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Green Chemistry: Principles and Practice

Paul Anastas* and Nicolas Eghbali

Center for Green Chemistry and Green Engineering at Yale, Yale Chemistry Department

USA. E-mail: paul.anastas@yale.edu; Fax: 1-203-436-8574; Tel: 1-203-432-5215

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Green Chemistry is a relatively new emerging field that strives to work at the molecular level to achieve sustainability. The field has received widespread interest in the past decade due to the need for chemical innovation to meet environmental and economic goals simultaneously. Green Chemistry is based on a framework of a cohesive set of Twelve Principles, which have been systematically summarized in this *review*. This article covers the concepts of design and the scientific philosophy of Green Chemistry through a set of illustrative examples. Future trends in Green Chemistry are discussed with the Twelve Principles as a cohesive design system (93 references).



Paul Anastas

Paul T. Anastas is the Teresa and H. John Heinz III Environment and the Director of the Center for Green Chemistry at Yale University. Trained as a synthetic organic chemist, he is credited with establishing the field of Green Chemistry. He has published ten books and numerous papers on sustainable chemistry.



Nicolas Eghbali

Nicolas Eghbali earned a BS in Molecular Biology from the University of Paris (France). After completing his PhD dissertation under the supervision of Professors Chao-Jun Li and David Harpp at McGill University, he joined the faculty of the Department of Chemistry and Green Engineering at Yale, where his PhD work was centered on the utilization of carbon dioxide in green organic synthesis to material science and catalysis.

I Introduction

Green Chemistry is defined as the “design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances.”^{1,2} This definition and the concept of Green Chemistry were first introduced by Paul Anastas and John Warner nearly 20 years ago.³ In the years since, there has been international adoption that includes national programs and governmental initiatives on Green Chemistry around the world with the United States, United Kingdom, and Italy.⁴ These have played a significant role in informing sustainable development. Examples include the US Presidential Green Chemistry Challenge Awards established in 1995 and 1997,⁷ and the publication of the first volume of the now well-established Green Chemistry book series in 1996.

in 1999.⁸

The most important aspect of Green Chemistry is the concept of design. Design cannot do design by accident. It includes novelty, planning and systematic concepts are “design rules” to help chemists achieve the intentional goal of sustainability. Green planning of chemical synthesis and molecular design to reduce adverse consequences synergies—not merely trade-offs.

The Green Chemistry approach strives to achieve sustainability at the molecular level. It has been applied to all industry sectors. From aerospace, automobile, cosmetic, electronics, pharmaceutical, to agriculture, there are hundreds of examples of successful applications of competitive technologies.⁹

The concept of Green Chemistry has had this large impact due to the fact that it has touched industry, education, environment, and the general public. The field of Green Chemistry can design next generation products and processes so that they are profitable and safe for the environment. Following the scientific enthusiasm of Green Chemistry, teaching in the field of Green Chemistry and Green Engineering. Some institutions offer degrees in the field of Green Chemistry and Green Engineering. Several countries around the world.¹⁰

II Framework of Green Chemistry

The three main points about the Green Chemistry framework can be summarized as follows:

1. Green Chemistry designs across all stages of the chemical life-cycle.
2. Green Chemistry seeks to design the inherent nature of the chemical products and processes.
3. Green Chemistry works as a cohesive system of principles or design criteria.

The Twelve Principles of Green Chemistry are design criteria or guidelines that provide a framework for the design of safer chemicals and chemical processes. They constitute an overarching construct for the design of safer chemicals and chemical processes. They are perceived as a dangerous science and often the public associates the word “chemical” with danger. Using safety precautions such as protective gear. When safety protections fail, the risk of injury and exposure, increases (Fig. 1). If the hazard is high and exposure controls fail, the risk of injury and death). By minimizing the hazard portion of the equation instead of focusing only on exposure, the risk is reduced even in cases of undesirable circumstances (accident, spills, sabotage, *etc.*). Designing safer chemicals requires striving to reduce the intrinsic hazards to a minimum and therefore limiting the risk of injury and exposure.

$$\text{Risk} = f(\text{hazard} \times \text{exposure})$$

The aim of Green Chemistry, to reduce hazards across all the life-cycle stages, has been defined as the ability to cause adverse consequence to humans or the environment. Hazard is defined as the ability to cause adverse consequence to humans or the environment. A substance or a chemical process can be designed to be minimized at every level of design (e.g., explosion, flammability) or global hazards such as stratospheric ozone depletion. Careful design will reduce or eliminate intrinsic hazards within chemicals and processes by the nature of the feedstock and raw materials that are used in the chemical transformation made. Careful design will reduce or eliminate intrinsic hazards within chemicals and processes by the Twelve Principles as one cohesive set.

III The Twelve Principles

The Twelve Principles of Green Chemistry were introduced in 1998 by Paul Anastas and John Warner as a framework for the design of new chemical products and processes, applying to all materials used to the efficiency and safety of the transformation, the toxicity and bioaccumulation. They were summarized recently into the more convenient and memorable acronym *12 Principles of Green Chemistry* intended to provide a general knowledge about Green Chemistry. For the convenience, each principle.

1. **Prevention.** It is better to prevent waste than clean up waste after it is formed.
2. **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis.** Wherever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no hazard to human health and the environment.
4. **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
5. **Safer Solvents and Auxiliaries.** The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, if unavoidable, should be innocuous.
6. **Design for Energy Efficiency.** Energy requirements for chemical processes should be recognized and minimized. Environmental and economic impacts should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives.** Unnecessary derivatization (including blocking groups, protection/ deprotection, modification of physical/chemical processes) should be minimized or avoided if possible, because these processes 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 degrade 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 enable real-time, in-process monitoring and control to minimize the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention.** Substances and the form of a substance used in chemical processes should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Fig. 2 The Twelve Principles of Green Chemistry.

1 Waste

Waste prevention is the first of the Twelve Principles of Green Chemistry. It is better to clean it up after the fact. The generation of any material that does not have a realized purpose is considered a waste. As mentioned above, waste can take many forms and may impact the environment based on its nature, its toxicity, its quantity, or the way it is released.¹² When large portions of the waste are generated because of the original design of the process itself then it will inexorably generate waste.

In 1992, the concept of what is now widely accepted as the E-Factor, or Environmental Factor, was introduced by Sheldon.¹³ This metric helps to quantify the amount of waste generated per kilogram of product, a measure of “environmental acceptability” of a manufacturing process.

The environmental factor which has been adopted by many in the chemical industry for evaluating industrial processes have been and opened the door to creative solutions. One well-known example is the synthesis of ethylene oxide which was prepared through a chlorohydrin intermediate ([Fig. 3a](#)). The E-Factor for this process is equal to 5. For each kilogram of product, 5 Kg of waste were to be disposed. This waste was heavily contaminated by chlorine by-products.¹²⁻¹⁴ When the synthesis was modified to use a different process without chlorine, the E-Factor dropped to 0.3 Kg of waste. The new process was generating 1 Kg of product for every 0.3 Kg of waste, eliminating the formation of waste water as well.¹⁵

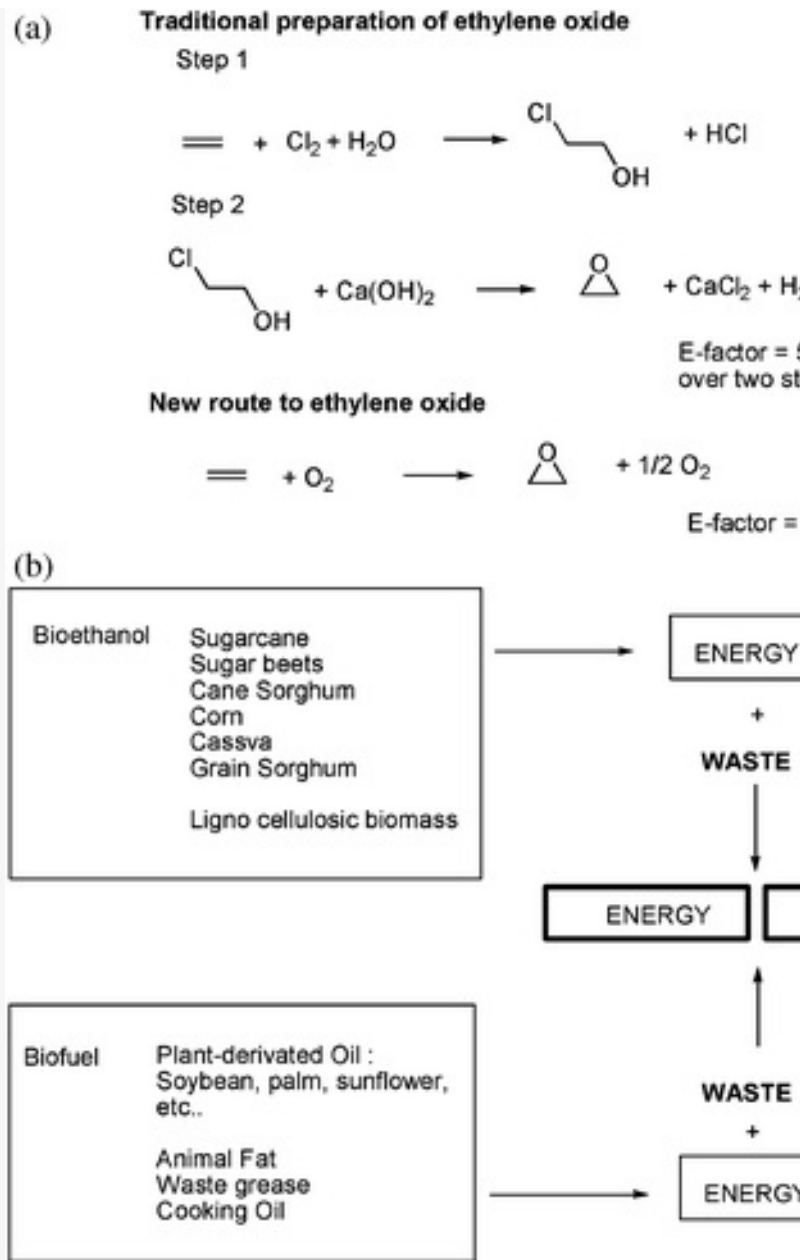


Fig. 3 (a) Traditional preparation of ethylene oxide route relying on molecular oxygen. (b) Revalorization of byproducts.

When byproducts cannot be avoided, other innovative solutions should be considered in an industrial ecology approach where waste can become a new raw material with significant value over the life-cycle. This approach is currently being applied to the production of biofuel.

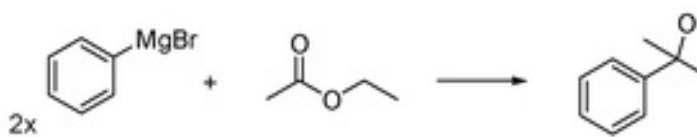
2 Atom economy

In 1990 Barry Trost introduced the concept of synthetic efficiency: Atom Economy. The concept of maximizing the use of raw materials so that the final product contains the maximum number of atoms from the reactants. The ideal reaction would incorporate all of the atoms of the reactants. The atom economy is the weight of the desired product over the molecular weights of all reactants used in the reaction. This is used to quickly assess how efficient a reaction will be.

The Atom Economy AE

$$AE = \frac{\text{MW Product}}{\text{MW of reagents}}$$

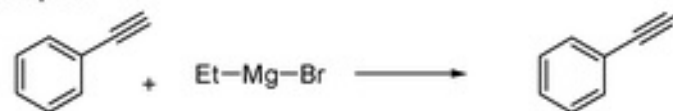
Example of a Grignard reaction



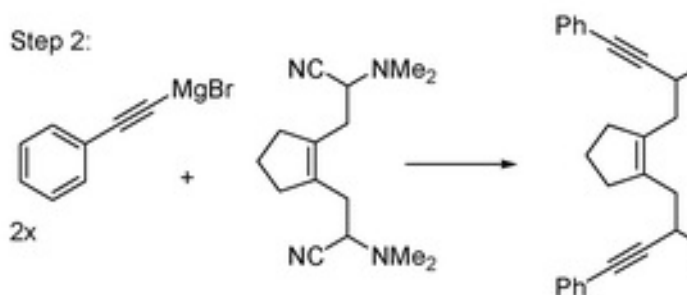
AE = 4

Grignard reagent, Application to the synthesis of a propargylic amine

Step 1:

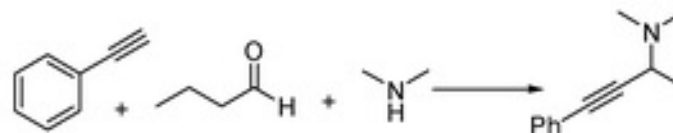


Step 2:



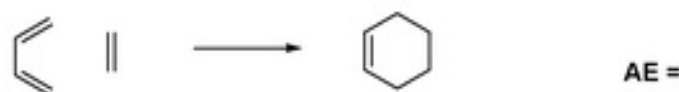
AE = 5
over 2

Alternative synthesis for propargylic amine: A3 Coupling



AE =

Diels-Alder reaction



AE =

Fig. 4 The Atom Economy AE and several illustrations

To illustrate this concept, a few examples such as the Grignard reaction, A3 coupling, and Diels-Alder reaction are shown below. The Grignard reaction, which received the recognition of the scientific community, is unfortunately a relatively poor atom-economical reaction due to the stoichiometric necessity to prepare the Grignard reagent separately.¹⁸ Fig. 4 presents a typical Grignard reagent to build a propargylic amine type structure.²⁰ The values of the AE are only half of the raw material. A solution in respect to the last example was proposed by the A3 coupling (Alkyne, Aldehyde and Amine).²¹ This one-step multicomponent coupling reaction of the original atoms used are found in the final product. The Diels-Alder reaction is an atom-economical reaction¹⁷ (Fig. 4). Its AE is equal to 100% since all atoms from the reactants

Diels–Alder type reactions belong to the category of cycloaddition which is among the most important reactions in organic chemistry.

3 Synthesis

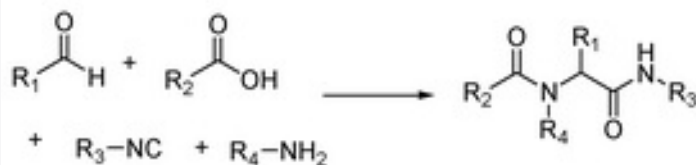
As illustrated in [Fig. 5](#), the synthetic toolbox of organic chemists has been improved in the past decade. Many of the new reactions that have been developed in the past decade add to the list of reactions discovered during the past century. Reactions based on cycloaddition,^{[17,22](#)} rearrangement reactions^{[24](#)} were already known and constitute one category of efficient reactions. Cross-metathesis,^{[27](#)} and enzymatic reactions^{[28,29](#)} are rather new approaches and illustrate the diversity of synthetic tools available to organic chemists. The Grubbs catalyst, for example, allows the synthesis of alkenes similar to Wittig-type reactions such as the Horner–Wadsworth–Emmons reaction (via a phosphonate intermediate, [Fig. 5](#)). It is an essential tool for the construction of larger molecules. Cross-metathesis reaction does not produce a large amount of waste. The formation of phosphonate reaction is unfortunately unavoidable since it is part of the design of the reaction and

Typical example of a rearrangement: the Cope rearrangement

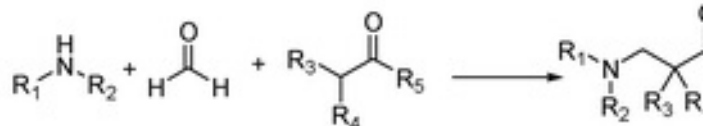


Examples of well-known multicomponent coupling reactions

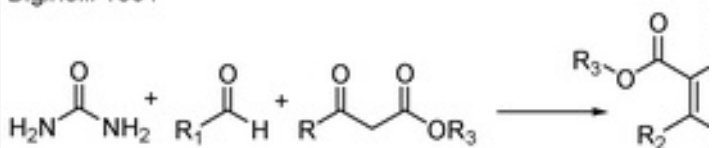
Ugi 1959



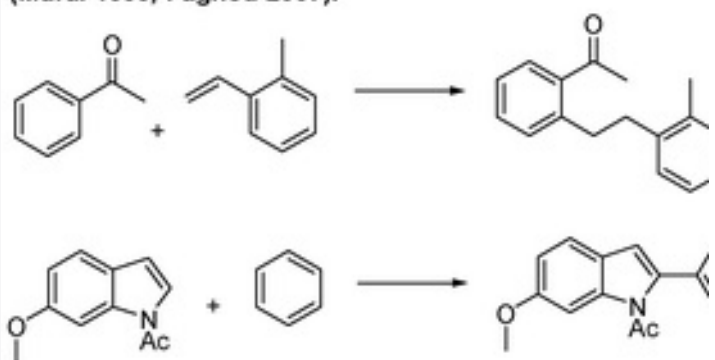
Mannich 1912



Biginelli 1891



Examples of C-H activation reactions (Murai 1993, Fagnou 2007):



Alternative synthesis: Grubbs metathesis



Traditional Wittig-Horner or Horner-Wadsworth-Emmons Reaction:

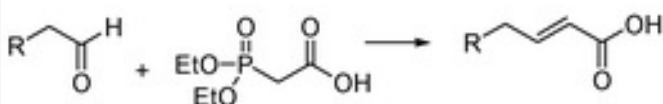


Fig. 5 Examples of green reactions.

C-H activation is another relatively new area of chemistry which holds great promise. In traditional reactions, activated carbon-halogen bonds are usually used because of their high reactivity. However, since they are not naturally occurring, it implies additional steps to produce the precursor. The replacement of these with C-H activation eliminates the need for halogenated precursors and therefore the halogenated waste.

Two famous examples of C-H activation were published in 1993 by Murai³¹ and

employed a ruthenium catalyst to couple the inactivated substrates acetophenone first examples of C–H activation and represents a milestone in the field. In the second aromatic compounds selectively without the need for any activating or directing groups C–H activation in advancing Green Chemistry.

4 Molecular design

While there has been significant focus on designing chemicals for various functions, there has been a surprising lack of interest in taking into consideration hazard in the design of molecules that have an impact on the environment and the transformations that take place. Through a mastery of this understanding, chemistry will be able to contribute to sustainability. Work by Ariëns³³ in 1984 and by Garrett and Devito³⁴ is not only highly needed for the advancement of Green Chemistry, but is also possible.

In recent decades, there has been a significant amount of work in the field of toxicology, moving from descriptive science to one that has a large mechanistic component,³⁵ and even more recently the incorporation of an *in-silico* component.³⁶ Because of that transition, it has been possible to develop models that relate structure, properties, and function. These approaches provide the development of a comprehensive design strategy. For instance the existing understanding can be used to establish some ground rules for designing less toxic chemicals *via* incorporation of safer groups into humans and many animal organisms.³⁷

5 Solvents

Solvents are perhaps the most active area of Green Chemistry research.³⁸ They represent a major area of concern in Green Chemistry because they often account for the vast majority of mass wasted in synthesis. Many conventional solvents are toxic, flammable, and/or corrosive. Their volatility and soot emissions, along with air pollution, have increased the risk of workers' exposure, and have led to serious accidents. These problems, often associated with energy-intensive distillation and sometimes cross contamination, have led to the shortcomings, chemists started a search for safer solutions. Solventless systems,⁴⁰ and more recently ionic liquids⁴³ are some examples of those new "green" answers.

Where possible, the ideal situation would be to not use any solvent because the energy and effort required to remove it from a designated system. Efforts have therefore been made to develop reactions that do not require solvents. This idea was reinforced by the finding that solvents account for most of the industrial waste. In many cases, the properties of the reagents used or the desired outcome of the transformation, the availability of a catalyst, or the chemistry to allow the reaction to proceed without the original solvent.

Water is the most abundant molecule on the planet and is sometimes referred to as the universal solvent. Running a reaction in or on water therefore has significant advantages. Water is safe and a good solvent for large scale process chemistry. The properties of water have even led to its use in microfluidics. The effect⁴⁴ and easier separation since a lot of organic substances do not dissolve in water. A reaction in water is one of the useful examples illustrating the advantages of water as a solvent. One of the main concerns in industrial applications and has yet to be addressed is the risk of water contamination. It must be kept clean.

SCF are another alternative to traditional organic solvents and have been extensively used for the extraction of substances which have been simultaneously heated and compressed above their critical points.

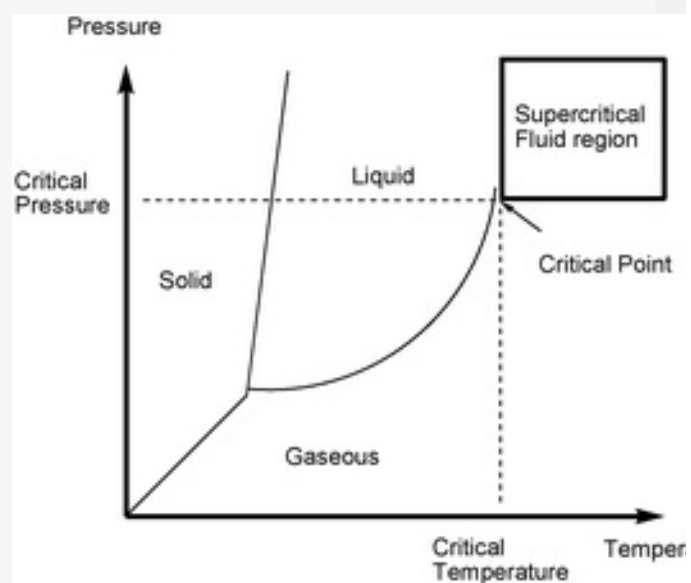


Fig. 6 Pressure-temperature phase diagram showing the supercritical region.

Common SCF are generated from water, carbon dioxide, methane, methanol, etc. The most widely used SCF is carbon dioxide. The resulting scCO_2 has proven to be a versatile solvent, safe and non-toxic. The work of Poliakov, Leitner, Jessop, DeSimone, and others.⁴⁵ What makes SCF so attractive is the change of state that occurs when cooling down the vessel or reducing the pressure. Above the critical temperature, which reactions can be performed and below, it will be a gas. Degassing the system scCO_2 has found a wide range of industrial applications with the most famous being the replacement of perchloroethylene in dry cleaning.⁴⁶ Supercritical fluids have properties that make them good solvents.

Another example of greener solvents would be ionic liquids pioneered in modern chemistry. Ionic liquids, or sometimes called room temperature ionic liquids, are liquid salts at room temperature and have low vapor pressure and very low flammability. What was discovered recently by Jessop *et al.* is

solvent” generated *in situ* just like the liquid scCO₂. Addition of pressurized carbon into an ionic liquid, generating a safer solvent *in situ*. Releasing the pressure reverse retransformed into the original mixture, thus removing completely the solvent and steps.

Another example based on the same concept is the development of fluorinated biphasic or solvent containing a catalyst suited for the desired transformation is usual temperature. When heated, they form a single media, allowing the reaction to proceed. After the reaction, the fluorinated solvent separate, simplifying the purification process. This is an attractive process because fluorinated solvents are expensive.

These last examples are good illustrations of one of chemistry’s major challenges in developing new systems, the new improved green solvents remain auxiliaries and therefore must be separated. This cannot be avoided then the issue of separation must be taken into consideration with the process.

6 Energy

Rising concerns over the depletion of petroleum feedstocks and the increase in energy costs have led to the development of more energy efficient processes and for the search for renewable energies; non-depletable and on a human scale.⁴⁹

As mentioned in the first section (first principle), unutilized energy may also be wasted in chemical reactions or systems that do not require intensive energy use is highly desirable. Research is being done on choosing appropriate reactants so that the transformation may proceed at room temperature. This can do to reduce energetic requirements, with all the direct and indirect benefits associated with it.

Increasing the energy efficiency of a chemical system is merely one part of the solution. Several of those renewable energies have been identified in biofuels production,^{49,50} wind power, hydro power, geothermal energy,⁴⁹ and hydrogen fuel cells.^{49,54} Once applied, they will play in this new challenge as they have the ability to design both energy efficient transformations and processes that can be used to harvest some of those renewable natural energies.

Solar energy, the primary sustainable energy source on earth, is one of those alternative sources that have been dedicated to understand and design chemical systems that can convert solar energy into chemical energy. Inorganic and hybrid solar cells have received interest although more focus has been on organic solar cells for higher efficiency. The principle of those cells relies on the ability of the material used to absorb solar radiations. The absorption leads to the formation of excited states that can be relayed to other molecules. Materials and polymers that can efficiently transform light into current remain a challenge in this approach.

Proton Exchange Membrane (PEM) fuel cells using hydrogen and oxygen gases c

upcoming increase in energy demand (Fig. 7).^{54,56} PEM fuel cells have generated research interest due to the development of increasingly efficient catalysts such as nanoparticles or even hydrogenases. A major consideration in this approach is the hazard of handling hydrogen gas, which is highly flammable.

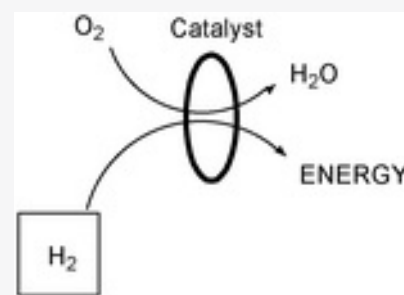


Fig. 7 General concept of a hydrogen fuel cell.

7 Renewable materials

It has been estimated that the vast majority of our manufacturing products are derived from fossil fuels.^{1,49,58} The depletion of those resources will touch many aspects of our consumer lifestyle. The shift from non-renewable feedstocks both for material and fuel has now become more urgent. The search for material and energy is bio-mass,⁵⁸ the material available from living organisms. This includes food, etc.⁵⁹

Examples of renewable material include cellulose, lignin, suberin and other wood components, chitin, starch, glycerol and oil.⁶⁰ Lignin, for instance, is a major waste of the pulp and paper production site to provide energy for many years. In recent years it has found new uses as a source of additives, and raw materials for the production of chemicals such as vanillin, DMSC, and natural polymer that constitutes the exoskeleton of arthropods (e.g. crustaceans). It can be transformed into chitosan by deacetylation.⁶² Numerous applications of chitosan include purification, biomedical applications and other industrial uses.^{62,63} Reusing this waste would reduce the amount of raw materials to replace the current petroleum feedstocks.

8 Derivatives

Covalent derivatization is a ubiquitous technique in chemistry whether it is employed in organic chemistry.⁶⁴ In the early 1990s, an innovative concept surfaced called non-covalent derivatization based on covalent bonding but rather on intermolecular interactions.⁶⁵ The work by Warr and others demonstrated that less material to achieve chemical modifications from the original system. An example is illustrated by the controlled diffusion and solubility of hydroquinones used in Polarographic analysis.

release hydroquinones at elevated pH. Instead of relying on base-labile covalent protecting groups, they developed a non-covalent protecting group in the form of a co-crystal of bis-(*N,N*-dialkyl)terephthalamides (Fig. 8). This approach was successful and viable for the in situ modification of the original hydroquinone structures and minimized waste material.

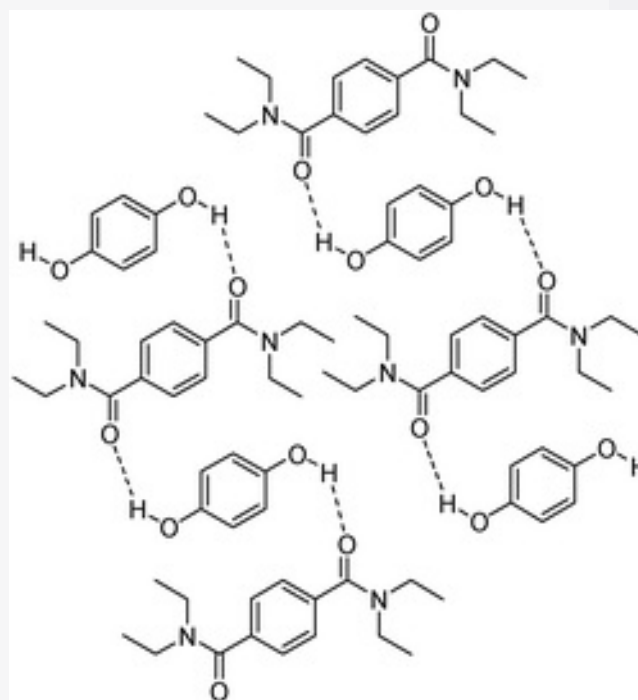


Fig. 8 Hydroquinones protected by non-covalent hydrogen bonding with bis-(*N,N*-dialkyl)terephthalamides.

9 Catalysis

In many cases, the formation of waste is linked to the traditional use of a stoichiometric amount of reagents. The transition from stoichiometric methodologies to catalytic processes is perceived as one major way to reduce waste in the chemical toolbox. Catalysis can improve the efficiency of a reaction by lowering the energy barrier, by using a sub-stoichiometric amount of reagents, and by greater product selectivity. This implies that catalysis can be a more sustainable approach. Moreover, it often opens the door to innovative chemical reactions and bring unexplored challenges.

Oxidation and reduction reactions illustrate this concept. Reduction employing stoichiometric reagents is an established procedure used by organic chemists.⁶⁹ It generates a significant amount of waste. A large amount of reducing agent is needed to complete the reaction. Switching to catalytic hydrogenation reduces the need for stoichiometric reagents and in consequence decreases the amount of waste generated (Fig. 9).

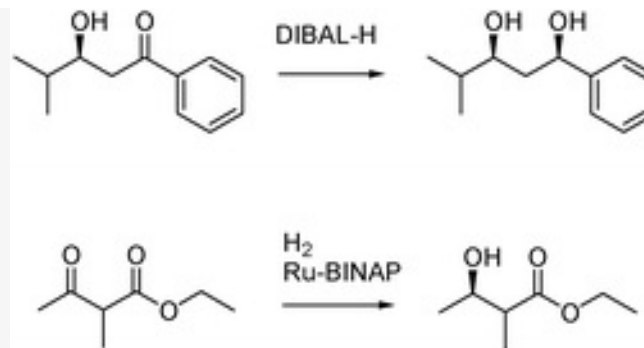


Fig. 9 Comparison between stoichiometric and catalytic reduction.

Beyond efficiency, catalysis can allow for otherwise unfavorable reactions to be performed. This led to the development of the Grubbs catalyst.²⁷ As illustrated in [Fig. 5](#), the Grubbs catalyst represents a groundbreaking approach to the formation of unsaturated compounds. The environmental innovation was important.

Biocatalysis is yet another example of “green” chemistry as it is a biomimetic approach inspired by enzymes.^{28–29,71} It usually refers both to the direct use of purified enzymes and the use of whole living organisms. Reaction conditions are relatively mild as the transformation can be performed at room temperature and ambient pressure. Moreover, enzymes have proven to be more chemo-, regio-, and stereoselective than traditional catalysts.

10 Biodegradation

The problem of persistence has been known for a long time and became apparent in the 1950s for instance, tetrapropylene alkylbenzene sulfonate (TPPS) was used as a detergent and accumulated into the water supply due to an incomplete degradation. The situation was described as “water tended to foam when coming out of the tap.”^{73,74} The public outcry prompted the search for a more biodegradable alternative and it was found that replacing the methyl branched chain of TPPS by a linear carbon chain resulted in a more biodegradable product. A common example is the replacement of TPPS by linear alkylbenzene sulfonate (LAS).

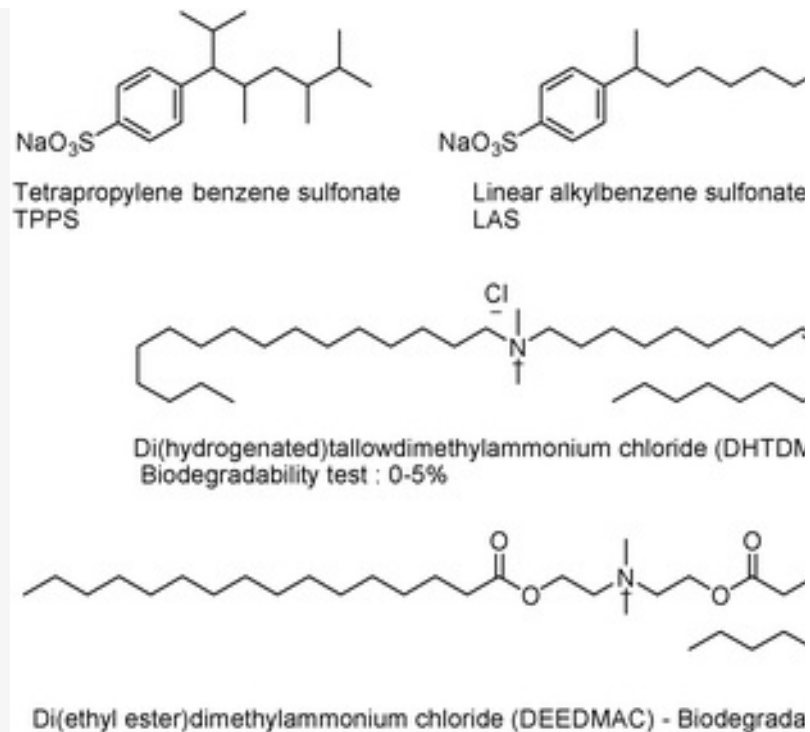


Fig. 10 Integrating biodegradability in the design

Designing biodegradable materials and chemicals is not a simple task as illustrated by the presence of environmental pollution. Trends have emerged following decades of data collection. Certain chemical structures, such as branched chains, quaternary carbons, tertiary amines, and certain heterocycles may hinder biodegradation. On the other hand, integrating functional groups such as esters or amides which are known to be biodegradable into the design of environmental degradable products.^{73,75} This strategy was applied to the design of biodegradable compounds used as household fabric softeners.⁷⁶ Until the 1990s, long chain ammonium salts such as dimethyl ammonium chloride (DHTDMAC) were released into the environment. Its biodegradation in aqueous sediment was low and the intrinsic ecotoxicity, high. In the 1990s, new ammonium salts were introduced. The new ammonium salts have proven to be more biodegradable than DHTDMAC by di(ethyl-ester) dimethyl ammonium chloride (DEEDMAC) which was followed by

11 Analysis

It is the goal of green analytical chemistry to measure chemicals without generating waste. The challenges associated with analytical chemistry are usually linked to the analytical approach itself. Real time monitoring is not possible as many methodologies still require a pre-treatment of the sample or rely on what is known as extractive chemistry⁷⁹ is defined as the ability to monitor a transformation and act immediately. This is not always possible, and therefore waste may be generated when the sample is analyzed. In the design of analytical methods, consideration the functional requirements of analytical methods since it will be considered. This can help to contribute to further environmental problems. Green analytical chemistry can be designed to be more sustainable, generate less waste and are safer to human health and the environment.⁷⁹ This definition of a chemical transformation and the environmental shortcomings associated with

reaction has significant advantages in terms of Green Chemistry. When action can energy, and/or prevent the formation of significant amounts of by-products that w

When it comes to the analytical methods themselves, most of them share two pr method: a pretreatment of the sample which includes extraction, separation or eve sample, and a signal acquisition step.⁷⁹ Since the pretreatment step usually calls fo of analytical chemists concerns. If the use of solvents can not be avoided for an ext Accelerated Solvent Extraction (ASE) or SCF extraction should be considered.^{79,80}

Material used in the manufacture of analytical apparatus should be taken into co engineers building new sensors should be aware of the toxicity and any potential e they handle. Mercury electrodes, for example, are often used for electrochemistry. F such as nanotubes or nanofibers has proven to be an effective solution.⁸¹

12 Accident prevention

Dangerous substances and processes have multiplied in our working environment. and the clean air act amendments of 1990,” preventing accidents starts by identify hazards whether it is toxicity, physical hazards such as explosivity or flammability, design of chemicals and processes in order to prevent accidents such as Bhopal or

A recent and shocking illustration of these dangers and hazards can be found in 2009.⁸⁴ Handling of the very common and highly flammable butyllithium reagent re the death of the research assistant involved. This accident should be a strong remi chemicals we still use present serious hazards and should be replaced by safer alter

IV Accomplishments by industry

There are numerous examples of successful industrial changes using Green Chemis present an exhaustive list of the awards winners but rather introduce a few key exa adapting to the new challenges of Green Chemistry.

As a first example, a greener synthetic pathway which was attributed to Eastmar biocatalytic process runs under mild conditions, minimizes the formation of bypro efficiency. Overall hundreds of litres of organic solvents were eliminated from the p

In 2008, researchers at Dow AgroSciences were rewarded for the design of green p structure–activity relationships of natural biopesticides in an effort to predict analc Spinetoram. The company expects that the production of this new pesticide will el organophosphate insecticides during its first five years of use.”⁸⁶

In 2006, Merck developed a greener synthetic pathway for Sitagliptin, a chiral α -glucosidase inhibitor for type 2 diabetes.⁸⁷ The approach was based on a novel asymmetric catalytic hydrogenation to avoid the need of excessive derivatization (Fig. 11).⁸⁸ Merck presented a three-step synthesis. Implementing the new route on a manufacturing scale showed a significant reduction in waste. The new process is a more cost-effective option.

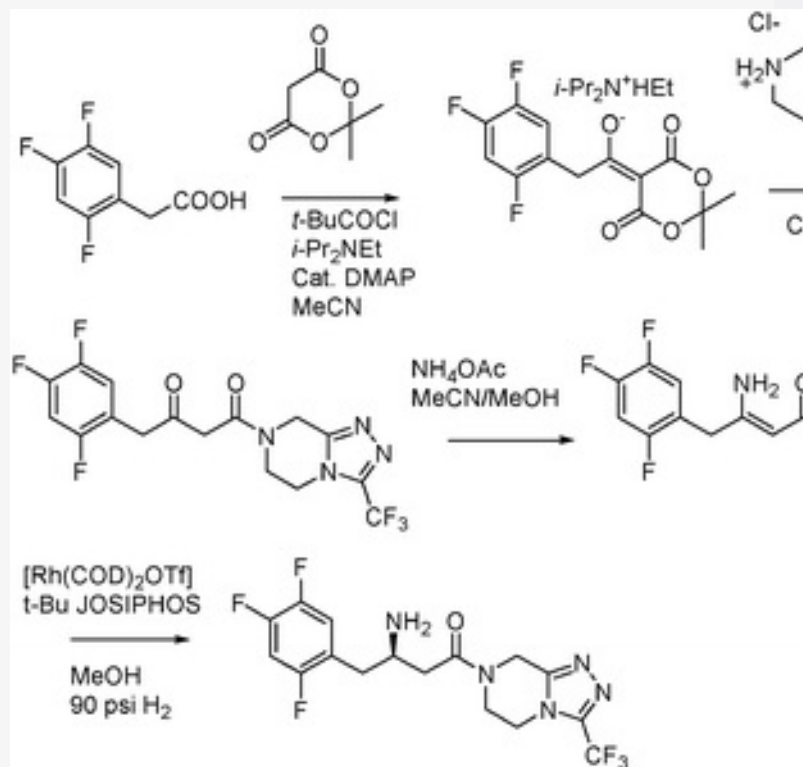


Fig. 11 New synthesis of Sitagliptin.

In 2004, BMS developed a new approach to Paclitaxel, the active ingredient in the drug Taxol, which is commercially produced from the naturally occurring precursor 10-deacetylbaccatin III. This approach, a “semisynthetic route”, which was first developed as an economically viable approach to Paclitaxel, addressed environmental concerns. A more sustainable process was therefore investigated by BMS. Instead of synthesizing Paclitaxel from a precursor, the active compound was extracted from the plant. This method eliminated all organic solvents, hazardous reagents, and additional steps associated with the traditional manufacturing of Paclitaxel using only plant cell cultures.

In 2002, Pfizer developed a new greener synthetic pathway for the redesigned synthesis of a drug to treat depression (Fig. 12).⁹⁰ The new process offered substantial environmental benefits due to the selectivity of the synthesis. Specifically, a three-step sequence in the original manufacturing process was eliminated. The last change eliminated the need to use, distill, and recover four toxic solvents (methyl acetate, toluene, hexane).

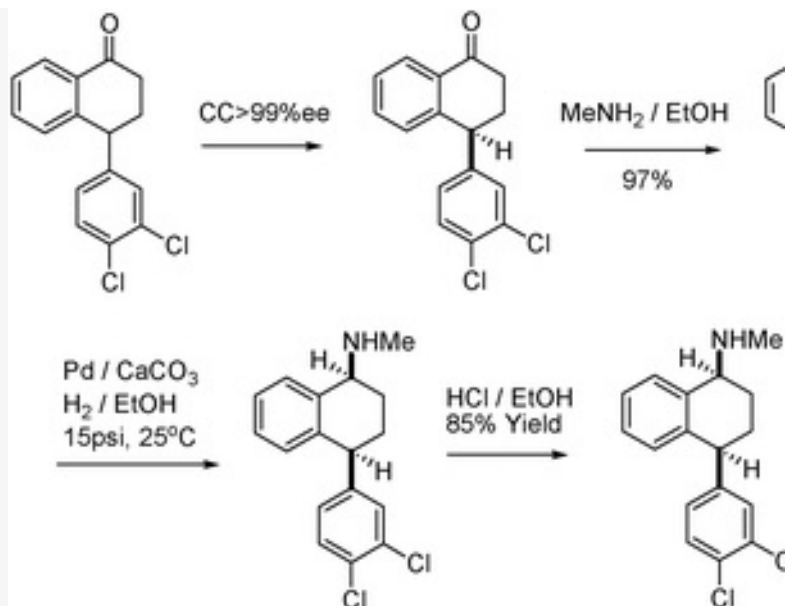


Fig. 12 New synthesis of sertraline.

One final noteworthy example is the work accomplished in 1998 by Solutia, Inc. of 4-aminodiphenylamine (Fig. 13).⁹² Researchers at the company explored new routes to 4-aminodiphenylamine (4-ADPA), in order to eliminate the formation of aqueous waste salts. There were also concerns about the hazard associated with storage and handling. The solution came with a new synthesis to 4-ADPA that utilizes the base-promoted, direct nitration of aniline. Environmental benefits were significant and included a dramatic reduction in waste.

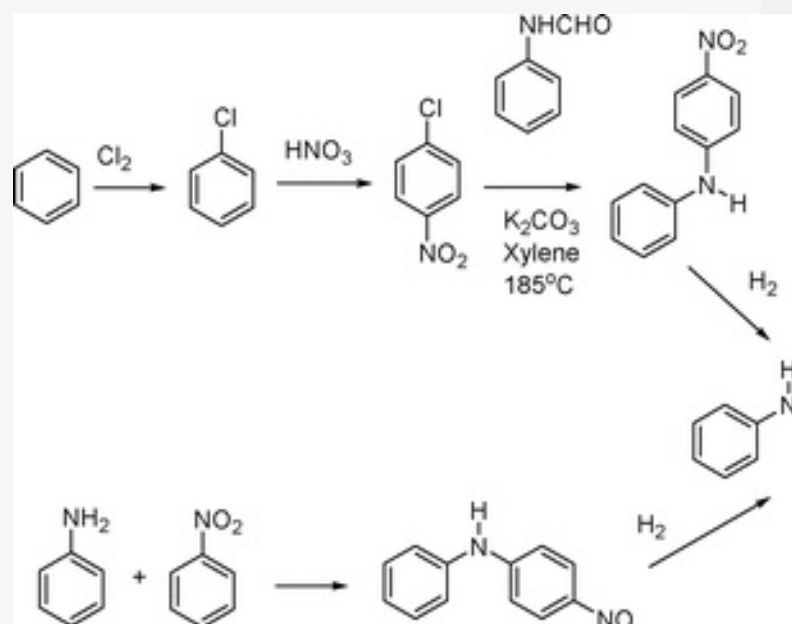


Fig. 13 Differences between the chlorine-based and direct nitration processes for the preparation of 4-ADPA.

V Future challenges

The accomplishments in the field of Green Chemistry thus far are impressive due to the research institutes around the world. However, the accomplishments achieved thus far are still limited, and there are many challenges ahead.

be addressed by the field. A few notable challenges are mentioned below.

Twelve Principles as a cohesive system

The design framework of the Twelve Principles of Green Chemistry has been a temporary detour. The Twelve Principles were not meant to be twelve independent goals but rather an integrated system. In the applications of all principles can one hope to achieve a truly sustainable process? If, by understanding the aspects of the principles, systemic sustainable design is possible and can facilitate incremental improvement.

Multi-functional catalysts

Catalysis has made significant progress during the past two decades. However, even in the area of transformation only and little is known about multi-functional catalysts, defined as a catalyst that can facilitate a series of transformations. If the same catalyst could be used for various independent transformations, it will bring chemistry to a new level as more complex molecules could be made.

Mastering weak forces for synthesis and properties

Non-covalent and weak-force interactions are likely to play an increasingly important role in the design of materials and properties through weak-forces and guiding synthetic pathways in the same manner. The use of weak forces in bond breaking and bond forming can result in significant advantages. These include reducing the amount of waste, and an increase in efficiencies. Mastering the weak forces in the same manner as mastered covalent forces holds great potential to help in reaching sustainability at the molecular level.

Integrative systems thinking

The traditional approach to scientific investigation has been largely based on the reductionist approach. It has resulted in a depth of understanding and discovery that have made the things of modern medicine—possible. It has also resulted in tremendous unintended and unforeseen consequences. By thinking in terms of systems, Green Chemistry can help in reaching sustainability while avoiding unintended results. Coupling reductive and integrated thinking can help in reaching sustainability.

Conclusion

For generations, molecular scientists have invented the molecules, materials, and processes that have driven economic and societal development. Green Chemistry is ensuring that all of that creativity is practised in a way that builds in impact on people and the planet as well as the economy.

has shown that through innovation companies can be economically more profitable over time. Although an impressive amount of work has been done by practitioners of Green Chemistry, the achievements of the past pale by comparison to the power and potential of the field.

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