# Green Chemistry: As an Alternative Tool for Reducing Pollution

**Veenu Gupta**

MSc Chemistry, M.Ed, CSIRNET (Chemistry)

**Abstract:** ***The concept of green processes and technologies is environmentally friendly, improved and utilized in such a way so that it doesn't disorganize the environment and conserve natural resources. Some people refer green technology as environmental technology and clean technology. The existing expectation is this field will bring novelty and innovation changes in diurnal life of same magnitude of information technology. Besides, today due to the importance of these technologies, most of the governments takes initiatives to promote it. Therefore, governments recommended many financial incentives which generate electricity from renewable resources. The goals of green technologies are as follow: to meet the needs of society in the way without depleting or damaging natural resources on earth which is the major target of green technologies. The concept is to make products which can be fully reclaimed or reused. Furthermore, by changing patterns of production and consumption, steps are being taken into account to diminish waste and pollution as one of the most indispensable aims of green technologies. Many companies have committed for establishing manufacturing practices and business regarding green technologies. Besides, this kind of technology implies to a system which utilizes innovative techniques to create environmental friendly products. Predominantly, it contains the various everyday cleaning products, waste, inventions, energy sources, clothing and host of others. Going green or using technologies which are environmental friendly is amongst the many methods which countries are looking in order to spur economic growth and develop the lives of its citizens. Green processes and technologies use renewable and natural resources which never depletes. Besides, green technology utilizes innovative and new techniques in terms of energy generation. Furthermore, green nanotechnology which utilizes green chemistry and green engineering is one of the newest in green technologies. One of the most important factors for pollution of environment is the disposal of waste which green technology has the answers to it as well. This kind of technology can easily alter the waste pattern and production in a way which it does not deteriorate the earth and people can go green. Furthermore, among the conceivable areas where these creations and growth are expected to come from involve organic farming, green energy, green building construction, eco-textiles, and manufacturing of relevant products and materials to support green business. Because it is new to the industries. Besides, it is also expected to absorb new clients who will see too many advantages of using green technologies in their places and others. Therefore, the main goal is to utilize green technology which has no adverse effects on the planet. Nowadays there are huge concerns regarding environmental pollution which bring attentions on the utilization of green products and processes. There are a great amount of researchers who have been conducted and are being conducted in different industries with various scopes in this term. However, the essential point is whether green technology are able to adapt in various industries. Certainly, one of the major problems in the globe is pollution which has created a huge concern in relation to the future human life. Therefore, this paper concentrates on the advantages and disadvantages of green technology. Green chemistry is a philosophy and study of the design of products or substances that will not Involve materials harmful to the environment. . It is a modern science of chemistry that deals with the application of environmentally friendly chemical compounds in the various areas of our life such as Industrial uses and many others. This area of chemistry had been developed by the need to avoid chemical hazards that organic and inorganic compounds had on the body of humans and animals. Chemistry plays a pivotal role in determining the quality of modern life. The chemicals industry and other related industries supply us with a huge variety of essential products, from plastics to pharmaceuticals. However, these industries have the potential to seriously damage our environment. Green chemistry therefore serves to promote the design and efficient use of environmentally benign chemicals and chemical processes.***

**Keywords:** atom economy, green engineering, bio plastics, biopolymers

## 1. Introduction

Green Chemistry is defined as invention, design, development and application of chemical products and processes to reduce or to eliminate the use and generation of substances hazardous to **human health and environment.** Thus, Green Chemistry can be thought as the production process which reduces pollution present in the atmosphere. During any of the process, the generation of byproducts takes place and if you don't utilize them in a proper manner, then they will create environmental pollution. These processes are too expensive, only if there's no utilization of byproducts.

**Green chemistry**, also called **sustainable chemistry**, is an area of chemistry and chemical engineering focused on the designing of products and processes that minimize or eliminate the use and generation of hazardous substances. While environmental chemistry focuses on the effects of polluting chemicals on nature, green chemistry focuses on the environmental impact of chemistry, including reducing consumption of nonrenewable resources and technological approaches for preventing pollution.

Green chemistry, also called the sustainable **chemistry or** environmentally friendly chemistry. According to chemist John Warner and Paul Anastas, **the green chemistry is "chemical products and process modeling" which lessens or eradicate the generation and use of hazardous substances.**

The green chemistry revolution is providing an enormous number of challenges to those who practice chemistry in industry, education and research. With these challenges however, there are an equal number of opportunities to discover and apply new chemistry, to improve the economics of chemical manufacturing and to enhance the much-tarnished image of chemistry.

Green chemistry is a philosophy and study of the design of products or substances that will not involve materials harmful to the environment. The ideal scenario is to virtually stop pollution before it can even begin through the use of non pollutants. Green chemistry is a relatively new area of chemistry that emerged by the need to reduce the hazardous effect of chemicals and to reduce the amount of environmental pollution that chemicals have.

Green Chemistry indulges itself in the use of environmental friendly and mild reagents like **sound waves, microwaves, sunlight, and enzymes.** These reagents are not dangerous in nature. In recent times, several photochemical reactions have been accomplished with the use of microwave arrangement. Rather than microwaves, sound waves are also used in carrying out specifically recognized chemical reactions. It's quite evident that when the continuous efforts will be in action to enhance the green chemistry, the pollution-free space will be the assured gift, given to us.

When we talk of chemical reaction, if the whole chemical reactants get converted into beneficial products, then surely no chemical waste will be produced. Therefore, our very own environment will be so free of any kind of pollution.

In the recent years, India has explored new techniques of farming, obtaining good quality seeds and irrigation. There is an increasing use of fertilizers and pesticides in order to become self-sufficient in the context of food generation. The over- exploitation of soil and excessive use of fertilizers has deteriorated the quality of soil, air and water. We cannot stop the methods of development instead look for methods which will help in reducing the environmental pollution. Hence, the concept of green chemistry comes into picture. It aims at minimizing the use and generation of hazardous substances.

Green chemistry is the process of thinking and utilizing the existing knowledge to reduce the adverse impact of pollution on the environment. Green chemistry can also be thought of as a production process which will reduce pollution in the environment. During any process, byproducts are generated and if not utilized properly then they add to the environmental pollution. These processes are cost ineffective if the byproducts are not utilized. Waste generation and disposal are economically unsound processes. The utilization of knowledge for reducing chemical hazardous with the development activities is the foundation of green chemistry.

**Green chemistry** is the design of **chemical** products and processes that reduce or eliminate the use or generation of hazardous substances to humans, animals, plants, and the environment. Green chemistry discusses the engineering concept of pollution prevention and zero waste both at laboratory and industrial scales. It encourages the use of economical and ecocompatible techniques that not only improve the yield but also bring down the cost of disposal of wastes at the end of a chemical process.
**Green chemistry** applies across the life cycle of a **chemical** product, including its design, manufacture, use, and ultimate disposal. MPaul Anastas is known as the '**Father of green chemistry**'. **Green Chemistry** and Clean Energy. ... At the same time, **green chemistry** can **save** companies **money** by reducing the need for costly **chemicals**, reagents and solvents, lowering insurance and legal costs, reducing waste disposal costs (which can exceed $5 per kg for some toxics), and **saving** energy.

Waste disposal and generation sounds an uneconomical process. The knowledge used in reducing hazardous chemical with the help of developmental activities is what Green Chemistry is all about.

## 2. History of Green Chemistry

Green chemistry emerged from a variety of existing ideas and research efforts (such as atom economy and catalysis) in the period leading up to the 1990s, in the context of increasing attention to problems of chemical pollution and resource depletion. The development of green chemistry in Europe and the United States was linked to a shift in environmental problem-solving strategies: a movement from command and control regulation and mandated reduction of industrial emissions at the "end of the pipe, " toward the active prevention of pollution through the innovative design of production technologies themselves. The set of concepts now recognized as green chemistry coalesced in the mid- to late-1990s, along with broader adoption of the term (which prevailed over competing terms such as "clean" and "sustainable" chemistry).

In the United States, the Environmental Protection Agency played a significant early role in fostering green chemistry through its pollution prevention programs, funding, and professional coordination. At the same time in the United Kingdom, researchers at the University of York contributed to the establishment of the Green Chemistry Network within the Royal Society of Chemistry, and the launch of the journal *Green Chemistry*.

In 1990 the Pollution Prevention Act was passed in the United States. This act helped to create a modus operandi for dealing with pollution in an original and innovative way. This paved the way to the green chemistry concept. Paul Anastas and John Warner coined the two letter word "green chemistry" and developed the twelve principles of green chemistry. In 2005, RyojiNoyori identified three key developments in green chemistry: use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations and the use of hydrogen in asymmetric synthesis.

### 1.1 Origins of Green Chemistry

It is a modern science of chemistry that deals with the application of environmentally friendly chemical compounds in the various areas of our life such as industrial uses and many others. This area of chemistry had been developed by the need to avoid chemical hazards that organic and inorganic compounds had on the body of humans and animals.

### 1.2 Concepts of Green Chemistry

The concept of green chemistry incorporates a new approach to the synthesis, processing and application of chemical substances in such manner as to reduce threats to health and environment.

This new approach is also known as:
- Environmentally benign chemistry
- Clean chemistry
- Atom economy
- Benign-by-design chemistry

**Green Chemistry or environmentally benign chemistry** is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green chemistry was developed by virtue of the need to overcome this hazardous effect that toxic compounds exert on the body. This relatively new area of chemistry uses water as the medium of chemical reactions that are done in the laboratory. Chemical reactions are usually done in a medium that is called solvent. An exception is reactions that take place in the gas phase where there is no need for medium there. Sometimes chemical reactions are done in a neat fashion.

Namely, the reacting compounds are mixed and reacted together with the need for a solvent. This is one of the methods that are used in green chemistry to avoid pollution and the hazardous effect of the volatile solvent. Green chemistry applies to organic chemistry, inorganic chemistry, biochemistry, analytical chemistry and physical chemistry to minimize west, utilize renewable resources.

### 1.3 Green Chemistry &Sustainable Development

The UN defines sustainable development as "meeting the needs of present without compromising the ability of future generation." Green chemistry focuses on how to achieve sustainability through science and technology

To better understand and solve the issue of environmental pollution, many approaches and models have been developed for environmental impact assessments.

The concept of end-of-pipe approaches to waste management decreased, and strategies such as environmentally conscious manufacturing, eco efficient production or pollution prevention gained recognition.

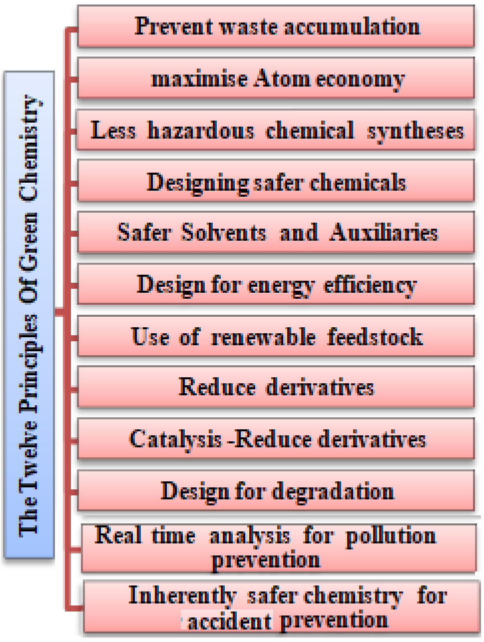
### 1.4 The Twelve Principles of Green Chemistry:

In 1998, Paul Anastas (who then directed the Green Chemistry Program at the US EPA) and John C. Warner (then of Polaroid Corporation) published a set of principles to guide the practice of green chemistry.[12] The twelve principles address a range of ways to reduce the environmental and health impacts of chemical production, and also indicate research priorities for the development of green chemistry technologies.

The principles cover such concepts as:
- The design of processes to maximize the amount of raw material that ends up in the product;
- The use of renewable material feedstocks and energy sources;
- The use of safe, environmentally benign substances, including solvents, whenever possible;
- The design of energy efficient processes;
- Avoiding the production of waste, which is viewed as the ideal form of waste management.

Green Chemistry is commonly presented as a set of twelve principles proposed by Anastas and Warner. The principles comprise instructions for professional chemists to implement new chemical compound, and new synthesis and technological processes.

1) **Prevention** -It is better to prevent waste than to treat or 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 syntheses** -Wherever practicable, synthetic methodologies 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 preserve efficacy of function while reducing 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** -The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used;
7) **Use of renewable feedstock** -Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure;
8) **Reduce derivatives** -A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable;
9) **Catalysis -** Unnecessary derivatization (blocking group, protection/ de protection, temporary modification) should be avoided whenever possible. 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 do not persist in the environment and break down into innocuous degradation products;
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 and
12) **Inherently safer chemistry for accident prevention** -Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions, and fires.




### 1.5 Progress in Green Chemistry

Over the past decade, green chemistry has convincingly demonstrated how fundamental scientific methodologies can be devised and applied to protect human health and the environment in an economically beneficial manner. Significant progress has been made in key research areas, such as atom economy, alternative synthetic route for feed stocks and starting materials, bio-catalysis, green solvent, bio sorption, designing safer chemicals, energy and waste management.

In a chemical reaction, if the entire chemical reactants are converted into useful products then no chemical waste will be generated. Hence the environment will be free from any pollution. This can only be achieved if the conditions are optimized for the reaction.

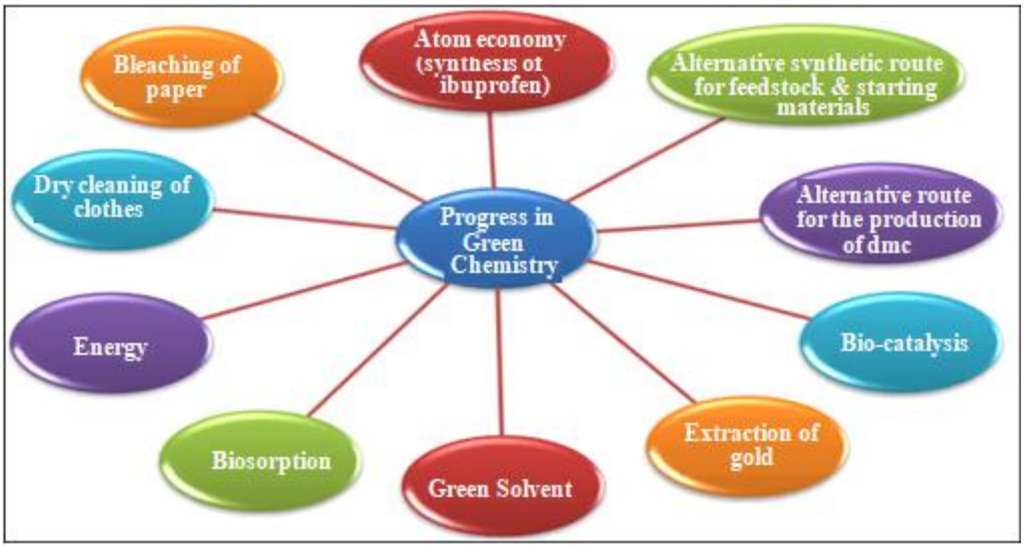
Attempts are being made not only to quantify the *greenness* of a chemical process but also to factor in other variables such as chemical yield, the price of reaction components, safety in handling chemicals, hardware demands, energy profile and ease of product workup and purification. In one quantitative 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 nanomaterials 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

And this can solely be attainable when conditions are optimized for reaction. There consist of various applications in our routine life. The below-mentioned points should be in our mind and they'll showcase its uses:

Green chemistry has many applications in our day to day life. The following points will show its uses:

1) **Dry cleaning of clothes** – In earlier days, tetrachloroethylene was used as a solvent for dry cleaning. This compound is carcinogenic and also pollutes the ground water. Nowadays, liquefied carbon dioxide with suitable detergent is used for this purpose. It generated liquid carbon dioxide as a byproduct and hence causes less pollution.
2) **Bleaching of paper** – Initially chlorine gas was used for this purpose but now it has been replaced by hydrogen peroxide. Hydrogen peroxide along with a suitable catalyst which promotes its bleaching action is used. Green chemistry is promoting a healthy environment for the human society, being responsible citizens we all should follow this. A world free from pollution will improve the living conditions and increase the age of life on this planet.
3) **Atomeconomy (Synthesis of Ibuprofen):** Atom economy is one of the fundamental principles of green chemistry. Atom economy looks at the number of atoms in the reactants that end up in the final product and by-product or waste. % Atom economy = 100 x (FW of product /FW of reactants)



### 4) Alternative synthetic route for feedstock &starting materials

Production of dimethylcarbonate (DMC) production DMC is a versatile and environmentally innocuous material for the chemical industry. Owing to its high oxygen content and blending properties, it is used as a component of fuel. Traditional method for the production of DMC This method involves the use of phosgene (COCl2) and methanol (CH3OH) as shown below: $COCl_2 + 2CH_3OH \rightarrow CH_3OCOOCH_3$ (DMC) + 2HCl

### 5) Alternative Route for the production of DMC

This involves the use of copper chloride (CuCl), methanol ($CH_3OH$), oxygen ($O_2$) and carbonmonoxide.

$2CuCl + 2CH_3OH + 1/2O_2 \rightarrow 2Cu(OCH_3)Cl + H_2O$

$2Cu(OCH_3)Cl + CO \rightarrow 2CuCl + CH_3OCOOCH_3$

### 6) Bio-Catalysis

Bioleaching is the extraction of specific metals from their ores through the use of microorganisms such as bacteria. This is much cleaner than the traditional heap leaching using cyanide in the case of gold extraction.

### 7) Extraction Of Gold

This can involve numerous ferrous and sulphur oxidizing bacteria, such as Acidithiobacillusferrooxidans and Acidithiobacillusthiooxidans (also referred to as Thiobacillus). For example, bacteria catalyse the breakdown of the mineral arsenopyrite (FeAsS) by oxidising the sulphur and metal (in this case arsenic ions) to higher oxidation states whilst reducing dioxygen by $H_2$ and $Fe^{3+.}$ This allows the soluble products to dissolve.

$FeAsS(s) \rightarrow Fe^{2+}(aq) + As^{3+}(aq) + S^{6+}(aq)$

This process occurs at the cell membrane of the bacteria. The electrons pass into the cells and are used in biochemical processes to produce energy for the bacteria to reduce oxygen molecules to water.

In stage 2, bacteria oxidise $Fe^{2+}$ to $Fe^{3+}$ (whilst reducing $O_2$). $Fe^{2+} \rightarrow Fe^{3+}$

They then oxidise the metal to a higher positive oxidation state. With the electrons gained, they reduce $Fe^{3+}$ to $Fe^{2+}$ to continue the cycle. The gold is now separated from the ore and in solution.

### 8) Green Solvent

During these early years, the chronic toxicological properties of chemicals were often completely unknown and many unwittingly became indispensable tools of the trade. Infamously, benzene was widely employed as a solvent, a hand-cleaner and even as an aftershave, decades before its carcinogenicity became appreciated. Today chemists are still taught the efficacy of chromium, osmium and lead compounds as oxidants, the virtues of chlorinated solvents and the use of atom-inefficient methodologies, while the curricula in most undergraduate chemistry programs provide little or no training in toxicology, environmental science or sustainable technology.

Solvents are consumed in large quantities in many chemical syntheses as well as for cleaning and degreasing. Traditional solvents are often toxic or are chlorinated. Green solvents, on the other hand, are generally derived from renewable resources and biodegrade to innocuous, often a naturally occurring product

One of the green solvents is supercritical carbon dioxide ($scCO_2$). Supercritical carbon dioxide refers to carbon dioxide that is in a fluid state while also being at or above both its critical temperature and pressure ($T_c = 31.3\ ^oC$, $P_c = 1071$ psi (72.9 atm) yielding rather uncommon properties. Supercritical carbon dioxide has been used as a processing solvent in polymer applications such as polymer modification, formation of polymer composites, polymer blending, microcellular foaming, particle production, and polymerization Reaction of amines with $CO_2$

$RNH_2 + CO_2 \longrightarrow RNHCOOH\ RNH_3 + RNHCOO^-$

$RNH_2 + 2H_2C\ (O)\ CH_2 \longrightarrow RN\ (CH_2CH_2OH)_2$

$H_2\ C\text{-}O\text{-}CH_2 + CO_3^{2-} \longrightarrow [COO\text{-}CR\text{-}C\text{-}O\text{-}]$ (polycarbonates)

### 9) Synthetic techniques

Novel or enhanced synthetic techniques can often provide improved environmental performance or enable better adherence to the principles of green chemistry. For example, the 2005 Nobel Prize for Chemistry was awarded, to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock, for the development of the metathesis method in organic synthesis, with explicit reference to its contribution to green chemistry and "smarter production." A 2005 review identified three key developments in green chemistry in the field of organic synthesis: use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations and the use of hydrogen in synthesis. Some further examples of applied green chemistry are supercritical water oxidation, on water reactions, and dry media reactions. Bioengineering is also seen as a promising technique for achieving green chemistry goals. A number of important process chemicals can be synthesized in engineered organisms, such as shikimate, a Tamiflu precursor which is fermented by Roche in bacteria. Click chemistry is often citedas a style of chemical synthesis that is consistent with the goals of green chemistry. The concept of 'green pharmacy' has recently been articulated based on similar principles.

### 10) Carbon dioxide as blowing agent[

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.

International Journal of Science and Research (IJSR)
ISSN: 2319-7064
ResearchGate Impact Factor (2018): 0.28 | SJIF (2019): 7.583

**11) Hydrazine**

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:

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

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

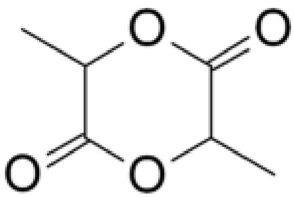
$2\ NH_3 + H_2O_2 \rightarrow H_2N\text{-}NH_2 + 2\ H_2O$

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.

**1, 3-Propanediol**

1, 3-propanediolis traditionally generated from petrochemical precursors. It can be produced from renewable precursors via the bioseparation of 1, 3-propanediol using a genetically modified strain of *E. coli*.This diol is used to make new polyesters for the manufacture of carpets.

**Lactide**

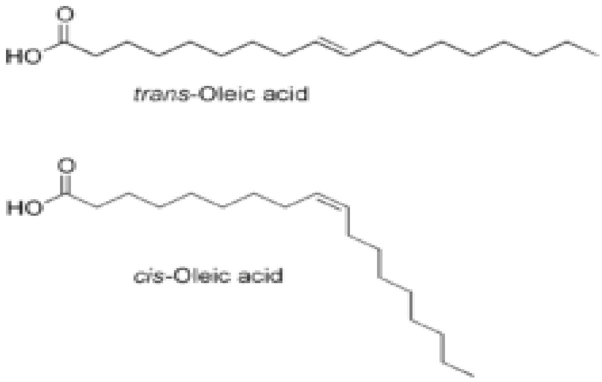


**Lactide**

In 2002, Cargill Dow (now NatureWorks) 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 NatureWorks 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.

**Carpet tile backings**

In 2003 Shaw Industries selected a combination of polyolefin resins as the base polymer of choice for EcoWorx due to the low toxicity of its feedstocks, 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.




*Trans* and *cis* fatty acids

**Transesterification of fats**

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 byproducts, and reduces the amount of fats and oils wasted.

**Bio-succinic acid**

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.

Several laboratory chemicals are controversial from the perspective of Green chemistry. The Massachusetts Institute of Technology created a "Green" Alternatives Wizard [2] to help identify alternatives. Ethidium bromide, xylene, mercury, and formaldehyde have been identified as "worst offenders" which have alternatives.Solvents in particular

International Journal of Science and Research (IJSR)
ISSN: 2319-7064
ResearchGate Impact Factor (2018): 0.28 | SJIF (2019): 7.583

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.

**Figure 1**

| *Red solvent* | *Flash point* | *Reason* |
|---|---|---|
| Pentane | –49 °C | Very low flash point, good alternative available. |
| Hexane(s) | –23 °C | More toxic than the alternative heptane, classified as a hazardous airborne pollutant (HAP) in the US. |
| Diisopropyl ether | –12 °C | Very powerful peroxide former, good alternative ethers available. |
| Diether ether | –40 °C | Very low flash point, good alternative ethers available. |
| Chloroform | N/A | Carcinogen, classified as a HAP in the US. |
| Dichloroethane | 15 °C | Carcinogen, classified as a HAP in the US. |
| Dimethyl formamide | 57 °C | Toxicity, strongly regulated by EU Solvent Directive, classified as a HAP in the US. |
| Dimethyl acetamide | 70 °C | Toxicity, strongly regulated by EU Solvent Directive. |
| N-Methyl pyrrolidinone | 86 °C | Toxicity, strongly regulated by EU Solvent Directive. |
| Pyridine | 20 °C | Carinogenic/mutagenic/reprotoxic (CMR) category 3 carcinogen, toxicity, very low threshold limit value TLV for worker exposures. |
| Dioxane | 12 °C | CMR category 3 carcinogen, classified as HAP in US. |
| Dichloromethane | N/A | High volume use, regulated by EU solvent directive, classified as HAP in the US. |
| Dimethoxyethane | 0 °C | CMR category 2 carcinogen, toxicity. |
| Benzene | –11 °C | Avoid use : CMR category 1 carcinogen, toxic to humans and environment, very low TLV (0.5 ppm), strongly regulated in the EU and the US (HAP). |
| Carbon tetrachloride | N/A | Avoid use : CMR category 3 carcinogen, toxic, ozone depleter, banned under the Montreal protocol, not available for large-scale use, strongly regulated in the EU and US (HAP). |

**Development of the solvent selection tool**

A number of companies have previously published solvent selection guides, more recently Fischer *et al* published a detailed and comprehensive approach to the environmental selection of solvents, though in our view this assessment is too generous to volatile solvents. Volatile solvents have more potential for environmental release and may also have more flammability issues (*e.g.*, pentane or diethyl ether). In reviewing previous work, we felt that because of the challenges and time pressures associated with the medicinal chemistry job, any tool needed to be extremely simple for the end user scientist. However, this does not mean that the information behind the tool is simple. The work to produce a tool was initiated in our environment, health and safety (EHS) group, and solvents were assessed in a thorough and systematic way in three general areas.

1) **Worker safety**– including carcinogencity, mutagenicity, reprotoxicity, skin absorption/sensitisation, and toxicity
2) **Process safety** – including flammability, potential for high emissions through high vapour pressure, static charge, potential for peroxide formation and odour issues.
3) **Environmental and regulatory considerations**- including ecotoxicity and ground water contamination, potential EHS regulatory restrictions, ozone depletion potential, photoreactive potential. Of course compliance with regulations and company guidelines provide the baseline of Pfizer's environmental policy.

Solvents, such as benzene and carbon tetrachloride, were included to reinforce the avoidance of their use.

In addition, the scientists in our green chemistry teams produced a simple solvent replacement table for each of the solvents in the red/undesirable category, with the philosophy of adopting a “use this instead” policy rather than a “don't use” policy. This replacement table is shown in Table 2. The replacements are either chemically similar (*e.g.*, heptane as a replacement for the high flammable pentane) or functionally equivalent (*e.g.*, ethylacetate, methyl *tert*-butyl ether (MTBE) or 2-methyltetrahydrofuran (2-MeTHF) as alternative extraction solvents to dichloromethane).

**Table 2:** Solvent replacement table

| Undesirable solvents | Alternative |
|---|---|
| Pentane | Heptane |
| Hexane(s) | Heptane |
| Di-isopropyl ether or diethyl ether | 2-MeTHF or *tert*-butyl methyl ether |
| Dioxane or dimethoxyethane | 2-MeTHF or *tert*-butyl methyl ether |
| Chloroform, dichloroethane or carbon tetrachloride | Dichloromethane |
| Dimethyl formamide, dimethyl acetamide or *N*-methylpyrrolidinone | Acetonitrile |
| Pyridine | $Et_3N$ (if pyridine used as base) |
| Dichloromethane (extractions) | EtOAc, MTBE, toluene, 2-MeTHF |
| Dichloromethane (chromatography) | EtOAc/heptane |
| Benzene | Toluene |

There are a number of points that need further comment. Many of our scientists are surprised that dichloromethane is the recommended alternative to other chlorinated solvents, such as chloroform. All that Table 2 is indicating is that if a chlorinated solvent needs to be used, dichloromethane is the best choice out of the four.

All of the solvents have good replacements, with the exception of one group, which is the dipolar aprotic solvents dimethyl formamide, dimethyl acetamide and *N*-methylpyrrolidinone. For this group of solvents, acetonitrile is a relatively poor substitute, especially for reactions involving a strong base. Due to the lack of good alternatives, Pfizer, with a group of other pharmaceutical companies, has identified finding replacements for these solvents as a key target in green chemistry research.

The guide and replacement table seem almost ridiculously simple but when used by our enthusiastic site teams they led to amazing results, including a 50% reduction in chlorinated solvent use across the whole of our research division (more than 1600 lab based synthetic organic chemists, and four scale-up facilities) during the time period 2004–2006. Even sites that had an increase in the number of chemists during that period were able to report a 50% reduction in chlorinated solvent use. In addition, we were able to reduce the use of an undesirable ether by 97% over the same two year period and substantially promote the use of heptane compared with hexane (more toxic) and pentane (much more flammable).

**The development of a reagent guide**

This was much more challenging than the solvent guide because of the wide variety of reagents and by the fact that reagents by their very nature are designed to be reactive (whereas solvents are ideally inert), potentially causing additional safety and environmental issues. To our knowledge, no other company has tried to develop a guide of this nature. We wanted the guide to achieve three purposes.

To provide a balanced assessment of chemical methodologies, taking into account the many constraints that scientists have to take into account when making decisions in their work. To our mind the ideal reagent would have three ideal characteristics:

- The ability to work in good yield in a wide variety of “drug like molecules” —this is a characteristic highly valued by medicinal chemists.
- The ability of a reagent to be used for scale-up to prepare multi-kilogram batches—a characteristic valued by our Chemical R and D, Kilo Lab and Pilot Plant chemists and engineers.
- To be as green as possible. Our green chemistry teams would like to introduce the greenest possible reagent as early as possible in the discovery/development process. The assessment of greenness included worker safety, ecotoxicity and atom economy.
- To provide easy access to the chemical literature or procedures for reagents that score well in the assessment. In the on-line Pfizer version of the guide, reagents that score well are linked directly through electronic links to key literature papers, internal procedures or both.
- To raise awareness of newer emerging green methodologies.

The three most common oxidants used by Pfizer's medicinal chemists for this transformation are Dess–Martin periodinaneor its precursor IBX, tetrapropylammoniumperruthenate (TPAP) and the Swern oxidation. All of these methods have significant scale-up issues, for example Dess–Martin periodinane is a high energy molecule that has poor atom economy and is prohibitively expensive for use on a multi-kilogram scale. The use of stoichiometric TPAP again has very poor atom economy and is also prohibitively expensive for large-scale use. A review of large-scale oxidations since 1980 revealed only one large-scale use of TPAP to catalyse an oxidation with a co-oxidant and no examples of stoichiometric use. The Swern oxidation is used at Pilot Plant scale but generates toxic by-products and the stench of dimethylsulfide. Hence, the purpose of the reagent guide is to influence the medicinal chemist away from the reliable but environmentally unfriendly methods to more friendly methods, such as the oxidation with bleach (NaOCl) catalysed by nitroxyl radicals, such as TEMPO and PIPO.In addition, there has been an explosion in the chemical literature of methods that use molecular oxygen as an oxidant, with more than 150 papers in the last 3 years. These methods carry some challenges on scale-up, as the use of molecular oxygen to aerate flammable solvents is a significant safety concern. These concerns can be reduced by using oxygen diluted with large volumes of nitrogen but still these methods lie on the edge of acceptability when judged against the scalability criteria. An improved safety profile and more acceptable scalability is obtained if the oxidation is performed in water. Again, the purpose of the reagent guide is to provide scientists with easy up-to-date access to developments in this exciting area of green oxidation.

For the oxidation grids we were able to set strict criteria for greenness (reaction by-products should be either water or sodium chloride and there should be no major process safety issues). For amide formation, the majority of literature methods had very poor atom economy. We decided to set the greenness criteria for this transformation as the following.

- Side products should have a molecular weight less than 200.
- No major process safety issues.
- No major environmental issues.

Uronium salts, such as HATUand HBTU, have become widely used in research laboratories but have many green chemistry issues. Their by-products have molecular weights of 398 and 397, respectively, for accomplishing a dehydration reaction (removing a molecule of water with a molecular weight of 18). They are both highly energetic molecules and HATU is shock sensitive.The phosphorus based reagent BOPand PyBOPare again energetic molecules and have even worse atom economy. BOP has the further major disadvantage that its manufacture and use involve HMPA (a class 1 carcinogen).

Dicyclohexylcarbodiimide (DCC) and di-isopropyl carbodiimide fail our green criteria because of their very strong sensitization properties and hence in recent years have become rarely used for scale-up in the pharmaceutical industry. Cyanuric chloride is similarly a very strong sensitiser. Oxalyl chloride does not meet our greenness criteria on account of its poisonous by-product carbon monoxide. 1-Chloro-4, 6-dimethoxy-1, 3, 5-triazine (CDMT) is a sensitiser but has been used by some process groups for scale-up. EEDQ, PPACA, and EDCI do not meet our greenness criteria on the basis of atom economy but are widely used for scale-up chemistry. Thionyl chloride and chloroformates are the most common reagents for this transformation used by the pharmaceutical industry, *N*, *N′*-carbonyldiimidazole (CDI) is growing in popularity and was used in the commercial synthesis of sildenafil and sunitinib. We judged that thionyl chloride did not fully meet our greenness criteria because of its worker safety issues but was preferred to oxalyl chloride for acid chloride formation. Although reagents such as CDI and isobutyl chloroformate are described as green, they are not without issue, for example, the synthesis of CDI uses highly poisonous phosgene, our assessment simply says they are greener than some of the alternatives available at this time.

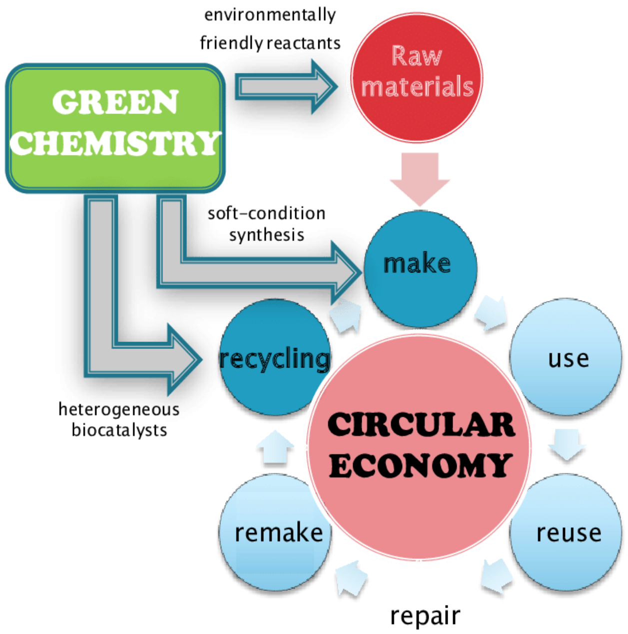
All of the reagents discussed so far are stoichiometric reagents but the real opportunity is in the development of catalytic reagents where the only by-product would be water. The use of boronic acids, and in particular boric acid, to catalyse amide formation is very exciting and works well in some substrates. In reality, boric acid is a poor catalyst for amide formation but it does help drive the reaction of acids and amines that undergo substantial uncatalysed reaction over to completion. For these substrates, boric acid catalysis represents a very green methodology. Enzymatic methods are another catalytic method where the only by-product is water.

The boric acid and enzymatic methodology are active research areas and the regularly updated Pfizer reagent guide gives Pfizer scientists easy access to the latest green advances in these areas. The grid also gives references to other reagents that meet two out of the three criteria.

A Venn diagram covering amide formation from acids, prone to racemisation, and amines can be found in the electronic supplementary information.

**Biosorption**
Biosorption is one such important phenomenon, which is based on one of the twelve principles of Green Chemistry, i.e., “Use of renewable resources.” It has gathered a great deal of attention in recent years due to a rise in environmental awareness and the consequent severity of legislation regarding the removal of toxic metal ions from wastewaters. In recent years, a number of agricultural materials have been used to remove toxic metals from wastewater.

**Energy**
Fossil fuel is dogged with many environmental pollution problems. There is, therefore, a growing need for alternative energy sources to replace fossil fuels. Renewable energy resources that are currently receiving attention include, solar energy, wind energy, hydro energy. Environmentally benign petrol can be obtained by the removal of Pb from petrol; by addition of ethanol produced from biomaterials to the petrol pool; by addition of methyl t-butyl ether (MTBE) to the petrol pool. MTBE has high octane and by use of electric vehicles powered by fuel cells.




## 3. Conclusion

Green chemistry addresses such challenges by opening a wide and multifaceted research scope thus allowing the invention of novel reactions that can maximize the desired products and minimize the waste and byproducts, as well as the design of new synthetic schemes that are inherently, environmentally, and ecologically benign.

**Therefore, combining the principles of the sustainability concept as broadly promoted by the green chemistry principles with established cost and performance standards will be the continual endeavor for economies for the chemical industry.**

The medicinal chemistry population is very receptive to changing work habits in response to our green chemistry outreach initiatives. Particularly encouraging has been the remarkable response to two separate solvent reduction campaigns targeting chlorinated solvents and selected ethers. In addition, the replacement of hexane and pentane in our stockrooms with the less toxic and less volatile heptane has been extraordinarily well received. Key to these successes has been the philosophy of encouragement and education rather than obligation and scrutiny. Chemists are highly creative individuals and when provided with the new guidance they have proved willing to adopt or invent new, greener practices. We are now moving forward with a new suite of on-line tools designed to promote greener synthetic reagents. These tools provide simple access to a diverse range of documentation and literature, which can rapidly provide the working chemist with the information they need to try new procedures. We are optimistic that this guide will share the success of our solvent initiatives and will influence our scientists to adopt safer and greener syntheses.It is, therefore, essential to direct research and development efforts towards a goal that will constitute a powerful tool for fostering sustainable innovation.

Green chemistry alone cannot solve the pressing environmental concerns and impacts to our modern era, but applying the twelve principles of green chemistry into practice will eventually help to pave the way to a world where the grass is greener.

## References

[1] S. Chandrasekaran, B.C.Ranu, G.D.Yadav & S. Bhanumati, Monographs on Green Chemistry Experiments, GC Task Force, DST, 2009
[2] P. Anastas and J. C. Warner, Green Chemistry: Theory and Practice; Oxford Science Publications, Oxford, 1998
[3] J. H. Clark, Chapman and Hall, Chemistry of Waste Minimisation, Corporate Image of the Chemical ed London, 1995 Industry, CIA (UK), 1993; Pan European Image Survey, CEFIC, 1994.
[4] K. Tanaka and F. Toda, Chem. Rev., 100, 1045. 2000
[5] James H. Clark, Green chemistry: challenges and opportunities, Green Chemistry February 1999
[6] R.A. Sheldon, Green solvents for sustainable organ S. Ravichandran, Int. J. ChemTech Res., 2(4)2191, 2010
[7] J. H. Clark, Catalysis of Organic Reactions by Supported Inorganic Reagents, VCH, New York, 1994