Al-Nahrain Journal of Science
ANJS, Vol. 28(2), June, 2025, pp. 48-61

Green Chemistry: Current State and Future Opportunities

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Article's Information

Received: 10.10.2024
Accepted: 03.04.2025
Published: 15.06.2025

Keywords:
Catalysis, Sustainable Development , Photochemistry

Abstract

Nowadays, there is no singular solution to all environmental issues; however, green chemistry, also referred to as clean chemistry, represents a fundamental strategy for pollution prevention. This approach offers a transformative perspective on various challenges associated with industrial chemical activities. Historically, industrialists and chemists have focused on minimizing exposure to hazards by managing toxic substances at every stage of the process, including usage, treatment, and disposal. The primary objective of green chemistry is to develop innovative processes that provide economic advantages over traditional methods, thereby encouraging their adoption within the industry. This discipline addresses the challenges of sustainable development by promoting practices that protect the environment and conserve natural resources. Ultimately, while green chemistry does not resolve all environmental problems, it remains a crucial approach for fostering a cleaner environment and ensuring the sustainability of our planet's resources.

http://doi.org/10.22401/ANJS.28.2.05
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1. Introduction

Whether it is food products, medicines, fertilizers, pesticides, material or most of the objects that surround us and that we use on a daily basis, they have all at some point in their manufacture undergone at least one chemical transformation.[1] Chemistry is an integral part of our daily lives without us necessarily realizing it. Thus, chemistry as an industry has experienced considerable development in the twentieth century to the point of becoming a basic industry of fundamental importance [2]. But due to its expansion, chemistry is a polluting industry. Let us cite as an example the manufacture of ibuprofen (nonsteroidal anti-inflammatory) by the Boots process (traditional synthesis) [3]. An annual production of 13,000 tons of anti-inflammatory is accompanied by 20,000 tons of waste. In this example, the chemical process generates more waste than product! This waste is not recyclable, and some is toxic. They must therefore be treated to detoxify or destroy them [4]. Since the beginning of industrial chemistry, waste has been systematically released into nature. The image of chemistry among the public has gradually deteriorated at the rate of catastrophes with serious human or ecological consequences [5]. Throughout its intensive development phase, the chemical industry has released substances in an uncontrolled manner into the air, water or soil. Indeed, dilution was then considered the best solution to pollution problems. But since the end of the 1960s, the persistence of certain molecules in the environment as well as their accumulation in living organisms has been noted. The toxicity of many compounds previously considered harmless has also been discovered. Diffuse chemical pollution threatens human health and reproduction. In 2008, Inserm (National Institute of Health and Medical Research) outlined the proven or possible links between environmental factors and a dozen or so cancers on the rise, in a report that summarized more than 1,800 scientific articles or reports on the subject: "Changes in the environment could be partially responsible for the observed increase in the incidence of certain cancers." Over the past thirty years, the development of new chemical products for construction, furniture and maintenance has been very rapid [6, 7]. But this change has not been followed by any control of building hygiene. Among these new products are VOCs (Volatile Organic

Compounds), including aldehydes (formaldehyde), benzene, toluene, and glycol ethers, which are currently highly present in the ambient air of homes. VOCs are substances composed of carbon and hydrogen present in most building materials. They constitute a new source of pollution of the ambient air in homes [8]. They can evaporate for months and years. One of the most harmful is currently formaldehyde. Its emissions vary according to the humidity and temperature of the room. The warmer and more humid the room, the greater the formaldehyde emissions. In 2005, its consumption in France reached 126,352 tons. Nearly half of this tonnage is used in the resin manufacturing sector, which is used, for example, to make varnishes or glues. The agrochemical manufacturing and industrial chemical manufacturing sectors consume more than 40% of the annual quantity, to produce disinfectants, antifungals and preservatives [9]. Many industrial sectors are therefore affected using formaldehyde solutions or resins: leather tanning, the manufacture of wood panels, glues and gelatin, synthetic rubber, pharmaceutical products, foundry molds, dyes, pigments, essential oils, perfumes, soaps, detergents, paints, fertilizers, animal feed. Another example is the case of fine particles from diesel engines that reach the pulmonary alveoli. Their role in lung cancer has been proven. According to studies conducted in Paris, Grenoble, Rouen and Strasbourg, 10% of lung cancers in these cities are attributable to them [10]. Every day, consumer items: cosmetics and food packaging. They are antiandrogens. Bisphenol A is used to make baby bottles, plastic bottles and other everyday products. In light of these recent and converging alerts, there is an awareness of indoor and diffuse chemical pollution. This is a major public health issue and an industrial, scientific and medical challenge. But what resources do the chemical industries have at their disposal?

2. Green Chemistry and Sustainable Development

2.1. Historical Context

Environmental concerns have increasingly become central to economic and industrial agendas. Over fifteen years ago, several researchers began to propose parameters for qualifying a reaction as "green chemistry." The concept of green chemistry emerged in the early 1990s, with the United States Environmental Protection Agency (EPA) launching its first research initiative focused on this area in 1991. In 1998, American chemists Paul Anastas and John C. Warner, affiliated with the EPA, formally defined the principles of green chemistry, establishing a framework aimed at reducing or eliminating the use and generation of hazardous substances in chemical processes [11].

2.2. Definition and Importance

Sustainable development is defined as a transformative approach that addresses the necessary changes required for both the environment and its inhabitants to thrive in a cleaner and more equitable world. This concept emphasizes the importance of respecting environmental integrity while promoting social equity. Furthermore, sustainable development relies on a long-term vision that integrates economic, social, and environmental dimensions in an inseparable manner. It serves as a framework for organizing efforts to meet the present and future needs effectively. The transition towards a more sustainable model is essential for ensuring health and equity while safeguarding the natural resources of our planet [12].

2.3. Foundations of Sustainable Development

Sustainable development is fundamentally based on three core pillars:

- Social Equity: Ensuring fairness and justice in the distribution of resources and opportunities among all individuals.
- Environmental Quality: Maintaining and enhancing the health of ecosystems and natural resources to support life.
- Economic Efficiency: Promoting economic practices that contribute to sustainable growth without depleting environmental resources.

These pillars collectively guide the pursuit of development that meets current needs without compromising the ability of future generations to meet their own needs [13].

2.4. Four Fundamental Principles of Sustainable Development

Sustainable development is predicated on four essential principles necessary for its success: solidarity, precaution, responsibility, and participation.

Figure 1: Fundamental principles of sustainable development.

- Solidarity

Solidarity must be established among nations, communities, and, at times, within members of a single society. This principle emphasizes the interconnectedness of all people and the necessity for mutual support in achieving sustainable outcomes.

- Precaution

The precautionary principle entails making informed decisions to prevent potential disasters that could adversely affect health and the environment, such as pollution, greenhouse gas emissions, and industrial accidents. For instance, limiting carbon dioxide emissions is crucial to mitigating climate change.

- Responsibility

Responsibility is a shared obligation among citizens, industries, and agricultural sectors to minimize environmental harm. This includes implementing measures such as imposing taxes on industries that contribute significantly to pollution.

- Participation

Participation involves the establishment of councils for children and youth to ensure inclusive engagement in sustainable project initiatives. This collective involvement is vital for the successful implementation and achievement of sustainability goals.

3. State of Play of the Chemical Industry

The first response to pollution problems was regulation. States sought to exercise control by imposing waste management rules. This approach is based on the fact that a reduction in exposure to a hazard factor results in a reduction in risk. The main flaw in this approach is its time lag compared to the hazard. In 1990, the United States adopted the Pollution Prevention Act. It constitutes a fundamental change in the treatment of risk. Indeed, it requires efforts to be concentrated upstream to reduce pollution at the source, as soon as processes are developed. This tackles the causes of the risk and avoids having to regulate exposure to the hazard. A reflection on a "reform of chemistry" has begun. The concept of "green chemistry" as developed in the United States around 1990 with the aim of providing a framework for the prevention of pollution linked to chemical activities [11]. "Green chemistry aims to design chemical products and processes that reduce or eliminate the use and synthesis of hazardous substances." In this definition, the term "hazardous" is taken in the broadest sense: the danger can be physical (flammable, explosive substance, etc.), toxicological (carcinogenic, mutagenic, etc.) or global (destruction of the ozone layer, climate change, etc.). A European regulation came into force on 1 June 2007: REACH (Registration, Evaluation and Authorisation of Chemicals) is a regulation establishing a new European policy on the management of chemical substances. Its objective is to improve the level of protection of health and the environment while strengthening competitiveness and innovation in the European Union. The main aim of this regulation is to improve knowledge of the intrinsic properties (hazards) of chemical substances and the risks associated with their uses. This project will integrate new substances into the same system and gradually (over 11 years) existing substances. Around 30,000 substances (as such or included in preparations) should be subject to registration. The main consequence of the REACH regulation will be to increase consumer safety and environmental protection. Since 1981, the chemical industry has conducted numerous tests to identify the risks associated with the production and use of chemical substances. Safety data sheets provide information to users on the optimal conditions for handling these substances. For example, toxicological, ecotoxicological and physicochemical data on 10,500 substances are now available. The European Commission has also carried out, in whole or in part, a risk assessment for 130 substances out of the 141 considered to be priorities. Ultimately, REACH will lead to complementing data on the hazards of substances (intrinsic properties) and to better controlling risks to health and the environment on the basis of a risk assessment throughout the product life cycle. In practice, manufacturers and importers of chemical substances will acquire knowledge about the substances, through laboratories that are most often external to the industry and will conduct a health and environmental risk assessment. Acquiring this knowledge will certainly improve the protection of employees, consumers and the environment. The chemical industry has also defined a code of good conduct for about twenty years. Synonymous with continuous progress in terms of safety, health and the environment, Responsible Care is a voluntary approach by the global chemical industry: independently of the standards and regulatory provisions that are imposed on it and that it complies with. By relying on guiding principles, good practices and management systems, this individual and collective approach allows the chemical industry to consolidate its reputation in a world where chemicals are considered more as potential hazards than as elements that contribute to everyone's well-being. It integrates the Health - Safety - Environment dimension of products throughout their life cycle, from their design in the laboratory to their fate after use. Its aim is to protect the men and women of the company, to change modes of transport, to save energy, to find new sources of energy, to treat waste and to innovate to be a driving force for sustainable development. It is a real "green business". Launched in France in 1990 by the Union of Chemical Industries, under the name of Commitment to Progress, the approach aims to implement the concept of sustainable development after those of North America and Western Europe, chemical companies in Eastern Europe, the Pacific and South America are also joining. To date, 53 national or regional federations are rolling out their national program, under the aegis of Responsible Care [14].

4. Green Chemistry

A chemist or engineer, even before creating a material, a product or a process, must ask themselves certain questions: what raw materials to use? What techniques to implement? What types of waste will be produced? The principles of green chemistry and green engineering only make sense if, when creating a project, the researcher integrates basic thinking guided by clear and simple principles into the early stages of design.[36]

The American government launched the "Pollution Prevention Act" in the 1990s. This federal directive aims to unify research around a new idea: designing new chemical products or processes or optimizing existing ones, with the aim of making them less dangerous to human health and the environment. In 1991, a project called "Alternative Synthetic Pathway for Pollution Prevention" was launched to distribute funds for research on these themes [15]. Green chemistry was born. It is based on the following simple idea: to eliminate pollution, let's ban pollutants! It is a vision of chemistry and not a discipline in its own right. Green chemistry applies naturally to organic chemistry, mineral chemistry, biochemistry, analytical chemistry as well as process engineering. In 1996, Paul Anastas (organic chemist) and a colleague Tracy Williamson published an article in ASC Journal that laid the foundations for green chemistry. It was not until 1998 that Paul Anastas and John Warner published a text that would make history. It was the first concrete tool for reflection based on 12 principles resulting from the work undertaken under the impetus of the "Pollution Prevention Act". We could say that green chemistry is designing industrial products and processes based on process engineering with a minimum impact on three areas: the health of operators and employees, the quality of the environment and the health of consumers. Green chemistry is governed by the following twelve principles [16]:

1. Prevention: it is better to limit pollution at the source rather than having to eliminate waste.
2. Economy of atoms: in a chemical reaction, it is necessary to optimize the incorporation of reagents into the final product.
3. Less harmful chemical syntheses: it is desirable to design less dangerous chemical syntheses that use and lead to products that are little or not toxic to health and the environment.
4. Design of safer chemical products: chemical products must be designed to preserve their function while reducing their toxicity.
5. Safer solvents and auxiliaries: the use of solvents and auxiliary substances should be reduced as much as possible.
6. Improving energy efficiency: energy expenditure should be reduced by favoring processes that take place at ambient temperature and pressure.
7. Using renewable raw materials: it is better to use renewable materials rather than fossil materials.
8. Reducing the quantity of by-products: by-products should be avoided as far as possible.
9. Catalysis: catalytic processes are superior to stoichiometric processes.
10. Design of non-persistent substances: chemicals will be designed by incorporating their final degradation mode.
11. Real-time analysis of pollution control: real-time methods will be developed to control the process before any formation of harmful substances.
12. Essentially safe chemistry to prevent accidents: processes will be chosen to minimize the risks of accidents, discharges, explosions and fires.

Green chemistry is set to develop for several reasons. The global awareness of the need to move towards sustainable development is reflected in increasing public pressure on polluting industries and the implementation of ever more restrictive legislation. It is also necessary to take into consideration the profit that an industrialist can derive from the development of a green process: cost reduction and technological advantage over the competition (business still present). Green chemistry must now overcome several barriers: technical and economic difficulties in developing processes, but above all a profound change in mentalities that must learn and adapt to the thought patterns of this new chemistry. Sustainable development has three dimensions: environmental, economic and social. Green chemistry naturally fits into these three dimensions and appears to be a major tool for sustainable development. It is therefore called sustainable chemistry (La Recherche, special issue, 420, June 2008). But green chemistry is often perceived in public opinion as "chemistry from plants", a chemistry transforming agricultural and forestry products for non-food purposes (energy, ubricants, surfactants, solvents, surface treatments, packaging and storage materials, etc.) described and summarized in the book "Green Chemistry" by Paul Colonna (2006) [17]. The advent of the concept of sustainable chemistry offers the opportunity to see if the evolutions of chemical processes towards greater sustainability could not imply a change in the relationships between chemistry and society, and in particular lead to a review of communication on chemistry. Communicating on sustainable, green and responsible chemistry will require moving from a defensive, positivist attitude to an approach of listening and respect for the concerns, interests and expectations of fellow citizens. Eastes (2010) believes that adopting such a communication posture seems inaccessible for the moment to the community of chemists [18]. We can see that with green chemistry we are entering an eminently subjective and above all evolving domains. Through the previous examples, we encounter even in the scientific community various definitions and possible variants. This is a positive sign because it shows that researchers and citizens are discussing this concept, making it a Socially Lively Question (SLV).

5. Examples of Green Chemistry

By taking the synthesis of ibuprofen, we can see green chemistry at work. In the 1990s, the BHC company developed a new process that respects the fundamental principles of green chemistry and in particular the "atom economy". It consists of minimizing the quantity of waste by using reactions during which the atoms of the reactants are integrated into the products as much as possible. In this process, the waste is reduced to a molecule: acetic acid. The latter is a basic product of the chemical industry, so it is recovered and sold. In the end, the synthesis does not generate any waste [19]. But we must also consider the economic aspect, which is essential from an industrial point of view.

The quantity of by-product, and therefore the reprocessing cost, is considerably reduced in the case of the green process compared to the traditional process. To optimize chemical processes to make them more environmentally friendly, in the case of the synthesis of ibuprofen, the development of a specific catalyst that made it possible to develop the BHC process. Stages 2 and 3 in the BHC process are catalyzed. (Catalysis is the action of a substance called a catalyst on a chemical transformation in order to modify its reaction rate. The catalyst is not consumed and is found unchanged at the end of the reaction. If it can be easily separated from the reaction medium, it can be recycled in a new synthesis). Through this example, we can observe that in the new process, there are no longer by-products that constituted the waste in the BOOTS process but only one, acetic acid $C_2H_4O_2$ which can therefore be reused. In addition, the manufacturing steps are reduced to 3 instead of 6 which constitutes a gain. And this thanks to catalysts that play an important role in green chemistry. More generally, catalysis is considered one of the pillars of green chemistry because it allows syntheses to be optimized at several levels. Two Nobel Prizes have recently rewarded advances in the field of catalysis. The 2005 Nobel Prize in Chemistry was awarded to three researchers, including Frenchman Yves Chauvin, for their work on the olefin metathesis reaction (change of positions of the substituents of double bonds by a catalyzed chemical mechanism), described by the Nobel Committee as "a step forward towards green chemistry, which is more environmentally friendly." The same committee considered it one of the most useful in organic chemistry, which has many applications and is widely used in the chemical industry [20]. It is used in syntheses as varied as the synthesis of products with biological activity (drugs, herbicides, insect pheromones) or materials (polymers with special properties, gasoline additives). In the context of research and development, we can take the example of hydrogen. Hydrogen can be one of the most promising factors in the search for alternatives to fossil resources. But it does not exist in its natural state. It must be produced from natural gas, biomass or water with different methods that are being validated such as thermal, electrochemical and biological methods. In fact molecular hydrogen is considered a green energy vector because it can be generated from renewable sources and its combustion only generates water. A detailed analysis on the green nature of the main hydrogen production processes by comparing them to each other based on the principles of green chemistry has been carried out. But the result is that these processes, although relatively green, are not viable at the present time from the point of view of competitiveness and economics. Indeed, adopting hydrogen as an energy vector requires storing it, distributing it and ensuring the safety of its use [20].

6. Challenges and Opportunities

Today, green chemistry must prove its industrial, economic and environmental efficiency, for this it must meet four main challenges that interlock with each other including:

- Technological Challenge.

Technologies can meet one or more of the principles of green chemistry and are expressed through 3 main themes: Those of processes, Substitute products and safety.

- Societal Challenge.

Today, environmental concerns are becoming widespread even if the change in behavior sometimes takes time to be implemented. On one side are the expectations of society in terms of health, non-toxicity of the products consumed, respect for the environment, eco-responsibility of companies, and on the other side are the expectations of companies that must combine environmental progress with competitiveness requirements.

On both sides, green chemistry, to be accepted, must be understood (societal acceptability). From this point of view, awareness and communication remain key factors for success.

- Industrial Challenge.

The industry has to deal with rising oil prices and the imminent depletion of oil resources. An obligation to drastically reduce polluting emissions from chemical processes, and particularly the release of greenhouse gases. Strong regulatory pressure on the use of raw materials, intermediates and products in the chemical industry, as well as several other but also with several other European directives concerning the end-of-life of materials.

- Economic Challenge

It is important to point out to economic operators the following: Make them accept that the requirements of sustainable development influence today's growth and that it is essential to anticipate the conditions of tomorrows. Make them aware of the fact that sustainable development can be a factor of competitive differentiation. Technological advances are probably one of the principles, driving forces of the development of green chemistry. Researchers must find new solutions or solutions that replace those already in place if they are competitive (economic challenge), that they are integrated into the overall balance sheet (industrial challenge) [11].

7. The Latest Advances in Green Chemistry

At a time when the term "chemistry" seems to be frightening, accused of many evils (Diseases, pollution) in a justified manner. The concept of ideal synthesis is put forward to meet the challenge of a more compatible green and clean chemistry The ideal synthesis takes into account economic concerns (high yield), social (safety of procedures etc.) and environmental (solvent-free reaction, absence of reaction waste) (Figure 2) [21].

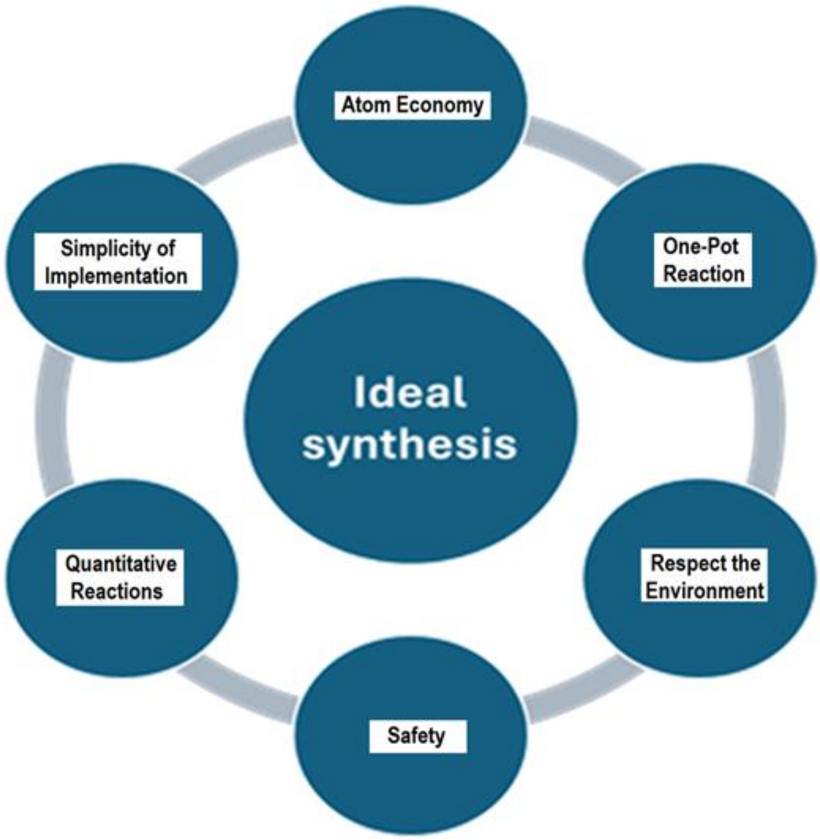

Figure 2: Schematics representation of ideal synthesis

7.1. Applications of catalysis

Catalysis is one of the approaches used to make chemical transformations efficient and less energetic. It allows to reduce the quantity of waste produced compared to the transformations (stoichiometric) i.e. there is no excess of reagents left at the end that could not react. In this sense, catalysis is a pillar of green chemistry, i.e. one of the approaches showing significant gains in terms of overall efficiency of chemical reactions. Catalytic reactions are reactions carried out in the presence of a catalyst that reduces energy requirements. This solid or liquid element increases the speed of the reaction without being consumed, by lowering the energy barrier, in other words the energy threshold required to allow the reaction to occur. The catalyst is generally in much smaller quantities than the reactants and is not consumed and is found unchanged at the end of the reaction [2]. Catalysis presents an alternative to solve many problems of green chemistry including:

- Use of non-toxic starting reagents.
- Lower energy cost related to the activation of molecules by catalysts.
- Selective combination of molecules with high efficiency to provide only the desired product without waste.

7.2. Catalysis and the use of non-toxic reagents without waste production

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In general, the lack of tolerance towards the environment of certain processes for the synthesis of highly useful products requires innovation to open new access routes to these essential products, implementing cleaner processes [22, 23].

7.2.1. Without the use of toxic reagents

Indeed, several efforts are being undertaken to discover new synthesis routes that replace those involving toxic reagents, for example the recovery of CO_2 to replace phosgene derivatives (a very toxic gas at room temperature). We therefore know how to use carbon dioxide in fine chemistry for the synthesis of optically active synthesis intermediates or for the preparation of polycarbonate (a transparent biodegradable material) (Figure 3). In this sense, the valorization of CO2 in organic synthesis is particularly interesting because it allows the use of a non-toxic and cheap raw material and contributes to reducing its emissions into the atmosphere in this case by reducing the greenhouse effect [24].

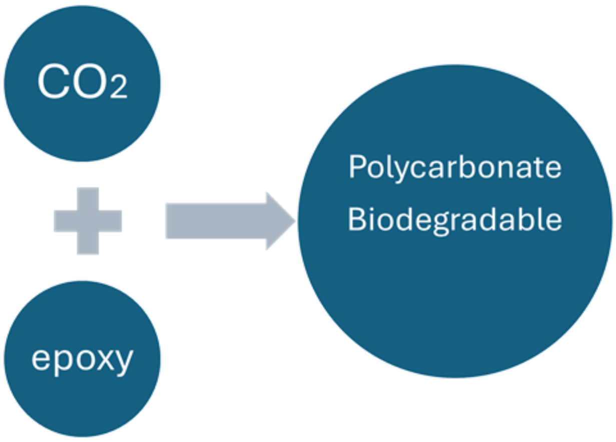


Figure 3: Schematic representation of production of transparent biodegradable material.

7.2.2. Without waste production

Nowadays, the production of secondary products in a process always requires the separation of the useful product from the by-products and entails an energy cost such as distillation or solvent in the case of chromatography or recrystallization and always with loss of material, time and thus money. Indeed, this type of process must be re-studied with the need to use only appropriate raw materials without unnecessary consumption of resources [25].

7.3. Catalysis, a tool for economy and selectivity

7.3.1. Energy saving

Indeed, catalysis has the effect of lowering the activation energy of a given chemical reaction. In this case, the direct consequence is an overall saving of the energy provided in the synthesis process. (figure 4)[26].

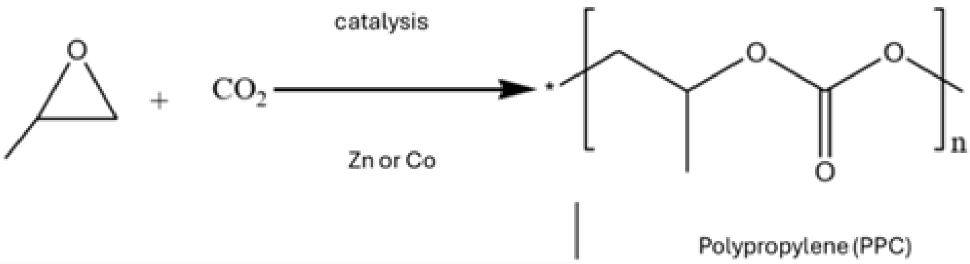


Figure 4: Example of energy saving reaction.

7.3.2. Selectivity and material saving

The reduction of the energy to be provided in a process also has the advantage of allowing chemical reactions at lower temperatures and increasing the selectivity of the processes for the formation of the desired products, which therefore limits the formation of secondary products during these reactions and consequently costly separations. On the other hand, efforts are being made to discover new reactions involving the combination of multiple reagents in a single derivative if possible without the use of solvents. Such catalytic reactions are carried out with retention of all the atoms involved, therefore it results in a saving of material, which therefore implies the absence of costly separation, time, equipment and also a saving of energy. Figure 5 show example of such reaction [26].

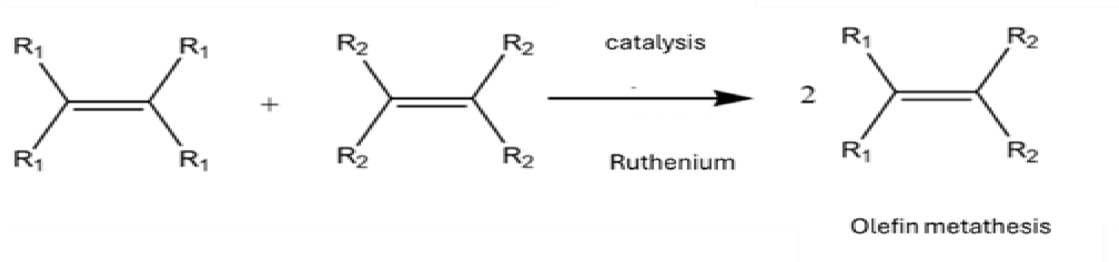


Figure 5: Example of selectivity and material saving reaction. R1= H , R2= C1…..C3

Undoubtedly, catalysis in all its forms represents an essential path towards green (clean) chemistry and contributes to restoring the image of chemistry, through its capacity to selectively transform molecules into useful products under mild conditions without producing waste at the end of the reactions (waste = 0).

8. Solvent-Free Chemistry

Most solvents are volatile organic compounds, which can therefore disperse easily in the environment. This is often accompanied by risks since they are very often flammable. In addition, they are harmful from an ecological and health point of view because many present both acute toxicity and also chronic toxicity. On the one hand, these concerns are all the more justified since organic solvents are used in large quantities. On the other hand, the latest studies have shown that: 80 to 90% of the waste generated by the pharmaceutical industry comes from the solvents used during synthesis. 35% of the volatile organic compounds free in the atmosphere are very toxic organic solvents. As well as the use of solvents is responsible for half of the greenhouse gas emissions in the world. The implementation of solvent-free reactions makes it possible to develop an efficient, clean and thus economical technology. Indeed, a liquid reagent is actually used as a solvent for the other reagents in the reaction. From a scientific and technical point of view, these reactions take place in the presence of a solvent, but they have the particularity of contributing to green (clean) chemistry by reducing the masses or volumes involved, because no additional solvent is added during the reaction used with large quantities. In addition, solid-solid or solid-gas reactions are different from this point of view, because no solubilization is possible during the reaction [27]. Currently, synthesis techniques in the absence of solvent can use conventional equipment in the case where one of the reagents is liquid. In the case of solid-solid reagents, they use more specific equipment such as a mortar or a grinder and also activation techniques other than a thermal effect, of which photochemistry or microwaves are particularly suitable since they can eliminate the use of solvent as a heat vector or as an activator.

9. Mortars

The use of a simple mortar operated manually has made it possible to carry out several chemical reactions. Indeed, the action caused by the friction between the bowl of the mortar and the pestle provides the energy necessary for the advancement of a reaction. In this case, the final product can be recovered directly in the mortar, therefore without the use of organic solvents [28]. For example (figure 6), Rong et al performed the condensation of an aldehyde and an aromatic ketone with malononitrile $CH_2(CN_2)$ in a single pot. This reaction usually takes place during 5 min of grinding. The expected product according to a multicomponent reaction, is isolated by a simple filtration in distilled water then a recrystallization in ethanol (EtOH). This example clearly shows that the use of a simple mortar allows a certain number of reactions to be carried out without the use of organic solvents for a reasonable time.

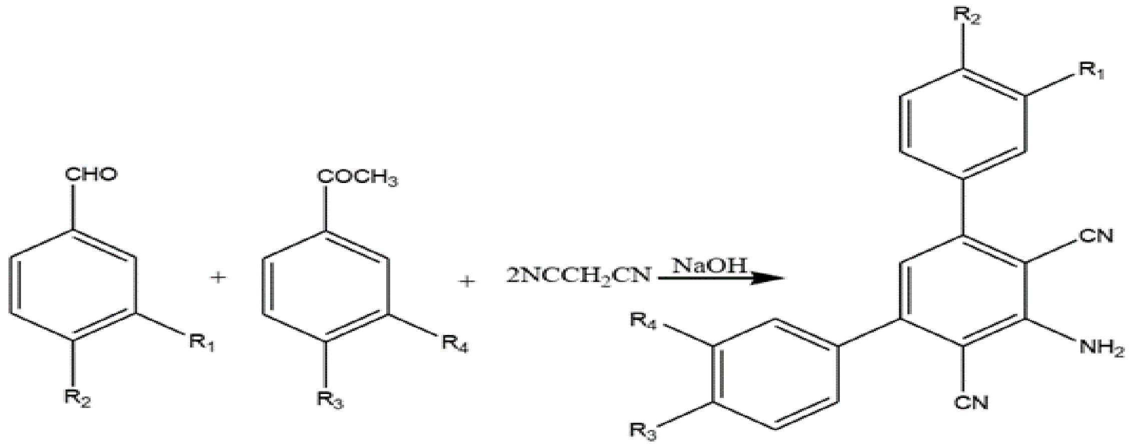


Figure 6: example of using mortors in green chemistry reaction. R1…R4=H,C1…..C4

10. Crushers

Vibrating and planetary motion crushers allow reactions to be carried out using solid reagents without having to dissolve them in a solvent but to carry out reactions with one or more reagents in the form of liquids associated with solids. For example, Knoevenagel (figure 7) studied condensation without the use of organic solvents in a vibrating mill. In this experiment, the only by-product formed is water (H_2O). The latter is eliminated by drying (drying agent such as Na_2SO_4) [29].

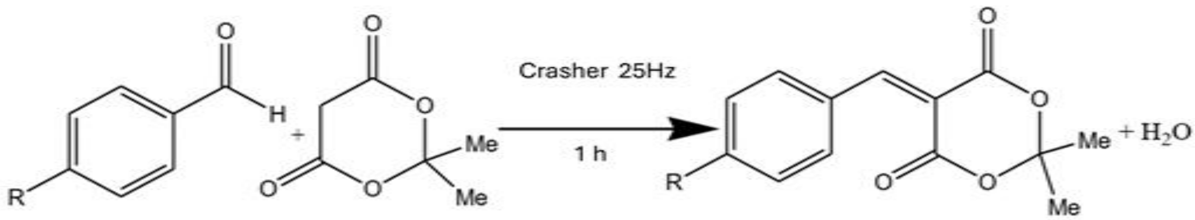


Figure 7: Example of using crushers in green chemistry reaction. R=H,C1….C4

11. Photochemistry

In general, photochemical reactions are most often used for the preparation of mono or polycyclic strained molecules, through the formation of carbon-carbon (C-C) bonds, thus avoiding the use of activating or protecting groups and the formation of by-products. In this case, it is essential to know the electromagnetic absorption spectrum of the irradiated substances before performing photochemical reactions, because the irradiation wavelength must always be selected first. The types of UV lamps used are UV (λ = 254 nm at low pressure) or UVvisible (λ > 320 nm, at high or medium pressure) [37]. Among the best-known photochemical reactions (figure 8), the synthesis of chiral phthalides. This reaction was carried out in the solid state. In this case, the initial solid sample is at the bottom of a reactor and is cooled to 15 ° C and then irradiated with a high-pressure mercury UV-visible lamp for about two hours. The phthalides obtained are optically pure and with a good yield [30].

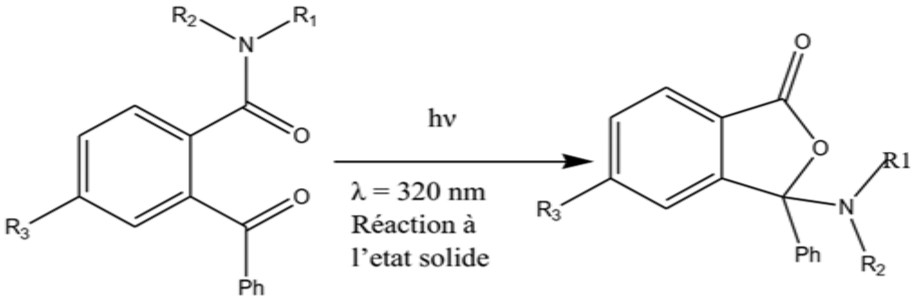


Figure 8: example of using photochemistery in green chemistry reaction. R1…R3=H,C1….C4

12. Microwaves

The use of microwaves to accelerate a chemical reaction is a valid alternative to other heating methods including oil bath (figure 9), sand and also reflux. In reality, the principle of microwaves is electromagnetic radiation at wavelengths λ (between 1 cm and 1 m). The interactions between this electronic radiation from microwaves and the substrate are responsible for heating [31].

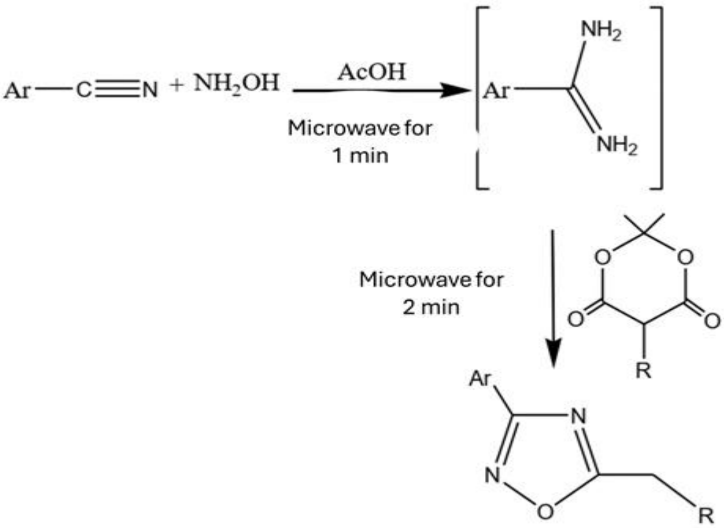


Figure 9: example of using microwave in green chemistry reaction. R=H,C1….C4

13. Green Solvents for Green Chemistry

Most organic solvents have a very high environmental impact and their uses are subject to significant restrictions because they are volatile organic compounds and are also very often flammable, harmful and toxic (Table 1). This has led to the development of processes using green solvents such as carbon dioxide CO2, water, ionic liquids and also fluorinated solvents [32]. Today, carbon dioxide in the supercritical state (intermediate between gas andliquid) is used as a substitute for apolar organic solvents. It replaces CCl_4 (methane tetrachloride), a very toxic compound in the decaffeination process.The advantages of using carbon dioxide CO_2 as a green solvent are: Non-flammable, It is a non-toxic compound and renewable.

Table 1: Alternative Solvents to Traditional Solvents

Traditional Solvents	Issues	Alternative Solvents
Volatile organic compounds	Toxicity Flammability Greenhouse gas emissions	Water Supercritical CO_2 Ionic liquids
Fluorinated solvents		

13.1. Water (H_2O)

Indeed, water is a green compound par excellence. It is used as a substitute solvent for polar organic solvents. Table (2) below includes the main advantages and disadvantages of using water as a green solvent. Since the beginning of organic synthesis, water has appeared as the greenest solvent. The emergence of the concept of green chemistry has generated a renewed interest in water as a solvent.

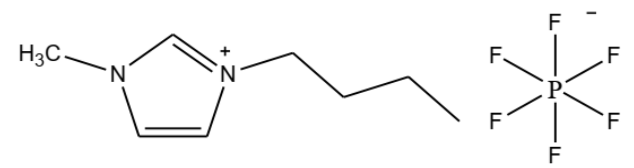
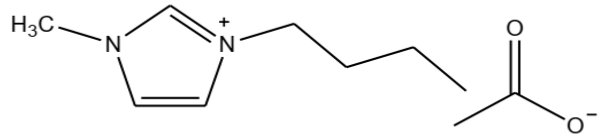
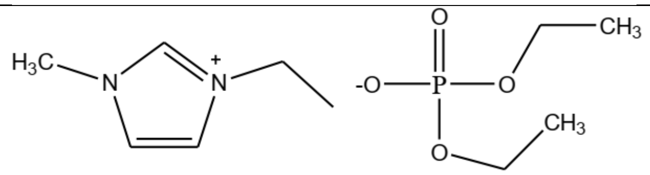
Table 2: Advantages and disadvantages of water as a green solvent

Advantages	Disadvantages
Non-toxic	Slow heating and cooling rates
Abundant source	Expensive distillation processes
No danger to health or the environment	
Cost-effective	
- Non-flammable	

13.2. Ionic liquids

Ionic liquids are salts that have a melting point of 100 °C and even lower than room temperature. These ionic liquids have a low viscosity and are colorless. These salts actually form a new class of solvents for green chemistry. In general, ionic liquids are formed of organic cations complexed with inorganic anions such as F^-, Br^- and Cl^- or organic ($CH_3CO_2^-$, $CFCO_2^-$ ....etc). Their advantages are multiple including: Non-flammable, i.e. reducing the risk of accidents. Not being volatile at ambient conditions, therefore no diffusion into the atmosphere. No risk of exposure Stable at high temperature. The yield, reaction speed and selectivity are often better. The following table (3) summarizes some of the most used ionic liquids.[33]

Table 3: The most used ionic liquids

Ionic liquids	Nomenclature	Structure
BMI MPF6 Soluble: Acetone, Dichloromethane and DMSO	1-Butyl-3-methylimidazolium hexafluorophosphate	
BMIM Acetate Soluble: H2O, Acetonitrile, Acetone and Dichloromethane	1-Butyl-3-methylimidazolium acetate	
EMIM diethyl phosphate Soluble: H2O, Methanol and Ethanol	1-Ethyl-3-methylimidazolium diethyl phosphate	

13.3. Fluorinated chemicals

Several fluorinated solvents or gases have toxicity, environmental impact and thus a reduced cost compared to those of halogenoalkane gas such as HFC (Hydrofluorocarbon) and HFE (Hydrofluoroethers). The latter are very toxic gases contained in refrigerants and air conditioning systems "known for the refrigeration industry" and they are greenhouse gases. Hydrofluoroethers (HFO) is a fluorinated solvent with a lower toxicity profile than hydrofluorocarbon and hydrofluoroethers [34].

14. Conclusions

Green chemistry represents a transformative and forward-thinking approach to addressing the environmental challenges posed by industrial chemical processes. Traditionally, the focus has been on managing hazards through regulatory frameworks, aiming to minimize exposure by carefully controlling toxic substances during handling, use, treatment, and disposal. While effective to an extent, this approach often treats the symptoms rather than the root causes of the problem. In contrast, green chemistry seeks to address these issues at their source by designing processes that are inherently free of hazards. However, achieving this ideal requires a nuanced and practical perspective. For example, the ability to perform a reaction using a new solvent does not, in itself, qualify that solvent as "green." A solvent can only be considered environmentally sustainable when it proves its capacity to reduce the ecological footprint of a process in real-world commercial applications. This perspective underscores a key principle of green chemistry: it is not an endpoint but a continuous journey toward aligning chemical innovation with sustainability. By rigorously evaluating and refining these advancements, we move closer to realizing a future where industrial practices can thrive in harmony with the environment.

Funding: No funding is received for this work.

Conflict of interest: The authors declare no conflict of interest.

Acknowledgement: Waleed N. Al-Darkazali would like to appreciate the support provided by the College of Science, Mustansiriyah University, for the support provided.

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