2. Green Chemistry and Technology for Sustainable Development. Basic Principles and Applications

2.1. Green Chemistry from Theory to Practice

Environmental issues in the past were considered as part of the economic system and the rapid exploitation of natural resources. It took many years to consider the established ways that materials were used (feedstocks), the initial design of chemical processes, the hazardous properties of products, the energy consumption and other parameters involved in the manufacture of products (life cycle, recycling, etc).

Green Chemistry was for many years a relatively abstract idea with no basic principles and definitions of practical applications. Now, the term Green Chemistry has been defined as “the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances for workers and consumers”.

The definition of Green Chemistry starts with the concept of invention and design. This means we, scientists and technologists, must take into account from the start what we are looking for, what kind of product, how we are going to design its manufacture and its use. The impact of chemical products and chemical processes must be included as design criteria. Hazard considerations for initial materials and final products must also be included in the performance criteria.

Another aspect of the definition of Green Chemistry is in the phrase “use and generation of hazardous substances”. We must think in advance if use of the product is going to be dangerous (workers, consumers) or if it is going to generate environmental pollution through their use or after their practical application (as waste). Rather than focusing only on those undesirable substances that might be inadvertently produced in a process, Green Chemistry also includes all substances that are part of the process. Also, Green Chemistry recognizes that there are significant consequences to the use of hazardous substances, ranging from regulatory, handling and transport, production of waste and liability issues.

Green Chemistry aims not only for safer products, less hazardous consequences to the environment, saving energy and water, but includes broader issues which can promote in the end Sustainable Development.

The rapid development of new chemical technologies and the vast number of new chemical products in the last decades turned the attention of environmentalists to remedial actions for the negative impacts (monitoring environmental pollution, reduction of pollutants, recycling, etc). But the fact is that the most effective way to reduce the negative impacts is to design and innovation in the manufacturing processes, taking into account energy,
materials, atom economy, use and generation of secondary materials which are dangerous and finally the life cycle of the products and their practical recycling into new materials.

In the last decades 600-700 million tones of chemical materials are produced every year (excluding fossil fuels, fertilizers and medicines) from the chemical industries of the world. More than 120,000 chemicals are in circulation for various applications, of which, approximately, 2,500 are high volume products. Some of these chemicals have been studied for their toxicological and ecotoxicological effects, but these studies are expensive and most of the ecotoxicological studies are lacking. Despite the stringent environmental laws and regulations in the developed countries, there are numerous environmental problems and adverse effects in sensitive ecosystems and habitats.

Figure 2.1. Green Chemistry is a new “philosophy” of how to make chemical products in the chemical industry and for chemical research. Innovative design and changes in chemical processes can eliminate hazards and help scientists to achieve the goals to sustainable development.

Green Chemistry or Sustainable Chemistry had to be invented and its inception in 1992 was very timely. Scientists and especially research chemists must start from the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. In the past chemists were limiting risk by controlling exposure to hazardous chemicals. In return Green Chemistry attempts to reduce or preferentially eliminate, through design and changing the terms of manufacturing process, hazardous effect of products and feedstocks for the environment.

In recent years Green chemistry has gained a strong foothold in the areas of research and development in both industry and academia, especially in the developed industrial countries. Several international conferences, scientific journals, numerous publications and new courses in universities testify to the increasing influence of Green Chemistry philosophy.
In a recent article Paul T. Anastas said for the twenty years progress of Green Chemistry: “….It is widely recognised that sustainable civilization requires both a healthy environment and a healthy economy. Green Chemistry with its applications has unequivocally demonstrated that creative scientific design can help achieve both those goals simultaneously and for societal benefit. …. As we celebrate the International Year of Chemistry, we should reflect upon the astounding advancements made by chemistry as a whole and the progress made over the past two decades by the filed of Green Chemistry…." [Anastas PT. Twenty years of Green Chemistry. Chem Eng News, 89(26): 62-65, 2011].

2.2. The Twelve Principles of Green Chemistry

The most important aims Green Chemistry were defined in twelve principles. The number twelve is highly significant and symbolic (like the twelve months of the year) as a complete sum of the most important things that we have to do to accomplish a multiple task.

Green Chemistry has to cover a broad section of chemical and technological aspects in order to offer its alternative vision for sustainable development. Green chemistry had to include fundamental ways to reduce or to eliminate environmental pollution through dedicated, sustainable prevention programs. Green Chemistry must focus on alternative, environmentally friendly chemicals in synthetic routes but also to increase reaction rates and lower reaction temperatures to save energy. Green Chemistry looks very carefully on reaction efficiency, use of less toxic solvents, minimizing the hazards of feedstocks and products and reduction of waste.

Paul T. Anastas, an organic chemist working in the Office of Pollution Prevention and Toxins at the EPA, and John C. Warner developed the Twelve Principles of Green Chemistry in 1991. These principles can be grouped into "Reducing Risk" and "Minimizing the Environmental Footprint." Risk has been a legacy of some chemical industries in the past. Hazardous chemicals to humans and environmental pollution risk was connected with new chemical products and that gave a “bad name” to synthetic chemical materials. The environmental footprint is more to do with energy consumption, the climate crisis and depleting natural resources.

A. Green Chemistry aims to Reduce Risk in the Laboratory
Use Safer Chemicals,
Design Less Hazardous Synthesis Methods
Use Safer Solvents and Reaction Conditions
Accident Prevention (minimize the potential for explosions, fires, etc)

B. Minimizing the Environmental Footprint
Waste Minimization and Prevention –
Use of Catalysts Instead of Stoichiometric Quantities
Reduce the Use of Chemical Derivatives
Synthetic Efficiency (Atom Economy)
Taking Advantage of Chemicals Designed for Degradation
Establishment of In Process Controls for Pollution Prevention –
Use of Renewable Feedstocks
Encourage Energy Efficiency
The **Twelve Principles of GC** can be analysed fully in the following set

1. **Principle No. 1. Prevention**: It is better to prevent than to clean or to treat afterwards (waste or pollution). This is a fundamental principle. The preventative action can change dramatically many attitudes among scientists developed in the last decades. Most of the chemical processes and synthetic routes produce waste and toxic secondary substances. Green Chemistry can prevent waste and toxic by products by designing the feedstocks and the chemical processes in advance and with innovative changes.

2. **Principle No. 2. Maximise synthetic methods, Atom Economy**: All synthetic methods until now were wasteful and their yields between 70-90%. Green Chemistry supports that synthetic methods can be designed in advance to maximize the incorporation of all reagents used in the chemical process into the final product, eliminating the need to recycling the by-products. The concept of **Atom Economy** was developed by Barry Trost of Stanford University (USA), for which he received the Presidential Green Chemistry Challenge Award in 1998. It is a method of expressing how efficiently a particular reaction makes use of the reactant atoms.

3. **Principle No. 3. Less hazardous chemical syntheses**: Green Chemistry must strive, wherever practical, to design safer synthetic methods by using less toxic substances as well as the products of the synthesis. Less toxic materials mean lower hazards to workers in industry and research laboratories and less pollution to the environment.

4. **Principle No. 4. Designing safer chemicals**: Designing must become a fundamental aim of Green chemists to effect the desired function and properties of the chemical product while minimizing their toxicity to human and the environment. At present, there are around 100,000 chemical substances and materials in the market. Most of these substances have been characterized as to their physiochemical properties and toxicities, but there is lack of ecotoxicological data for most of them. From the 1980s there are more stringent regulation and new chemicals are monitored more effectively.

5. **Principle No. 5. Safer solvents and auxiliary substances**: Solvents, separation agents and auxiliary chemicals used in synthetic chemistry must be replaced or reduced with less toxic chemicals. Green Chemistry initiated big changes in chemical laboratories and in the last decade there are less toxic solvents in chemical laboratories and alternative techniques.

6. **Principle No. 6. Design for energy efficiency**: Chemists must recognize that until now there was very little thought to energy requirements in chemical synthetic chemical processes Designing more efficient methods is a necessity and if possible synthetic methods should be conducted at room temperature and pressure to reduce energy requirements.

7. **Principle No. 7. Use of renewable raw materials and feedstocks**: Starting raw material for synthetic processes are mostly petrochemical substances and products of refining. Raw materials must have very low
toxicity and if possible to be renewable, rather than depleting. We know that there are many practical problems in finding renewable raw materials. Green chemists must change the manufacturing process by discovering renewable chemicals. Development with depleting natural resources is a negative aspect of economic growth.

8. Principle No. 8. Reduce intermediate derivatives: Chemists must aim for reducing unnecessary derivatization (use of blocking groups, protection/deprotection techniques and temporary modification of physical and chemical processes) in the synthetic routes. These derivatizations use additional reagents, are wasteful and produce large amounts of by-products and waste. The principle reminds chemists to change their old ways of producing chemicals with more chemical steps and additional materials. Designing new chemical synthetic routes are desirable.

9. Principle No. 9. Catalysis, catalytic reagents: The use of catalysts is well known that can change dramatically the efficiency of chemical reactions and the yield of products. Catalytic reagents with great selectivity can be superior to stoichiometric reagents. New catalysts and more emphasis on catalytic processes is the future of green chemistry techniques.

10. Principle No.10. Design products which degrade easily: Most chemical products and consumer items do not degrade very easily, thus causing environmental problems. Green Chemistry aims at designing products so that at the end of their useful life to break down into innocuous materials. Persistence into the environment is a negative aspect of many consumer products (e.g. plastic products) and this can be reversed by designing products which degrade in a short time.

11. Principle No. 11. Real- time analysis for pollution prevention: Analytical methodologies need to be further developed to allow for real time, in-process monitoring and control prior to the formation of hazardous substances

12. Principle No. 12. Inherently safer chemistry for accident prevention. Raw materials and chemical substances used in chemical process should be inherently safe, i.e. their properties and their degradation products to be non-toxic and not dangerous (e.g. to explode, to be flammable, allergic to humans, cause burns to skin, etc). Green Chemistry aims to stop the use of dangerous materials for the health and safety of workers and the consumer.

These principles are obviously very difficult to apply immediately for many chemical processes. After twenty years of Green Chemistry initiatives and industrial applications it is amazing to see many creative innovations at various scientific and industrial processes. The cooperation of chemists, engineers, material scientists, bioscientists and technologists has achieved interesting results. The interdisciplinary approach has expanded the fields of green chemistry and produced some excellent non-toxic materials and feedstock savings in chemical industries.
2.3. Green Chemistry and Sustainable Development. International Organization and Industries Promoting the Aims of Green Chemistry

In the last 250 years chemistry has improved our quality of life, and made thousands of useful products and materials possible. But this achievement has come at a price: for the global environment and non-renewable natural resources. Sustainability is at stake and continuation of the quality of life is under threat. Many chemicals work their way up the food chain and circulate round the globe, pesticide residues were found in the tropics and in the Arctic; flame retardants from electronics are now commonly found in aquatic organisms, especially in marine mammals.

Green chemistry and its principle want to change all these negative impacts and through design, innovation and green processes to restore the planet’s sustainable development. A typical example is the use of non-renewable fossil fuels. Today’s chemical industry relies almost entirely on petroleum as the primary building block to create chemicals. This type of chemical production typically is very energy intensive, inefficient, and toxic, resulting in significant energy use, and generation of hazardous waste. One of the principles of green chemistry is to prioritize the use of alternative and renewable materials including the use of agricultural waste or biomass and non-food-related bioproducts.

The term “sustainable chemistry” proposed in the beginning was changed into “green” because it contains the meaning of radical change, innovation, rejection of old attitudes and practices.

Figure 2.2. Logos of various organizations of Green Chemistry.
From the beginning many international organizations embraced the principles of Green Chemistry and recognised its significance in chemical processes and in particular for the chemical industry. Environmental Protection Agency, with its internationally recognised advances in environmental protection and the American Chemical Society adopted the aims and principles of Green Chemistry. The Royal Society of Chemistry in Great Britain was also from the beginning on board the green chemistry movement.

Green Chemistry initially promoted safer chemicals and protection of the environment, but at the same time introduced the principles of energy efficiency, atom economy in chemical processes with reduction of waste. These green chemical principles concerning economical benefits were the first to be taken up by big chemical industries in their research and development departments. Green chemistry applications made financial sense in many syntheses of chemical substances, use of green solvents and renewable feedstocks. Also, new green techniques, like the supercritical CO₂ replacing volatile organic solvents, catalysis and lower temperature reactions showed great promise and higher yields. Reduction of waste in chemical processes is also part of the “green” changes in industry due to higher environmental taxes. Some governments introduced lower taxes for industries which applied voluntarily alternative “greener” methodologies. Scientific papers in the fields of green chemistry, alternative syntheses, green solvents, catalysis and waste minimization increased exponentially in 1991-2010 period.

Green Chemistry principles give great emphasis to the scientific term “hazardous”, for processes and the life cycle of chemical substances. Green chemistry is a way of dealing with risk reduction and pollution prevention by addressing the intrinsic hazards of substances rather than dealing with the conditions of their use that might increased their risk (e.g. exposure in the working environment, or uses of the products with exposure potential)

Risk, in its most fundamental terms, is the product of hazard and exposure:

\(\text{Risk} = f(\text{Hazard} \times \text{Exposure})\)

To calculate the risk associated with a certain substance we have to quantify its hazard (how toxic or dangerous to humans and the environment it is) and multiply it with a quantifiable exposure (dose, time, etc). In the past, all common approaches to risk reduction focused on reducing exposure to hazardous substances and regulations often required increases in control technologies and treatment technology (i.e. personal protective equipment in order to reduce risk by restricting exposure). Green Chemistry goes to the heart of risk prevention or adequate reduction in advance before the substance is made or used. Green Chemistry demands to design products and use raw materials with lower hazardous properties, as practical as possible. Green chemistry takes into account the difficulties and practical considerations in industrial processes, but puts first prevention than remedial action afterwards.

The definition of Green Chemistry and Its Principles illustrates another important point about the use of the term “hazard”. This term is not restricted to physical hazards such as explosiveness, flammability, and corrosibility, but
includes acute and chronic toxicity, carcinogenicity, environmental pollution to water, air and soil (aquatic organisms, mammals, etc) and ecological toxicity.

2.4. Green Chemistry is Part of the Environmental Movement of the Last Decades

Green Chemistry traces back several decades and can be linked to the public awareness on environmental pollution, the environmental movement in the USA and other industrial countries of the 1960s and 1970s. Environmental pollution and its negative effects were recognised much earlier in the most advanced industrial country and by its rapidly increasing scientific community. In 1969 the U. S. government under pressure from society established the Citizen’s Advisory Committee on Environmental Quality and a Cabinet-level Environmental Quality Council The Environmental Protection Agency (EPA) in the USA was formed in 1970 and is considered a leading innovator of environmental protection, a cause that has paved the way to current green chemistry practices.

Two decades after the implementation of the EPA, The Pollution Prevention Act (1990) was created to enforce eco-friendly strategies, and provide grants to states in the effort to reduce source waste. Shortly after the passage of the PPA, the Office of Pollution Prevention and Toxics (OPPT) explored the idea of developing new or improving existing chemical products and processes to make them less hazardous to human health and the environment. In 1991, OPPT launched a model research grants programme called “Alternative Synthetic Pathways for Pollution Prevention”.

This programme provided unprecedented grants for research projects that include pollution prevention in the design and synthesis of chemicals. In 1993, the program was expanded to include other topics, such as greener solvents and safer chemicals, and was renamed “Green Chemistry.” Since then, the Green Chemistry Programme has built many collaborations with academia, industry, other government agencies, and non-government organizations to promote the use of chemistry for pollution prevention through completely voluntary, non-regulatory partnerships. Paul Anastas, a chemist, who was responsible for these programmes and coined the term “Green Chemistry”. P. Anastas worked very hard for many years and great enthusiasm to promote the principles of green chemistry and rightly is considered as the “father” of Green Chemistry.

President Bill Clinton devised the Presidential Green Chemical Challenge Awards during his presidency to reward those practicing sustainable chemistry. By the end of the 1990s, “Twelve Principles of Green Chemistry” was published. The guidelines served as a reference for processes and practices to lessen negative environmental impact by the chemical industry.

In 1993 the Interuniversity Consortium Chemistry for the Environment (INCA) in Italy promoted the cooperation of universities for green chemistry issues in industry and research laboratories in Italian universities. In 1993 in Venice organized the first meeting of scientists concerned with green chemistry applications under the title «Processi Chimici Innovativie Tutela dell’ Ambiente".
The International Union for the Pure and Applied Chemistry (IUPAC, Paris) in 1996 decided to establish a group on Green Chemistry. In 1997 the First International Green Chemistry Conference took place in Venice under the auspices of IUPAC.

In 1997 **The Green Chemistry Institute** of the American Chemical Society was established. The GCI with its international prestige promoted a series of research projects and grants for an array of Green Chemistry projects and played an important role in new methodologies and innovations.

![Green Chemistry Institute](image1.png)  
**Figure 2.3.** The Green Chemistry Institute (USA), the Summer School of Green Chemistry (University of Venice, Prof. P. Tundo) and other organizations all over the world promote the aims of Green Chemistry.

The European Union financed the **International Green Chemistry Summer School** in the University of Venice. The summer school has been a very important initiative of Professor Pietro Tundo who is an enthusiastic supporter of the Green Chemistry goals in education (under the auspices of the organization INCA in Italy. ([www.unive.it/inca](http://www.unive.it/inca)).

In 2001 the Engineering and Physical Sciences Research Council (EPSRC) financed the proposal of the Royal Society of Chemistry (RSC) for the establishment of a network of scientists and university research laboratories on Green Chemistry (GCRN, **Green Chemistry Research Network**). The headquarters of the GCRN is in the Chemistry Department of the University of York in England. The Chemistry Department, under the director Prof. James Clark has one of the most active research centre of Green Chemistry in England ([www.chemsoc.org/networks/gcn/discuss.htm](http://www.chemsoc.org/networks/gcn/discuss.htm)).

The **Green Chemistry Centre of Excellence** at the University of York's Department of Chemistry is a world leading research centre which aims to promote the development and implementation of green and sustainable chemistry and related technologies into new products and processes.

The Centre offers the postgraduate degree MSc Green Chemistry and Sustainable Industrial Technology. The Centre is involved with a number of green chemistry activities in the areas of research, industrial collaboration, the development of educational and promotional materials and networking both with academia and industry.

The European Directorate for R &D (DG Research) started many years ago an active promotion of Green Chemistry issues in Europe and financed many research projects (European Fifth Framework Programme).
The United Nations also promoted the activities of Green Chemistry through its International Centre UNIDO-ICS. The **International Centre for Science and High Technology of the United Nations Industrial Development Organization** developed many programmes and supported projects for Green Chemistry.

Also, the OECD (**Organization for Economic Co-operation and Development**) which promote policies that improve the economic and social well-being of people around the world has very active programmes for Green Chemistry issues among industrial nations.

Figure 2.4. Some very important scientists who worked all these years to promote Green Chemistry and Green Engineering Issues. Prof. Paul Anastas (Yale, US), Prof. James Clark (University of York, England), Prof. Pietro Tundo (Venice) and Prof. Michael Braungart (Process Engineering, Suderburg University), author with W. McDonough of the bestseller “Cradle-to-Cradle. Remaking the Way We Make Things”, 2002)
In the last decade Green Chemistry institutes and organizations were established in many countries: Sweden, China, Italy, Spain, Taiwan, Canada (Canadian Green Chemistry Network), Australia (Centre for Greene Chemistry, Japan (Green and Sustainable Chemistry Network).

In Greece there is the Hellenic (Greek) Network of Green Chemistry (Ελληνικό Δίκτυο Πράσινης Χημείας) which connects various chemists of Chemistry Departments of Greek universities. The coordinator is Prof. Konstantinos Poulos of the Chemistry Department of the University of Patras. (C.Poulos@chemistry.upatras.gr, http://www.chemistry.upatras.gr). The Greek Network of GC organizes every two years a national conference on various themes of GC and sustainable development. Professors A. Maroulis and Hadjiantoniou-Maroulis are very active in the Department of Chemistry of the University of Thessaloniki on educational and research porjects of GC.

Another very interesting development which is very positive for Green Chemistry is the establishment of undergraduate and postgraduate courses in universities all over the world. Some examples:

i) Green Chemical Engineering Material Framework, University of Texas, Austin, USA,

ii) Green Chemistry for Process Engineering, University of Nottingham, England,

iii) Industrial and Applied Green Chemistry, University of York, England,

iv) Center for Green Chemistry and Green Engineering, Yale University,

v) Greener Education Materials for Chemists, University of Oregon, USA

Finally, many chemical and pharmaceutical industrial companies industries have active research institutes and laboratories devoted in promoting and research and development of green chemistry innovations. For example, Goodrich Corporation, Dow Chemical Company, E.I. DuPont de Nemours, Eastman Kodak Company, etc.

2.5. Designing Products Under the Holistic Approach “Cradle-to-Cradle”

The design of commercial products under the “Cradle-to-cradle” approach is a modern and innovative concept to make products through a continuous use and recycling (or regenerative circle) of biological and technological materials, thus avoiding waste and using renewable materials.

The “Cradle-to-cradle” design (it appears also under other names, such as C2C, or cradle 2 cradle, or is referred as regenerative design) is a new philosophy of how to make green things without pollution and waste. It is a biomimetic approach to the design of systems. Its basic idea is to model human industry on nature’s processes in which materials are viewed as nutrients circulating in healthy, safe metabolisms. I

In its idealistic way, Cradle-to-cradle for its innovators wants industry to protect and enrich ecosystems and nature’s biological metabolism while also maintaining safe, productive technical metabolism for the high-quality use and circulation of organic and synthetic materials. It is a holistic economic, industrial and social framework that seeks to create systems that are not just efficient but essentially waste free. The cradle-to-cradle model is not limited only to industrial design and manufacturing; but it can be applied to many
different aspects of human civilization (urban environments, buildings, economics and social systems).

The phrase "Cradle-to-Cradle" was first used by the architect Walter Stahel in the 1970s but it was made more known by the American architect William McDonough and the German chemist, Professor. Michael Braungart. In 2002 they published the book "Cradle-to-Cradle: Remaking the Way We Make Things", presenting their ideas on the concept with a simple way and excellent methodological examples. The book became a bestseller and their idea was promoted all over the world and implemented by companies, organizations and governments.

Certain materials, including metals, fibers and dyes, may be reused without causing a negative impact on the environment. According to McDonough and Braungart, they are called "technical nutrients," and they maintain their integrity even after being used in several products. Similarly, some organic or "biological nutrients" may be used and then returned to the earth to decompose. In either case, the materials provide regenerative.

The Cradle to Cradle Certified programme is a multi-attribute eco-label that assesses a product’s safety to humans and the environment and design for future life cycles. The programme provides guidelines to help businesses implement the Cradle to Cradle framework, which focuses on using safe materials that can be disassembled and recycled as technical nutrients or composted as biological nutrients. The model has been implemented by a number of companies, organizations and governments around the world, predominantly in the European Union, China and the United States. Cradle to cradle has also been the subject matter of many other studies.

![Image](image.png)

"Cradle-to-Cradle: Remaking the Way We Make Things" (2002)

Cycles “cradle to cradle”

**Figure 2.5.** The revolutionary idea for the design products under the sign «Cradle-to-cradle» was very innovative, Technical materials can be used as biological nutrients and can be used in several products. After their use can return to the earth to decompose. The book became a bestseller in 2002.
2.6. Scientific Areas for Practical Applications of Green Chemistry

Already from the 1980s, chemical industries under the pressure of new environmental laws and regulations for workers health and safety and environmental pollution, changed their processes and introduced new technologies. The economic incentives and the avoidance of litigations from the state, citizens and environmental organizations were major factors in changes towards more benign technological applications. But in most areas of industrial production old methods prevailed, for example the use of petroleum products for feedstocks, in organic synthetic routes and in the use of organic chlorinated solvents for separation. But the first seeds of green chemistry ideas started to have a more pronounced effects in the chemical industry.

From the beginning of the 1990s the ideas of Green Chemistry started to have a more international outlook. In 1998 the OECD through programmes such as “Risk Management Programme”, promoted new and innovative activities under the broader umbrella of “Sustainable Chemistry”. The purpose was to initiate alternative practices in the chemical industry and processes more benign to the environment. A committee of scientists and technological experts was convened from many industrial countries (Japan, USA, Germany, Sweden, Canada, etc) to propose the basic areas of research and development for Green Chemistry applications.

The areas proposed for special focus under the green chemistry principles were the following. They were selected with emphasis on economic considerations and for their future contribution to sustainable development.

1. **Use of alternative feedstocks.** There are already many new developments in this field, but the emphasis on renewable raw materials and a shift from fossil fuels is very desirable for sustainability. The starting materials for the chemical industry must be renewable and less toxic for workers and the environment.

2. **Use of less hazardous reagents.** There are now enough data for the toxicological and for the long term ecotoxicological properties of most of the high volume chemicals used for industry. Chemists and technologists must divert their efforts to use less dangerous raw materials and reagents for the synthetic routes of the production of chemical products. But if there are major obstacles they must choose less toxic substances and change their technologies accordingly, for example using catalysts and new synthetic techniques.

3. **Use of natural processes, like biocatalytic techniques.** New biosynthetic methods were developed in the last decades which are more selective, use less energy, lower temperatures, higher yields and demand raw materials which are less toxic. Green Chemistry research in the last decades replaced many old methods and introduced some innovative catalytic methods with high yields and less waste.

4. **Use of alternative solvents.** Many solvents, especially polychlorinated and aromatic solvents, were used for decades for extraction techniques in synthetic organic chemistry. Some of these solvents (e.g. carbon tetrachloride) were banned and some others are restricted. Chemists use now less toxic solvents and their waste can be recycled or decomposed at high temperatures. The chemical industry invested, under the Green
Chemistry principles, in new solvents which are less toxic to workers and can disintegrate more easily under environmental conditions.

5. **Design of safer chemicals and products.** Many new developments in methodology and toxicological tests improved our understanding of the toxicity and their mechanisms of new chemicals and products. The methodology of **Quantitative structure-activity relationships, QSARs** can be used to speed up the estimation of toxicity, carcinogenicity or other toxicological property of a new substance. Thanks to Green Chemistry principles and applications most new chemical products have very low toxicity and are more benign to the environment.

![Figure 2.6](image)

**Figure 2.6.** Industrial chemists have changed to a great extend the synthetic routes used for the production of chemical products. Renewable raw materials, lower temperature, energy savings, less waste, alternative solvents.

6. **Developing alternative reaction conditions.** In recent years there are many more alternative or “greener” reaction techniques improving substantially the product yield, saving energy and minimize waste. Photochemical reactions, microwave and ultrasound assisted organic synthetic techniques, reactions using water as solvent, catalytic reactions, etc are some of the new techniques in synthesizing chemicals.

7. **Minimizing energy consumption.** This is a very important goal considering the energy savings and the climatic change which has become a global environmental problem. The chemical industry has invested enough resources to reduce energy demands with innovations and changes in synthetic reactions (lower temperatures, reducing steps). Green Chemistry is very interested to contribute through research to minimize energy consumption in every step of the industrial process. This was a very brief description of the most important changes in future industrial processes which are going to improve efficiency, save energy, minimize waste, and produce safer products and with less environmental impacts.
2.7. Use of Alternative Basic Chemicals as Feedstoks in Chemical Industry and Research

In 2007 the U.S. Department of Energy commissioned a report for the future of alternative and renewable feedstocks for its chemical industry. The U.S. has the biggest chemical industry in the global arena producing almost 1/3 of chemical products. U.S. scientists are considering from now that the time is approaching for the natural gas and petroleum production will “peak,” plateau and then decline. Prices also increased substantially in the last decades contributing to the uncertainty. These trends and the uncertain future inevitably influence other industrial nations and especially the European Union countries which produce the other 1/3 of chemical products (U.S. Department of Energy. Energy Efficiency and Renewable Energy. Chemical Industry Vision 2020 Technology Partnership. Alternative, Renewable and Novel Feedstocks for Producing Chemicals. Oak Ridge National Laboratory, July 2007).

In the preface of the report we read “... Industrial chemistry has evolved from using natural plant oils, coal tars and wood tars to an industry that today generates in the United States alone over 160 million tons/yr of products from petroleum (~85%) and natural gas (~15%). The change in feedstock choice over the last century is the result of the components in petroleum and natural gas providing chemists with the lowest combined cost of raw materials and processing. Starting in 2000, the United States experienced a rapid increase in the price of petroleum and natural gas. ... The rapid increases with significant fluctuations were the result of numerous production trends, booming Asian growth, short-term events (e.g., hurricanes), and the geopolitics of oil. These rate increases and fluctuations..."
contribute to uncertainty in the near-term price of feedstocks and encumber U.S. chemicals producers ....”.

“.... It is well recognized that the natural gas and petroleum production will "peak," plateau and then decline. Although, when the "peak" will occur is speculative, its eventual arrival is not. Approaching the "peak" will be disruptive, add considerably to supply and price pressures and hasten the industry's move from petroleum and natural gas to less volatile "alternative" feedstocks such as coal or biomass. Alternative feedstocks will consume more energy and emit more CO₂ per unit of product produced. Biomass may be an exception to higher energy and CO₂ emissions depending on how the CO₂ is accounted for. Planning for and developing new technologies to ease the eventual transition to alternatives and manage CO₂ needs to be initiated by all industry stakeholders....”.

Until now we know from experience of the last 50 years that the majority of raw chemicals and starting materials not only for the chemical industry but also for other industries and workshops were products of the petrochemical industry. This total reliability to fossil fuels and their products (for chemicals and transport) had a great impact on resources, sudden increase on prices, economic crisis for certain countries and an uncertain future for availability of feedstocks. It is known that 20-25,000 basic chemicals are relying on petrochemical feedstocks due to low cost and the established technological means. But the future is not very promising. Scientists and technologists who are following trends on sustainability and natural resources urge industries to change into alternative resources and develop new approaches into more efficient chemical processes. Green Chemistry and Green Engineering are striving to produce new methodologies for sustainable development. Their proposals focus on:

a) Renewable feedstocks and raw materials

Green Chemistry wants to change into renewable feedstocks. The second most desired property of basic starting materials is their lower toxicity and their environmental impact. Health and safety protection of workers and the environment is a top priority. Green Chemistry proposes change of direction into biological raw materials (plant and animal waste, products from fermentation of plant waste, biogas, etc). There are many difficulties in the use of these materials, but in the last years there are encouraging new prospects for large scale production and use of alternative, renewable materials.

b) Oleochemistry. New biological starting materials

Fats and oils (from plants and animals) as oleochemical raw materials can become a new source of chemical feedstocks. Already a series of raw materials exist in the market with many applications in cosmetics, polymers, lubricating oils and other products.

c) Photochemistry. New Chemical Processes with the Aid of Light

Green Chemistry puts a lot of emphasis on photochemical reactions in chemical processes. Light (ultraviolet and visible) can become an important catalyst for many reactions, replacing toxic metals in many reactions. Scientists think that photochemistry has great potential and many research innovations and applications were introduced in the last years. Ultraviolet is considered a renewable energy sources and through photochemistry can contribute to green synthetic chemistry applications.
d) Photocatalytic synthetic routes with Titanium dioxide (TiO$_2$)

In the last decades numerous research studies have been shown great promise for using TiO$_2$ dioxide for photocatalytic industrial reactions under visible light. The energy use is minimized, waste products are very low and the yields are much higher than conventional reactions.

**e) Photocatalytic oxidations. Waste and toxic chemicals decomposition**

Also, TiO$_2$ and other metallic oxides (Fe$^{2+}$) can be used in photocatalytic oxidations for the decompositions of toxic and waste chemical materials. These decompositions, especially for polychlorinated compounds, phenols, etc., can produce neutral chemicals with minimum toxicity. A useful mixture is Fe$^{2+}$/H$_2$O$_2$ (Fenton reagent) with the aid of light can decompose toxic industrial waste. Various techniques are already applied in industrial effluents with very good results in environmental protection. These oxidations under the name **Advanced Oxidation Processes** (AOP) have become a standard technology for liquid waste elimination in industry and destruction of chemical substances which pollute the environment.

**f) Waste Biomass as chemical feedstock, biomaterials and biofuels**

The advances of the last decade into the use of biomass for the production of various materials was very impressive. It was known for decades that biomass from agricultural processes was wasted. Scientists for year researched many aspect of biomass and its effective. Biomass is considered a very important problem of sustainability with increasing fossil fuel prices. In recent years many new technologies showed the use of biomass as biofuel, raw material for the production of biomaterials, polymers and various other applications.

**g) Biodegradation of biomass for biogas and biodiesel**

Biomass is well known for its use for biofuel, especially from organic waste in landfills. Biomass, through chemical and physical processes can be used for the production of biodiesel. Biomass in 2005 offered the opportunity for the production of 19% of energy on a global scale. Now, it is estimated that 4% of all fuel products in cars is produced from biomass.

![Biomass Energy Diagram](image)

**Figure 2.9.** Biomass can become the starting material for the production of biofuel, biomaterials, biopolymers and for the production of engine fuels.
h) Biocatalysis and biotransformations in the chemical industry

Biocatalysis is considered particularly green technology with many applications which are considered benign for the environment and energy efficient. Enzymes have been used for many synthetic chemical routes with great advantages in the food and pharmaceutical industries. Biocatalysis is in the interface of fermentation techniques (food and alcoholic drink industries) with other industrial processes which use enzymes for higher yields and low energy consumption. Biotransformation can be achieved through biocatalysis and are considered good green techniques for a series of chemical industries and a variety of chemical products.

i) Capture or sequestration of carbon dioxide

Green Chemistry is involved in carbon dioxide reduction in chemical industries. Climate change and the phenomenon of greenhouse effect due to CO₂ emissions is considered by Green chemists a very important environmental problem. Any effort to reduce CO₂ emissions during the industrial processes is very important goal for GC. Also, any design in chemical process which sequester or capture or can use CO₂ is worth for the GC aims.

2.8. Green Chemistry and Reduction of Solvent Toxicity. Alternative Solvents or Replacement

Green Chemistry is concerned with the amounts of toxic organic solvents used in synthetic routes and overall chemical processes. One principle of green chemistry is to reduce the use of solvent as much as possible, or if possible to replace with a less toxic or to use alternative techniques in which solvents are not needed. Solvents in the chemical industry is one of the major problems concerning workers health and safety and environmental pollution because of waste. Synthesis, separation of product, cleaning, drying, analysis and recycling, etc. are some of the processes where solvents are used. Changing solvents and technological processes is not an easy task. There are many alternatives but can be more expensive, time consuming or difficult to implement under the established order of chemical methodologies. Although environmental pollution from solvents can be a serious problem for many chemical industries, the solutions are not always there to replace solvents or to reduce their use.

In recent years, under the influence of green chemistry principles, some solvents have been replaced and methodologies changed to more benign techniques. Some of these changes are listed briefly below.

a) Oxidations under Green Chemistry principles to reduce solvents

Many oxidation techniques in chemical processes have changed under green chemistry principles. Many oxidations now are performed in water, in supercritical CO₂ or with less toxic solvents and under room temperatures. The hydrogen peroxide (H₂O₂) is considered as a very good oxidative reagent that performs at normal temperatures. There are numerous research efforts to apply oxidations with high selectivity and as by-production only water. Homogeneous and heterogeneous reactions in combination with catalysts are used in many oxidations. Oxidations are very important in the pharmaceutical industry and in many petrochemical processes. Oxygen and nitrogen oxides
(NOx) are oxidative agents with green chemistry credentials which are used in the oxidation of benzene, cyclopentanone and propylene.

In recent years for oxidations chemists use catalytic methods with metallic complexes. Some of these are: metal-peroxo systems, polyoxometallates (POM), metal oxide clusters, especially metal Volfram (or Tungsten, W), and heteroanions. Heterogeneous catalysis for oxidations with zeolitic materials are some other techniques used in recent years. Many research projects of these types of oxidation agents can be found in scientific journals for selective oxidations.

b) Catalytic selectivity in synthesis to reduce solvents

Catalytic selectivity can be another research effort for the reduction in the use of solvents and with higher yields and lower amounts of waste. Many industrial processes are based in new catalysts, such as inorganic polyacids and heteropolyacids which act as green catalysts in oxidations, in the hydration of butane mixtures and in the polymerization of tetrahydrofuran (THF). The heterogeneous catalytic method showed cleaner products, minimum waste and easy separation of the products. Various porous materials with small pore diameter can be used as catalytic surfaces for the regulation of the dissipating reactants (mesoporous solid acids). Selectivity and higher yields are achieved in this type of reactions.

Polymer chemistry and production of plastics have achieved recently green credentials with new methodologies. Renewable starting materials, higher yields with biocatalytic methods, minimum use of solvents and less waste are some of the achievements in the production of well known commercial polymers.

2.9. Applications of New Methodologies in the Synthesis of Chemical Compounds

In this brief presentation we provide a short description of some of the important changes in the synthesis of chemicals under green chemistry principles and alternative methods.

a) Ionic liquids in organic synthetic routes

Ionic liquids are used extensively in recent years as alternative solvents in organic synthesis. These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses. Ionic liquids have many applications, as powerful solvents and electrically conducting fluids (electrolytes). Salts that are liquid at near-ambient temperature are important for electric battery applications. Ionic liquids are mixtures of anions and cations, fused salts with melting point less than 100 °C. Although ionic liquids do no fit to the principles of green chemistry, they are considered as good candidates for future improvements that can give “green” credentials to their use and applications.

b) Organic synthesis in water

Water was considered for many decades as a medium that was to avoided as solvent for synthetic organic chemistry. Water proved to be an excellent solvent for many synthetic methods. The most interesting example of water as a solvent is the Diels-Alder organic synthesis. Water has been proved very good for selectivity even for reagents which are not very soluble or insoluble in water.
c) Organic synthesis in polyfluorinated phases

In these techniques chemists are using polyfluorinated two phase systems of solvents which dissolve a catalysts with a long hyperfluorinated alcylo- or aliphatic chain. Reagents are dissolved in an organic solvent which is insoluble in the hyperfluorinated phase. Warming up the mixture accelerates the reaction with excellent yield of products.

d) Supercritical carbon dioxide and supercritical water

Supercritical fluid is called any liquid substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be “fine-tuned”. Supercritical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon dioxide and water are the most commonly used supercritical fluids. They are use for supercritical fluid extraction (SFE). These supercritical properties can be applied as “green chemistry” credentials in chemistry with high yields and minimum waste.

e) Use of microwave techniques for organic synthesis

Microwave furnaces are widespread now for food warming and cooking. Their use in organic synthesis started many years ago and their success in organic synthesis with “green” criteria is very well established. Already, there are numerous research papers and applications for microwave organic synthesis with high yields, without solvents, low waste and very low energy requirements.

f) Sonochemistry. The use of ultrasound for synthesis

Chemical reactions can start and enhanced by sonic waves. Sonochemical reactions by ultrasound is very advanced “green” techniques with exceptional high yields. There are three classes of sonochemical reactions: homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid-liquid or solid–liquid systems, and, overlapping with the previous techniques, sonocatalysis. The chemical enhancement of reactions by ultrasound has been explored and has beneficial applications in mixed phase synthesis, materials chemistry, and biomedical uses.

Other techniques advanced in the last decade in organic synthesis, with emphasis on toxic solvent minimization, are soluble polymers as catalysts, thermoregulated systems, and enzymes. All these techniques have been advanced with green chemistry principles in mind, since industrial production of chemical substances is the fundamental technology producing environmental problems, waste and toxic by-products.

Green Chemistry Has Advanced from Theory to Practice

As we can see from all the above technological advances, Green Chemistry principles have advanced considerably in the last decades. Research on various industrial applications have been very successful and with considerable advantages for energy consumption, less toxic products and minimum waste. These advances have contributed first of all in the safety and health of workers who work in chemical industries, making of products with basic materials workshops and other professional people involved in the
transport and distribution of these products. Secondly, green chemistry found alternative ways to cut energy consumption, or by changing processes, or through new catalytic routes, in order to shave energy. Energy consumption by industry is not only an economic advancement, but also an important environmental problem. Thirdly, the use of alternative solvents (e.g. toluene than of benzene, cyclohexane than carbon tetrachloride, dichloromethane than chloroform) green chemistry reduced substantially environmental problems. Fourthly, green chemistry introduced innovations for the industrial products during their use or after their useful life cycle as waste. These are some very important changes for sustainable development goals.

Green Chemistry, through design and better synthetic routes focused on cleaner production techniques and less toxic consumer products. From pesticides, fertilizers, elastomers, plastics, medicines, analytical reagents, and other commercial products, the major industrial players now concentrating in the production of safer, healthier and more benign products for the environment. At the same time industry takes part in the goals of sustainability and the prevention of environmental damage, not only because technological advances provide alternative methodologies but because it makes economic sense and averts the future lack of resources for feedstocks and energy.
References

Green Chemistry Frontiers, Challenges and Advances

**Alternative Feedstocks, Oleochemistry, Biomass, etc**

**Photochemistry, Catalysis, Organic Synthesis**

Photocatalytic Degradation-Advanced Oxidation Processes)

Biomass, Biomaterials, Biofuels

Biocatalysis, Biotransformations

Sequestration of Capturing of CO₂

Reaction of Green Chemistry: Oxidations, Catalysis, ionic Liquids

Selective Catalysis, Heteropolyacids, Oxometallates, etc

Green Chemistry and Methods of Polymerization


**Chemical Reactions in Unusual Media**


77. West A. Promising a greener future: Ionic liquids have long been hailed as the future of green chemistry but can they live up to their promise? *Chemistry World*, RSC, March, 33-35, 2005.


**Design of Safer Chemicals, Solvents and Materials**


**Green Chemistry in Education and Green Chemistry Experiments**


