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Green Chemistry and Environmentally Friendly Technologies: A Review

[1]Rajiv Dua, [1]Suman Shrivastava, [1]Suman Lata Shrivastava and [2]S.K. Srivastava

[1]Department of Chemistry, Govt. Post Graduate College, Guna (M.P.) 473001, India
[2]Department of Chemistry, Synthetic Organic Medicinal Chemistry Laboratory,
Dr.H.S. Gour University, Sagar (M.P.) India

Abstract: The principles of green chemistry guide firms in designing new products and processes in such a way that their impact on the environment is reduced. This article begins with an overview of green chemistry, including its development, its definition, its codification in principles of best practice and its ethical premises.

Key words: Green Chemistry · Atom Economy · Synthetic Efficiency · Sustainable Chemical Feedstocks · Green Solvents

INTRODUCTION

The "green chemistry" concept was introduced in the early 1990s in a special program launched by the US Environmental Protection Agency (EPA) and soon adopted by mass-media as the new approach of chemistry in opposition to the pollute-and-then-clean-up approach considered the common industrial practice.Their early definition of the subject is still widely quoted: *"'Green Chemistry' is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products".* However in practice 'Green Chemistry' is nowadays taken to cover a much broader range of issues than the definition suggests. As well as using and producing 'better' chemicals with less waste, 'Green Chemistry' also involves reducing other associated environmental impacts, in particular reducing the amount of energy used in chemical processes [1]. In 1995 President Bill Clinton established the *Presidential Green Chemistry Challenge Awards* to recognize chemical technologies that incorporate the principles of sustainable chemistry into chemical design, manufacture and use.

EPA identified the following main areas for green chemistry:

- Use of alternative synthetic pathways (examples, are natural processes such as photochemistry and biomimetic synthesis or alternative feedstocks that are more innocuous and renewable such as biomass).
- Alternative reaction conditions (examples are use of solvents that have a reduced impact on human health and the environment), or increased selectivity and reduced wastes and emissions.
- Design of eco-compatible chemicals (less toxic than current alternatives or inherently safer with regard to accident potential).

Ideally, the application of green chemistry principles and practice renders control, regulation, clean-up and remediation unnecessary and the resultant environmental benefit can be expressed in turns of economic impact [2].

It is science based non regulatory and economically driven approach to achieving the goals of environmental protection. The major difference between a green chemistry approach to environmental issues and more traditional approaches is that green chemistry utilizes the creativity of the scientists and engineers to develop novel and benign approaches to processes from the start rather than relying on regulatory restrictions after the process has been discovered to be toxic or polluting. Green chemistry is a tool for chemists, chemical engineers and others who design materials to help move society toward the goal of sustainability. Design at the molecular level allows decisions to be made that impact how materials will be processed, used and managed at the end of their life. Green chemistry principles were first published in the 1998 book "Green Chemistry: Theory and Practice," by Paul T. Anastas and John C. Warner, as a means to make the concepts of green chemistry accessible to the scientific community [3]. It is now being explored and used by many

Corresponding Author: Rajiv Dua, Department of Chemistry, Govt. Post Graduate College, Guna (M.P.) 473001, India.

countries including UK, Canada, Australia and Germany. Being one of the leading producers of pesticides and pharmaceutics, India has also realized the need to go green. Green chemistry methodologies can be viewed through the framework of the "Twelve Principles of Green Chemistry"

The 12 Principles of Green Chemistry: The 12 Principles focus on reducing the volumes of chemicals used and pollution prevention.

Waste Minimization and Prevention: It is better to prevent waste than to treat or clean up waste after it has been created. Generally speaking, waste minimization involves the reduction of waste toxicity by reducing the volume or quantity of highly toxic chemical constituents through substitution, recycling, recovery and reuse efforts. The old adage: ''An ounce of prevention is worth a pound of cure'' applies here. It is better to prevent waste than clean it up after-the-fact. Throughout history there have been many cases of environmental disasters such as Bhopal gas tragedy, India; The Love Canal disaster, New York; Times Beach, Missouri; Cuyahoga River, USA, The Exxon Valdez oil spill occurred in Prince William Sound, Alaska.

Waste Reduction Possibilities

Inputs

- eco friendly solvents, high purity reagents, recyclable auxiliaries, lass hazardous materials

Production

- change time, temperature and pressure, reactor types, mixing, heat transfer
- new route, appropriate cleaning

Discharges

- reduce water volume, improved scrubbers, waste water clean up, mineralization of organics

By-Products

- Maximise use, research and development, marketing, site integration

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

Atom economy answers the basic question, "How much of what you put into your pot ends up in your product?" The concept of Atom Economy was developed by Barry Trost of Stanford University (US), for which he received the Presidential Green Chemistry Challenge Award in 1998 which includes reducing the use of nonrenewable resources, minimizing the amount of waste and reducing the number of steps used to synthesize chemicals. It is a method of expressing how efficiently a particular reaction makes use of the reactant atoms [4].

The atom economy of a reaction can be calculated:

Atom economy % atom economy = $MW_{(desired\ products)} / MW_{(all\ reactants)} \times 100\ \%$

Reaction Yield

$$\%\ yield = \frac{(\text{Actual quantity of products achieved})}{(\text{Theoretical quantity of products achievable})} \times 100$$

Inefficient, wasteful processes have low atom economies. Efficient processes have high atom economies and are important for sustainable development, as they use fewer natural resources and create less waste.

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. Synthetic methodologies must be designed such that the chemicals used and by-product, if generated, are not or less harmful to human health and the environment. A better example is the formation of alkenes through more safe Grubbs catalyst produces very less waste in comparison with Witting reaction. Green chemistry can lead to dramatic changes in how we interact with chemicals on a daily basis as in the case of the 2005 Nobel Prize in Chemistry has been awarded to Yves Chauvin, Robert Grubb and Richard Schrock for theircontribution to the development of metathesis, an energetically favored and less hazardous method in organic synthesis [5]. Metathesis is used daily in the chemical industry, biotechnology, mainly in the development of pharmaceuticals and of advanced plastic materials. This represents a great step forward for "green chemistry", reducing potentially hazardous waste through smarter production.

Designing Safer Chemicals: Chemical products should be designed to affect their desired function while minimizing toxicity. The design of chemicals with minimal toxicity reduce the potential risk to human health and the environment; decrease the costs of production and site remediation; and increasing team commitment to workplace health and safety. For instance, prefer public transport instead of own vehicles, thereby mininising the CO_2 emission, use recyclable paper in order to minimize the burden on natural resource and also to lessen the amount of toxic products coming out after bleach during paper production. Develops efficient methods of converting solar energy into chemical energy and electrical energy to avoid the necessity of generating power from nuclear plants, which produces a lot of nuclear waste, gaseous emission and chemical pollutants.

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. The idea of "green" solvents expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production. Many organic solvents such as benzene, chloroform, toluene, carbon tetrachloride etc are volatile organic compounds (VOCs) and it means that their high volatility, very useful for industrial applications, contributes both to increase the risks of fire and explosion and to facilitate the release in the atmosphere in which these solvents can act as air pollutants causing ozone depletion, photochemical smog and global warming. In the interest of green chemistry, commonly used five main solvent systems which are currently considered as "green" are: (i) solventless systems, (ii) water, (iii) ionic liquids, (iv) fluorous solvents and (v) supercritical fluids. In 2005 Ryoji Noyori identified three key developments in green chemistry: use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations and the use of hydrogen in asymmetric synthesis [6]. Examples of applied green chemistry are supercritical water oxidation, on water reactions and dry media reactions.

Design for Energy Efficiency: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure. Rising consumption and heavy future demand on energy that is primarily generated from petroleum and depleting resources has raised serious concerns in the international community. The solution would not lie in digging in more deeper to use up all the available resources, instead it lies in designing energy efficient processes and generating alternative sources of energy production. In line with this, chemist can design reactions that could take place at moderate temperature using catalyst or other methods, thereby reducing more demand on energy.

Use of Renewable Feedstocks: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable. Renewable feedstocks are often made from agricultural products or from wastes of other processes; depleting feedstock are made from fossil fuels or are mined. Significant developments in using renewable feedstocks to make fuels and chemicals are blooming and efforts are being put in to produce organic chemicals; related products to be obtained from natural resources other than petroleum and depleting resources [7]. This is not a very novel field to mankind, because since long ethanol has been developed from variety of sources like sugarcane (molasses), beet roots, grapes etc. So, ethanol producers are looked at and examine which are developing alternative downstream products aside from fuel ethanol. Diesel is the commonest form of transportation fuel with a demand higher than for petrol. Jatropha curcus, the chosen feedstock, has been under intensive development over the past few years and the volume of planting is slowly beginning to approach levels whereby it can start to fulfill its promise as a key biodiesel feedstock [8].

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 [9]. Methylene chloride, a common solvent in organic synthesis, is a suspected carcinogen made from fossil fuel based raw materials. Methyl-tetrahydrofuran has been identified as an alternative with similar solvent properties that can be made from renewable, bio-based resources. Benzene used in the commercial sythesis of adipic acid which is required in the manufacture of nylon, placticizers and lubricants, has been replaced to some extent by the renewable and nontoxic glucose and the reaction is carried out in water.

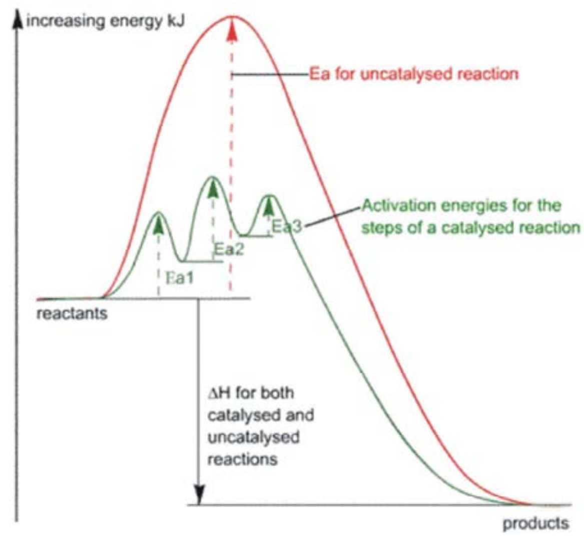
Biomass Conversion and Biorefinery

Inputs	Building	Outputs(Conversion
Corn	Starch	Butadiene
Potatoes	Cellulose	Organic acids
Sorghum	Lignin	Furfural
Apple pomace	Suberin	Resorcinol
Beet molasses	Chitin	Levulinic acid
Sugar cane	Oils & Glycerol	Levoglucosan
Wood Residues	Poly hydroxy alkanoate	Per acetic acid

Reduce Derivatives: Unnecessary derivatization (use of blocking groups, protection/deprotection and temporary modification of physical / chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste. In many traditional chemical reaction based routes, elegant multistep syntheses were designed that employed increasingly clever ‘‘protecting groups’’ that would temporarily block the reactivity of a specific functional group until a deprotecting group was introduced to remove it. Unnecessary derivatisation (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimised or avoided from an environmental impact perspective if possible, because such steps can generate more waste [10]. Once such process designed in the industry is in Polaroid films, where researchers sought to release hydroquinone at elevated pH, which being highly basic trends to cleave covalent protecting groups also. Hence, a non-covalent protecting group in the form of co-crystal was developed which minimized lot of waste thus making the process green.

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

Catalytic chemistry is one of the most important aspects of eco-friendly chemistry which promotes most of the green chemistry goals in terms of atom efficiency, lower energy use, higher yields, attaining high levels of selectivity at minimal waste through biocatalysis most of which is fast biodegradable and non polluting, decreased use of separating and processing agents and the activation of inert material, thereby reducing reliance on toxic materals.98,99 It is for this central role it plays that catalysis is referred to as a foundational pillar of green chemistry. Catalytic reagents also eliminate need of stoichiometric amounts of it in the reaction. An example of this includes use of noyori chirally catalyzed hydrogenation in place of Diisobutylaluminium hydride (DIBAL-H) [11]. The Grubbs Catalyst is often used in organic synthesis to achieve olefin cross-metathesis, ring-opening and ring-closing metathesis polymerization an energetically favoured and less hazardous method in organic synthesis [12].



New approaches in the design and development of second generation titanium oxide photo catalysts which can operate effectively under visible light and/or solar beam irradiation, have drawn attention to the vital need for totally new environmentally friendly, clean chemical technologies and processes, the most important challenge facing chemical scientists in the field of green chemistry [13].

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. 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 that they perform their intended function. Simple Green products are designed to provide cleaning function with chemicals that are nontoxic and biodegradable.The surfactants, chemicals that remove soil and suspend it in water, in

Simple Green are designed to maximize effective cleaning while minimizing health and environmental impacts. The cleaners are a milder alternative to traditional cleaning products, with less impact on the user and the environment. The use of a water solvent provides a safer alternative to the volatile hydrocarbon solvents typically used to remove grease and oil.

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. There are two aspects of this principle time and materials. Real time analysis for a chemist is the process of "checking the progress of chemical reactions as it happens." If better, more responsive monitors can be designed, then the use of ''just-in-time'' reagents and techniques can be employed to improve process yields, product consistency, use of raw materials that will minimize the environmental toll. Also there is a need to improve analytical techniques to consume less material. New chromatographic methods (HPLC) that use less solvent or do not require complex mixtures of solvents need to be developed.

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 Bhopal gas Tragedy (1984) in India is the worst reminder of an industrial tragedy, 40 tons of methyl isocyanate (MIC) was accidentally released when a holding tank overheated at a Union Carbide pesticide plant. Some diseases which became famous by the discharge of poisonous pollutants from the industries were Minamata disease (mercury poisoning), Itai-Itai Disease (cadmium poisoning), Methaemoglobinaemia (excessive amount of nitrogen fertilizers) etc.

Green Chemistry Principles into Practise

S.No	Principle	Examples
1.	Waste Minimization and Pre an Prevention	Sample preparation techniques,concentrating especially on the green advantages of so-called solvent less sample preparation.[14]
2.	Atom Economy	A Diels-Alder reaction is an example of a potentially very atom efficient reaction that also can be chemo-, regio-, diastereo-nd enantioselective.[15]
3.	Less Hazardous Chemical Syntheses	eplacement of amalgam cells (mercury containing) with polymer membranes in chlor-alkali industry.
4.	Designing Safer Chemicals	ea-nine antifoulant; an environmentally acceptable alternative to organotin antifoulants. [16]
5.	Safer Solvents and Auxiliaries	Usage of bio-solvents, supercritical fluids ionic liquid and solvent-less reactions. [17]
6.	Design for Energy Efficiency	Improving the energy efficiency of current polymerization systems through creating better stereospecific catalysts, biocatalytic eactions and condensation polymerization reactions [18]
7.	Renewable Feed stocks	Developments of new class of surfactants (sugar fatty acid esters) are readily biodegradable and is based on renewable resources. [19]
8.	Reduce Derivatives	Lipase catalysts for polymerizations, eliminates the need for protecting/deprotecting groups and solvents as well as enabling milder reaction conditions.[20]
9.	Catalysis	Use of mesoporous solid acids based on silica and sulfated zirconia in many important organic reactions.[21]
10.	Design for Degradation	Synthesis of Biodegradable surfactant (linear alkyl benzene sulphonate, alkyl phenol ethoxylates) and polymers (Polylactic acid; PLA).[22]
11.	Real-time analysis for Pollution Prevention	Green approaches to colorimetric monitoring of calcium in water.[23]
12.	Inherently Safer Chemistry for Accident Prevention	Dimethyl carbonate is ecofriendly than dimethyl sulfate and methyl chloride in methylation reaction. [24]

These principles reveal why green chemistry is unique within the field of chemistry: green chemistry is not just prescriptive but normative. The distinction between prescriptive and normative propositions is that prescriptive propositions do not depend on the value of the result, whereas normative propositions require a value judgment about the worthiness of the result.

Current State of Implementation of Green Chemistry: The Presidential Green Chemistry Challenge was established to recognize and promote innovative chemical technologies that prevent pollution and have broad applicability in industry. The Challenge is sponsored by the Office of Chemical Safety and Pollution Prevention of the United States Environmental Protection Agency (EPA) in partnership with the American Chemical Society Green Chemistry Institute and other members of the chemical community. EPA typically honors five winners each year, one in each of the following categories:

- Academia
- Small business
- Greener Synthetic Pathways, such as the use of innocuous and renewable feedstocks (e.g., biomass, natural oils); novel reagents or catalysts including biocatalysts and microorganisms; natural processes including fermentation and biomimetic syntheses; atom-economical syntheses; or convergent syntheses

- Greener Reaction Conditions, such as the replacement of hazardous solvents with greener solvents; solventless or solid-state reactions; improved energy efficiency; novel processing methods; or the elimination of energy-and material-intensive separations and purifications
- Designing Greener Chemicals, such as chemicals that are less toxic than current alternatives; inherently safer chemicals with regard to accident potential; chemicals recyclable or biodegradable after use; or chemicals safer for the atmosphere [25].

Collectively, these award-winning technologies have eliminated more than 1.3 billion pounds of hazardous chemicals and solvents, saved over 42 billion gallons of water and eliminated nearly 460 million pounds of carbon dioxide releases to air.

The research, development and implementation of green chemistry has already led to significant economic gains for many private firms with accompanying environmental, health and safety benefits for society. The breadth of Green Chemistry's applicability can be seen through its many areas of accomplishment spanning agriculture, energy, materials, electronics, automotive and consumer goods. Several industrial sectors have been true pioneers in their adoption of green chemistry principles by recreating the approach to designing the next generation of chemicals and materials. These include polymer manufacturers, textile producers and pharmaceuticals developers.

Some illustrative examples of Green Chemistry accomplishments include:

Categories	Winners	Innovation and Benefits
Year: 2011Academic Award	Bruce H. Lipshutz,	Developed a novel, second-generation surfactant called TPGS-750-M. It is a "designer" surfactant composed of safe, inexpensive ingredients: tocopherol (vitamin E), succinic acid and methoxy poly(ethylene glycol) (a common, degradable hydrophilic group also called MPEG-750). TPGS-750-M forms "nanomicelles" in water that are lipophilic on the inside and hydrophilic on the outside.
Small Business Award	BioAmber, Inc.	Integrated Production and Downstream Applications of Biobased Succinic Acid. BioAmber is producing succinic acid that is both renewable and lower cost by combining an *E. coli* biocatalyst licensed from the Department of Energy with a novel purification process. BioAmber's process uses 60 percent less energy than succinic acid made from fossil fuels, offers a smaller carbon footprint and costs 40 percent less.
Greener Synthetic Pathways Award	Genomatica	Production of High-Volume Chemicals from Renewable Feedstocks at Lower Cost. 1,4-Butanediol (BDO) is a high-volume chemical building block used to make many common polymers, such as spandex. Using sophisticated genetic engineering, Genomatica has developed a microbe that makes BDO by fermenting sugars.
Greener Reaction Conditions Award	Kraton Performance Polymers, Inc.	Developed NEXA polymer membrane technology for applications requiring high water or ion flux. NEXAR polymers are block copolymers with separate regions that provide strength (poly(*t*-butyl styrene)), toughness and flexibility (poly(ethylene-propylene)) and water or ion transport (styrene-sulfonated styrene).NEXAR polymers use up to 50 percent less hydrocarbon solvent and completely eliminates halogenated cosolvents.
Designing Greener Chemicals Award	The Sherwin-Williams Company	Developed water-based acrylic alkyd paints with low volatile organic compounds (VOCs) that can be made from recycled soda bottle plastic (PET), acrylics and soybean oil.
Year: 2010 Academic Award	James C. Liao, Easel Biotechnologies, LLC University of California, Los Angeles	Butanol, isobutanol and other C_{3-8} alcohols made from glucose or directly from CO_2 using genetically engineered microorganisms including photosynthetic microorganisms.
Small Business Award	LS9, Inc.	Engineered established industrial microorganisms convert fermentable sugar selectively to alkanes, olefins, fatty alcohols, or fatty esters; includes Ultra Clean Diesel fuel.
Greener Synthetic Pathways Award	The Dow Chemical Company BASF	Developed a new route to make propylene oxide with hydrogen peroxide that eliminates most of the waste and greatly reduces water and energy use.
Greener Reaction Conditions Award	Merck and Co., Inc. Codexis, Inc.	Developed a second-generation green synthesis of sitagliptin, the active ingredient in Januvia, a treatment for type 2 diabetes. This collaboration has lead to an enzymatic process that reduces waste, improves yield and safety and eliminates the need for a metal catalyst.
Designing Greener Chemicals Award	Clarke	Formulating spinosad and reduced risk pesticide that is unstable in water, within a plaster matrix creates a time-release pesticide for aqueous environments.
Year: 2009 Academic Award	Krzysztof Matyjaszewski, Carnegie Mellon University	Atom Transfer Radical Polymerization was developed for manufacturing polymers using environmentally friendly, such as ascorbic acid as a reducing agent, requires less catalyst and reduces risks from hazardous chemicals.
Small Business Award	Virent Energy Systems, Inc.	Gasoline, diesel and jet fuel made from sugars, starch, or cellulose by the BioForming process.
Greener Synthetic Pathways Award	Eastman Chemical Company	Immobilized enzymes, such as lipase, used to make a variety of esters for cosmetics and personal care products thereby saving energy and avoiding both strong acids and organic solvents.
Greener Reaction Conditions Award	CEM Corporation	Innovative Analyzer Tags Proteins for Fast, Accurate Results without Hazardous Chemicals or High Temperatures.
Designing Greener Chemicals Award	The Procter and Gamble Company Cook Composites and Polymers Company	Chempol alkyd resins and Sefose biobased oils used to reformulate alkyd paints and coatings with lower levels of volatile organic compounds
Year: 2008 Academic Award	Robert E. Maleczka, Jr. and Milton R. Smith, III, Michigan State University	Iridium catalysts used in a halogen-free synthesis of boronic esters, which are intermediates for many important, complex molecules
Small Business Award	SiGNa Chemistry, Inc.	Encapsulated sodium, lithium and other alkali metals maintain the reactivity of the metals but are safe to handle, store, transport and increasing their usefulness in a wide variety of synthetic reactions.

Continued

Some illustrative examples of Green Chemistry accomplishments include:

Categories	Winners	Innovation and Benefits
Greener Synthetic Pathways Award	Battelle	Biobased resins for toners used in laser printers and copiers are easily removed from paper making it easier to recycle
Greener Reaction Conditions Award	Nalco Company	Fluorescent-tagged molecules in the 3D TRASAR system detect the formation of mineral scale, microbial growth and corrosion in cooling water systems, minimizes the use of water-treatment chemicals and decreases environmental damage from discharged water
Designing Greener Chemicals Award	Dow AgroSciences LLC	Spinetoram, a new environmentally favorable insecticide, as a reduced-risk pesticide replacing organophosphate pesticides for use on many crops including pome fruit, stone fruit and tree nuts
Year: 2007 Academic Award	Michael J. Krische University of Texas at Austin	A class of chemical reactions makes bonds between carbon atoms using hydrogen and catalysts, with minimal waste.
Small Business Award	NovaSterilis Inc.	Terminal sterilization of allograft tissue, medical devices and biopolymers using supercritical CO_2 and peroxyacetic acid to replace hazardous ethylene oxide and gamma radiation
Greener Synthetic Pathways Award	Kaichang Li, Oregon State University; Columbia Forest Products; Hercules Incorporated	Wood adhesive made from soy flour replaces toxic urea-formaldehyde in manufactured wood products such as plywood, medium-density fiberboard and particleboard
Greener Reaction Conditions Award	Headwaters Technology Innovation	Hydrogen peroxide made directly from hydrogen and oxygen, by a selective nanocatalyst and without hazardous chemicals, can replace chlorine-containing bleaches and oxidants
Designing Greener Chemicals Award	Cargill, Incorporated	BiOH polyols made from renewable, biological sources replace petroleum-based polyols in flexible polyurethane foams
Year: 2006 Academic Award	Galen J. Suppes University of Missouri-Columbia	Process to convert glycerin, a waste product of biodiesel production, into propylene glycol, a higher-value product that can replace ethylene glycol in automotive antifreeze and lower the cost of biodiesel fuel thereby reducing emissions and conserving fossil fuels.
Small Business Award	Arkon Consultants NuPro Technologies, Inc.	Environmentally Safe Solvents and Reclamation in the Flexographic Printing Industry The new system eliminates hazardous solvents, reduces explosion potential and emissions during solvent recycling and increases worker safety in the flexographic printing industry
Greener Synthetic Pathways Award	Merck and Co., Inc.	Sitagliptin, the active ingredient in Januvia, used to treat type 2 diabetes, made by a novel green synthesis for ß-amino acids
Greener Reaction Conditions Award	Codexis, Inc.	Directed Evolution of Three Biocatalysts to Produce the Key Chiral Building Block for Atorvastatin, the Active Ingredient in Lipitor
Designing Greener Chemicals Award	S.C. Johnson and Son, Inc.	Green list process, a system that rates the environmental footprint of the ingredients within 17 functional categories, to reformulate consumer products
Year: 2005 Academic Award	Robin D. Rogers The University of Alabama	A Platform Strategy Using Ionic Liquids to Dissolve and Process Cellulose for Advanced New Materials which can potentially save resources, time and energy.
Small Business Award	Metabolix, Inc.	Bioplastics (polyhydroxyalkanoates) made within genetically engineered organisms replace petroleum-based plastics in a wide variety of uses. PHAs biodegrade to harmless products in the environment, reducing the burden of plastic waste on landfills and the environment
Greener Synthetic Pathways Award	Archer Daniels Midland Company Novozymes	Low Trans Fats and Oils Produced by Enzymatic Interesterification of Vegetable Oils Using Lipozyme, saves hundreds of millions of pounds of soybean and other vegetable oils, processing chemicals and water resources each year.
Greener Reaction Conditions Award	Merck and Co., Inc.	Aprepitant, the active ingredient in Emend, used to treat chemotherapy-induced nausea and vomiting, made by a convergent, highly atom-economical safer synthesis that also saves water
Greener Reaction Conditions Award	BASF Corporation	UV-curable, one-component, low-VOC primer free of diisocyanates for automotive refinishing that performs better than conventional urethane technologies
Designing Greener Chemicals Award	Archer Daniels Midland Company	Archer RC, a new biobased coalescent to replace traditional coalescents that are volatile organic compounds (VOCs).
Year: 2004 Academic Award	Charles A. Eckert, Charles L. Liotta. Georgia Institute of Technology	Supercritical carbon dioxide ($scCO_2$), near critical-water and CO_2-expanded liquids; tunable benign solvents that facilitate reactions with increased selectivity, no waste and facile separations
Small Business Award	Jeneil Biosurfactant Company	Rhamnolipid biosurfactant, a natural, low-toxicity alternative to synthetic surfactants made by soil bacteria using a simple fermentation.
Greener Synthetic Pathways Award	Bristol-Myers Squibb Company	Paclitaxel, the active ingredient in Taxol, used to treat ovarian and breast cancer, synthesized by plant cell fermentation
Greener Reaction Conditions Award	Buckman Laboratories International, Inc.	More efficient processing of recycled papers and the production of higher-quality paper using Optimyze to hydrolyze polyvinyl acetate and other major sticky contaminants of recycled paper
Designing Greener Chemicals Award	Engelhard Corporation (now BASF Corporation)	Coloring plastics with RightFit pigments: organic azo pigments in the red, orange and yellow range with brilliant colors, high color strength and good heat stability
Year: 2003 Academic Award	Richard A. Gross Polytechnic University	Reactive components of polyurethane coatings: polyol-polyesters made by immobilized yeast lipases
Small Business Award	AgraQuest, Inc.	Serenade, EPA-registered biofungicide, made by a naturally occurring bacterium.
Greener Synthetic Pathways Award	Süd-Chemie Inc.	Solid oxide catalysts made in a wastewater-free process produce clean fuels from natural gas, generate hydrogen from carbon monoxide and water and carry out other high-volume catalytic reactions.
Greener Reaction Conditions Award	DuPont	Sorona polyester, made from bioderived 1,3-propanediol, adds resilience and other beneficial characteristics to automotive upholstery or coatings
Designing Greener Chemicals Award	Shaw Industries, Inc.	EcoWorx carpet tiles for commercial applications: the nylon yarn and polyolefin backing can be separated after use, providing complete "cradle-to-cradle" recycling
Year: 2002Academic Award	Eric J. Beckman University of Pittsburgh	Detergents (polydimethylsiloxanes (PDMS), poly(ether carbonates) and acetate-functional polyethers) increase the solubility of many compounds in supercritical CO_2
Small Business Award	SC Fluids, Inc.	Supercritical CO_2 removes photoresist from semiconductor wafers, replacing hazardous solvents and corrosive chemicals
Greener Synthetic Pathways Award	Pfizer, Inc.	Sertraline, the active ingredient in Zoloft, used to treat depression, synthesized by a process that eliminates waste, reduces solvents and doubles overall product yield
Greener Reaction Conditions Award	Cargill Dow LLC (now NatureWorks LLC)	Solvent-free production of NatureWorks polylactic acid (PLA), a biobased plastic, overcomes previous economic hurdles to high-volume production

Continued

Some illustrative examples of Green Chemistry accomplishments include:

Categories	Winners	Innovation and Benefits
Designing Greener Chemicals Award	Chemical Specialties, Inc. (CSI) (now Viance)	ACQ Preserve®, an arsenic-and chromium-free wood preservative, registered by EPA as a pesticide for use in pressure treatment of wood products
Year: 2001 Academic Award	Chao-Jun Li Tulane University	Transition metal catalysts for carbon-carbon bond formation in air and water under ambient conditions that eliminate volatile solvents and generate less waste
Small Business Award	EDEN Bioscience Corporation	Messenger proteins: nontoxic, naturally occurring harpin proteins produced by fermentation, stimulate plant growth and defenses against disease and pests
Greener Synthetic Pathways Award	Bayer Corporation Bayer AG (technology acquired by LANXESS)	Baypure CX iminodisuccinate, a biodegradable, nontoxic chelating agent used in household and industrial cleaning formulations
Greener Reaction Conditions Award	Novozymes North America, Inc.	Cotton wax from cotton fiber, yarn and fabric is removed by BioPreparation enzyme technology in preparation for dyeing and finishing the cotton; this technology eliminates corrosive chemicals and saves water
Designing Greener Chemicals Award	PPG Industries	Corrosion-resistant electrodeposition coatings, used primarily in the automotive industry, contain yttrium instead of lead
Year: 2000 Academic Award	Chi-Huey Wong The Scripps Research Institute	Enzymes and environmentally acceptable solvents replace traditional reactions requiring toxic metals and hazardous solvents; enzymes also enable otherwise impossible or impractical reactions
Small Business Award	Rev Tech, Inc.	Envirogluv process: solvent-and heavy metal-free, UV-cured inks for decorating glass bottles and ceramic ware, such as for beverages and cosmetics
Greener Synthetic Pathways Award	Roche Colorado Corporation	Ganciclovir, the active ingredient in Cytovene, a potent antiviral agent, synthesized by the Guanine Triester Process, eliminates two hazardous solid waste streams and 11 chemicals
Greener Reaction Conditions Award	Bayer Corporation Bayer AG	Two-component waterborne polyurethane coatings provide soft, leather-like coatings for hard plastic interior automobile surfaces such as instrument panels
Designing Greener Chemicals Award	Dow AgroSciences LLC	Sentricon termite colony elimination system (active ingredient: hexaflumuron), registered by EPA as a reduced-risk pesticide
Year: 1999 Academic Award	Terry Collins Carnegie Mellon University	Transfer of dyes between fabrics during laundering may be prevented by TAML catalysts and peroxide; TAML catalysts also enhance stain removal and allow washing machines to use less water and energy
Small Business Award	Biofine, Inc. (now BioMetics, Inc.)	Levulinic acid, a building block for more than a dozen commodity chemicals, is synthesized by high-temperature, dilute-acid hydrolysis of cellulosic biomass
Greener Synthetic Pathways Award	Lilly Research Laboratories	A drug candidate for the treatment of epilepsy, synthesized by a process including a yeast-mediated asymmetric reaction that eliminates chromium waste and large volumes of solvent
Greener Reaction Conditions Award	Nalco Chemical Company	Wastewater streams treated with polyacrylates dispersed in aqueous ammonium sulfate, eliminating hydrocarbon solvent and surfactants required in traditional emulsion polymerizations
Designing Greener Chemicals Award	Dow AgroSciences LLC	Spinosad, a highly selective, environmentally friendly insecticide made by a soil microorganism, does not persist in the environment; low toxicity to mammals and birds.
Year: 1998 Academic Award	Barry M. Trost Stanford University Dr. Karen M. Draths, John W. Frost Michigan State University	Atom economy: maximizing the incorporation of atoms from the starting materials into the reaction product, thus minimizing both hazardous and other waste Catechol is a feedstock for some major pesticides; genetically manipulated microbes convert glucose to catechol, replacing the traditional synthesis of catechol from petroleum-derived benzene
Small Business Award	PyROCOOL Technologies, Inc.	Pyrocool fire extinguishing foam, a highly effective formulation of biodegradable surfactants: less toxic than alternatives, inherently safer to use, far less potential for environmental damage
Greener Synthetic Pathways Award	Flexsys America L.P.	-Aminodiphenylamine, a key intermediate for a rubber preservative, is synthesized without using chlorine
Greener Reaction Conditions Award	Argonne National Laboratory	Ethyl lactate potentially replaces hazardous petroleum-derived solvents in electronics manufacturing and many other applications due to its favorable economics
Designing Greener Chemicals Award	Rohm and Haas Company (now The Dow Chemical Company)	Diacylhydrazines, a class of insecticides that disrupts molting in target species, contained in Confirm™, MACH, and INTREPID; registered by EPA as reduced-risk pesticides
Year: 1997 Academic Award	Joseph M. DeSimone University of North Carolina at Chapel Hill (UNC) and North Carolina State University (NCSU)	Garment cleaning in liquid or supercritical carbon dioxide ($scCO_2$) made possible by surfactants that greatly increase the solubility of many other substances in CO_2; this cleaning system replaces hazardous solvents
Small Business Award	Legacy Systems, Inc.	Coldstrip, an environmentally friendly, wet cleaning technology for the semiconductor, flat panel display and micromachining industries, replaces highly corrosive Piranha solutions
Greener Synthetic Pathways Award	BHC Company (now BASF Corporation)	Ibuprofen, the active ingredient in Advil™, Motrin™ and other over-the-counter pain relievers, synthesized in three catalytic steps with virtually no wasted atoms
Greener Reaction Conditions Award	Imation (technology acquired by Eastman Kodak Company)	Medical imaging using DryView photothermographic technology to replace silver halide photographic films and other hazardous photographic chemicals
Designing Greener Chemicals Award	Albright and Wilson Americas (now Rhodia)	Tetrakis (hydroxymethyl) phosphonium sulfate (THPS) a biodegradable, less-toxic biocide, a class of antimicrobial chemicals with low overall toxicity and rapid breakdown in the environment
Year: 1996 Academic Award	Mark Holtzapple Texas A and M University	Sea-Nine marine antifoulant, the first new antifoulant, replaces persistent, bioaccumulative and toxic tin-containing antifoulants
Small Business Award	Donlar Corporation (now NanoChem Solutions, Inc.)	Biodegradable thermal polyaspartic acid (TPA) replaces nonbiodegradable polyacrylates, increasing a plant's ability to take up nutrients and improving crop yields
Greener Synthetic Pathways Award	Monsanto Company	Redesigned synthesis of disodium iminodiacetate (DSIDA) eliminates cyanide, formaldehyde and ammonia; DSIDA is the key intermediate in Roundup herbicide, registered by EPA
Greener Reaction Conditions Award	The Dow Chemical Company	Polystyrene foam sheet made with 100 percent carbon dioxide as the blowing agent, replacing chlorofluorocarbons (CFCs) or flammable hydrocarbons
Designing Greener Chemicals Award	Rohm and Haas Company (now The Dow Chemical Company)	Sea-Nine marine antifoulant, the first new antifoulant replaces persistent, bioaccumulative and toxic tin-containing antifoulants

CONCLUSION

To combine the technological progress with the safeguard of the environment is one of the challenges of the new millennium. Chemists will play a key role in the realization of the conditions for a sustainable development and green chemistry may be their winning strategy.

Green chemistry addresses such challenges by inventing novel reactions that can maximize the desired products and minimize by-products, designing new synthetic schemes and apparati that can simplify operations in chemical productions and seeking greener solvents that are inherently environmentally and ecologically benign.

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