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GREEN CHEMISTRY: PRINCIPLE AND PRACTICE

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ABSTRACT:

In order to attain sustainability, the area of "green chemistry," which is still in its early stages of development, works at the molecular level. The topic has attracted a lot of attention in the last ten years because it can use chemical innovation to simultaneously achieve economic and environmental goals. The Twelve Principles that make up the framework of Green Chemistry have been extensively examined in this critical assessment. This article uses a number of illustrative examples to discuss design ideas and the scientific theory behind green chemistry. The difficulty of employing the Principles as a cogent design framework is highlighted along with upcoming trends in green chemistry (93 references).

INTRODUCTION:

According to its definition, green chemistry is the "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances." Nearly 20 years ago, at the beginning of the 1990s, this definition and the idea of green chemistry were first put forth 1, 2. 3 Since then, there has been an international adoption that has led to the development of literally hundreds of programmes and governmental initiatives on green chemistry all over the world, with the initial leading programmes being located in the U.S., the UK, and Italy. 4 Informing sustainable design has largely been a result of these. 5 The US Presidential Green Chemistry Challenge Awards, established in 1995, the Green Chemistry Institute, established in 1997, and the publication of the first volume of the now-defunct.

Important early initiatives include the 1995-founded US Presidential Green Chemistry Challenge Awards, the 1997-founded Green Chemistry Institute, and the 1999 release of the inaugural issue of the Royal Society of Chemistry's now-established Green Chemistry magazine. 8The idea of design is the key component of green chemistry. Design cannot be done by accident because it is a statement of human intention. It includes innovation, preparation, and methodical conception. The Twelve Principles of Green Chemistry are "design guidelines" for chemists to follow as they work toward the deliberate objective of sustainability. Careful planning of chemical synthesis and molecular design to minimise unfavourable

effects is a hallmark of green chemistry. One can achieve synergy through proper design—not just trade-offs.

The goal of the Green Chemistry method is to establish molecular sustainability. It is hardly unexpected that it has been used in various industry areas given this objective. There are countless examples of successful uses of honourable, commercially viable technology in industries as diverse as agriculture, automotive, cosmetic, electronics, energy, household goods, and pharmaceuticals. 9

Because it has impacted industry, education, the environment, and the general public in addition to the research laboratory, the idea of "green chemistry" has had a significant impact. The field of "green chemistry" has shown how chemists can create profitable new products and processes that are also good for the environment and people. Teaching programmes, governmental funding, and the creation of Green Chemistry Research Centers have increased during the past 20 years in response to the scientific fervour of Green Chemistry.

Green Chemistry and Green Engineering courses are currently being offered at numerous universities. Degrees in the area are offered by some institutions. Several nations around the world have seen a rise in government support. 10

The Green Chemistry Framework:

The three key components of the Green Chemistry framework are as follows:

1. Green Chemistry plans take into account the entire chemical life-cycle.

2. Green chemistry aims to eliminate the inherent risk of chemical products and processes by designing them from the ground up.

3. Green Chemistry functions as a coherent set of guiding principles or design standards.

The Twelve Principles of Green Chemistry are a set of design standards or principles that serve as the foundation for environmentally friendly design. They serve as a unifying framework for the development of safer chemicals and chemical reactions. The word "chemical" is frequently associated with the word "toxic" in the general population, and chemistry has long been seen as a dangerous subject. Risk can be decreased by taking safety procedures and wearing protective gear. The risk, which is determined as a function of the danger and exposure, rises when safety precautions are ineffective (Fig. 1). If exposure controls are ineffective and the risk is substantial, the results could be disastrous (injury or death).

Even in times of unfavourable circumstances (accident, spills, sabotage, etc.), the risk can be controlled by limiting the hazard component of the equation rather than only concentrating on exposure management. Designing safer, more environmentally friendly chemicals and methods necessitates minimising inherent risks in order to lower the possibility of accidents and property damage.

$$Risk = f(hazard \times exposure)$$

Fig. 1 Risk is a function of hazard and exposure.

It has been established that Green Chemistry's goal of reducing risks at every stage of the life cycle is financially advantageous. A hazard is something that has the potential to harm people or the environment. A chemical substance's or process' intrinsic risks can be minimised at every stage of the process, whether

they be health risks like toxicity, physical risks like explosions and flammability, or environmental risks like stratospheric ozone depletion. The nature of the feedstock and raw materials employed in the chemical transformations as well as the produced final products may give rise to risks based on these hazards. A thoughtful design that incorporates the Twelve Principles as a single, cohesive set will reduce or eliminate intrinsic hazards in chemicals and processes.

The Twelve Principles:

Paul Anastas and John Warner introduced the Twelve Principles of Green Chemistry in 1998. (Fig. 2). These principles serve as a framework for the design of new chemical products and processes, and they apply to all facets of the process life-cycle, including the raw materials used, the effectiveness and safety of the transformation, the toxicity and biodegradability of the products and reagents used. Recently, they were condensed into the more useful and memorable acronym PRODUCTIVELY. 11 The parts that follow are meant to give a general understanding of green chemistry. Each premise is supported by a technological illustration for the reader's convenience.

- Prevention. It is better to prevent waste than to treat or clean up waste after it is formed.
- Atom Economy. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Less Hazardous Chemical Synthesis. Whenever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment.
- Designing Safer Chemicals. Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
- Safer Solvents and Auxiliaries. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
- 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.
- Use of Renewable Feedstocks. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- Reduce Derivatives. Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- Catalysis. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- 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.
- 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.

Fig. 2 The Twelve Principles of Green Chemistry

WASTE

The first of the Twelve Principles of Green Chemistry is waste prevention. Avoiding waste formation is preferable to cleaning up after it has already occurred. Waste can be defined as the creation of any material with unrealized worth or the loss of energy that is not put to use. As was already established, garbage can come in a variety of shapes and sizes, and its type, toxicity, quantity, and method of release can all have an impact on how it interacts with the environment. 12 A process will unavoidably produce waste, which is by definition unwanted, if significant amounts of the initial raw materials employed in the process are lost due to the process's original design.

Roger Sheldon first proposed the idea of what is now often referred to as the E-Factor, or Environmental Impact Factor, in 1992. 13 This measure aids in calculating the waste produced per kilogramme of product. It is a method for judging whether a manufacturing process is "environmentally acceptable."

The environmental concern, which is now widely accepted in the chemical sector, highlights how ineffective some industrial methods have been and makes way for original solutions. The early synthesis of ethylene oxide, which was made via a chlorohydrin intermediate, is one prominent example (Fig. 3a). As shown earlier, the whole synthesis's E-Factor was 5. Five kilogrammes of waste were to be disposed of for every kilogramme of product.

This does not account for the waste water that has been tainted with chlorine by-products. 12–14 The E-Factor decreased to 0.3 Kg of waste when the synthesis was changed to use molecular oxygen, eliminating the need for chlorine. The creation of waste water was also prevented by the new procedure, which produced more than 16 times less trash than the old one. 15



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

When byproducts are unavoidable, creative alternatives should be considered. One effective option is to pursue an industrial ecology approach, in which waste can be transformed back into a new raw material with substantial value as it enters the life cycle. Currently, this strategy is being used to produce biofuel (Fig. 3b). 16

ATOM ECONOMY:

Atom Economy (AE), also known as Atom Efficiency, is a synthetic efficiency concept that was first developed by Barry Trost in 1990. 17 It refers to the idea of utilising raw materials as efficiently as possible so that the finished product has the most atoms from the reactants. All the atoms of the reactants would be included in the ideal reaction. The molecular weight of the desired product divided by the molecular weights of all the reactants used in the reaction is used to calculate the AE. It is a theoretical value designed to determine an action's potential efficiency quickly.

The Atom Economy AE



Fig. 4 The Atom Economy AE and several illustrations.

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The Grignard reaction, A3 coupling, and the Diels-Alder reaction are just a few examples used to demonstrate this idea. Due to the usage of a stoichiometric amount of metal reactant and the requirement to synthesise the Grignard reagent separately, the Grignard reaction—which the scientific world has recognised for its significance in organic synthesis—is regrettably a relatively poor atom-economical reaction. 18 Fig. 4 shows a typical Grignard reaction19 and how the Grignard reagent is used to create a structure resembling a propargylic amine. 20 The values of the AE are 44 and 56 percent, respectively, showing a loss of 50 percent of the raw material. C.-J. Li et al. presented an answer for the last example using the A3 coupling in 2002. (Alkyne, Aldehyde and Amine). 21 Since 92% of the original atoms employed in the reaction are present in the final product, this one-step multicomponent coupling reaction is more effective and conserves atoms. Another great illustration of an atom-economical reaction is the Diels-Alder reaction17 (Fig. 4). Since every atom from the reactants is included in the finished product, its AE is equal to 100%. Cycloaddition, one of the classical chemistry's greenest reaction categories, including Diels-Alder type reactions.

SYNTHESIS:

As shown in Fig. 5, a large amount of novel work has been done to enhance the synthetic toolbox of organic chemists. The green reactions that have already been identified over the past century are expanded upon by many of the novel reactions that have been produced in the last ten years. One category of effective reactions consists of previously known cycloaddition,17,22, rearrangement,23, or multi-component coupling reactions24. Enzymatic reactions28,29, C-H activation28, metathesis29, and cascade or tandem reactions25 are relatively new techniques that serve as excellent illustrations of the cleaner, more effective synthetic tools available to organic chemists.

For instance, the Wittig-type reactions like the Horner-Wadsworth-Emmons reaction are comparable to the mechanism used by the Grubbs catalyst to enable alkene metathesis (formation of a four membered ring as reaction intermediate, Fig. 5). It is a crucial component in the creation of bigger compounds. The metathesis reaction does not, however, generate as much waste as the Wittig reaction does. In the case of the Wittig reaction, the creation of phosphonium salts is regrettably inevitable because it is a component of the reaction's design and its primary driving force.

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.

Another recent development in chemistry that has a bright future is C-H activation. 26 Because of their high reactivity, activated carbon-halogen bonds are frequently employed in conventional coupling reactions. It means more steps are required to create the precursor because halogenated molecules are rarely found in nature. The necessity for halogenated precursors and the resulting halogenated waste products are eliminated when conventional coupling processes are replaced with C-H activation.

In 1993, Murai31 and Fagnou both published two well-known examples of C-H activation. 32 Acetophenone and 2-methylstyrene, two substrates that had been rendered inactive, were coupled in the first instance by Murai et al. using a ruthenium catalyst. This research marks a turning point in the science as one of the earliest examples of C-H activation. In the second instance, Fagnou and Stuart selectively combined two aromatic compounds without the aid of any directing or activating groups. These illustrations show how C-H activation might advance green chemistry.

Although there has been a lot of attention paid to creating chemicals for a variety of uses, from medicines to materials, there has been a startling lack of focus on taking danger into account during the design process. Sustainability requires an understanding of the characteristics of molecules that affect the environment and the changes that occur in the biosphere. Chemistry will be able to legitimately build molecules that are safer for people and the environment once it has mastered this understanding. The work of Arins33 in 1984 and Garrett and Devito in 1996 demonstrated the necessity and viability of creating safer compounds for the growth of green chemistry. 34

A substantial amount of work has been done in the field of toxicology in recent decades to transform it from a descriptive science to one with a significant mechanistic component,35 and more recently, progressively towards the introduction of an in-silico component. 36 This transformation has made it possible to link structure, properties, and function through correlations, equations, and models. These methods serve as the cornerstone for the efforts being made to create a thorough design plan. For instance, by incorporating certain design elements that prevent their entry into humans and many animal creatures, the existing knowledge of medicinal chemistry can already assist define some guidelines for producing less harmful compounds. 37

SOLVENTS:

The most active field of Green Chemistry research may be solvents. 38 They pose a significant obstacle for green chemistry since they frequently make up the majority of the mass lost during synthesis and processing. 39 In addition, a lot of common solvents are poisonous, flammable, or caustic. Their ephemeral nature and solubility have resulted in serious accidents, increased worker exposure risk, and air, water, and land contamination. When feasible, recovery and reuse are frequently linked to energy-intensive distillation and occasionally cross contamination. Chemists began looking for safer alternatives to address each of these flaws. These modern "green" solutions include solventless systems, water, supercritical fluids (SCF), and more recently, ionic liquids (43).

The ideal condition would be to avoid using any solvent whenever possible because choosing to add an auxiliary always entails work and energy to get it out of a specified system. Therefore, efforts have been made to create systems without solvents. 40 The discovery that solvents make up the majority of industrial waste served as further support for this notion. 39 The method frequently needs new or redesigned chemistry to enable the reaction to continue without the original solvent. This depends on the physical properties of the reagents used or the desired outcome of the transformation.

The most prevalent molecule on Earth is water, which is also sometimes referred to as a safe "universal solvent." 41 Therefore, there are many benefits to doing a reaction in or on water. Water is risk-free and safe to drink. It can be an effective solvent for large-scale chemical processing. Due to the hydrophobic effect44 and the fact that many organic compounds do not dissolve in water, the characteristics of water have even increased reaction speeds. One of the helpful instances demonstrating the benefits of using water as a solvent is the case of an enhanced Diels-Alder process in water. 17,41

The risk of water pollution, which can be difficult to clean and slow down industrial applications, is a problem that hasn't yet been solved.

SCF are another option to conventional organic solvents and have been substantial research in recent years. 42 They are substances that have been heated and compressed at temperatures exceeding their critical points at the same time (see Fig. 6).



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

Water, carbon dioxide, methane, methanol, ethanol, or acetone are frequently used to create SCF. Among SCF, carbon dioxide is one of the most frequently used. The research of Poliakoff, Leitner, Jessop, DeSimone, and others has shown that the resulting scCO2 is a flexible solvent that is safe and simple to manage. 45 The change in condition that happens when the vessel is cooled or the pressure is reduced is what makes SCF so alluring, but especially scCO2. CO2 will be a gas below critical points and a liquid above them, where reactions can take place. The solvent can be completely removed from the system by degassing it. The decaffeination of green coffee beans and the replacement of perchloroethylene in dry cleaning are two of the most well-known uses of ScCO2 in industry. 46 One effective substitute for conventional solvents has been demonstrated to be supercritical fluids.

Ionic liquids, developed in contemporary times by Seddon43, are another instance of greener solvents. As their name implies, ionic liquids, also known as room temperature ionic liquids, are liquid salts at room temperature. They are extremely flammable and have almost minimal vapour pressure. A "switchable" ionic liquid that was recently discovered by Jessop et al.47 is a "smart-obedient solvent" produced in situ, much like the liquid scCO2. An organic mixture becomes an ionic liquid when pressurised carbon dioxide is added, creating an in-place safer solvent.

When the pressure is released, the phenomenon is reversed, and the ionic liquid transforms back into the original combination, entirely getting rid of the solvent and skipping the time-consuming purification and extraction stages. Horvath's advancement of fluorous biphasic catalysis is another instance based on the same idea.

48 At room temperature, organic reagents are typically not miscible with a fluorous phase or solvent containing a catalyst suitable for the desired transformation. They combine into a single medium when heated, enabling the reaction to take place. The organic phase and the fluorous solvent separate when the mixture cools, streamlining the purifying procedure. Despite the drawback of the cost of fluorous solvents, this strategy is appealing.

These last examples provide as effective representations of separation, one of chemistry's most difficult problems. The new, enhanced green solvents are still auxiliaries, with the exception of some solventless

systems, and must be kept separate from the desired result. The problem of separation must be taken into account when selecting the right solvent if their use cannot be avoided.

ENERGY:

The development of more energy-efficient processes and the hunt for renewable energies—non-depleting resources in a time frame relevant to human scale—have been driven by growing worries over the depletion of petroleum feedstocks and the increase in energy demand. 49

Unused energy can be regarded as a waste, as was said in the first part (first principle). It is highly desirable to develop chemical processes or systems that don't consume a lot of energy. One example of what chemists can do to reduce energetic requirements is to lower the energy barrier of a chemical reaction or select suitable reactants so that the transformation can happen at ambient temperature, with all the direct and indirect benefits associated with it. 1

Increasing a chemical system's energy efficiency is just one aspect of the answer. Alternative forms of energy are also required. Biofuel production, solar power (thermal and photovoltaic), wind power, hydro power, geothermal energy, and hydrogen fuel cells are a few examples of these sustainable energies. 49,54 Green chemists, who are skilled at creating materials or chemical systems that may be used to gather part of those renewable natural energies, once again have a crucial role to play in addressing this new challenge.

One of the substitutes for petroleum is solar energy, which is currently the world's main sustainable energy source. It has taken a lot of work to comprehend and develop chemical systems that can transform solar radiation into voltaic energy. 53,55 Although interest has been shown in organic, inorganic, and hybrid solar cells, organic solar cells have attracted the most attention due to their higher efficiency. The ability of the material employed to absorb photonic energy from solar radiations is the foundation of such cells. As a result of the absorption, excited states are created that can be relayed and produce electronic current. The development of materials and polymers that effectively convert light into current is still a difficult task, but it is essential to the success of this strategy.

Another possibility for addressing the impending rise in energy demand is proton exchange membrane (PEM) fuel cells using hydrogen and oxygen gases (Fig. 7). Particularly in the last ten years, with the creation of increasingly effective catalysts like nanoparticles or even hydrogenase enzymes, PEM fuel cells have attracted study attention. 57 The risk of handling hydrogen gas, which is very volatile and explosive, is a key factor in this method.



Fig. 7 General concept of a hydrogen <u>fuel cell</u>.

RENEWABLE MATERIALS:

According to estimates, the great majority of our manufactured goods come from natural gas or petroleum feedstock. 1,49,58 Numerous facets of our consumer culture and economy will be impacted as a result of the depletion of those resources. It is now more important than ever to switch to renewable feedstocks for both fuel and building materials. Biomass, or the material derived from living beings, is the primary renewable feedstock on the planet for both material and energy. This comprises food, agricultural waste, wood, and other materials. 59

cellulose, lignin, suberin, and other wood components, as well as polyhydroxyalkanoates, lactic acid, chitin, starch, glycerol, and oil, are examples of renewable materials. 60 For instance, lignin is a significant waste product of the pulp and paper sector. It has long been used as fuel for burning at the industrial site. It has discovered new uses recently, such as dispersants, additives, and raw materials for the manufacture of compounds like vanillin, DMSO, or humic acid. 61 Another prevalent natural polymer that makes up the exoskeleton of arthropods is chitin (e.g. crustaceans). It is a significant byproduct of the seafood industry and can be deacetylated to become chitosan. 62

DERIVATIVES:

Whether used for analytical chemistry or organic synthesis, covalent derivatization is a widely used process in chemistry. 64 Non-covalent derivatization is a novel idea that emerged in the early 1990s. This derivatization relies on intermolecular interactions rather than covalent bonds. 65 The work by Warner was created as a way to achieve chemical alterations from the original system while using minimal energy and less material. The regulated diffusion and solubility of hydroquinones employed in Polaroid films provide as an early illustration of non-covalent derivatization. 66 At Polaroid, researchers wanted to release hydroquinones at a high pH.

They created a non-covalent protective group in the form of a co-crystal between hydroquinones and bis-(N,N-dialkyl)terephthalamides, as opposed to the conventional method of base-labile covalent protecting groups (Fig. 8). This strategy worked well and was practical for the industrial process. The problem was resolved with minimal energy and waste production while maintaining the original hydroquinone structural integrity.



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

CATALYSIS:

The typical use of a stoichiometric number of chemicals often results in waste.67 One significant way to increase the effectiveness of the synthetic toolbox is to move away from stoichiometric techniques and toward catalytic processes. By reducing the amount of energy needed, eliminating the usage of stoichiometric amounts of chemicals, and increasing product selectivity, catalysis can increase a reaction's efficiency. This implies less need for energy, feedstock, and waste. In addition, it frequently allows for novel chemical reactions and offers novel approaches to resolving conventional chemical problems.

Reactions of oxidation and reduction serve as examples of this idea. Organic chemists frequently perform reduction using DIBAL-H as the hydride donor, but this method produces a lot of waste because a stoichiometric amount of reducing agent is required to complete the reaction. By using catalytic hydrogenation, such as the Noyori hydrogenation70, the amount of feedstock required and the amount of waste produced are reduced because the necessity for stoichiometric reagents is eliminated (Fig. 9).



Fig. 9 Comparison between stoichiometric and catalytic reduction.

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Beyond effectiveness, catalysis can promote processes that wouldn't occur naturally. In the case of the metathesis reaction and the creation of the Grubbs catalyst, this was the situation. 27 As shown in Fig. 5, the invention of a metathesis catalyst made it possible to produce unsaturated molecules in a novel way. Both the innovation and the environmental benefit were significant.

Another example of "green" chemistry is biocatalysis, which uses natural or modified enzymes in a biomimetic manner.28-29,71 It often refers to both the direct usage of pure enzymes and the transformations carried out by created living organisms. As the transformation can be carried out in water at atmospheric pressure and ambient temperature, reaction conditions are rather mild. Enzymes have also shown to be more stereo-, chemo-, and regioselective.

BIODEGRADATION:

In the 1950s, for example, tetrapropylene alkylbenzene sulfonate (TPPS) was used as a surfactant for laundry detergents and accumulated into the water supply as a result of an incomplete degradation. This is an example of the persistence problem, which has been known for a long time and first became apparent in the early stages of industrial development.72,73 The situation was so dire that in some cases "water tended to foam when coming out of the tap."73,74 The public outcry prompted the industry to look for a quick fix, and it was discovered that substituting a linear carbon chain for the methyl branched chain of TPPS reduces the biopersistence. A typical example is the substitution of linear alkylbenzene sulfonate for TPPS.



Di(ethyl ester)dimethylammonium chloride (DEEDMAC) - Biodegradability test : 76%

Fig. 10 Integrating biodegradability in the design of surfactants.

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The ongoing issues with environmental pollution serve as a reminder of how difficult it is to design biodegradable materials and chemicals. After decades of data collection, trends have become apparent. Halogenated moieties, branching chains, quaternary carbons, tertiary amines, and certain heterocycles are among the chemical structures that should be avoided since they may have increased persistence. On the other hand, including functional groups like esters or amides that are recognised by common enzymes could aid in the creation of products that are environmentally friendly. 73,75 Surface-active quaternary ammonium compounds that are utilised as domestic fabric softeners were the subject of this approach. 76

Long chain ammonium salts were released into the environment up to the 1990s, including di(hydrogenated)tallow dimethyl ammonium chloride (DHTDMAC). It was later found that their inherent ecotoxicity was high and their rate of biodegradation in aqueous sediment was poor. Hydrolyzable amide or ester bonds were developed in response. According to Fig. 10, where DHTDMAC was replaced by di(ethyl-ester) dimethyl ammonium chloride (DEEDMAC), there was a 70% increase in the biodegradability of the new ammonium salts.

ANALYSIS:

Analytical chemistry that produces no waste when it measures substances is called "green chemistry." 77– 79 Analytical chemistry-related environmental issues are frequently related to the analytical methodology. Unfortunately, real-time direct analysis is not systematic because many approaches still ask for pretreating the sample or using what is known as "ex situ analysis." Process analytical chemistry79 is the capacity to watch a transformation and take quick action to stop undesirable results. When the sample is tested, waste may be produced because it isn't always possible. Since it will be ineffective if the chosen analytical methods add to more environmental issues, green chemists must take into account the functional requirements of analytical methods.

"Green chemistry" refers to analytical chemistry that doesn't waste anything when measuring compounds. 77–79 Environmental problems in analytical chemistry are typically connected to the analytical process. Unfortunately, because many approaches still call for pre-treating the sample or using "ex situ analysis," real-time direct analysis is not systematic. Process analytical chemistry79 is the ability to observe a change and act quickly to halt undesirable outcomes. Waste may be created during the testing of the sample because it isn't always possible. Green chemists must consider the functional requirements of analytical methods because it will be ineffective if the methods they select cause more environmental problems.

When it comes to the analytical techniques themselves, the majority of them have two issues that are connected to the two main steps of a technique: a pretreatment of the sample, which may involve extraction, separation, or even occasionally chemical modification of the sample, and a signal acquisition step. 79 The pretreatment step has been the focus of analytical chemists' worries because it typically requires large amounts of solvent. Innocent substitutes like Accelerated Solvent Extraction (ASE) or SCF extraction should be taken into consideration if the use of solvents for an extraction step cannot be avoided. 79,80

Analytical equipment's construction materials should be taken into account. Building new sensors, green chemists and green engineers should be cognizant of the material's toxicity as well as any potential environmental issues. Electrochemistry frequently employs electrodes made of mercury, for instance. It has been found to be successful to replace them with carbon-based electrodes, such as nanotubes or nanofibers. 81

ACCIDENT PREVENTATION:

The number of hazardous materials and procedures has increased in our workplace. The "Chemical Accident Prevention and the Clean Air Act Amendments of 1990" state that identifying and evaluating the hazards is the first step in preventing accidents. 82 Toxicological, physical, such as flammability or explosivity, and global hazards should all be taken into consideration when developing new chemicals and manufacturing techniques to avoid accidents like the Love Canal or Bhopal. 83

The UCLA catastrophe that took place in January 2009 serves as a stunning and current example of these risks. 84 Unfortunately, improper handling of the widely used and highly combustible butyllithium reagent led to the research assistant's tragic death. The scientific community should take this disaster as a powerful wake-up call that many of the chemicals we still use pose serious risks and should be replaced with safer alternatives to minimise the risk of mishaps.

Accomplishments by industry:

There are various instances of Green Chemistry-based industrial innovations that have been successful. 85 The purpose of the following section is not to enumerate all of the award recipients; rather, it is to provide a few notable instances of how the business world has responded to the problems posed by green chemistry.

A first illustration is a greener synthesis process that Eastman is credited with developing because of its enzymatic esterifications.

85 Increased efficiency is the result of the mild conditions, less byproduct generation, and energy savings that characterise this biocatalytic process. In total, the prior approach resulted in the elimination of hundreds of litres of organic solvents.

For creating eco-friendly herbicides, Dow AgroSciences researchers received recognition in 2008. They created Spinetoram while attempting to comprehend the structure-activity correlations of natural biopesticides in an effort to foretell analogues that would be more active. During its first five years of use, the company projects that the production of this new pesticide will eliminate "about 1.8 million pounds of organophosphate insecticides." 86

A more environmentally friendly synthesis method for Sitagliptin, a chiral -amino acid derivative used to treat type 2 diabetes, was created by Merck in 2006. 87 The method eliminates the requirement for extensive derivatization by using an unique asymmetric catalytic hydrogenation of unprotected enamines (Fig. 11). 88 With a three-step synthesis, Merck claimed a higher overall yield. The amount of waste was significantly reduced when the new method was put into practise on a production scale, making it a more economical choice.



Fig. 11 New synthesis of Sitagliptin.

The anticancer medication Taxolactive [®]'s component, Paclitaxel, was the subject of a novel strategy developed by BMS in 2004. 89 Through an 11 step synthesis, paclitaxel is commercially synthesised from the naturally occurring precursor 10-deacetylbaccatin III (10-DAB). There were several environmental issues with this "semisynthetic pathway," which was initially designed as a commercially feasible method of producing the chemical.

In order to find a more sustainable method, BMS used the most recent biotechnological developments. The active component of Paclitaxel was directly isolated from plant cell cultures as opposed to being created from a precursor. With this approach, all organic solvents, risky chemicals, and extra processes from the earlier procedure were completely eliminated. Paclitaxel is now produced by BMS exclusively using plant cell cultures.

Sertraline, an active component used to treat depression, was revamped in 2002, and Pfizer created a new, more environmentally friendly synthetic process for its manufacturing (Fig. 12). 90 The novel method increased the synthesis's overall efficiency and selectivity while providing significant environmental benefits. In the original manufacturing process, a three-step sequence was condensed into a single step. 91 The method was improved such that all processes could be completed in ethanol, and the amount of raw materials used was greatly reduced. The requirement to utilise, distil, and recover four harmful solvents was eliminated by the most recent revision (methylene chloride, tetrahydrofuran, toluene, and hexane).

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Fig. 12 New synthesis of <u>sertraline</u>.

The work done in 1998 by Solutia, Inc. on the removal of chlorine from the synthesis of 4aminodiphenylamine (Fig. 13) is a final noteworthy example.92 Researchers at the company looked into new ways to make a variety of aromatic amines, including 4-aminodiphenylamine (4-ADPA), in order to avoid the creation of aqueous waste streams with high levels of inorganic salts. Concerns were also raised regarding the risk involved with handling and storing significant amounts of chlorine gas. The answer comprised a brand-new synthesis for 4-ADPA that makes use of the base-promoted, direct coupling of aniline and nitrobenzene.93 The environmental advantages included a notable decrease in waste production.



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

Future challenges:

The experts in academia, business, and research facilities throughout the world have made tremendous advancements in the field of green chemistry thus far. The big challenges that the field still needs to tackle are, however, preceded by the successes thus far. The challenges listed below are a few of note.

Twelve Principles as a cohesive system:

The Twelve Principles of Green Chemistry were intended to be an integrated, coherent system of design rather than twelve separate objectives, and their design framework has served as a model for numerous advancements in the area. A truly sustainable process can only be achieved by putting all the principles into practice. Systemic sustainable design is possible and can support transformative innovation rather than incremental improvement by looking for the aspects of the principles that mutually reinforce one another.

Multi-functional catalysts:

Over the past two decades, catalysis has advanced significantly. However, even today, most catalysts are made to work on just one transformation, and little is understood about multi-functional catalysts, which are described as having more than one catalytic function. Chemistry would advance to a new level if the same catalyst could be used for numerous separate reactions or to complete a full synthesis in one pot. This would allow for the production of more complex compounds with increased material and energy efficiency.

Mastering weak forces for synthesis and properties:

Future developments in chemistry are projected to place a greater emphasis on non-covalent and weakforce interactions. There are considerable benefits to imparting characteristics by weak forces and directing synthetic pathways in the same way while reducing the quantity of bond breaking and bond forming. These include lowering the amount of energy required, reducing waste, and improving efficiencies. The ability to control weak forces in the same way that chemistry has controlled covalent forces has a great deal of potential to aid in achieving molecular sustainability.

Integrative systems thinking:

The reductionist methodology has traditionally formed the foundation of scientific inquiry. This method has led to a depth of understanding and discovery that has enabled contemporary life's conveniences, like communication, transportation, and medical. Additionally, it has had significant unexpected and unanticipated impacts that have harmed both people and the environment. Green Chemistry can seek important advancements while avoiding unexpected outcomes by adopting a systems perspective. Innovations that are truly transformative are produced when reductive and integrated thinking are combined.

CONCLUSION:

For many years, molecular scientists have developed the chemicals, materials, and production techniques that have facilitated societal and economic advancement. In order to practise chemistry in a way that incorporates impact on people and the environment as a design criterion, one must adhere to the historical heritage of green chemistry.

In doing so, Green Chemistry has demonstrated how businesses may innovate in a way that makes them both more profitable and environmentally friendly. Although Green Chemistry practitioners all over the world have accomplished a commendable amount of work, the field's strength and potential far outweigh its past successes.

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