins is called DCOI whose structure is as depicted below.

![DCOI structure](image)

These compounds rapidly degrade in the environment and partition to the sediment, non-hazardous at environmental concentrations, limited bioavailability, be toxic only to target organisms and result in minimum bio-concentration. It has a bio-concentration factor of only 13 as compared to 1500 for TBTO. Bio-concentration levels of 100 or more are generally considered to be of significantly toxic. It degrades to less toxic forms (Fig 9).

![Decomposition of DCOI](image)
Principle 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.

Many chemical reactions are done in a solvent. And, traditionally organic solvents have been used that pose hazards and many are highly toxic. They also create volatile organic compounds (VOC's) which add to pollution and can be highly hazardous to humans. This principle focuses on creating products in such a way so that they use less hazardous solvents.

Many solvents have been implicated in environmental damage such as ozone depleting chlorofluorocarbons and trichloroethane, smog producing Volatile Organic Compounds, and ground-water polluting trichloroethylene. Some solvents are implicated in human health effects and are in EPA’s list of toxic materials such as ethylene glycol ethers, chloroform, benzene, xylene, carbon tetrachloride, and toluene. Others are implicated in long term carcinogenicity such as methylene chloride. And many are flammable and/or corrosive.

Carbon dioxide as a supercritical fluid is most frequently used as medium for reactions. It is inflammable, easily available (from natural sources, from power engineering) and cheap. Its application gives considerable energy savings because the critical point is easy to reach due to a low evaporation heat of CO₂. Carbon dioxide as a supercritical fluid dissolves non-polar compounds and some polar (e.g. methanol, aceton) like fluorocarbon solvents. The discovery of a new surfactant with high surface activity in supercritical carbon dioxide opened a way to new processes in textile and metal industries and for dry cleaning of clothes. Micell Technologies Company offers technology for removal of stains using liquid carbon dioxide instead of the perchloroethylene more commonly applied. [4]

Fig. 10. Phase diagram showing supercritical fluid regions of CO₂.
While supercritical fluids in general exhibit interesting physical properties \[5\] specific interest in CO\(_2\) is magnified by its perceived "green" properties—carbon dioxide is non-flammable, relatively nontoxic, and relatively inert. In addition, unlike water, the supercritical regime of CO\(_2\) is readily accessible, given its critical temperature of only 304 K. CO\(_2\)’s critical pressure (and hence its vapor pressure in the "near-critical" or liquid regime) is significantly higher than analogous values for alkane, fluoroalkane or hydrofluoroalkane fluids. CO\(_2\)’s anomalously high critical pressure is but one result of the effect that CO\(_2\)’s strong quadrupole moment exerts on its physical properties. While the high critical pressure is problematic, the most unfortunate outcome of the effect of quadrupole moment on physical properties was the premise, first advanced during the late 1960s, that CO\(_2\) might prove to be a solvent whose strength would rival or surpass that of alkanes and ketones \[6\].

**Case Study 5:** The simultaneous use of both hydrogen and oxygen in a reaction is obviously problematic from a safety standpoint, given that H\(_2\)/O\(_2\) mixtures are explosive over a broad concentration range. Addition of CO\(_2\) to mixtures of H\(_2\) and O\(_2\) expands the non-explosive regime (in the gas phase), more so than if either N or water vapor was added. Because CO\(_2\) is inert towards oxidation and is also non-flammable, CO\(_2\) is one of the very few organic solvents that could be considered for the direct reaction of hydrogen and oxygen to form hydrogen peroxide. \[7\]

DuPont scientists discovered that addition of CO\(_2\) to tetrafluoroethylene enhances the stability of that notoriously difficult-to-handle monomer, although the exact mechanism for the enhanced stability has not been published. \[8\] What has been revealed is that addition of CO\(_2\) to TFE vapor inhibits runaway decomposition and explosion of the monomer. In addition, the CO\(_2\)/TFE mixture behaves like an azeotrope, in that boiling of a mixture of the two does not significantly change the concentration of either the liquid or the vapor. According to the DuPont patent, this "azeotropelike" behavior persists over a wide concentration range, behavior that is quite unlike that of typical azeotropic mixtures.

CO\(_2\) is generally immune to free radical chemistry. Because carbon dioxide does not support chain transfer to solvent during free-radically initiated polymerization, it is an ideal solvent for use in such polymerizations, despite the fact that it is typically a poor solvent for high molecular weight polymers. In chain transfer, a growing chain (with a terminal
radical) abstracts hydrogen from a solvent molecule, terminating the first chain. The solvent-based radical may or may not support further initiation, and hence chain transfer to solvent can lead to diminished molecular weight and diminished polymerization rate. Research conducted during the 1990s showed that CO\(_2\) does not support chain transfer, as it is inert towards polymer-based free radicals. Other researchers have examined small-molecule free radical chemistry in CO\(_2\) to be viable as well. Indeed, it is likely that most of the polymerizations currently conducted by DuPont in its semi-works facility are precipitation polymerizations, where the improved control over molecular weight and the enhanced safety inherent to use of TFE/CO mixtures more than makes up for any difficulties caused by polymer precipitation during the reactions.

CO\(_2\) is miscible with gases in all proportions above 304\(^\circ\)K. The rate of most processes where a gas reacts with a liquid is limited by the rate at which the gas diffuses to the active site (either within a catalyst particle or simply to the liquid reactant). Gases, such as hydrogen and oxygen, are poorly soluble in organic liquids and water and hence in many two- and three-phase reactors, the rate is limited specifically by the rate at which the gas diffuses across the gas–liquid interface. Although phase separation envelopes exist with gases at lower temperatures, liquid CO\(_2\) can absorb much higher quantities of H\(_2\) or O\(_2\) than typical organic solvents or water. Hence, one can eliminate the dependence of the rate on gas transport into the liquid phase by employing CO\(_2\).

CO\(_2\) exhibits a low dielectric constant. Carbon dioxide exhibits a dielectric constant of 2.2-2.5 in the liquid state; supercritical CO\(_2\) will exhibit values generally between 1.1 and 1.5, depending upon density. This low dielectric can be both a process disadvantage and a chemistry disadvantage. Some reactions, for example, require polar solvents for best results. Further, low dielectric constant also suggests poor solvent power, and hence solubility in CO\(_2\) can require much higher pressures for certain classes of solute than more polar compressible fluids (fluoroform, for example, which exhibits a liquid dielectric of \(~\)10).

**Principle 6: 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. If possible, synthetic methods should be conducted at ambient temperature and pressure. This principle focuses on creating products and materials...
in a highly efficient manner and reducing the energy associated with creating the products, therefore reducing associated pollution and cost.

Pollution reduction has been achieved through the use of catalytic technologies in the generation of clean fuels and chemicals. However, traditional preparation of the catalysts used generate large amounts of wastewater, utilize large amounts of energy and oftentimes generate nitrate and sulfate emissions which contribute to acid rain. Sud-Chemie, has developed an efficient method for manufacturing catalysts to be used in the generation of clean fuels and chemicals that has drastically decreased the amount of water and energy utilized. The new process also reduces emissions down to just pure water vapor and a small amount of $\text{CO}_2$. This technology won a Green Chemistry Challenge Award in 2003.

Principle 7: Renewable Feedstock
A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable. 90-95% of the products we use in our everyday lives are made from petroleum. Our society not only depends on petroleum for transportation and energy, but also formaking products. This principle seeks to shift our dependence on petroleum and to make products from renewable materials that can be gathered or harvested locally. Biodiesel is one example of this where researchers are trying to find alternative fuels that can be used for transportation. Another example is alternative, bio-based plastics. PLA (polylactic acid) is one plastic that is being made from renewable feedstocks such as corn and potato waste.

Case Study 7: From the point of view of green chemistry, combustion of fuels obtained from renewable feedstock is more preferable than combustion of fossil fuels from depleting finite sources.

For example, many vehicles around the world are fueled with diesel oil, and the production of biodiesel oil is a promising possibility. As the name indicates, biodiesel oil is produced from cultivated plants oil, e.g. from soya beans. It is synthesized from fats embedded in plant oils by removing the glycerine molecule (Fig. 11)-valuable raw material for soap production.
Biodiesel oil also can be obtained from wasted plant oils, e.g. oils used in restaurants. In the technological process, a potential waste product is transformed into valuable fuel. (Combusted biodiesel oil smells like fried potatoes.) The advantages of using biodiesel oil are obvious. It’s fuel from renewable resources and contrary to normal generates sulphur compounds and generally does not increase the amount of carbon dioxide in the atmosphere. CO2 formed in the combustion of fuel was removed earlier by plants from which biodiesel is produced. Asnake and Satishkumar in 2010 carried out cost benefit analysis of biodiesel from castor and jatropha seeds and found they are economically feasible over petro-diesel11.

8. Reduce Derivatives

Unnecessary derivatization (blocking group, protection/deprotection, and temporary modification of physical/chemical processes) should be avoided whenever possible. Because such steps require additional reagents and can generate waste. This principle is perhaps the most abstract principle for a non-chemist. The methods that chemists use to make products are sometimes highly sophisticated. And, many involve the manipulation of molecules in order to shape the molecules into what we want them to look like. This principle aims to simplify that process and to look at natural systems in order to design products in a simplified manner.

Case Study 8: A 2001 winner, Quasi-Nature Catalysis invented by Chao-Jun Li at Tulane University, enables “natural” catalytic reactions that are aqueous and at ambient conditions. It will help replace traditional use of transition metal catalysts in pharmaceuticals, fine chemicals, petrochemicals, agricultural chemicals, polymers, and plastics. A 2003 winner, lipase catalysts for polymerizations, developed by Richard Gross
of Polytechnic University, eliminates the need for protecting/deprotecting groups and solvents as well as enabling milder reaction conditions.

9. Catalysis
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. In a chemical process catalysts are used in order to reduce energy requirements and to make reactions happen more efficiently (and many times quicker). Another benefit of using a catalyst is that generally small amounts (catalytic amount versus a stoichiometric amount) are required to have an effect. And, if the catalyst is truly a —green‖ catalyst it will have little to no toxicity and it will be able to be used over-and-over again in the process.

In order to make transition state energies more accessible in a chemical transformation, the use of catalysts can be quite beneficial. There are countless examples of stoichiometric reactions that might have catalytic alternatives. Provided the catalyst employed is not orders of magnitude more toxic than the stoichiometric reagents they replace, their use will be quite beneficial.

Case Study 10: In 1999 the Academic Award in the Green Chemistry Challenge was given to the Collin’s group for the design of a benign oxidation catalyst called TAML. TAML catalysts are nontoxic iron-based catalysts that are being used to clean up wastewater streams in the pulp and paper industry. Environmental benefits include decreased energy requirements, elimination of chlorinated organics from the waste stream, and decreased water usage. The catalysts are also completely degradable into benign components. TAML Oxidant Activators provides an option for low temperature, chlorine-free means of bleaching important to both the Pulp and Paper industry as well as household laundering. They are currently being investigated as oxidation catalysts for many purposes involving wastewater treatment.

10. Design for Degradation
Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products. Not only do we want materials and products to come from renewable resources, but we would also like them to not persist in the environment. There is no question that many products we use in our daily lives are far too persistent. Plastics do not degrade in our landfills and
pharmaceutical drugs such as antibiotics build up in our water streams. This principle seeks to design products in such a way so that they perform their intended function and then, when appropriate, will degrade into safe, innocuous byproducts when they are disposed of.

**Case Study 10:** PYROCOOL developed a non-toxic, completely degradable fire-extinguishing and cooling agent. Traditional extinguishers have utilized halogens, ozone depleting chemicals, or fluorinated materials that leak into the environment harming aquatic systems and contaminating water supplies. The PYROCOOL extinguishers replace the traditional extinguishers that are just as effective in putting out fires and does not deplete the ozone layer or persist in the environment. This product won a Green Chemistry Challenge Award in 1998.

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. How long do they allow the reaction to run for? When do they know it will be —done? If there was a way to see inside the reaction and to know exactly when it would be done, then this would reduce waste in the process and ensure that your product is —done and is the right product that you intended to make.

**Case Study 11:** Quantitative determinations of contaminants and pollutants in the environment are another important aspect of analytical chemistry. Dr. Albert Robbat, Jr. of Tufts University has developed analytical methods for hazardous waste sites that enable quick and easy determinations and assessments. By designing mobile systems, the measurements can be made on-site and in a fraction of the time regular methods require. This also allows for a reduction in the amount of waste generated in operating the instruments. [12, 13, 14]

12. **Inherently Safer Chemistry for Accident Prevention**
Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires. This principle focuses on safety for the worker and the surrounding community where an industry resides. It is better to use materials and chemicals that will not explode, light onfire, ignite in air, etc. when making a product.
Novel solvents called ionic liquids are being developed by a number of research groups in Green Chemistry 14. Ionic liquids are liquids composed of ions, which have a very low vapor pressure and therefore are virtually non-volatile. They are being used for a number of purposes including as alternative solvents in organic synthesis15 and as a media to dissolve cellulose to be used for materials 16. Ionic liquids can be used to replace flammable and potentially explosive organic solvents, therefore drastically reducing the potential for accidents.

**Case Study 12:** Ionic liquids (ILs) have been accepted as a new green chemical revolution which excited both the academia and the chemical industries. This new chemical group can reduce the use of hazardous and polluting organic solvents due to their unique characteristics as well as taking part in various new syntheses. The terms room temperature ionic liquid (RTIL), nonaqueous ionic liquid, molten salt, liquid organic salt and fused salt have all been used to describe these salts in the liquid phase.

Researchers explained that ILs remain liquid at room temperature due to the reason that their ions do not pack well. Combination of bulky and asymmetrical cations and evenly shaped anions form a regular structure namely a liquid phase. As solvents, ILs possess several advantages over conventional organic solvents, which make them environmentally compatible.

ILs have the ability to dissolve many different organic, inorganic and organometallic materials. They are highly polar and consist of loosely coordinating bulky ions. They do not evaporate since they have very low vapor pressures. They are thermally stable. ILs have high thermal conductivity and a large electrochemical window. ILs are immiscible with many organic solvents. ILs are nonaqueous polar alternatives for phase transfer processes.

Two important groups of ILs are those based on imidazolium and pyridinium cations with PF6- and BF4- anions 15-17. Fig 12 illustrates the imidazolium and pyridinium derivatives of ILs and their possible anions which are extensively investigated in literature. ILs tend not to give off vapors in contrast to traditional organic solvents such as benzene, acetone, and toluene.
Although ILs are studied by a great number of research groups, there are still many questions that scientists are not able to answer. For example, one of the basic rules of chemistry — like dissolves like — seems to be broken by some ILs: Nonpolar benzene is up to 50% soluble (by volume) in polar tetrachloroaluminate-based ILs. Therefore, studies on why ILs are able to dissolve uncharged covalent molecules are continuing.

Barriers
Economic and Financial Barriers
There are also other financial barriers. Many chemical enterprises are highly capital intensive, and firms are reluctant to abandon their previous investments. The costs of shutting down an old, inefficient plant can be very high, leaving firms without the resources to then re-invest in new technologies. Building new chemical infrastructure can also be very expensive, and the high upfront costs can be a significant barrier to implementation of greener chemical processes. Depending on the sector, many operations that fall under the chemical umbrella fall under the commodities classification, or may not enjoy high enough margins to overcome the financial and economic barriers to change.

Regulatory Barriers
The significant growth in environmental regulations over time has had an important impact on the chemical enterprise. And given the increasing globalization of the chemical enterprise, many firms must also cope with regulations (which may differ significantly) in all of the nations where they produce and sell their products. While green chemistry is interested in reducing inherent risk through the reduction of hazard, most environmental, health and safety regulations focus instead on reducing risk through reductions in exposure. This means that many firms find themselves in situations where they must spend precious resources on regulatorily mandated, and often expensive, end-of-pipe
technologies, instead of investing in research and development to move towards inherently safer products and processes. The focus on risk control, rather than risk prevention, can be a serious barrier. Under control-oriented regulation, firms have little incentive to invest in prevention, and may be forced to divert resources to control instead.

**Technical Barriers**

The science behind green chemistry is often complex and multi-disciplinary. While the underlying chemistry has made great progress, there are many reactions and processes for which greener substitutes remain unknown. Even where academic or industrial research has devised a new reaction or synthetic pathway to a given chemical, this knowledge may not be readily available to the chemists within industry. Some of it remains in the firms that develop it, protected as trade secret for competitive advantage. Some of it is buried within the vast chemical literature, and may not even be labeled anywhere as being a—green—alternative. As of yet, there is no formal collection and dissemination (such as a large-scale green chemistry database), although the Green Chemistry Institute has started to work on this problem with its GreenChemEx database. But as of yet this is still very small, and does not solve the problem of a comprehensive reference.

**Organizational Barriers**

Within firms, the implementation of green chemistry can run into problems that are the result of the organization’s structure. For example, a division may be reluctant to change to a greener production process that may produce costs for their own bottom-line, even if the results benefits the firm as a whole, since this could negatively impact evaluations of the division’s performance. The same problem can occur even more locally, when a particular facility is reluctant to implement a change which would be good for a division overall, but that would be locally costly.

In general, green chemistry aims at designing of products and processes that reduce or eliminate the use and generation of hazardous substances. It targets pollution at the design stage, before it even begins. The Principles of Green Chemistry can be viewed as imperatives or directives that address alternative starting and target materials, alternative reagents and solvents, catalysts, and improved processes and process control. It encompasses —Benign by Design: Source Reduction Rather than End of Pipe”—24-26.
It means that as designers of molecules, materials, products, processes and systems, chemists play an important role in developing the future healthy chemicals economy. Besides, it addresses —Reducing Risk by Addressing the Hazard, Not Just Exposure”. That means, another reason for the chemistry community to pursue green chemistry (and green engineering) vigorously is because it is based on fundamental molecular science providing the root of the solutions, rather than on applying a bandage or patchwork approach to risk reduction.\textsuperscript{[27, 28]}

Frankly speaking, green chemistry is by far socially sound, economically feasible and/or environmentally friendly over the former red chemistry challenges. However, implementation of twelve principles of green chemistry comes across with different barriers-economic, financial, regulatory, organizational, technical and other more obstacles. The implementation needs participation of society via creating awareness of green chemistry principles merits. It also involves government to induce action of public and government sectors through making taxe incentives, land loan, carbon credit, infrastructure facilitating, crowning awards and so forth.

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REFERENCES


