Green Chemistry for a Sustainable Future

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ABSTRACT

For more than three decades, Green Chemistry has provided a framework for chemists and chemical engineers to do their part in contributing to the broad scope of global sustainability. American Chemical Society journals are a great venue for these scientists to share their latest results and provide a resource to the chemistry community and beyond for understanding current problems and envisioning solutions. Sustainability in organic chemistry, especially in organic synthesis, has been driving innovation for decades. With the amount of waste generated in many synthetic chemistry routes, especially at scale in manufacturing, we are faced with not only an ethical imperative to develop more sustainable chemical processes and products but also a financial imperative. Metrics to gauge our progress, including process mass intensity (PMI), have been developed that allow all aspects of a process to be compared. For example, conducting a reaction in water may not necessarily be an improvement if several volumes of an organic solvent are needed to extract/purify the product. One could even argue that water can be problematic because its high boiling point makes recycling energy intensive, but we do not know these details without consciously thinking about them. A recent perspective highlights the need to explicitly include the assessment of sustainability using Green Chemistry metrics.

KEYWORDS: *green chemistry, sustainable, economy, waste, global, manufacturing, metrics, recycling*

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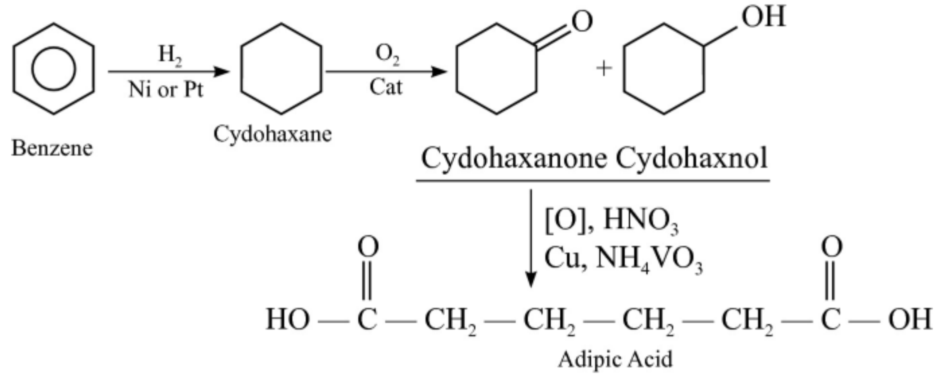
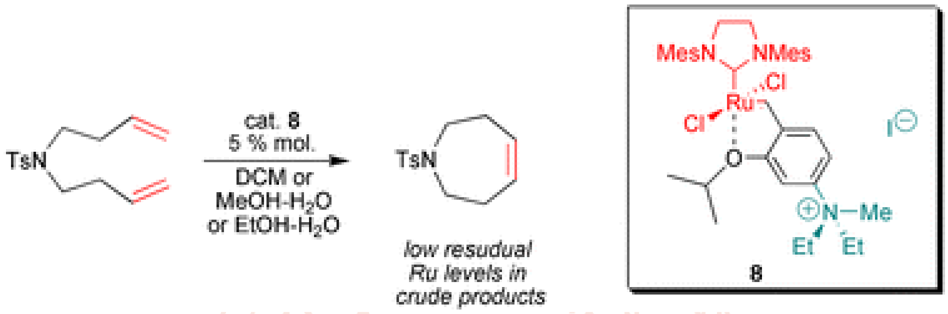
INTRODUCTION

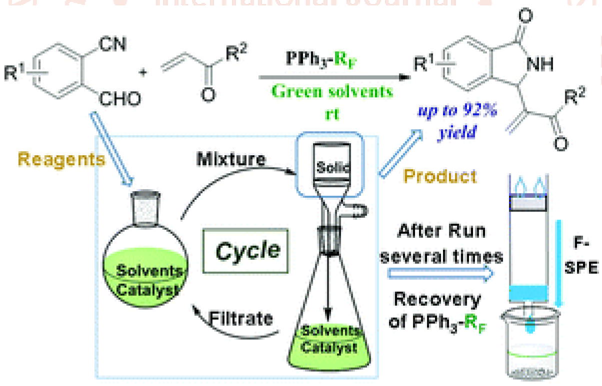
Sustainable development is one of the most frequently used terms in today's political debate. Our current understanding of sustainable development as a regulatory idea was basically defined by the Agenda 21: "Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs." As a consequence, all our individual and political actions should be reflected in the light of their societal, economical and ecological sustainability. This claim concerns every field of society, among them particularly chemistry and chemistry education. Both fields should reflect on how chemistry and chemistry education can contribute to more sustainability in our society, today and in future. One of chemistry's contributions to meeting the challenge of more sustainability in the development of our society is the promotion of a sustainable chemistry, in research and industrial production. Under the name of green chemistry (or in Europe also sustainable chemistry) a lot of effort has been undertaken to make future chemistry less poisonous and less hazardous. Green chemistry aims at making chemistry more energy efficient, at reducing waste disposal, and/or producing innovative products with less consumption of natural resources. Alternative processes and reaction pathways are designed, new materials and products are developed contributing to meet our needs today, but with taking more care of the interests of future generations.[1,2]



Modern chemistry education is challenged by both the political aim of a sustainable development of our society in general as well from the call for green chemistry strategies in chemical research and industry in particular. School chemistry education should promote competencies of the young generation to become scientifically literate.



Environmentally benign access to isoindolinones: synthesis, separation and resource recycling - Green Chemistry

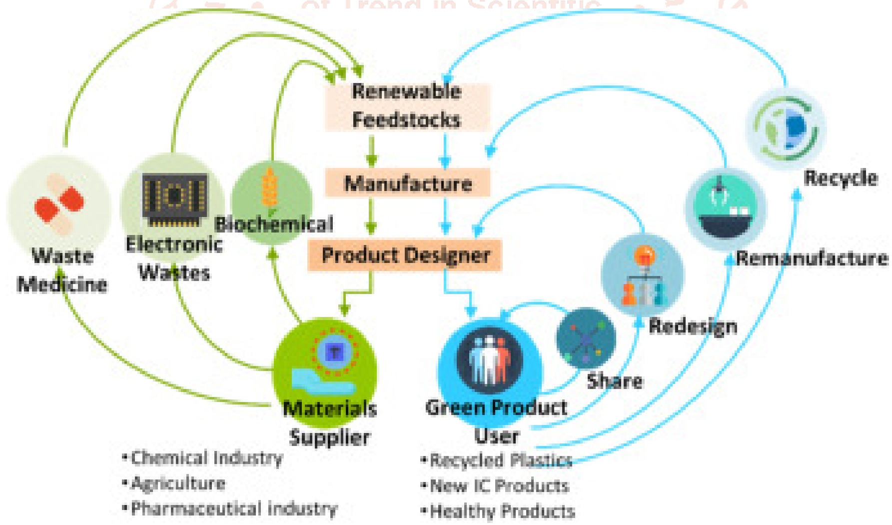


This means chemistry education has to contribute to making students capable of actively participating in society. Competencies need to be promoted to allow students to understand and participate in societal debate about applications of chemistry and technology. One prerequisite is that students should achieve substantial chemistry knowledge in the context of respective sustainability issues to understand the underlying developments, alternatives and dilemmas. But, subject matter knowledge will not be enough. The students as future citizens also need to learn how societal debate about questions related to chemistry, industry and the environment functions as well as develop skills to involve themselves together with others in the societal processes of democratic decision making.[3,4]

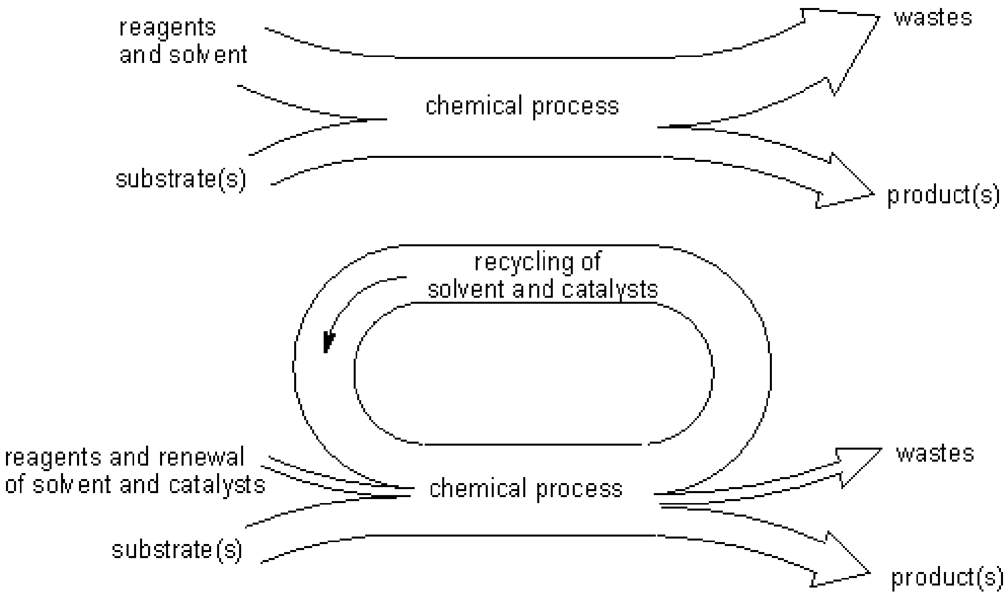
Potential points include:

- Sustainable bio production of safer chemicals from food waste
- Bioconversion of food waste into environmentally friendly reagents
- Production, importation, utilization, development, adoption, and disposal of safer chemicals
- Risk assessment and management associated with human health effects from chemical reagents
- Green chemistry application to manage water engineering and water quality
- Environmental chemistry approaches for pollution and accident prevention, safety and resource sustainability, and energy and resource sustainability
- Management of local, regional, and global impacts of air pollutants, including SOX, NOX, PM10/2.5, and trace metals, with the design and implementation of safer chemicals, materials, and products
- Environmental pollution and conservation, along with economic development, based on green chemistry
- Regulatory aspects and hierarchy concepts of chemical waste management and pollution prevention principles, utilizing knowledge of treatment, storage, and disposal facilities
- State and federal agencies that govern the role of chemical technology in the industrialization of developed and developing countries
- Efficient use of natural resources through the utilization of renewable feed stocks

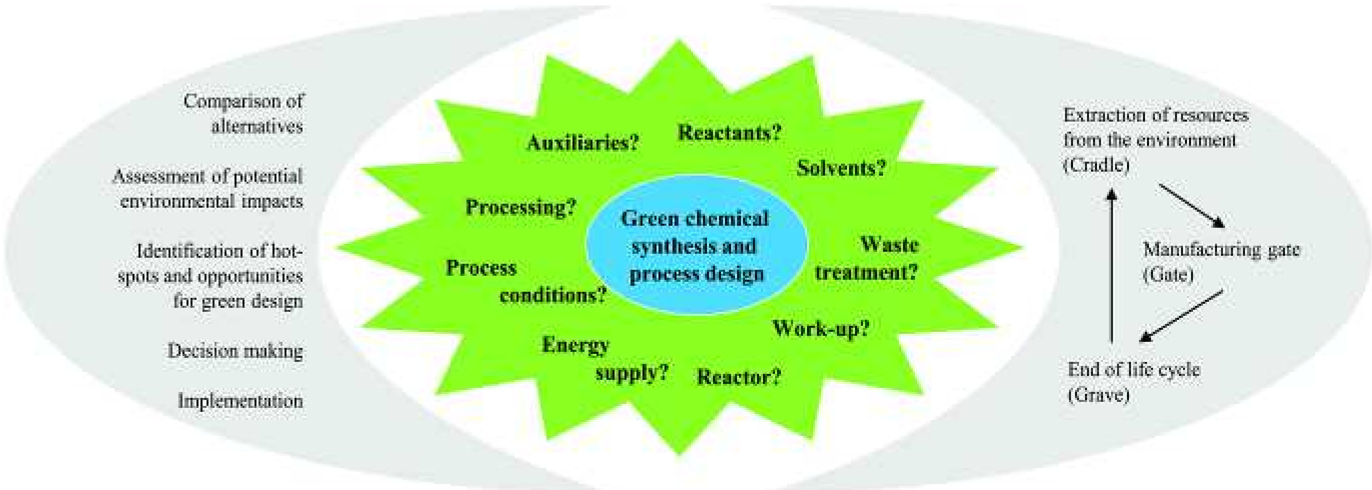
Green chemistry is the design of high-performing, cost-effective technology that is safer for the environment and human health.[5,6]



"We're in a world where it's unequivocal that there are hazardous materials in commerce," he says. "There are carcinogens, endocrine disruptors, neurotoxins. There are materials that are causing global climate change and ozone depletion. As a first step, we have to accept that these things are out there." The next step, Warner attests, is to assess how we got to this point in the first place. "Let's assume that there are no monsters in the world," Warner says. "Let's assume this really isn't an epic battle of good and evil." No scientist sets out to invent a red pigment that causes cancer. No company prizes a plastic additive that can lead to birth defects over a safer alternative. Why, then, do we continue to bring hazardous materials to market? The current state of regulation is one problem (we'll get to that later). But Warner says that the crux of the issue lies in what chemists are taught—or rather not taught—in school. Warner arrived at this revelation through personal tragedy. In the 1990s, he was a decade into his career as an industrial chemist. He had over 2,500 synthesized compounds to his credit, when a rare birth defect led to the death of his two-year-old son. In grief, he was left to wonder about the chemicals he'd created. Could any have contributed to his son's illness? Not once in his many years in school, including a PhD program at Princeton, did Warner take a course in toxicology. He hadn't studied how molecules persist in the environment. Today, nearly three decades later, such topics remain absent from core chemistry curricula in the United States. "Pick up any organic chemistry textbook and compare it to one from 1980, [7,8] and I challenge you to find a significant difference," he says. You won't even find references to the chemical transformations that drive many industries today. "How in the world can we ask the inventors of technology to make safe material if it's not part of how they've learned to do chemistry?" Warner asks. "This is not an issue of desire. It's an issue of ability."[9,10]



Important examples of green chemistry include: phasing out the use of chlorofluorocarbons (CFCs) in refrigerants, which have played a role in creating the ozone hole; developing more efficient ways of making pharmaceuticals, including the well-known painkiller ibuprofen and chemotherapy drug Taxol; and developing cheaper, more efficient solar cells.



Making chemical compounds, particularly organic molecules (composed predominantly of carbon and hydrogen atoms), is the basis of vast multinational industries from perfumes to plastics, farming to fabric, and dyes to drugs. In a perfect world, these would be prepared from inexpensive, renewable sources in one practical, efficient, safe and environmentally benign chemical reaction. Unfortunately, with the exception of the chemical processes found in nature, the majority of chemical processes are not completely efficient, require multiple reaction steps and generate hazardous by-products. [11,12]

While in the past traditional waste management strategies focused only on the disposal of toxic by-products, today efforts have shifted to eliminating waste from the outset by making chemical reactions more efficient.

This adjustment has, in part, led to the advent of more sophisticated and effective catalytic reactions, which reduce the amount of waste. The 2001 Chemistry Nobel Laureate Ryoji Noyori stressed that catalytic processes represent "the only methods that offer the rational means of producing useful compounds in an economical, energy-saving and environmentally benign way".

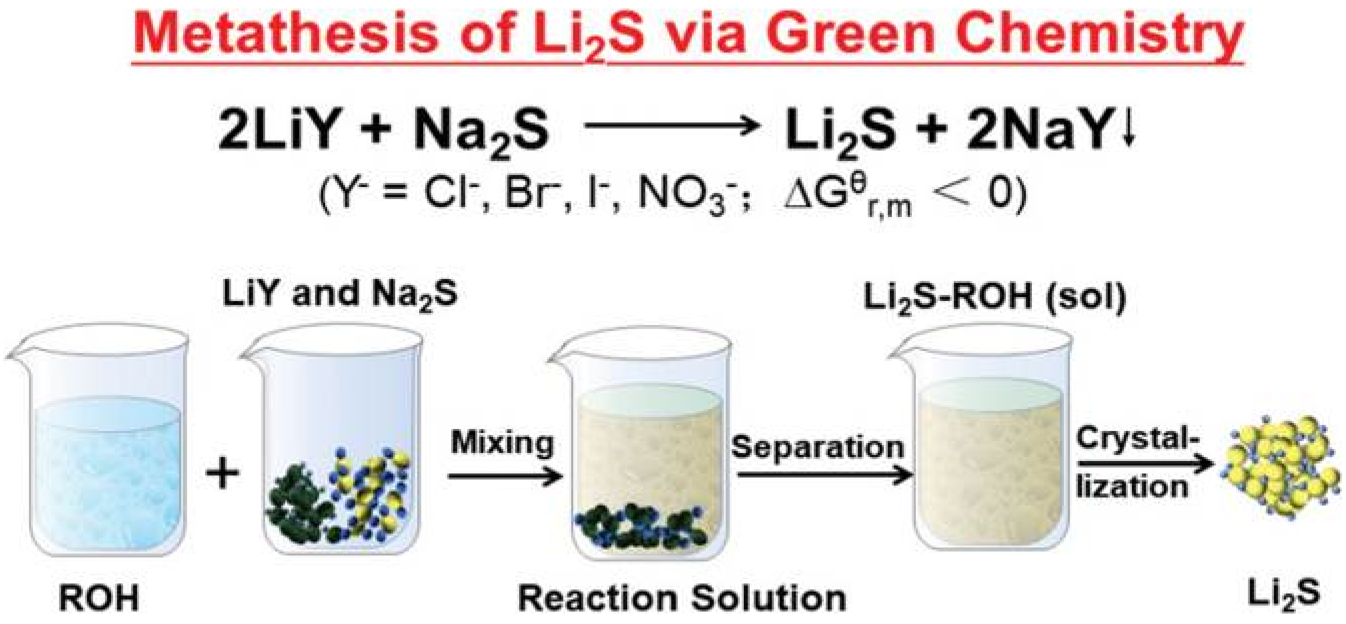
Green chemistry will be one of the most important fields in the future. Although this field has developed rapidly in the last 20 years, it is still at an early stage. Promoting green chemistry is a long-term task, and many challenging scientific and technological issues need to be resolved; these are related to chemistry, material science, engineering, environmental science, physics and biology. Scientists, engineers and industrialists should work together to promote the development of this field. There is no doubt that the development and implementation of green chemistry will contribute greatly to the sustainable development of our society.[13,14]

Discussion

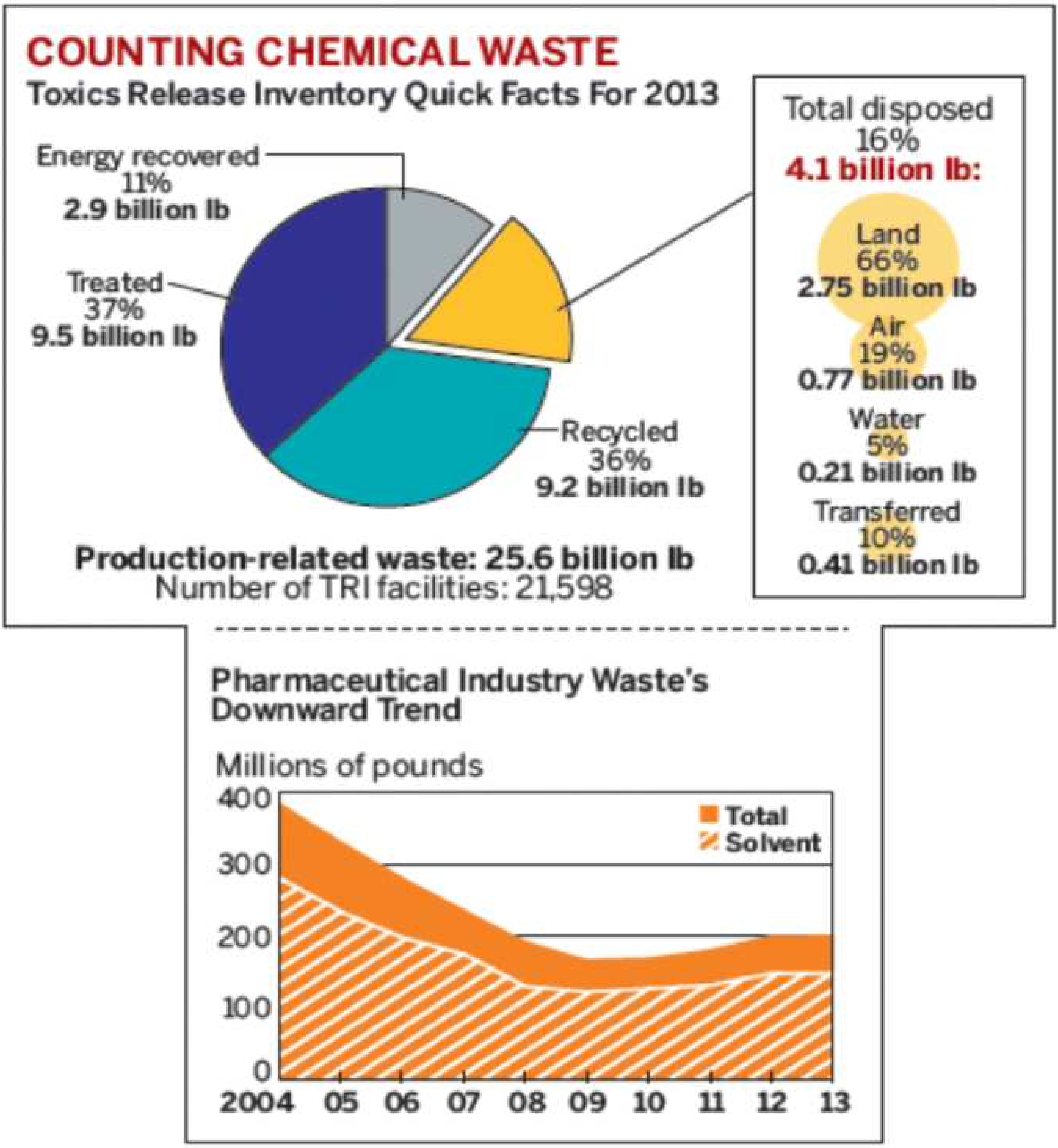
Principles of Green Chemistry

1. Prevention: It is better to prevent waste than to treat or clean up waste after it has been created.
2. Atom Economy: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Less Hazardous: Chemical Syntheses Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Designing Safer Chemicals: Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. Safer Solvents and Auxiliaries: The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used
6. Design for Energy Efficiency: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. Use of Renewable Feedstock: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. Reduce Derivatives: Unnecessary derivatization (use of blocking groups, protection/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.
9. Catalysis: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Design for Degradation: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. Real-time analysis for Pollution Prevention: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Inherently Safer Chemistry for Accident Prevention: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

Sustainable chemistry also embraces environmental chemistry, whereby fundamental chemical concepts such as the p-block elements – C, N, O, P and S – are termed 'nutrients' and 'salts' are responsible for 'salinity' of soils and surface waters. Pollutants disturb the natural nutrient cycles and salinity reduces soil and freshwater quality with overall degradation of the natural environment. Similarly, increasing acidity of rivers and oceans disturbs aquatic ecosystems and is a direct consequence of increased levels of carbon dioxide in the atmosphere. Furthermore, increasing toxicity of the environment due to chemical waste in soils, air and surface waters is of greatest concern in terms of addressing environmental sustainability.[15,16]



Sustainable chemistry intuitively involves engagement with the generation of new smart materials, and hence, with nanotechnology and its envisaged linkages to global clean energy requirements. The rapidly advancing nano-chemistry is perhaps the most significant exemplar of leading edge sustainable chemistry with its focus on the development of new smart materials for energy storage, production and conversion, for advancing agricultural productivity, water purification and desalination food processing, building construction, health monitoring and for pest control. Of these applications, rapid advancement in the production of photo-voltaic devices and carbon nano-tube solar cells is accelerating the solar energy industry. Similarly, the development of nano-catalysts for hydrogen production, coupled with carbon nano-tube hydrogen storage systems are promoting hydrogen as a viable, alternative clean energy resource. Thus, sustainable chemistry via nano-chemistry directly engages with environmental sustainability by providing processes and products which directly benefit humanity without harming the environment.[17,18]



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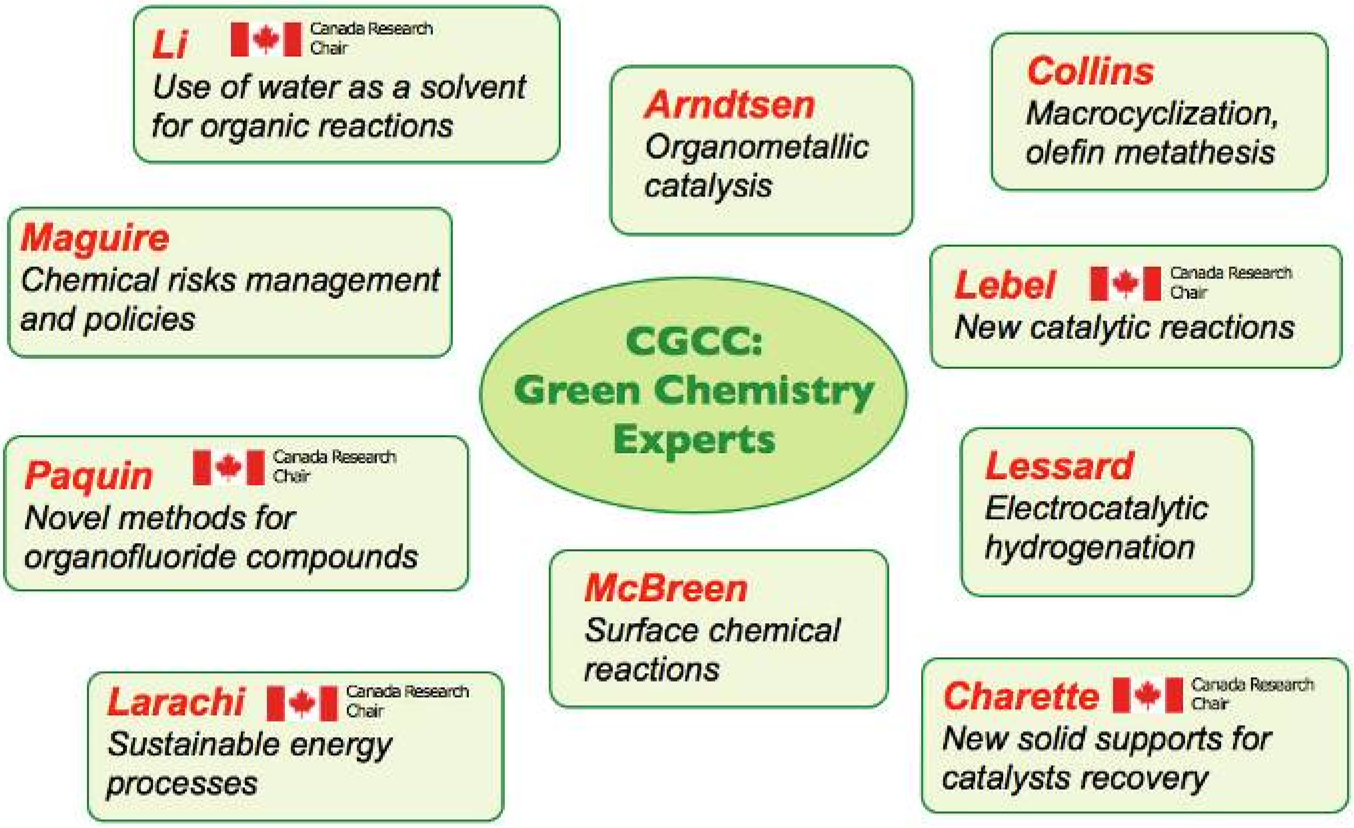
Attempts are being made not only to quantify the greenness of a chemical process but also to factor in other variables such as chemical yield, the price of reaction components, safety in handling chemicals, hardware demands, energy profile and ease of product workup and purification. In one quantitative study, the reduction of nitrobenzene to aniline receives 64 points out of 100 marking it as an acceptable synthesis overall whereas a synthesis of an amide using HMDS is only described as adequate with a combined 32 points.

Green chemistry is increasingly seen as a powerful tool that researchers must use to evaluate the environmental impact of nanotechnology. As nano materials are developed, the environmental and human health impacts of both the products themselves and the processes to make them must be considered to ensure their long-term economic viability. There is a trend of nano material technology in the practice, however, people ignored the potential nanotoxicity. Therefore, people need to address further consideration on legal, ethical, safety, and regulatory issues associated with nanomaterials [19]



In 1996, Dow Chemical won the 1996 Greener Reaction Conditions award for their 100% carbon dioxide blowing agent for polystyrene foam production. Polystyrene foam is a common material used in packing and food transportation. Seven hundred million pounds are produced each year in the United States alone. Traditionally, CFC and other ozone-depleting chemicals were used in the production process of the foam sheets, presenting a serious environmental hazard. Flammable, explosive, and, in some cases toxic hydrocarbons have also been used as CFC replacements, but they present their own problems. Dow Chemical discovered that supercritical carbon dioxide works equally as well as a blowing agent, without the need for hazardous substances, allowing the polystyrene to be more easily recycled. The CO_2 used in the process is reused from other industries, so the net carbon released from the process is zero.

Addressing principle #2 is the Peroxide Process for producing hydrazine without cogenerating salt. Hydrazine is traditionally produced by the Olin Raschig process from sodium hypochlorite (the active ingredient in many bleaches) and ammonia. The net reaction produces one equivalent of sodium chloride for every equivalent of the targeted product hydrazine:[27]

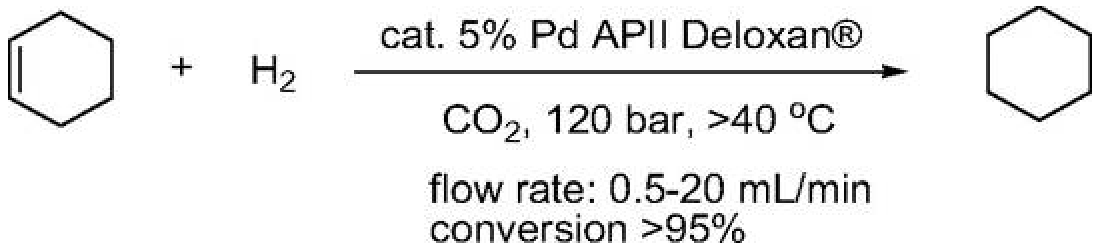
$$NaOCl + 2\ NH_3 \rightarrow H_2N\text{-}NH_2 + NaCl + H_2O$$

In the greener Peroxide process hydrogen peroxide is employed as the oxidant and the side product is water. The net conversion follows:

$$2\ NH_3 + H_2O_2 \rightarrow H_2N\text{-}NH_2 + 2\ H_2O$$

Addressing principle #4, this process does not require auxiliary extracting solvents. Methyl ethyl ketone is used as a carrier for the hydrazine, the intermediate ketazine phase separates from the reaction mixture, facilitating workup without the need of an extracting solvent.

In 2002, Cargill Dow (now Nature Works) won the Greener Reaction Conditions Award for their improved method for polymerization of polylactic acid . Unfortunately, lactide-base polymers do not perform well and the project was discontinued by Dow soon after the award. Lactic acid is produced by fermenting corn and converted to lactide, the cyclic dimer ester of lactic acid using an efficient, tin-catalyzed cyclization. The L,L-lactide enantiomer is isolated by distillation and polymerized in the melt to make a crystallizable polymer, which has some applications including textiles and apparel, cutlery, and food packaging. Wal-Mart has announced that it is using/will use PLA for its produce packaging. The Nature Works PLA process substitutes renewable materials for petroleum feedstocks, doesn't require the use of hazardous organic solvents typical in other PLA processes, and results in a high-quality polymer that is recyclable and compostable.[20]



In 2003 Shaw Industries selected a combination of polyolefin resins as the base polymer of choice for Eco Worx due to the low toxicity of its feed stocks, superior adhesion properties, dimensional stability, and its ability to be recycled. The EcoWorx compound also had to be designed to be compatible with nylon carpet fiber. Although EcoWorx may be recovered from any fiber type, nylon-6 provides a significant advantage. Polyolefins are compatible with known nylon-6 depolymerization methods. PVC interferes with those processes. Nylon-6 chemistry is well-known and not addressed in first-generation production. From its inception, EcoWorx met all of the design criteria necessary to satisfy the needs of the marketplace from a performance, health, and environmental standpoint. Research indicated that separation of the fiber and backing through elutriation, grinding, and air separation proved to be the best way to recover the face and backing components, but an infrastructure for returning postconsumer EcoWorx to the elutriation process was necessary. Research also indicated that the postconsumer carpet tile had a positive economic value at the end of its useful life. EcoWorx is recognized by MBDC as a certified cradle-to-cradle design.

In 2005, Archer Daniels Midland (ADM) and Novozymes won the Greener Synthetic Pathways Award for their enzyme interesterification process. In response to the U.S. Food and Drug Administration (FDA) mandated labeling of trans-fats on nutritional information by January 1, 2006, Novozymes and ADM worked together to develop a clean, enzymatic process for the interesterification of oils and fats by interchanging saturated and unsaturated fatty acids. The result is commercially viable products without trans-fats. In addition to the human health benefits of eliminating trans-fats, the process has reduced the use of toxic chemicals and water, prevents vast amounts of by products, and reduces the amount of fats and oils wasted.

In 2011, the Outstanding Green Chemistry Accomplishments by a Small Business Award went to BioAmber Inc. for integrated production and downstream applications of bio-based succinic acid. Succinic acid is a platform chemical that is an important starting material in the formulations of everyday products. Traditionally, succinic acid is produced from petroleum-based feedstocks. BioAmber has developed process and technology that produces succinic acid from the fermentation of renewable feedstocks at a lower cost and lower energy expenditure than the petroleum equivalent while sequestering CO_2 rather than emitting it. However, lower prices of oil precipitated the company into bankruptcy and bio-sourced succinic acid is now barely made

Several laboratory chemicals are controversial from the perspective of Green chemistry. The Massachusetts Institute of Technology created a "Green" Alternatives Wizard to help identify alternatives. Ethidium bromide, xylene, mercury, and formaldehyde have been identified as "worst offenders" which have alternatives. Solvents in particular make a large contribution to the environmental impact of chemical manufacturing and there is a growing focus on introducing Greener solvents into the earliest stage of development of these processes: laboratory-scale reaction and purification methods. In the Pharmaceutical Industry, both GSK and Pfizer have published Solvent Selection Guides for their Drug Discovery chemists.[19,20]

Results

In 2007, The EU put into place the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) program, which requires companies to provide data showing that their products are safe. This regulation (1907/2006) ensures not only the assessment of the chemicals' hazards as well as risks during their uses but also includes measures for banning or restricting/authorising uses of specific substances. ECHA, the EU Chemicals Agency in Helsinki, is implementing the regulation whereas the enforcement lies with the EU member states. The United States formed the Environmental Protection Agency (EPA) in 1970 to protect human and environmental health by creating and enforcing environmental regulation. Green chemistry builds on the EPA's goals by encouraging chemists and engineers to design chemicals, processes, and products that avoid the creation of toxins and waste.

The U.S. law that governs the majority of industrial chemicals (excluding pesticides, foods, and pharmaceuticals) is the Toxic Substances Control Act (TSCA) of 1976. Examining the role of regulatory programs in shaping the development of green chemistry in the United States, analysts have revealed structural flaws and long-standing weaknesses in TSCA; for example, a 2006 report to the California Legislature concludes that TSCA has produced a domestic chemicals market that discounts the hazardous properties of chemicals relative to their function, price, and performance. Scholars have argued that such market conditions represent a key barrier to the scientific, technical, and commercial success of green chemistry in the U.S., and fundamental policy changes are needed to correct these weaknesses.

Passed in 1990, the Pollution Prevention Act helped foster new approaches for dealing with pollution by preventing environmental problems before they happen.

Green chemistry grew in popularity in the United States after the Pollution Prevention Act of 1990 was passed. This Act declared that pollution should be lowered by improving designs and products rather than treatment and disposal. These regulations encouraged chemists to reimagine pollution and research ways to limit the toxins in the atmosphere. In 1991, the EPA Office of Pollution Prevention and Toxics created a research grant program encouraging the research and recreation of chemical products and processes to limit the impact on the environment and human health. The EPA hosts The Green Chemistry Challenge each year to incentivize the economic and environmental benefits of developing and utilizing green chemistry.

In 2008, the State of California approved two laws aiming to encourage green chemistry, launching the California Green Chemistry Initiative. One of these statutes required California's Department of Toxic Substances Control (DTSC) to develop new regulations to prioritize "chemicals of concern" and promote the substitution of hazardous chemicals with safer alternatives. The resulting regulations took effect in 2013, initiating DTSC's Safer Consumer Products Program.

There are ambiguities in the definition of green chemistry, and in how it is understood among broader science, policy, and business communities. Even within chemistry, researchers have used the term "green chemistry" to describe a range of work independently of the framework put forward by Anastas and Warner (i.e., the 12 principles).While not all uses of the term are legitimate many are, and the authoritative status of any single definition is uncertain. More broadly, the idea of green chemistry can easily be linked (or confused) with related concepts like green engineering, environmental design, or sustainability in general. The complexity and multifaceted nature of green chemistry makes it difficult to devise clear and simple metrics. As a result, "what is green" is often open to debate. [18,19]

Green chemistry metrics describe aspects of a chemical process relating to the principles of green chemistry. The metrics serve to quantify the efficiency or environmental performance of chemical processes, and allow changes in performance to be measured. The motivation for using metrics is the expectation that quantifying technical and environmental improvements can make the benefits of new technologies more tangible, perceptible, or understandable. This, in turn, is likely to aid the communication of research and potentially facilitate the wider adoption of green chemistry technologies in industry.

For a non-chemist, an understandable method of describing the improvement might be a decrease of X unit cost per kilogram of compound Y. This, however, might be an over-simplification. For example, it would not allow a chemist to visualize the improvement made or to understand changes in material toxicity and process hazards. For yield improvements and selectivity increases, simple percentages are suitable, but this simplistic approach may not always be appropriate. For example, when a highly pyrophoric reagent is replaced by a benign one, a numerical value is difficult to assign but the improvement is obvious, if all other factors are similar.

Numerous metrics have been formulated over time. A general problem is that the more accurate and universally applicable the metric devised, the more complex and unemployable it becomes. A good metric must be clearly defined, simple, measurable, objective rather than subjective and must ultimately drive the desired behavior.

Conclusions

Green chemistry is the design of chemical products and processes that reduce and/or eliminate the use or generation of hazardous substances. This approach requires an open and interdisciplinary view of material and product design, applying the principle that it is better to consider waste and hazard prevention options during the design and development phase, rather than disposing, treating and handling waste and hazardous chemicals after a process or material has been developed. Green chemistry is an opportunity for introducing innovative solutions to chemical problems and applying sustainability towards molecular design. Chemists have the ability to design products and processes that have reduced impacts on humans and the environment and therefore creating sustainable chemical building blocks for materials and products in our society.[21]

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