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Green Chemistry and New Technological Developments

New Avenues for the Green Economy and Sustainable Future of Science and Technology

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Abstract

The chemical industry plays a fundamental role in sustaining the world economy and underpinning future technologies and scientific advances in new materials, less toxic products, renewable energy sources, environmental protection, industrial processes with energy efficiency and renewable raw materials. Green Chemistry (GC) or Sustainable Chemistry aims, under greater societal expectations, for a sustainable global future of the planet Earth, for the design of chemical products that eliminate the use of hazardous substances for man and the environment. In this respect Green Chemistry fields initiated in the 1990s are rapidly developing technological innovations providing the most environmentally suitable solutions for a sustainable development of future science and technology. GC offers enhanced chemical process economics, concomitant with a reduced environmental burden. GC can be applied to design environmentally benign synthetic protocols, to produce life-saving medicines, environmentally friendly agrochemicals, new enzymes for biocatalytic chemical processes, innovative renewable energy sources, energy efficiency in chemical reactions, and innovative materials while minimizing environmental impact.

Directed evolution produced by biotechnological methods a great array of enzymatic catalysts that are extremely efficient to catalyze chemical reactions of industrial and fine chemicals. The “bionic leaf” method achieved the splitting of water by sunlight, the production of hydrogen and with the help of bacteria the formation of isopropanol as biofuel. Biocatalysts employed on large scale in the pharmaceutical synthesis delivering low cost and high quality intermediates and drugs. Biodegradable polymers and polymers from carbon dioxide have been advanced by many chemical companies. Organic photovoltaic solar cells have been developed for low-energy-production photovoltaic solutions providıvγ electricity at a lower cost than first- and second-generation solar technologies. The use of “green” solvents and industrial reactions in water have been applied in the last decade to numerous industrial processes. Vegetable oils have been used in numerous applications, including oil-based paints. The replacement of oil with biomass as raw material for fuel and chemical production is an interesting option for the development of biorefinery complexes. Green Chemistry envisaged technological interventions for traditional farming practices that will reduce environmental pollution and increased yields of many crops. There is intensive research on renewable energy sources for sustainable storage technologies (batteries). This review contains and presents selected research papers and projects on innovative green chemistry and green engineering which are aiming to a sustainable future for science and technology and innovative chemical products.

1. Introduction: Global Environmental Challenges, Green Chemistry and Sustainable Development

Trends and rapid developments of the global economic and technological growth in the 20th century, forced scientists and technologists to realize that further development of human civilization and the fulfillment of socio-economic needs of the present generation will be only possible if the natural resources are properly managed and the relationship between economic growth and caring for the environment of the present and future generations is consciously maintained.

Ten years after the 1972 United Nations Conference on the Human Environment (Stockholm), most of the global environmental challenges had clearly not been adequately addressed. Particularly, the problems poverty in developing and Third World countries through more productive and industrialized economies, the global and local environmental pollution, and the non-sustainable use of natural resources. Environmental pollution threats, ranging from atmospheric pollution in cities, municipal solid waste, acid rain, deforestation and desertification, the reduction of ozone layer and signs of climate change were overlooked. The idea of sustainable eco-development was presented for the first time in 1987 in the report of the World Commission on Environment and Development of the United Nations.[1]

In the report, it was stated that the further development of human civilization and the fulfillment of socio-economic needs of the present generation will be only possible if the natural resources are properly managed and the relationship between economic growth and caring for the environment of the present and future generations is consciously maintained, while the long-term effects of industrial activities are also considered. The global chemical industry plays a fundamental role in important scientific and technological fields associated with the future of sustainable development in developed and developing countries. From the beginning, the leaders of the major chemical industries participated in the debate on the actions and changes needed to achieve goals of Sustainable Development and identified their share of responsibility towards these goals. Chemists and engineers are embracing sustainability challenges in order to minimize potential environmental and health implications of their technologies. The American Chemical Society (ACS) in the 1990s promoted sustainability, green chemistry, and green engineering, combined with incentives for the adoption of sustainable technologies and new regulatory strategies.[2,3]

The term Green Chemistry (or Sustainable Chemistry) was coined by Paul Anastas in 1991 within the framework of the U.S. Environmental Protection Agency (EPA) program. As a result, the comprehensive US Green Chemistry Program was established in 1993 which involved the cooperation among many governmental agencies and research institutions, international scientific cooperation as well as worldwide activities in the field of education and information dissemination.[4-8]

The European chemical industry published its first sustainability report (2012), outlining the sector's vision to play a key role in global sustainable development. The chemical industry strives to be sustainable in terms of its operations and to be a key enabler of a sustainable society by implementing environmentally friendly science and technologies, natural resource efficiency, and safe chemical products for chemical workers and consumers. [9]

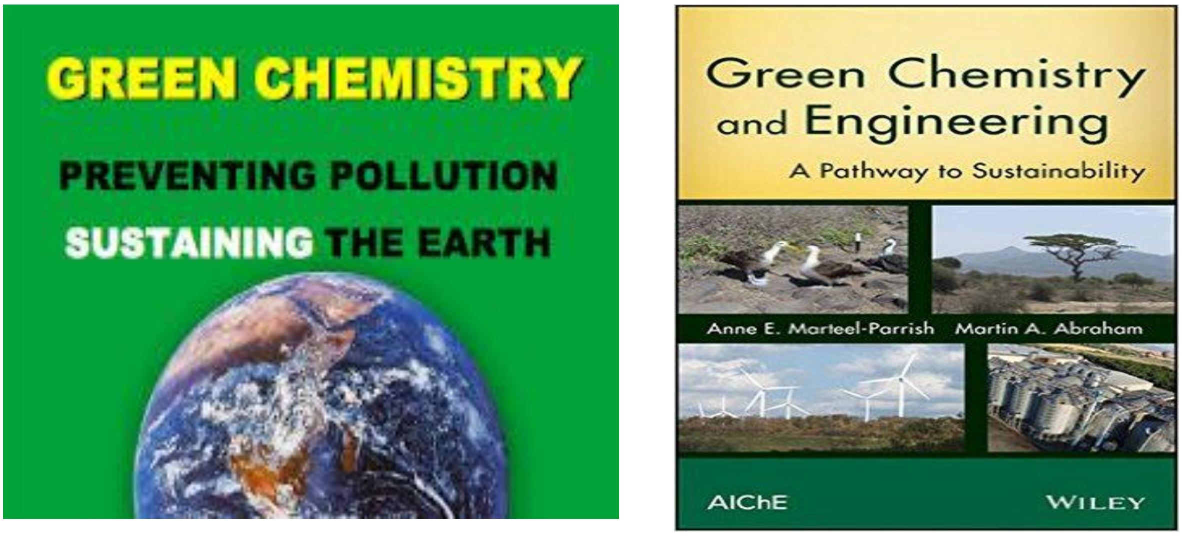


Figure 1. Various books have been published on the subject of Green Chemistry and Sustainable Development. Marteel-Parrish AE, Abraham MA. *Green Chemistry and Engineering: A Pathway to Sustainability*. Wiley-AIChE New York, 2013.

2. Green Chemistry and Green Engineering Principles

From the beginning Paul Anastas and John Warner emphasized the new principles of Green Chemistry and the new "philosophy" that has to be followed to achieve the sustainable eco-development of the chemical industry in the future. The following list of 12 principles outlines an early conception of what would make a greener chemical, process, or product.[10,11]

1. Preventiont is better to prevent waste than to treat or clean up waste after it has been created.

2. **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. **Less Hazardous Chemicals.** Syntheses wherever practicable, should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing Safer Chemicals** with desired function while minimizing their toxicity.

5. **Safer Solvents** and auxiliaries substances (e.g., solvents, separation agents, etc.) for workers and the environment.

6. **Design for Energy Efficiency**. Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized.

7. **Use of Renewable Feedstocks**. Raw materials or feedstock should be renewable rather than depleting.

8. **Reduce Derivatives**. Unnecessary derivatization (blocking groups, protection/deprotection, temporary modification, etc) should be minimized or avoided if possible.

9. **Catalysis and new catalytic reagents** (enzymes, as selective as possible) are superior to stoichiometric reagents.

10. **Design Products for Degradation**. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

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. **Inherently Safer Chemistry for Accident Prevention.** Substances and chemical process should be chosen to minimize the potential for chemical accidents.

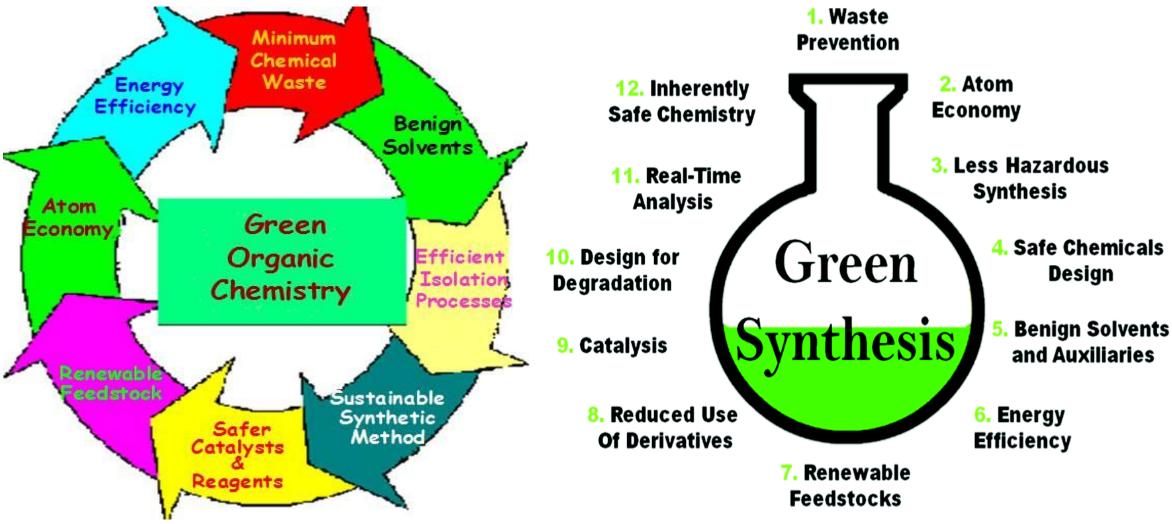


Figure 2. Green Chemistry has established firm ground providing essential design criteria for the development of efficient chemical syntheses. The 12 principles of GC have been recognized as fundamental principles for future sustainable chemical industry and environmental protection.

2.1. Green Engineering Principles for Sustainable Technology

The 12 Principles of Green Chemistry have been supplemented later with 12 Principles of Green Engineering which support and promote similar green and eco-friendly aspects of mechanical engineering, industrial processes in various industries, design features for recycling in products, energy efficiency and renewable raw materials. The 12 Principles of Green Engineering have been developed in order to provide a framework for scientists and engineers to engage in when designing new materials, products, processes, and systems that are benign to human health and the environment.

1: **Designers need to strive to ensure** that all material and energy inputs and outputs are as inherently nonhazardous as possible.

2: **It is better to prevent waste** than to treat or clean up waste after it is formed.

3: **Separation and purification operations** should be **designed to minimize energy consumption** and materials use.

4. Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.

5: **Products, processes, and systems should be "output pulled**" rather than "input pushed" through the use of energy and materials.

6: **Embedded entropy and complexity** must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.

7: **Targeted durability, not immortality**, should be a design goal.

8: **Design for unnecessary capacity or capability** (e.g., "one size fits all") solutions should be considered a design flaw.

9. **Material diversity** in multicomponent products should be minimized to promote disassembly and value retention.

10. **Design of products,** processes, and systems must include integration and interconnectivity with available energy and materials flows.

11. **Products, processes, and systems** should be designed for performance in a commercial "afterlife".

12. **Material and energy inputs** should be renewable rather than depleting.

These principles take into account the large scale of industrial processes which are more complicated than lab-scale syntheses and where cost and economics become a driving force. Health and safety of workers, environmental impacts are much higher, since large amounts of solvents, chemicals and waste are involved. [12-14]

3. Fields of Green Chemistry with New Technological Developments

In the last decade Green Chemistry and Green Engineering have advanced for a great variety of research and technology fields providing cutting-edge research and practical applications for a wide spectrum of chemical products and technological innovations. The most important research and technological fields of GC and GE include solutions. Among other things, reduction of global warming and use of CO_2 as a raw material for chemical synthesis, microwave, electrochemical and ultrasound synthetic methods, solvent free reactions (or water as a solvent), phytoremediation, waste management and wastewater, eco-friendly dyes and pigments, innovative food products, catalysis and biocatalysis, biopolymer technology, renewable materials, renewable energy sources, etc.

Although there are many fields of innovation for GC and GE products we list below some of the basic.[15-17]

a. Biocatalysis and biotransformations processes for practical synthetic reactions
b. Directed evolution. New enzymes for organic synthesis
c. Green chemistry and synthetic processes in the pharmaceutical industry
d. Hydrogen production via catalytic splitting of water
e. Green and renewable energy sources
f. Green chemistry and agricultural technologies benign to environment
g. Green chemistry. Multicomponent reactions
h. Green flow chemistry and continuous processes in chemical industry
i. Green chemistry and biodegradable polymers
j. Green chemistry and organic solar cells
k. Solvent and solvent selection in industrial synthesis

Except for the above, there are also numerous other technological; fields of Green Chemistry and Green Engineering that have been advanced in the last years. Already, some these innovative inventions have been applied and improved sustainability, reduced environmental pollution and released less hazardous chemical products.[18-20]

4. 'Directed Evolution', Green Chemistry and Biocatalysis

In 2016 the biochemical engineer Frances Arnold (CALTECH) received the Millennium Technology Prize (1 million Euros, awarded by Technology Academy Finland, Helsinki) in recognition of her discoveries and research on the field of '**directed evolut**ion', which mimics natural evolution to create new and better proteins (enzymes for biocatalysis) in the laboratory. This technology have solved many important synthetic industrial problems, often replacing less efficient synthetic methods and sometimes harmful technologies. Thanks to directed evolution, sustainable development and clean technology (biocatalysis) become available in many fields of chemical industry.[21,22]

The Millennium Technology Prize is one of the world's most prestigious science and technology prizes. Professor Arnold is the first woman to win the award, underscoring her status as a strong role model for women working in technology. Past winners were World Wide Web creator Sir Tim Berners-Lee, inventor of bright blue and white LEDs Shuji Nakamura and ethical stem cell pioneer Shinya Yamanaka. In 2012, US President Barack Obama awarded Prof. Frances Arnold the National Medal of Technology and Innovation, established by the US Congress in 1980. Arnold's scientific work has been recognized by many awards, including the 2011Draper Prize and a 2013 National Medal of Technology and Innovation. She was elected to the American Academy of Arts and Sciences in 2011. Arnold has the rare honor of being elected to all three National Academies in the USA.[23.]

Figure 3. The Millennium Technology Prize (Helsinki, Finland) was awarded to Professor Frances Arnold (CalTech) for her innovative research on directed evolution. This prestigious award is presented to a well known scientist whose research was innovative and contributed to the welfare of the society.

Frances Arnold, (Professor of chemical engineering at California Institute of Technology) advanced many years ago the '***directed evolution'*** method for the production of new proteins in the laboratory with desired properties that can be used for biocatalytic reactions. This technology used the power of biology and evolution to solve many important catalytic problems. Thanks to directed evolution, sustainable development and clean technology become available in many areas of industry that no longer have to rely on non-renewable raw materials. Arnold's method generated random mutations in the DNA – just as it happens in nature. The modified genes produce proteins with new properties, from which the researcher can choose the useful ones, repeating the process until the level of performance needed by industry is achieved. Directed evolution can produce enzymes that are used in industries that utilize biotechnology. It has been adopted in areas of Green Chemistry and renewable energy. For example, directed evolution is used to improve enzymes that convert cellulose or other plant sugars to biofuels and chemicals. The facilitation of a green chemical industry, based on renewable raw materials and biotechnology, has in fact been one of Arnold's greatest goals.[24-26]

4.1. Enzymes Can be Tailored by Directed Evolution for Optimal Performance

The most attractive technological achievement of directed evolution is the engineering of tailored (rational design) industrial enzymes for biocatalysis. In the last decade the scientific literature is full of innovative examples. For example, CalTech laboratory developed produced an efficient para-nitrobenzyl esterase over six generations of random point mutagenesis and recombination. The best clones identified after four generations of sequential random mutagenesis and two generations of random recombination displayed more than 150 times the *p*-nitrobenzyl esterase activity of wild type. The accumulation of multiple mutations by "directed evolution" allowed significant improvement of the biocatalyst for reactions on substrates. [27] These innovations have revolutionized the slow and costly process of protein modification. Directed evolution is used in hundreds of laboratories and companies around the world. Modified proteins are used to replace processes in the production of fuels, paper products, pharmaceuticals, textiles and agricultural chemicals.[28,29]

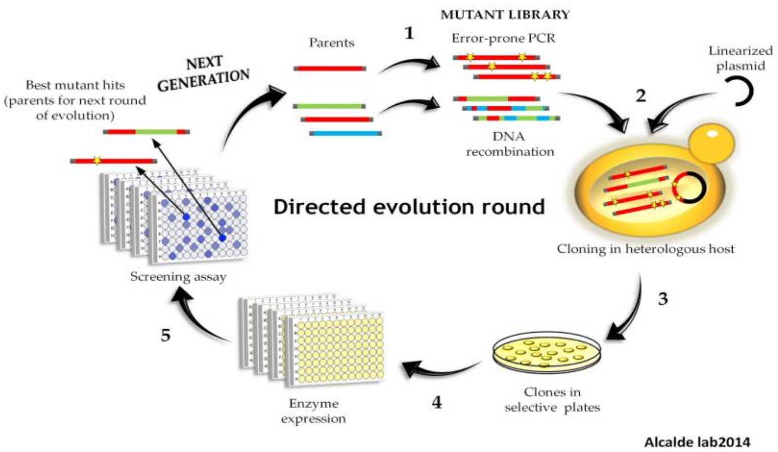
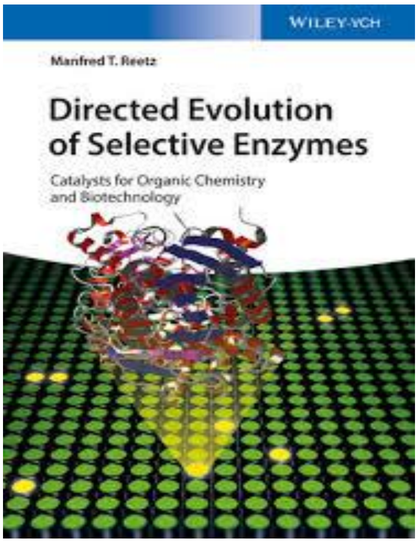


Figure 4. Directed evolution for protein modification to catalyze industrial reactions. Diversity is mimicked by inducing mutations in the gene encoding a specific protein. The best performers are selected and used as the parental types for a new round of evolution. The process is repeated as many times as necessary until a biocatalyst is obtained that exhibits the desired traits [http://www.miguelalcaldelab.eu/].

The cytochrome P450 (CYPs) constitutes the major enzyme family capable of catalyzing xenobiotic metabolism, the oxidative biotransformation of most drugs and other lipophilic xenobiotics and are therefore of particular relevance for clinical pharmacology. Discovering enzymes for catalyzing new reactions is important to chemical industry but highly challenging to laboratory experimentalists. Scientists investigated if Cytochrome P450 enzymes can be engineered by directed evolution to catalyze industrial synthetic reactions. However, desirable transformations are not easy to achieve. Recent scientific research has revealed that P450-derived enzymes can also catalyze useful reactions previously accessible only to synthetic chemistry. The evolution and engineering of these enzymes provides an excellent case study for how to genetically encode new chemistry and expand biology's reaction space.[30] Directed evolution achieved to convert these promiscuous generalist enzymes into specialists capable of mediating reactions of industrial interest with exquisite regio- and stereo- selectivity. Progress has been made by altering properties of biocatalysts P450s (substrate range, cofactor preference and stability) with emphasis in industrial applications.[31]

This methodology has been helped by many advances in DNA technologies, metagenomics, and bioinformatics that have enabled the use of biological systems (i.e., enzymes, metabolic pathways, and cells) for chemical synthesis and production of chemicals from renewable resources (such as sugars). There are many examples of enzyme and metabolic engineering for the synthesis of organic molecules with high efficiency and selectivity.[32]



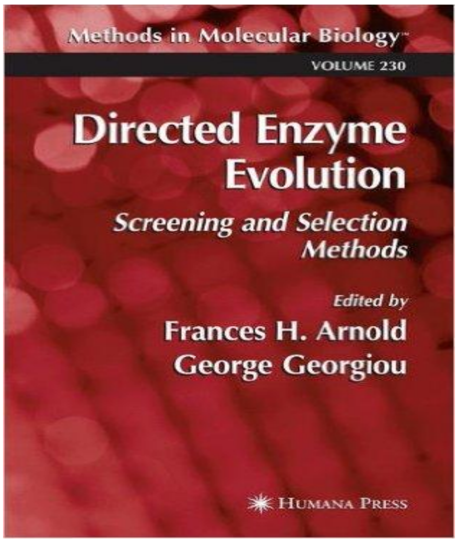


Figure 5. Directed evolution Books. Reetz MT. *Directed Evolution of Selective Enzymes. Catalysts for Organic Chemistry and Biotechnology*. Wiley-VCH, Berlin, 2016. Arnold FH, Georgiou G (Eds). *Directed Enzyme Evolution. Screening and Selection Methods*. Humana Press, Totowa, NJ, 2003.

5. The ‘Bionic Leaf’. Sunlight Splits Water and Bacteria Produce from Hydrogen Liquid Fuels

Hydrogen generated from solar-driven water-splitting has the potential to be a clean, sustainable and abundant energy source. Inspired by natural photosynthesis, artificial solar water-splitting devices are now being designed and tested for efficiency. Although sunlight-driven water splitting is a promising process to sustainable hydrogen (H_2) production as fuel, widespread implementation is hampered by the expense of the photovoltaic and photoelectrochemical apparatus. Various catalysts and integrated systems have been used for the production of hydrogen from water.[33,34] International teams of researchers have succeeded to increase the efficiency for direct solar water splitting with a tandem solar cell whose surfaces have been selectively modified with as new record of 14% efficiency.[35]

At present there is in use of new generation of hydrogen fuel cell vehicles with zero emissions. The H_2 car runs on compressed hydrogen fed into a fuel cell "stack" that produces electricity to power the vehicle. A fuel cell can be used in combination with an electric motor to drive a vehicle – quietly, powerfully and cleanly. Great attention has been focused on hydrogen as a potential energy vector and on the use of water-splitting technology as a clean and renewable means to generate hydrogen using solar energy. Numerous attempts have been made to develop photo-catalysts that work not only under UV light but also under visible-light illumination to efficiently utilize solar energy. Some potential sources of hydrogen are electrical, thermal, biochemical, photonic, electro-thermal, photo-thermal, photo-electric, photo-biochemical, and thermal-biochemical. Such forms of energy can be derived from renewable sources, and from energy recovery processes for hydrogen production purposes.[36,37]

5.1. The Idea of the ‘Bionic Leaf 2.0’ for Photochemical Use of Sunlight

In the last decade new research activities introduced the idea of “bionic leaf” for the efficient splitting of water by photochemical use of sunlight. This research started in the University of Harvard (Massachusetts, USA) and the goal has always been to harness sunlight and use it to create liquid fuel rather than electricity that must then be stored in a battery. The experimental set was designed to use solar power to separate oxygen atoms in water from hydrogen, which is then converted into isopropyl alcohol by bacteria. But prior efforts had used a nickel-molybdenum-zinc (NiMoZn) catalyst and the resulting reactive oxygen species (reactive oxygen species, ROS) would destroy the bacteria’s DNA.

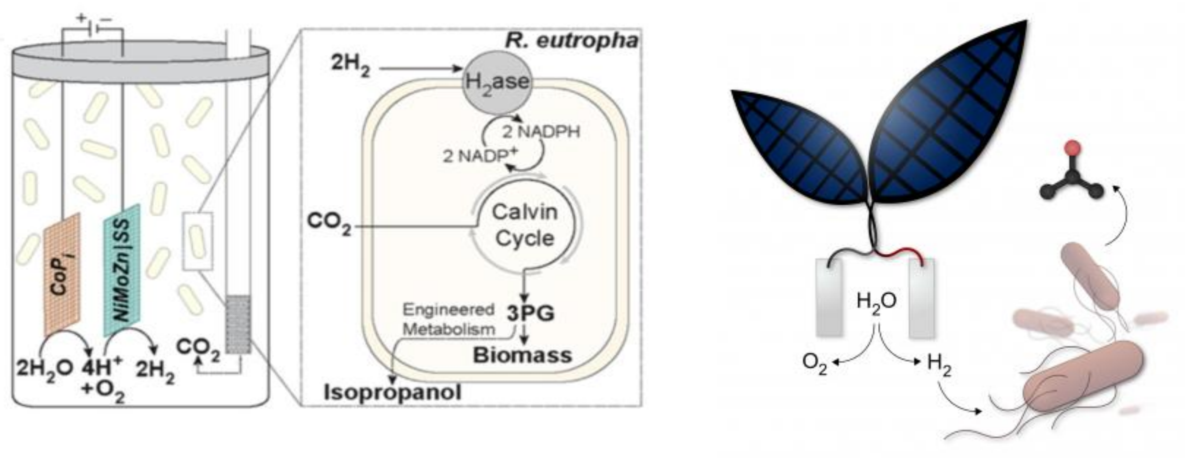


Figure 6. Scientists at Harvard University have created an artificial photosynthetic system (changing the NiMoZn catalyst with a new cobalt-phosphorus alloy catalyst) that uses solar energy to split water molecules. The produced hydrogen is consumed by bacteria (*Ralstonia eutropha*) to produce liquid fuels (isopropanol). The system can convert solar energy to biomass with 10 % efficiency, far above the 1 % seen in the fastest-growing plants.

The initial research on the ‘bionic leaf’ was a research idea of chemist Prof. Daniel Nocera (Patterson Rockwood Professor of Energy at Harvard University). In the second stage of the research Nocera cooperated with Prof. Pamela Silver (Elliott T. Adams and Onie H. Adams Professor of Biochemistry and Systems Biology at Harvard Medical School). The team recently (2016) published a new paper in the journal *Science* that described their new breakthrough.

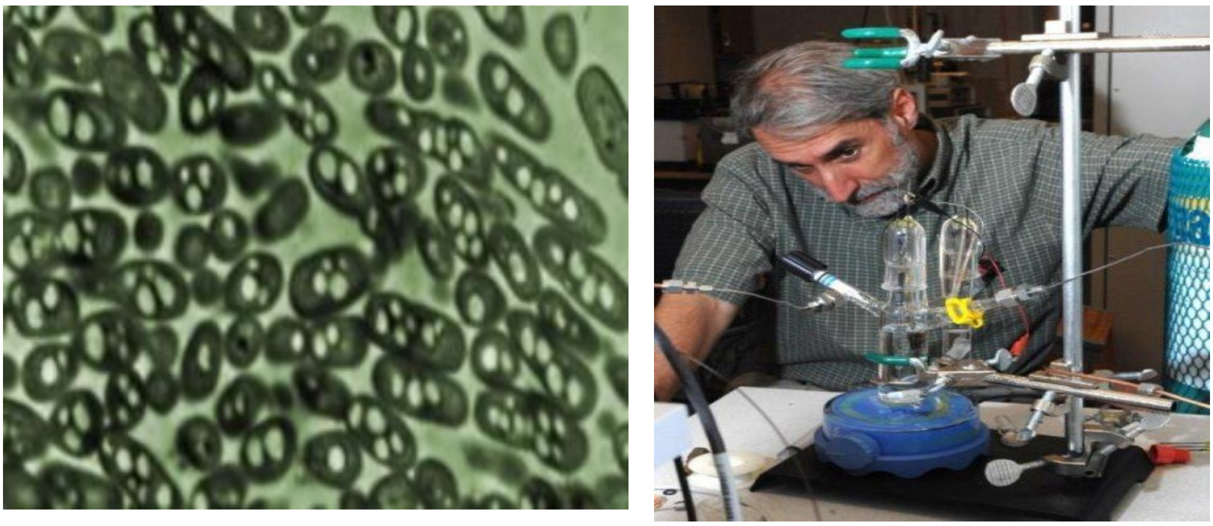


Figure 7. The ‘Bionic Leaf 2.0’. *Ralstonia eutropha* bacteria which are used in the ‘Bionic Leaf 2.0’ producing fuel (isopropanol) using the H_2 produced via catalysts powered by electric current from a photovoltaic panel. Prof. Daniel Nocera in his research laboratory of the University of Harvard (MA, USA).

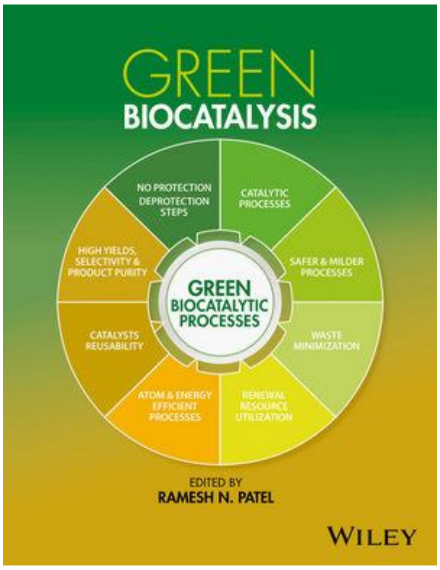
The paper describes an artificial photosynthetic system (dubbed 'bionic leaf 2.0') that can store solar energy and chemically reduce CO_2. Scientists developed a hybrid water-splitting system with a biocompatible inorganic catalysts (replaced the older Nickel-Molybdenum-Zinc by a Cobalt-phosphorus alloy catalyst). The new catalyst does not produce ROS which were damaging the bacteria. The splitting of water produced H_2 and O_2 at low voltages. The hydrogen in contact with the bacterium *Ralstonia eutropha* was consumed to synthesize biomass and fuels products (isopropanol). The scalable system has a CO_2 reduction energy efficiency of ~50% when producing bacteria biomass and liquid alcohols scrubbing 180 g of CO_2 per kilowatt-hour of electricity. Coupling this hybrid device to existing photovoltaic systems can yield a CO_2 reduction energy efficiency of ~10%, exceeding that of natural photosynthetic systems.[38]

According to Prof. Nocera "….this is a true artificial photosynthesis system which is well over the efficiency of photosynthesis in nature." While the study shows the system can be used to generate usable fuels, its potential doesn't end there. The system can now convert solar energy to biomass with 10% efficiency far above the 1% seen in the fastest growing plants.

6. Green Biocatalysis for the Pharmaceutical Industry

Aftrer an initial lag phase the pharmaceutical industry embraced Green Chemistry from the beginning for economic and prestige purposes with emphasis in greener synthetic methods, less solvents and environmental protection. In the last decades biocatalysis has established itself as a scalable and green technology for the production of a broad range of pharmaceutical compounds and intermediates. Biocatalysts employed on large scale in pharmaceutical synthesis deliver cost- and quality- advantages to the pharmaceutical industry. To this respect there are many discoveries of innovative biocatalytic processes using hydrolases, reductases, transaminases, oxidases etc., which are used for the preparation of therapeutic agents. A recent review included 25 recent biocatalysis case studies for pharmaceuticals manufacture. Innovative enzymes used for biocatalysis offered substantial economic benefits to the pharmaceutical industry.[39,40]

The biosynthesis in organic synthesis in the pharmaceuticals, flavour and fragrance, vitamin and fine chemicals industries is not fully expanded yet, so there are more to be done in the use of new catalytic enzymes in organic synthesis of drugs and other therapeutic ingredients.[41,42] In the past ten years new scientific and technological developments have advances DNA sequencing and gene synthesis for tailoring biocatalysts by protein engineering and design, and the ability to reorganize enzymes into new biosynthetic pathways.[43-46]



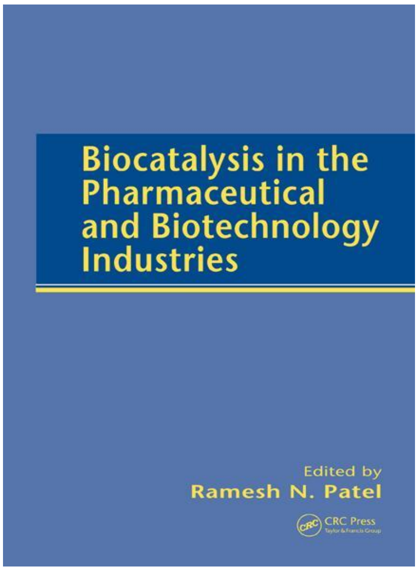


Figure 8. Green Biocatalysis has advanced in the last decade as the most important and effective methodology for the preparation of pharmaceuticals and active intermediates. Patel RN (Ed). *Green Biocatalysis*. John Wiley & Sons, Chichester, W. Sussex, 2016. Patel RN (Ed). *Biocatalysis in the Pharmaceutical and Biotechnlogy Indiustries*. CRC Press, Boca Raton, Fl.2006.

7. New Developments in Degradable and Recycled Polymers

The green economy strives to promote sustainability and alternative methods for reduction of the demand for raw material resources and energy, to minimize wastes, to prevent environmental pollution and hazards, to reduce greenhouse gas emissions, to optimize manufacturing processes, and effective recycling of end-of-life products and wastes. In the first decades of industrial processes the polymer production was using mainly petroleum raw materials, high energy inputs, and produced non-degradable plastics and large amounts of waste. In the 1930s, the first industrial process for making polyethylene (PE) required temperatures above 150°C and very high pressures exceeding 1000 bar. Catalytic olefin polymerization was discovered during the 1950s with low pressures below 10 bar and at temperatures below 100 °C.[47]

- The global polymer and plastic material production increased substantially in the last decade reaching in 2014 the staggering amount of 311 million metric tons. China is the largest producers with around 25% of the global production and 20% by NASFTA countries (USA, Canada, Mexico). In Europe, there are 60,000 plastics factories, with direct employment of 1.45 million people. Today, an average person in developed countries consumes 100 kg of plastic each year (packaging materials and household items).[48,49]

During the 1980s, in the aftermath of the first oil crisis in 1973, the energy-efficient catalytic copolymerization of ethylene for manufacturing linear low-density polyethylene

(LLDPE), used in food packaging, became a million ton business. In the last decades the variety of plastic materials increased substantially and the first biodegradable plastic products were introduced. Plastic littering problems increased at a fast rate and plastic pollution of oceans became a serious and emerging issue of environmental pollution. This was the result from a lack of recycling and illegal dumping of garbage in most developing countries. The Green chemistry of polymers with degradable products and bio-based plastics are considered in the right direction for sustainability in the polymer field.[50]

In 1997, scientists working for the chemical company Dow formed a joint venture aiming at converting PolyLactic Acid (PLA) into a commodity plastic which was biodegradable. The L-lactic acid monomer was produced by fermentation of dextrose from forage maize or other plant sources for sugar without requiring genetically modified plants. The PLA was globally marketed in 2003 by the newly formed company NatureWorks under the trade name Ingeo™. In 2009, NatureWorks established an annual nameplate production capacity of 140.000 tons of the Ingeo biopolymer. The biodegradable PLA applications included packaging, durable plastics, and fibers. Like the paper waste PLA does not degrade in landfills.[51,52]

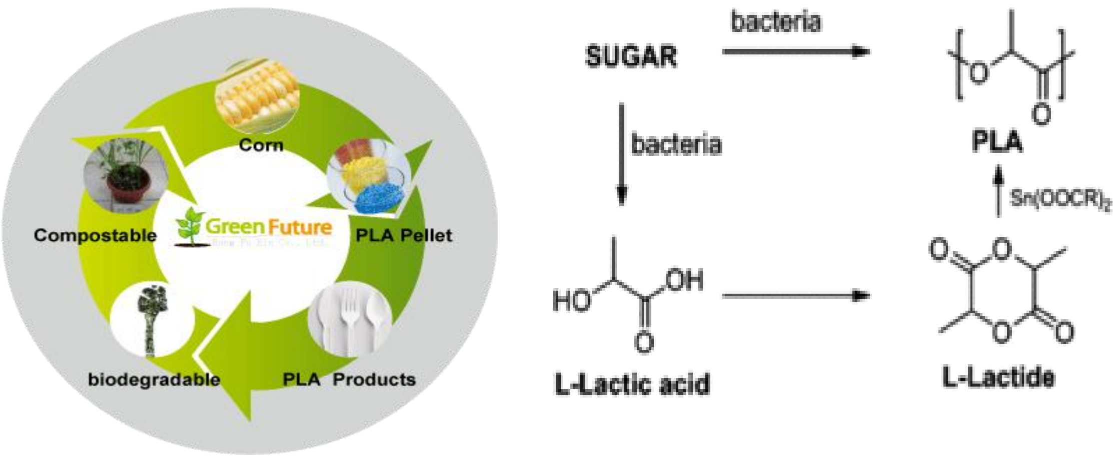


Figure 9. Poly(L-lactic acid) from bacteria and by melt polymerization of lactide, prepared from bio–based L-lactic acid. The polylactic acid polymer is a promising biodegradable polymer with many plastic products in the market.

There are several promising markets for biodegradable polymers such as polylactide. Plastic bags for household bio waste, barriers for sanitary products and diapers, planting cups, disposable cups and plates are some typical applications. Commercial markets for biodegradable polymers are expected to increase substantially in the coming years. Since PLA is compostable and derived from sustainable sources, it has been viewed as a promising material to reduce the societal solid plastic waste disposal problem. Its low toxicity along with its environmentally benign characteristics, has made PLA an ideal material for food packaging and for other consumer products. Also, due to their excellent biocompatibility and mechanical properties, PLA and their copolymers are becoming widely used in tissue engineering for function restoration of impaired tissues.[53-55]

Figure 10. The PlantBottle is the new biobased bottle for Coca-cola drinks. It uses "plant-based material", mainly sugar cane to create a necessary ingredient in PET plastic called monoethylene glycol. The "oxo-biodegradable" plastic contains additive 1-3% (metal salts) to help the degradation process in the presence of oxygen, light, heat and moisture after use of the plastic material.

In 2009, the world's largest beverage company Coca-Cola Co introduced the first generation of recyclable PET bottle (PlantBottle™) using up to 30% bio-based monomers. In the new generation of 100% bio-based PlantBottle™, the terephthalic acid will also be bio-based using bio-based *p*-xylene as an intermediate. In 2011, Coca-Cola Co. announced a partnership with three biotechnology companies with the aim of producing plastic bottles made from 100% bio-based materials. Coca-Cola showed off its new bottle at the Expo Milano (2015) food technology conference as a part of the company's efforts to make its containers from renewable ingredients. The new recyclable PlantBottle™ (2015) was the first plastic to be made 100% from sugar cane in Brazil.[56,57]

Biobased polymers are being tackled by start-up firms and industrial big chemical companies. Invista and Genomatica announced that they will pursue making nylon intermediates from sugar. A partnership of BASF, Cargill, and Novozymes has selected a method to make biobased acrylic acid for superabsorbent polymers. And Coca-Cola, pleased with progress toward a 100% biobased soda bottle (PlantBottle), has upped its funding of partner Virent, maker of a key raw material. Invista, the synthetic fibers maker that was once part of DuPont, plans to make biobased polymers. In May 2014 the company introduced a new version of its Lycra brand spandex that it touts as being 70% from dextrose derived from corn. [58,59,60]

The chemical giant BASF developed a compostable polyester film that called Ecoflex®. BASF produced fully biodegradable bags, Ecovio®, made of this film along with cassava starch and calcium carbonate. Certified by the Biodegradable Products Institute (BPI), the bags completely disintegrate into water, CO_2, and biomass in industrial composting systems. The bags are tear-resistant, waterproof and elastic. They can be used as conventional plastic bags in the house and will quickly degrade in municipal composting systems [American Chemical Society, 2016, Examples of Green Chemistry. Biodegradable plastics, available at https://www.acs.org/content/acs/en/greenchemistry/what-is-green-chemistry/examples.html].

7.1. Polymers from Carbon Dioxide

Reducing anthropogenic carbon dioxide (CO_2) emission has become an urgent environmental and climate issue of our age. As a naturally occurring, abundant, inexpensive, nonflammable, and renewable chemical compound, carbon dioxide (CO_2) is an attractive feedstock for the chemical industry. Carbon dioxide can be recovered on a large scale in carbon capture of power plants, burning fossil fuels, and in steam-reforming to produce hydrogen from water and coal. Carbon capture materials will need to be coupled with a method for releasing the CO_2 for further transport and storage or utilization. A number of processes have been studied for CO_2 recovery.[61]

In industrially viable processes, carbon dioxide is reacted with energy-rich strained rings, for example, oxiranes, to produce cyclic carbonates. The nontoxic and biodegradable cyclic carbonates with their high boiling and flash points are readily produced from oxiranes such as ethylene oxide and propylene oxide in the presence of tetrabutylammonium bromide. Applications include their use as green solvents for degreasing oily steel, paint stripping, and various other cleaning applications.[62]

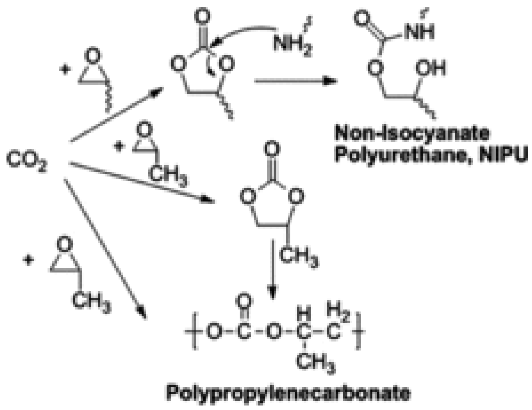


Figure 11. Non-isocyanate polyurethanes (NIPU) and polypropylenecarbonates prepared from cyclic carbonates starting from carbon dioxide (CO_2).

Green Polyurethane™ was the first-ever modified hybrid polyurethane (PU) manufactured without using hazardous isocyanates at any point in the production process. Green Polyurethane's™ unique formulation combines the best mechanical properties of polyurethane and chemical resistance properties of epoxy binders.[63]

In the last years many new catalytic mechanism have been developed for the synthesis of cyclic carbonates. One method used an active bifunctional porphyrin catalyst showing a high turnover number for the synthesis of cyclic carbonates from CO_2 and epoxides under solvent-free conditions.[64] Another research team reported that the cyclic amidine hydroiodide effectively catalyzed the reaction of CO_2 and epoxides under mild conditions such as ordinary pressure and ambient temperature, and the corresponding five-membered cyclic carbonates were obtained in moderate to high yields.[65]

The severity of the future problem of global warming have triggered global efforts to reduce the concentration of atmospheric carbon dioxide (CO_2). Carbon dioxide capture and storage is considered a crucial strategy for meeting CO_2 emission reduction targets. At present there are many research projects and various technologies for CO_2 capture, separation, transport, storage, leakage, monitoring, and life cycle analysis.[66]

Converting captured CO_2 into products such as chemicals, plastics, fuels, building materials, and other commodities has become an important component of the Office of Fossil Energy's Carbon Capture and Storage program (U.S. Department of Energy) , managed by the National Energy Technology Laboratory. This approach could be especially valuable in reducing carbon emissions in areas of the country where geologic storage of CO_2 is not practical. Research focused on PPC (polypropylene carbonate) polymer production conducted by Novomer in collaboration with specialty chemical manufacturer Albemarle Corporation tested scale-up of Novomer's novel catalyst technology.[67]

8. Green Chemistry and Organic Photovoltaic Solar Cells

Organic photovoltaic (OPV) solar cells aim to provide an Earth-abundant and low-energy-production photovoltaic solution. This technology has the potential to provide electricity at a lower cost than first- and second-generation solar technologies. Because various absorbers can be used to create colored or transparent OPV devices, this technology is particularly appealing to the building-integrated PV market. Organic photovoltaics have achieved efficiencies near 11%, but efficiency limitations as well as long-term reliability remain significant barriers. Unlike most inorganic solar cells, OPV cells use molecular or polymeric absorbers, which results in a localized exciton. The absorber is used in conjunction with an electron acceptor, such as a fullerene, which has molecular orbital energy states that facilitate electron transfer.[68]

In 2011, the U.S. Dpt of Energy announced $24.5 million to fund the next generation photovoltaics II projects. This early-stage applied research investment seeks to not only demonstrate new photovoltaic concepts, but also to train the next generation of graduate students and post-doctoral fellows who will ultimately lead the development and commercialization of PV technologies in future years. Current research focuses on increasing device efficiency and lifetime. Substantial efficiency gains have been achieved already by improving the absorber material, and research is being done to further optimize the absorbers and develop an organic multijunction architectures. Improved encapsulation and alternative contact materials are being investigated to reduce cell degradation and push cell lifetimes to industry-relevant values. The benefits promised by OPV solar cells include: Low-cost manufacturing, abundant materials and flexible substrates: The ability to be applied to flexible substrates permits a wide variety of uses.[69]

Organic photovoltaic solar cells are regarded as low-cost and potentially environmentally benign sources of power. π-Conjugated (semiconducting) polymers—the components of organic solar cells are responsible for absorbing light and transporting charge—are not typically synthesized in laboratories in ways that are amenable to manufacturing with low environmental impact. The principles of green chemistry, applied to the synthesis of conjugated polymers, are identified as important guidelines for the multi-ton manufacturing of these materials. A general theme in both green chemistry and process research is that low cost can be correlated to environmental benignity when the costs of disposing wastes are high.[70]

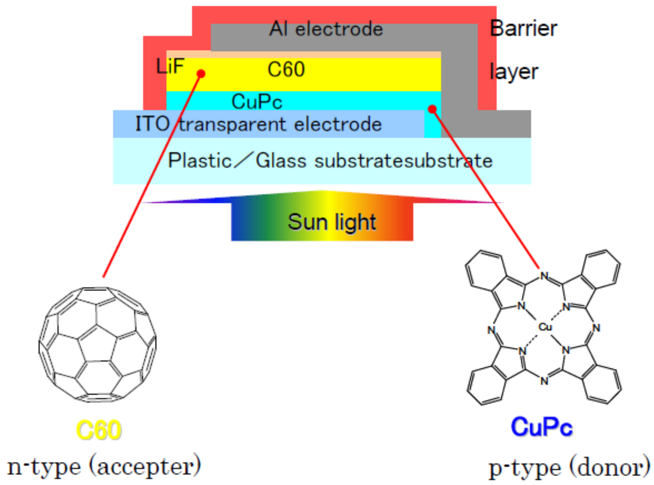


Figure 12. Highly-integrated, organic solar photovoltaic (OPV) modules. These new panels have a P-N diode junction using CuPc and C60 (phthalocyanine and fullerene).

The use of perovscite solar cells has advanced substantially the efficiency of organic photovoltaic solar cells. There is already certified energy conversion efficiencies for perovskite solar cells above 20%. In the last years researchers are exploring other critical area of solar cells, such as understanding device hysteresis and film growth, as well as the replacement of lead and the development of tandem cell stacks. Another important and critical research issue is cell stability.[71]

Scientists are working with various projects to improve polymer solar cell efficiency by using tandem structure. A broader part of the spectrum of solar radiation is used and the thermalization loss of photon energy is minimized. In the past, the lack of high-performance low-bandgap polymers was the major limiting factor for achieving high-performance tandem solar cell. As a result of this innovative approach, a single-junction device shows high external quantum efficiency of >60% and spectral response that extends to 900 nm, with a power conversion efficiency of 7.9%. The polymer enables a solution processed tandem solar cell with certified 10.6% power conversion efficiency under standard reporting conditions.[72]

9. Green Solvents, Catalyst-free Reactions and in Water

Environmental protection and worker safety in chemical; and pharmaceutical manufacture play an increasingly instrumental role in solvent selection. Most companies now use greener solvents. Also, consumers are starting to turn towards “greener” replacements to conventional solvents. Selection of the right solvent has always had the power to increase competitiveness, but environmental benefits and worker/user safety will be the key to product differentiation and better margins as the industry enters into this era of improved environmental awareness. Maintaining process compatibility and solvent functionality will continue to be the top priority when selecting a green solvent replacement, but financial performance and environmental performance need not be mutually exclusive. Green solvents currently represent around 10% of the total solvent market. Green solvent consumption growth through 2014 was assisted by the higher prices of conventional solvents that began escalating in 2004 as a result of record high feedstock pricing. Despite current low oil and gas prices, a market forecast showed that green solvents growth to markedly outpace the conventional solvents market.[73,74]

During the last decade industrial manufacturing and laboratory synthesis changed into catalyst-free reactions and later into catalyst-free reactions in-water and on-water. Various named reactions, multi-component reactions and the synthesis of heterocyclic compounds are some typical examples. Also, in these reactions alternative energy input systems were used, such as microwave and ultrasound irradiation. Synthetic organic chemistry in academic laboratories and in industry changed drastically in the last years by designing methodologies for organic synthesis in aqueous media under catalyst-free conditions and in water.[75]

Organic solvents with inherent toxicity and high volatility were replaced over the past two decades by ionic liquids (ILs) that have gained enormous attention from the scientific community, but their “greenness” is often challenged, due to their poor biodegradability. An alternative type of solvents, representing green chemistry principles are deep eutectic solvents (DES). Deep eutectic solvents are defined as a mixture of two or more components, which may be solid or liquid and that at a particular composition present a high metling point depression becoming liquids at room temperature. DES can be used for biocatalysis, electrochemistry and extraction.[76]

Sanofi is a big international pharmaceutical company. The manufacturing branch has core strengths in diabetes solutions, human vaccines, innovative drugs, consumer healthcare, animal health and Genzyme. Recently Sanofi-Aventis Research and Developments, Sanofi Chemie Industriepark and Sanofi Pasteur published a solvent selection guide in order to help chemists in the drug industry to select sustainable solvents that will be accepted in all production sites. Solvents are divided into four classes, from “recommended” to “banned”. Each solvent has its own ID card that indicates the overall ranking hazard, physical properties, cost, and substitution advice.[77]

10. Green Chemistry and Oil-Based Paints

Vegetable oils are generally considered to be the most important class of renewable resources, because of their ready availability and numerous application, including oil-based paints. Recently, a variety of vegetable oil-based polymers have been prepared by free radical, cationic, olefin metathesis, and condensation polymerization. The polymers obtained display a wide range of thermophysical and mechanical properties from soft and flexible rubbers to hard and rigid plastics, which show promise as alternatives to petroleum-based plastics and oil paints.[78]

The chemical industry treats vegetable oils as one of the most important renewable platform chemicals due to their universal availability, inherent biodegradability, low price, and superb environmental credentials (i.e., low toxicity and ecotoxicity). These natural properties are now being taken advantage of in research and development, with vegetable oil derived polymers and composites being used in numerous applications including paints and coatings, adhesives, and biomedicine.[79] A recent review described the importance of

Vegetable oils (VO) as raw materials for the production of materials such as alkyds, polyesteramides, polyetheramides, polyurethanes, epoxies, polyols, and their applications as protective coatings.[80]

Oil-based "alkyd" paints give off large amounts of volatile organic compounds (VOCs). These volatile compounds evaporate from the paint as it dries and cures and many have one or more environmental impacts. Procter & Gamble and Cook Composites and Polymers created a mixture of soya oil and sugar that replaces fossil-fuel-derived paint resins and solvents, cutting hazardous volatiles by 50 %. Chempol® MPS paint formulations use these biobased Sefose® oils to replace petroleum-based solvents and create paint that is safer to use and produces less toxic waste. Chempol® MPS is an innovative, Sefose(R)-based alkyd resin technology that enables formulation of paints and coatings with less than 50% of VOC's, of traditional, solvent-borne alkyd coatings. The "Presidential Green Chemistry Challenge Award for Designing Greener Chemicals" for 2009 was awarded in the P&G Company for the formulation and manufacture of Chempol MPS technology, which was collaboratively developed and commercialized.[81]

11. Green and Renewable Energy Sources

Governments and scientific communities throughout the Earth recognize that the availability of fossil fuels (petroleum, coal, natural gas) will eventually dwindle, becoming too expensive or too environmentally damaging. In contrast, the many types of renewable energy resources-such as wind, solar, geothermal, hydroelectric, biomass, and ocean energy-are constantly replenished and will never run out. It is hoped that future sustainable development and increasing the supply of renewable energy at global scale will replace carbon-intensive energy sources and significantly reduce global warming emissions. It is obvious that the practice of Green Chemistry and Green Engineering not only leads to a cleaner and more sustainable earth, but also is economically beneficial with many positive social impacts, especially in the acceptance and application of renewable energy resources. These benefits encourage businesses and governments to support the development of sustainable energy processes. In the last decade there are many examples of green chemistry accomplishments in the fields of renewable energy (biomass, biorefineries).[82-85]

The replacement of oil with biomass as raw material for fuel and chemical production is an interesting option for the development of biorefinery complexes. In biorefinery, almost all the types of biomass feedstocks can be converted to different classes of biofuels and biochemicals through jointly applied conversion technologies. This technological change needs an integration of Green Chemistry into biorefineries, and the use of low environmental impact technologies, future sustainable production chains of biofuels and high value chemicals from biomass.[86,87]


Figure 13. Biofuels present an immediate means of reducing the environmental impact of vehicle emissions, particularly heavy vehicles (like buses, trucks, etc), as the global trend is to continue the transition to an electric vehicle future.

Biomass (especially woody biomass, forest residues, agricultural residues and energy crops) is by far the most widely used raw material for the production of renewable energy fuels. Woody biomass is preferred material in thermochemical processes due to its low ash content and high quality bio-oil produced. Thermal conversion by fast pyrolysis converts up to 75% of the starting material into renewable biofuel suitable for transportation. Formulation or blending of various feedstocks, combined with thermal and/or chemical pretreatment, could facilitate a consistent, high-volume, lower-cost biomass supply to an emerging biofuels industry. A recent review summarized the results of numerous research papers that have been published in the last decade projecting the current state of knowledge regarding the effect of feedstock and pretreatments on the yield, product distribution, and upgradability of bio-oil.[88]

Science has advanced substantially in the last years for the third-generation biofuels (low input-high yielding feedstock), specifically the biofuels that are derived from microalgae and which are considered to be viable renewable energy resources. The third generation is devoid of the major drawbacks associated with first-generation biofuels (mainly terrestrial crops, e.g. sugarcane, sugar beet, maize and rapeseed) and second-generation biofuels (derived from lignocellulosic energy crops and agricultural and forest biomass residues). Industrial experience in the production of biofuels showed the importance of integrating biofuels production with the production of high-value biomass fractions in a biorefinery concept. The sustainability of these renewable resources can be achieved through the synergistic coupling of microalgae propagation techniques with CO_2 sequestration and bioremediation of wastewater treatment.[89]

12. Green Chemistry and Innovative Agricultural Technologies

From the 1990s Green Chemistry envisaged technological interventions and applications for traditional farming practices that will reduce environmental pollution (pesticides, fertilizers, intensification of agricultural soil use, excessive water use, etc) and increase the sustainability of agricultural methods. Most scientists agree that Green Chemistry alternatives are vital to sustainably producing agricultural goods without continued dependence on toxic chemicals and technologies that cause occupational hazards to farmers and pollute important environmental resources (soil erosion, water sources, ecosystems). Already, promising scientific and technological practices have been applied to agriculture, new less toxic pesticides and biopesticides (derived from plant or microbes) are in use. At the same time a great variety of innovative green technologies, such as protecting soil from erosion, conservation of biodiversity, climate change adjustments, water management of irrigation, and intensive research of green techniques for biomass transformation into fuels and platform chemicals are promoted in the last decade in many countries. [90,91,92]

Agricultural sustainability and innovative green practices are essential to address environmental problems in a world that must soon support and feed more than 7 billion humans. Despite the progress achieved in the last decades there are more than 2 billion malnourished poor in Third World countries who need short-term food security and live in areas with problems of soil erosion, lack of water resources and agricultural land scarcity because of intensification.[93,94]

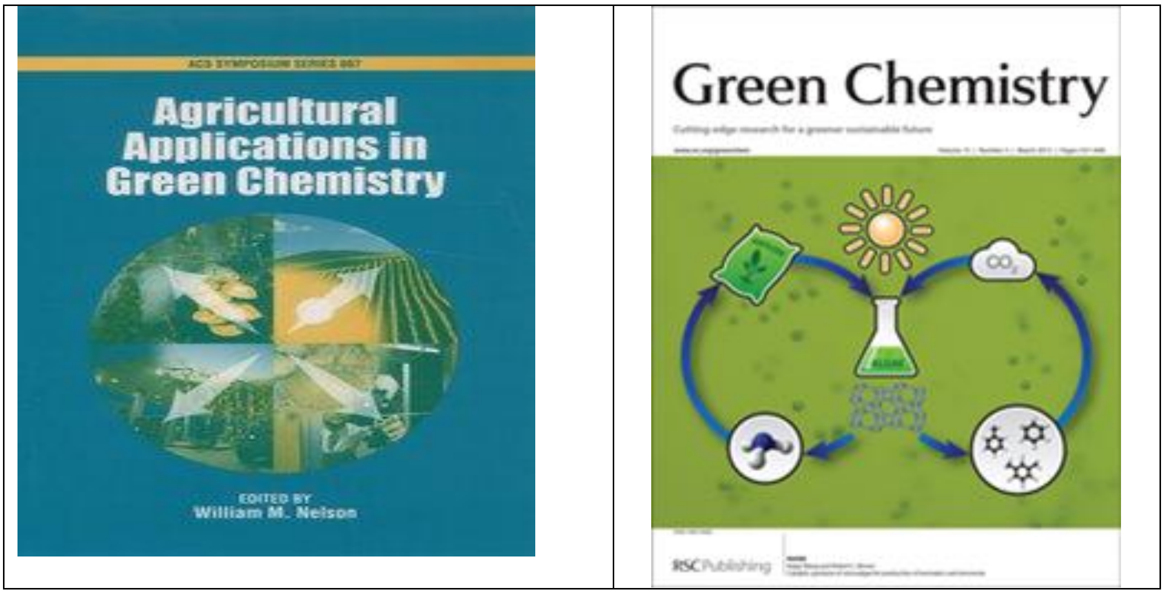


Figure 13. Green chemistry and Green engineering innovations are needed to transform the sustainability of agricultural practices. Nelson WM (Ed*). Agricultural Applications in Green Chemistry.* ACS Symposium Series, Oxford University Press, Oxford, 2004.

The initial “Green Revolution” (GR) in developing countries in the 1960s and 1970s (India, Pakistan, Philippinesd, Brazil, Mexico, etc) was credited with saving over a billion people from starvation. The GR produced an intensification of agriculture with the development of high-yielding varieties of cereal and rice grains, expansion of irrigation infrastructure, modernization of management techniques, distribution of hybridized seeds, synthetic fertilizers, and pesticides to farmers. The spread of Green Revolution in agriculture affected both agricultural and wild life biodiversity, increased environmental pollution, caused water management problems and other negative effects (agricultural soil scarcity).[95,96]

Heavy reliance on use of nitrogen fertilizer to support high yields is perhaps the Achilles heel of modern crop production. However, its misuse has negative impacts on water quality (nitrogen pollution) and climate through emissions of nitrous oxide (N_2O). Of particular note is that the potential improvements will be achieved equally from increased efficiency of fertilizer production and from its more efficient on-farm use.[97,98] Unlike chemical fertilizers, biofertilizer technology (advanced by Green chemistry technologies) is based on renewable resources of energy and does not contribute to environmental pollution. As a low-cost green technology it is most suitable for developing nations where labour is inexpensive. Various micro-organisms and associations with plants which are involved in biofertilizer production as well as their usage on the farm are considered as advantageous. Research showed benefits to small farmers who used these biofertilizers in India. In addition to nitrogen, phosphorus also plays a vital role in plant growth and metabolism. Micro-organisms responsible for phosphate dissolution occur in intimate symbiotic association with plant roots and function as the liaison between the plant and the surrounding soil. Future innovative biofertilizers will probably contain a blend of nitrogen-fixing and phosphate-mobilizing micro-organisms.[99]

Conventional over-fertilization in green leafy vegetables has promoted the need for alternative nitrogen management practices. Recently, a novel slow-release fertilizer, coated with inorganic minerals was developed. A relatively smooth surface, coating layer of the newly developed fertilizer stacked by bonded multi-layer of polyaryl polymethylene isocyanate was formed by tightly arraying solid phosphate rock powder granules. After immersing the fertilizer in water, there was about 13% nitrogen released after 24 h and 30% of nitrogen released in 7 days.[100]

13. Greener Electrochemical Storage Systems.

In the last decade scientists investigating renewable energy sources realized that greener and more sustainable storage technologies (batteries) are needed. It was therefore essential for researchers to incorporate material abundance, eco-efficient synthetic processes and life-cycle analysis into the design of new electrochemical storage systems. At present, a few innovative existing technologies address these issues, but fundamental technological hurdles remain to be overcome. Here we provide an overview of the current state of energy storage from a sustainability perspective. A recent review highlighted the current and future electrochemical storage systems beyond lithium-ion batteries, their complexity and importance of recycling battery materials from a sustainability perspective.[101]

Sodium ion batteries (NIBs) based on intercalation materials that employ non-aqueous electrolytes—akin to lithium ion batteries—were first explored in the mid-1980s. They have undergone a renaissance in the last few years because they hey offer a higher energy density than aqueous batteries and lower cost than Li ion batteries, The sodium ion batteries offer sustainability and cost-effectiveness and are considered as a green alternative for storage of energy.[102]

The innovative material **Graphene** (which was isolated in 2004) has become one of the hottest topics in the field of materials science for its highly appealing properties. Among the many affected areas of materials science, this 'graphene fever' has influenced particularly the world of electrochemical energy-storage devices. But despite widespread initial enthusiasm from many scientists for the role of graphene as material for energy storage there is no any advances in the field. In recent years research was performed on the applications of graphene (as an active material and as an inactive component) in lithium-ion batteries and electrochemical capacitors. Also, grapheme materials were used in emerging technologies such as metal–air and magnesium-ion batteries.[103]

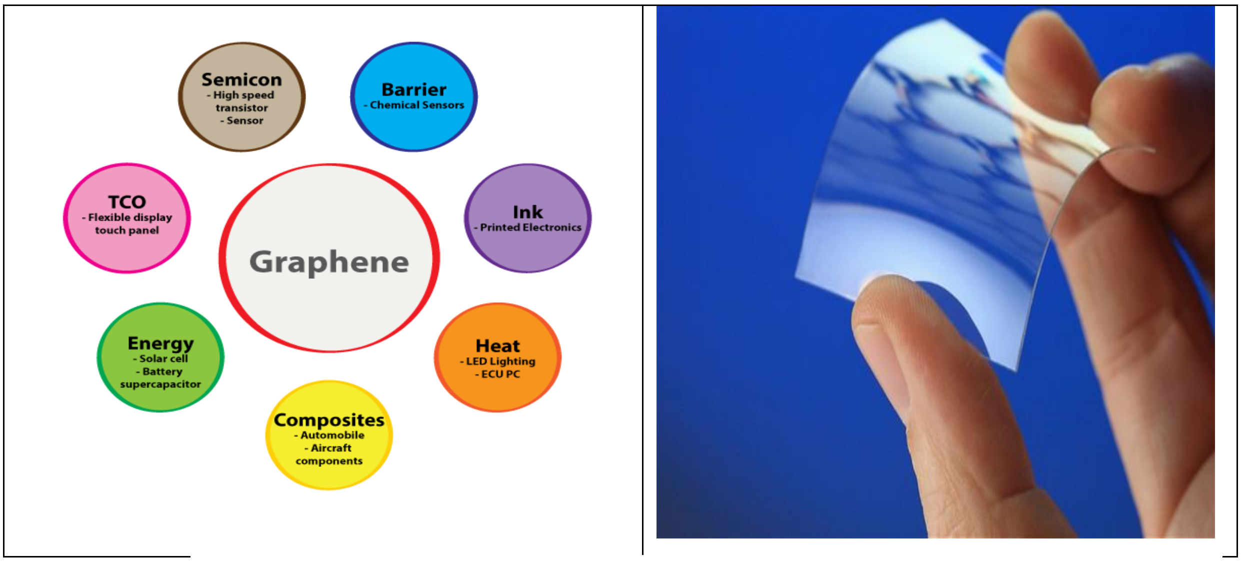


Figure 14. Graphene is an atomic-scale honeycomb lattice made of carbon atoms fascinating physicochemical properties. Graphene is emerging as one of the most promising nanomaterials which opens a way for its exploitation in a wide spectrum of applications ranging from electronics to optics, sensors, and biodevices.

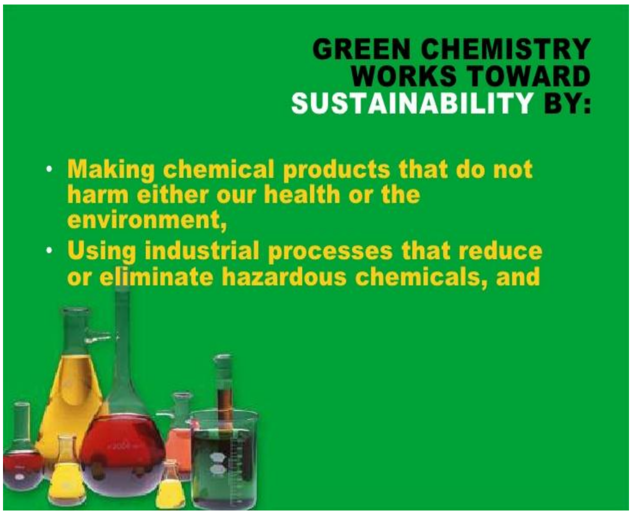
The scientific core efforts in the last decade, following green chemistry principles, were to improve the ability for efficient conversion, storage, transport and access to renewable energy. Also, research efforts focused on using Earth-abundant and nontoxic compounds so that whatever developments were made will not create new environmental problems. Although insertion electrode materials for Li(Na)-ion batteries met initially these requirements, scientists advanced their research into many different areas and re-engineered for extension to larger-scale applications.[104]

14. Green Chemistry and Green Engineering for Sustainability

Green Chemistry and Green Engineering are gaining substantial importance in the chemical and pharmaceutical industries and for new technological developments in a great variety of industries. This is the result of their sustainable nature, energy efficiency, reliance on renewable raw materials, less toxic chemicals and consumer products and lower cost. New green products and consumer items have establish many practical applications in everyday life in recognition of the previous states of environmental pollution by solid municipal waste. All these green-technology ventures are increasingly gaining importance in the face of global environmental degradation in many parts of the Earth and the increasing population.

Scientists and technologists recognize that the rapid industrialization of the past decades has led to widespread global warming, air pollution, depleting natural resources, greenhouse gas emissions, soil erosion, water pollution, and negative impact on sensitive ecosystems. The legislation of a great number of political and environmental initiatives in developed countries in the last decades, encouraged the development of environmentally friendly programmes and green technologies in every aspect of industry. On top of these programmes Green Chemistry and Green Engineering initiated innovative ideas to overturn serious environmental problems, to provide safer products. The most important sectors of the chemical industry, pharmaceuticals, polymers, food and consumer products increased their participation and invested in green technologies. Already there are many examples of successful ventures and products.[105]

Access to affordable and reliable energy sources (coal, petroleum, gas) has been a cornerstone of the world's increasing prosperity and economic growth since the beginning of the industrial revolution. But in 21st century with the problems of environmental pollution and climate change, scientists realized that our use of energy in the twenty must be sustainable and from renewable sources. Solar, air, wave and water–based energy generation, and engineering of microbes to produce biofuels are a few examples of the alternatives. Green engineering solutions are the future opportunities and pathways that could lead to a prosperous, sustainable and secure energy future on a global scale.[106]



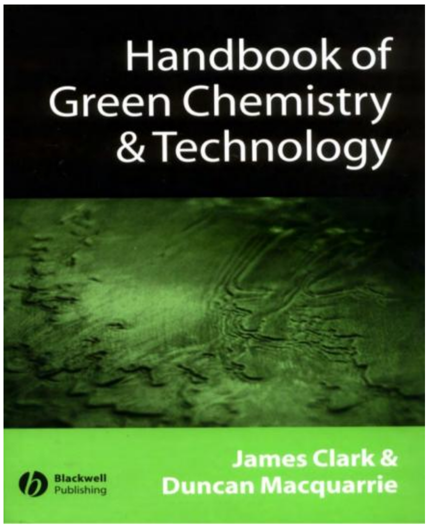


Figure 15. Green Chemistry and Green Engineering introduce innovative industrial processes that aim to produce sustainable chemicals and products. Clark J, McQuarrie D (Eds). *Handbook of Green Chemistry and Technology*. Blackwell Science Publishing, Oxford, 2002 and 2014.

For several years in the last decades, the importance of the management of Green Chemistry and Green Engineering innovations and applications has been growing, both in the industrial institutions and in the academic research laboratories. Although major engineering disciplines already dedicate significant research to Green and sustainable solutions there are more to be achieved in “Green” management disciplines.[107]

The challenge for future generations of chemists, chemical engineers and environmental specialists is to develop and master the technical tools and approaches that will integrate environmental objectives into design decision in the modern chemical industry. This review presents a selection of the most important innovative developments in green chemistry and green engineering fields in the last five years after researching the scientific literature and research projects. Also, in the last years there were numerous publications covering Green Chemistry and Green Engineering fields.[108- 115]

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