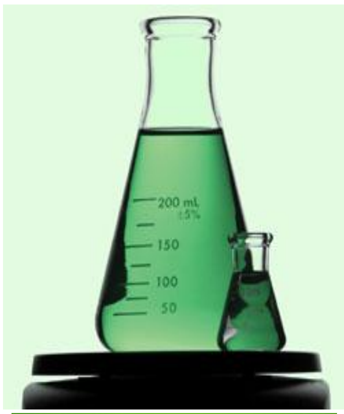
ATHANASIOS VALAVANIDIS
AND
THOMAIS VLACHOGIANNI

GREEN CHEMISTRY
and
GREEN ENGINEERING

From Theory to Practice for the Protection of the Environment and Sustainable Development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Οπισθόφυλλο

Athanasios Valavanidis and Thomais Vlachogianni

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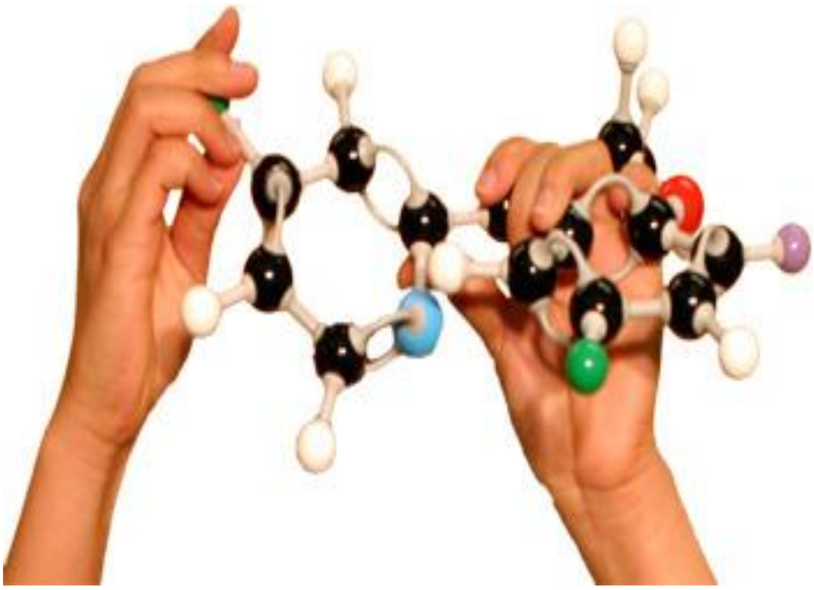
In this book we sought to teach students the core principles of Green Chemistry and Green Engineering and the various practical and technological applications that save energy, water and precious natural resources. We sought to illustrate the green chemical and engineering concepts (recycling, hazard reduction, solvent alternatives, renewable energy, atom efficiency in organic synthesis, etc) and provide a platform for discussion and environmental issues in the classroom environment. We are covering most of the aspects of Green Chemistry and Green Engineering and some important subjects and applications. The interested reader can find additional information and technological developments in the numerous publications and recent books which are included in our book. Also, postgraduate courses and educational initiatives all over the world are included as well as additional scientific papers on recent "green" scientific research projects



Professor Athanasios Valavanidis, is in the Chemistry Department of the University of Athens, Greece. He teaches Environmental Chemistry and Ecotoxicology
Dr. Thomais Vlachogianni (2007) is an ecotoxicologist who works on applied environmental issues and environmental management. She is a scientific officer in the Mediterranean Information Office (MIO) for Environment., Culture and Sustainable Development (Athens, Greece)

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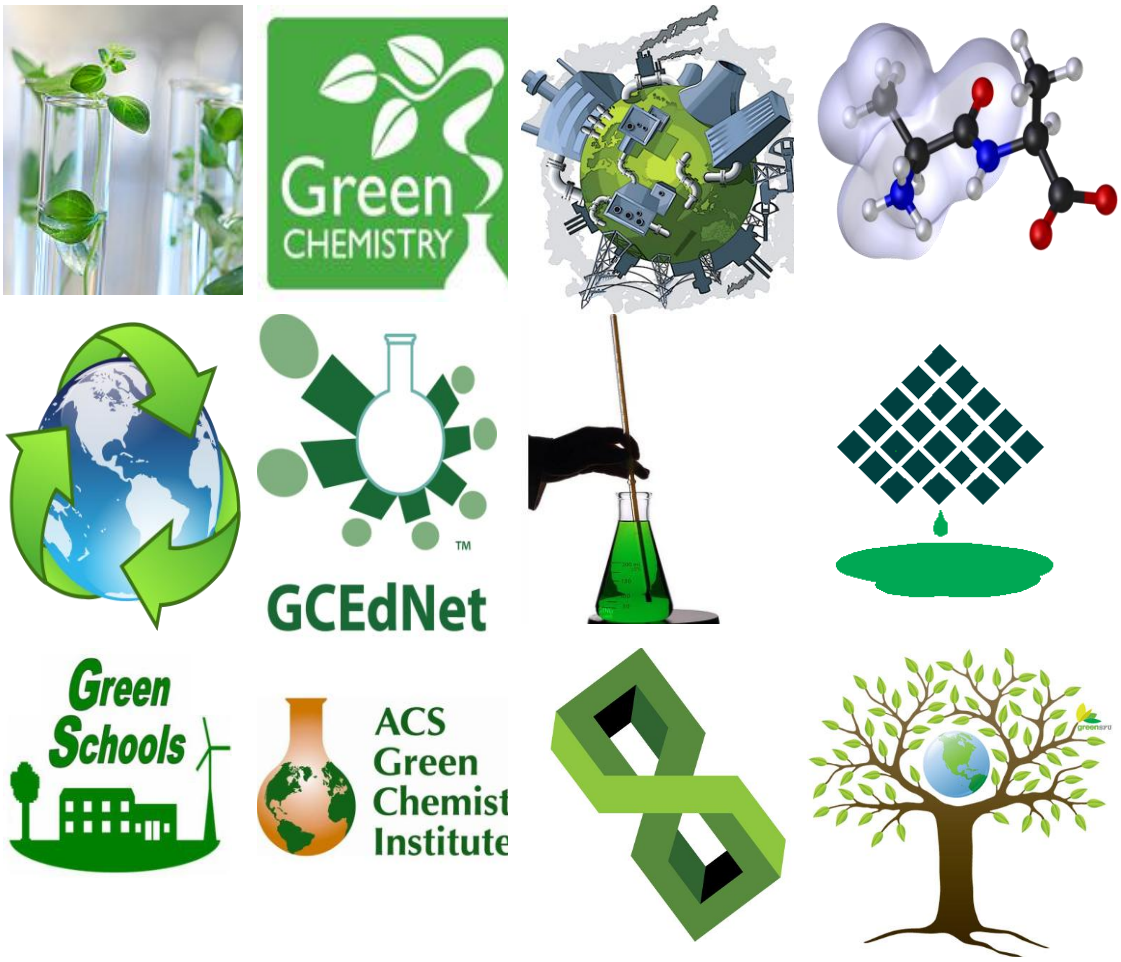

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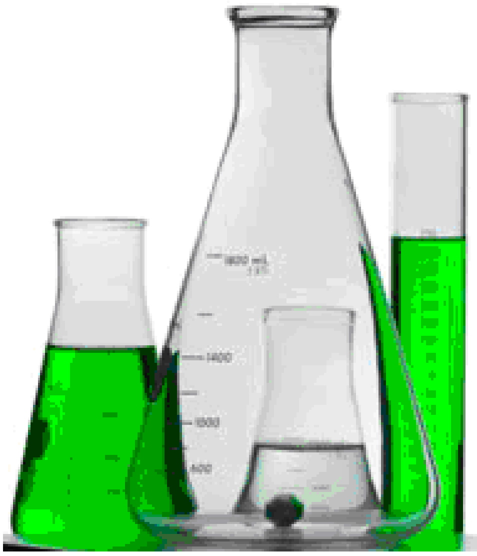

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CONTENTS IN BRIEF

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Συνοπτικά Περιεχόμενα

GREEN CHEMISTRY and GREEN ENGINEERING
Educating the Next Generation of Environmental Scientists for Sustainable Development

Synchrona Themata
ATHENS 2012

GREEN
CHEMISTRY

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PREFACE

Green Chemistry and Green Engineering are two new scientific "philosophies" that strive to promote Sustainable Development through science and technology and achieve the goals of environmental protection, health and safety of workers and consumers and less toxic products.

Green Chemistry and Green Engineering provide 12 Principles as a framework for scientists and engineers to promote the designing of new processes and materials, new energy sources, alternative methodologies and renewable sources for the research laboratory and the manufacturing industries.

Green Chemistry and Green Engineering in Greece has been promoted in higher education level to a certain extent but there is no an informative textbook on all aspects of GC principles and their innovative applications. This new book (in English and in Greek language) was written with the environmental scientists in mind, in order to provide a series of interesting topics and issues related to environmental problems and health and safety issues from toxic chemical substances and manufacturing processes. It covers a variety of issues relating to the use of depleting natural resources, recycling, waste minimization, alternative synthetic routes in industry, use of less toxic solvents, renewable starting materials, etc. It covers new developments with alternative methodologies, innovative applications and design strategies that will promote sustainability. All the chapters in the book are covered by general and specialized references of scientific papers, popular papers, reports and books on Green Chemistry and Green Engineering.

A Note to the Student

Green Chemistry and Green Engineering to the Greek student is a new subject with very important subjects but also expressed with complicated scientific terms and advanced technologies and innovative methodologies. Each chapter has a introductory section with facts and figures followed by GC and GE advances and applications. Each section is covered with scientific literature and websites for additional methods and highly technological advances. We hope this book in Greek and English languages to promote the important aspects and ideas of GC and GE. .

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Athanasios Valavanidis and Thomais Vlachogianni,

Athens
March 2012

ACKNOWLEDGEMENTS

We are especially grateful to various colleagues and other scientists, without whom this book many never have passed from concept to reality. Some of these scientists are in Greece and abroad. Especially, Prof. Konstantinos Poulos in the Department of Chemistry in the University of Patras for his enthusiasm and dedication to initiate the Hellenic Green Chemistry Network and to organize the conferences on Green Chemistry and Sustainable Development in various universities in Greece. Also, many thanks to Prof. James Clark in the Department of Chemistry of the University of York (UK) who was the pioneer many years ago on Green Chemistry subject in the Department of Chemistry of the University of York. I was a postdoctoral researcher in the Department when I heard for the first time about Green Chemistry in the 1990s.

I am grateful especially to Professor Paul T. Anastas who came many years ago in Greece and gave an inspirational lecture in the University of Athens on Green Chemistry. All these years we followed very closely his papers, articles and books on the subject of Green Chemistry and Green Engineering that gave us the ideas to start research projects on “green” organic synthesis with postgraduate students. We noticed for many years that there is no book on “Green Chemistry and Green Engineering” in Greece and limited information on the subjects of CG and GI for schools and teachers.

We are very indebted to several colleagues for many stimulating discussions and insights in the Department of Chemistry of the University of Athens (Greece) into the subjects of Green Chemistry, green organic synthesis, ionic liquids, microwave synthetic routes and Green Engineering.

We would like also to thank several friends who have read and commented on large parts of the manuscript. Dr Thomais Vlachogianni, despite her busy projects on environment with MIO, contributed fully by researching many aspects of GC and CE, writing parts of the book and reading the manuscript. Also, she helped with the problems of the electronic version of the book, the designing of the cover, the layout of the pages with diagrams and photos..

Athanasios Valavanidis
and Thomais Vlachogianni
Athens
March 2012,

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CREDITS Photos, Illustrations, Logos, Websites, Diagrams, Pictures, etc

This book aims to promote the principles and applications of Green Chemistry and Green Engineering for High Schools and Higher Education students in Greece. In the last few years we received many demands for teaching Green Chemistry ideas, innovations and research projects by Greek teachers. The book through GC and GE principles promote the ideas of Sustainable Development and its significance for the future of Our Planet. .

This book “Green Chemistry and Green Engineering” is going to be a free electronic edition for students, teachers and educationalists who would like to teach aspects of Green Chemistry and Green Engineering in schools and universities. The book is full of data, research reports, projects and innovative applications in every aspect of chemical industry and engineering with clean, renewable and non-toxic materials and products..

A limited printed edition without change is going to be available for academics in Higher Education institutions of Greece only on demand from the authors.

The publication of the book will be supported by the non-profit Publishing House in Greece ”Synchrona Themata” (Athens, Greece).

We would like to thank all Green Chemistry and Green Engineering websites, research institutes, universities, industrial enterprises, educational initiatives, publishers of books, non-governmental organizations (NGOs) and institutions for providing designs, diagrams, covers of their publications, logos, illustrations, photos and other illustrative material for use in the book. In most cases we provide the website of the illustration, photo or diagram in the appropriate Figure. The covers of books on GC and GE are included in order to provide students with an illustrative example of the increasing research interest .among scientists and manufacturers of the Green Chemistry and Green Engineering innovations and applications in a variety of sustainable technologies. In every part of the book that contains a picture, photo, diagram and relevant information we included the website. References are fully supported by the scientific journal, date, volume and pages. All websites or reports of data are also included in some references

Professor Athanasios Valavanidis
and Dr. Thomais Vlachogianni
Athens
March 2012

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ANALYTICAL CONTENTS

GREEN CHEMISTRY and GREEN ENGINEERING

APPENDICES

1. Global Environmental Challenges and Economic Growth in the Last Centuries Green Chemistry and Green Engineering for Sustainable Development

1.1. Industrial and Technological Revolutions

The “Industrial Revolution” started 250 years ago and its technological applications in the production of energy, synthetic organic chemicals, fossil fuels, transport and consumer products changed dramatically human life and civilizations as well the face of our planet Earth.

The Industrial Revolution marks a major turning point in human history. Every aspect of daily life was influenced. Average income and population began to exhibit unprecedented sustained growth. In the two centuries following 1800, the world's average per capita income increased ten times, while the world's population increased over six times. These unprecedented increases inevitably depleted the natural resources of our planet, especially fresh water, agricultural soil, and the quality of atmosphere.

Industrial production of textiles, metallurgy, mining, large scale production of chemicals, machine tools, steam power, paper and glass production, transport machines, mechanization of agriculture, and other innovations were largely influential in changing the face of human civilization and the face of the Earth.

In our days we hear or read continuously about the damaging effects on our environment and future quality of life. Sustainable Development (SD) has become a vital issue for survival of human societies and the planet.

All statistical data showed that the 20th century (1900-2000) witnessed the most dramatic developments in science and technology, population increases and acceleration of environmental damages.[1-3]

A) The **population** from 1 billion in 1820, increased to 2,5 billions in 1950 and in the last 50 years reached 6,2 billions (2000). In the end of 2011 (15/12/2011) the world population stands at 6.981.000 (~7) billions.

B) The **world economy** in the last 100 years increased in absolute numbers by 14 times and the **industrial production** by 40 times. In 2007 there were 800 million cars in the streets of the world and their production is increasing.

C) **Urbanization**. Earth witnessed increases of 14 times of people moving to big cities. In 1900, 13% of the population lived in towns and cities, but now the percentage is over 50%. It is estimated that in the next few decades will see an unprecedented scale of urban growth in the developing world. (in Africa and Asia where the urban population will double between 2000 and 2030). By 2030, the towns and cities of the developing world will make up

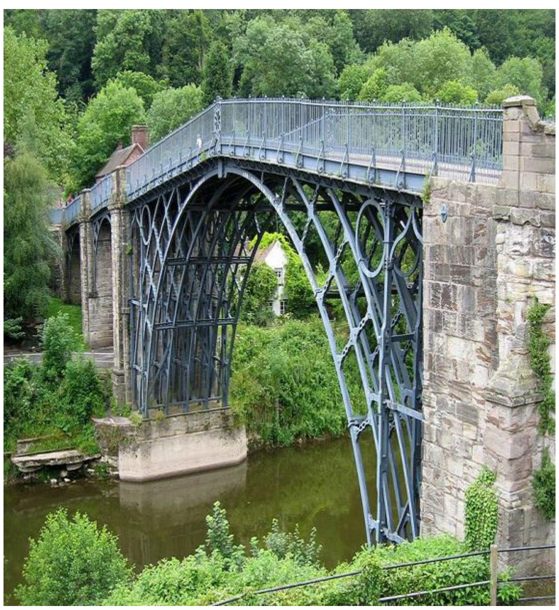
81% of urban humanity. Cities also embody the environmental damage done by modern civilization. Scientists, experts and policymakers increasingly recognize the potential value of cities to long-term **sustainability**. The potential benefits of urbanization far outweigh the disadvantages: The challenge is in learning how to exploit its possibilities.

D) **Energy**. In the last 100 years the production and consumption of energy and various energy resources increased by 13 times and the emissions of **carbon dioxide** (CO_2) in the atmosphere increased by 17 times.

E) **Fossil Fuels**. The production and consumption of fossil fuels (carbon, petroleum, gas) increased dramatically. Petroleum and its products from 800 million metric tones (mt) in 1900, increased to 10.000 mt in 2000. Estimates showed that in 2010 world consumption was 87 million barrels of crude oil (petroleum) (1 barrel of oil = 0.146 tones of oil equivalent, toe).

F) **Fresh Water consumption.** The world consumption of fresh water was increased by 9 times. Fresh water is a very precious natural resource**.**

G) **Agriculture (farming), Animal husbandry, Commercial fishing.** The fishing activity increased by 35 times, and Animal husbandry increased by 9 times. The agricultural land only doubled in the last 100 years but agricultural production increased by 10 times (thanks to fertilizers and pesticides and improved seeds).



Iron Bridge Coalbrookdale, Coalport, England 1779.

Industrial production and industrial installations in an idealized picture of 18th century

Figure 1. The Iron Bridge and idealized pictures of industrial development were inevitable because improved the standards of life and increased wealth and well being. Tall chimneys and black smoke was conceived as pictures of progress.

From the historical point of view the most important revolutions in the history of mankind are the “Neolithic revolution”, the “industrial revolution” and the last one is the “technological revolution” (1860-1920). The **Second Industrial Revolution** was market by discoveries and innovations of electricity, machines, new modes of production, synthetic chemical production, transport and new forms of communication. It is considered to have begun with Bessemer steel in the 1860s and culminated in mass production and the production line. The Second Industrial Revolution saw rapid industrial development in Western Europe (Britain, Germany, France, etc) as well as the United States and Japan. After the Second World War (1945) there were many improvements, innovations and numerous applications of new technologies and dramatic improvements in automated industrial production, housing and road construction, aviation transport, communications and in electrical and microelectronics equipment.

1.2. The Illusion of Material Progress and Growth Without Limits

Theses rapid changes in the last decades formulated the illusion that material progress and well being was in grasp of humanity and that natural resources do not pose limits to development. Man was feeling that nature is there to serve humanity’s needs. Environmental protection and sustainability were not in the agenda. The idea that economic and consumer growth is necessary for human development was deeply rooted in Western culture and forms the basis of the economic strategies in developed and developing countries around the globe. The same applied to the revolutionary Russia and later in socialist Eastern Europe countries. The Growth illusion is part of capitalist development in market economies, as well in the so-called “socialist” economies (with advanced economic planning or command economy with high bureaucratic administration and central planning agency) through the industrial revolution in the following decades.[4]

In the last decades of the 20th century there were many important achievements for most developed and developing countries : widespread electrification, widespread education, clean and safe water supply and distribution, agricultural mechanization, fossil fuel exploitation, improved housing and roads, vaccination, control of infectious diseases, decline of maternal and infant deaths, safer and healthier food, safer workplaces, high-performance materials, spacecraft and satellite technologies, widespread telephone, computer and internet communications, modern household appliances, effective medical and pharmacological interventions, etc.

These achievements and technological progress in all aspects of life of modern societies formulated the illusion that man can use nature for its own goals. Natural; resources of the planet in many parts of the world were overexploited. Mining of minerals, fossil fuels, intensified agriculture, fisheries were exploited ruthlessly. Man expanded its activities into sensitive ecological regions of the planet. Environmental pollution and degradation of water and soil caused many sustainability problems.

It is not often recognized that man and human societies is a product of nature and evolutionary developments. What distinguishes man from the animal kingdom is the fact that man can produce its means of subsistence. This is true since the dawn of human civilization and the start of agriculture. The existence of mankind in the planet has always been dependent on the exploitation of nature and natural resources. The most important question of our era is how humanity can stop exploiting without limits the natural resources and introduce sustainable and ways in the use and limited resources and recycling our waste.

A typical example of environmental degradation and environmental pollution was the case of "socialist countries" and their type of economical planning and administration. In the old Soviet Union there was a vast body of environmental laws and regulations that purportedly protected the public interest, but these constraints have had no perceivable benefit. Like all socialist countries, S. Union suffered from a massive "tragedy of the commons". Where property is communally or governmentally owned and treated as a free resource, resources will inevitably be overused with little regard for future consequences.

The imperatives for economic growth in the S. Union and other Eastern Europe countries (competing for power and prosperity with other western countries), combined with communal ownership of virtually all property and resources, caused tremendous environmental damage. According to Marshall Goldman (economist), who studied and traveled extensively in the S. Union "The attitude that nature was there to be exploited by man was the very essence of the Soviet production ethic." A typical example of the environmental damage was the exploitation of the Black Sea. To comply with five-year plans for housing and building construction, gravel, sand, and trees around the beaches were used for decades as construction materials. This practice caused massive beach erosion which reduced the Black Sea coast by 50 percent between 1920 and 1960.

1.3. The Environmental Awareness in the 1960s

Environmental awareness was initiated in the 1950s but an active environmental movement (especially in the USA and other western countries) was rapidly increased in the 1960s with recruitment of new members and environmental protection activities. The Sierra Club in the USA is well known as one of the first and active environmental Non-Governmental Organization (NGO) which helped raise public environmental awareness . Many new organizations were becoming part of a new kind of activism called **environmentalism** that combined the conservationist ideals, lobbying, book distribution, letter writing campaigns, and more. In the 1960s, the Sierra Club and other groups broadened their focus to include such issues as air and water pollution, population control, and curbing the exploitation of natural resources.

In 1962, the book "*Silent Spring",* by Rachel Carson (biologist) left a very strong legacy in the new environmental movement and initiated the logic of environment6al protection. The book cataloged the environmental impacts of the indiscriminate spraying of DDT in the US and questioned the logic of releasing large amounts of chemicals and their effects on ecology or human health.[5]

Also, scientists and natural science experts recognized the environmental effects of synthetic chemicals and new technological developments. The well known American environmentalist B. Commoner with his book "***Science and Survival***" (1968) described in his little book the basic aspects and problems of environmental pollution. The economist E.F. Schumacher in his seminal book "***Small is Beautiful***" (1973) described with lucid arguments the logic and challenges of growth against the natural order and limits. This development and exploitative industrialization causes a dangerous imbalance and lack of sustainable thinking in most industrial developed countries.[6,7]

The first international conference of the United Nations took place in Stockholm in 1972. The conference report "***The Human Environment***" collected numerous studies and reviews on the state of the environment in the planet and painted an alarming picture for rapid industrialization, intensive agriculture and exploitation of natural resources.

Academic scientists and university institutes (such as MIT) initiated systematic studies of environmental pollution and aspects of exploitation of natural resources in various areas of the planet. In the 1970s a well known team of scientists in the Massachusetts Institute of Technology with the support of the organization of Club of Role (industrialists with sensitivities towards the environment) introduced computer programmes to study the long term trends in development, natural resources, population and environmental pollution. They published their finding in the seminal book "***The Limits to Growth***" (1972). The book was a computerized modeling of the consequences of a rapidly growing world population, environmental pollution and finite natural resource supplies. The book used the World3 model to simulate the consequence of interactions between the resources of the planet Earth and human systems. Five variables were examined in the original model, on the assumptions that exponential growth accurately described their patterns of increase, and that the ability of technology to increase the availability of resources grows only linearly. These variables are: world population, industrialization, pollution, food production and resource depletion. This seminal study was followed by very important [8-14]

In 1987 we had the Brundtland Report "***Our Common Future***").[15] The Report presented for the first time the case of sustainable development and the available political decisions and changes which are needed in order to achieve the important among human development and a finite environment on Earth.[15]

The Conference of UN in 1992 (UNCED, United Nations Conference on Environment and Development, Rio de Janeiro, 1992) resulted to the signing of two actions **Agenda 21**, and **Biodiversity**. These were very important action plans with international environmental consequences. The Agenda 21 is related to sustainable development. It was a comprehensive blueprint of action to be taken globally, nationally and locally by organizations of the UN, governments, and major groups in every area in which humans directly affect the environment. The Convention of Biological Diversity (or biodiversity) is a global agreement which give "sovereign national rights over biological resources" .The agreements commit countries to conserve biodiversity, develop resources for sustainability and share the benefits resulting from their use. Biodiverse countries that allow bioprospecting or collection of natural products, expect a share of the benefits rather than allowing the individual or institution that discovers/exploits the resource to capture them privately.

Figure 1.2. The International Conferences of Rio de Janeiro (1992) and Johannesburg (2002) produced very important agreements for the environment.

Environmental pollution and overexploitation of natural resources were widespread in the Eastern European countries and in China. The rapid industrialization and the lack of environmental protection (despite the legal framework which was not applied) was revealed after the 1989-1990 collapse. Many publications described the vast environmental damage in Soviet Union and various other "socialist" countries.[16-22]

Figure 1.3.. Posters of the (old) Soviet Union in the 1930s depicting the "ideal" of industrial development, the happy faces of workers and the "glorious" smoke of the chimneys from factories.

1.4. Natural Resources and Sustainable Development

One of the most precious natural resource is fresh water (for drinking, cleaning and for agriculture and industry) on planet Earth and its sources are very limited. It is called the ‘elixir of life’ or the ‘matrix’ of life and is the cornerstone of the survival of all living organisms on Earth. Despite its importance, fresh water natural sources are overexploited and consumption is beyond the limits of sustainability. It is recognized as a very vital environmental problem and its waste will bring great economic, social and environmental problems. People around the world, when asked about fresh water management, conservation and sustainability, view water issues as the planet’s top environmental problem, greater than pollution, climate change and depletion of other natural resources. Agriculture uses a large proportion of fresh water resources and the problem is accelerating in recent decades. Water is considered the number one problem for sustainable development in many developing countries.

Other important environmental problems of sustainable development are considered air pollution in the cities and industrial areas, climate change and abrupt changes in weather patterns due to the increased concentrations of carbon dioxide, loss of habitats, biodiversity and sensitive ecosystems.

RIO+20
United Nations Conference
on Sustainable Development

The Committee for Sustainable Development of the United Nations was established as a continuation of the International Conference of 1992 (United Nations Conference on Environment and Development, Rio de Janeiro, 3-14 June, 1992). In the World Summit of 2002 in Johannesburg (WSSD, World Summit for Sustainable Development, 2002) the delegates underlined the environmental obligations at the national and international level for sustainable development. Although big decision were discussed and signed the results were limited, but the conferences gave the opportunity to NGOs and state organizations to voice their objections and solutions. Also, delegates from developing and Third World countries (which are among the most poorest countries on Earth) were able to voice their environmental problems. The new UN Conference called RIO+20 for Sustainable Development is considered very important for the whole of the planet and it will take place in Rio de Janeiro on 20-22 June 2012.

The environmental crises of the planet are now recognized as part of the history human civilizations and their expansion and growth in the last centuries after the industrial revolution. There are numerous examples of civilization failures and collapses throughout of human history. The importance for sustainability and the limits to growth have been recognized but action is needed and not just words.[23-25]


Figure 1.4. Large industrial installations and automated technology for assembly and mass production are considered the "jewel" of developed industrial countries.

1.5. Global Economic Growth and Sustainable Development

Sustainable Development is often an over-used word, but goes to the heart of tackling a number of inter-related global issues such as poverty, inequality, hunger and environmental degradation. In theory, development that is sustainable and not damaging to the planet is very possible. The idea of sustainable development grew from numerous environmental movements in last decades and in Global summits, such as the Earth Summit in Rio de Janeiro, 1992. However, the record on moving towards sustainability so far appears to have been quite poor. The concept of sustainability means many different things to different people, and a large part of humanity around the world still live without access to basic necessities

The continuous global economic growth, the increasing industrial production, the rapid development of the emerging economies (China, India, Brazil, etc) and the large population increases are major trends which were expected. The big question is if the planet can sustain such rapid and damaging expansion with the limited natural resources and fragile environments and ecosystems. Scientists and technologists agree that this unprecedented global growth is not sustainable and that damages through environmental degradation and exhaustion of natural resources is irreversible. The planet is confronted with big challenges and needs a form of development which takes into account the limits to growth.

When we talk about Sustainable Development (SD) we mean that is a pattern of resource use, that aims to meet human needs while preserving the environment so that it meets not only the present, but also for generations to come. The term SD was used first by the Brundtland Commission which coined the most often-quoted definition of SD "meets the needs of the present without compromising the ability of future generations to meet their own needs. SD takes into account the carrying capacity of natural systems with the social challenges facing humanity. Already from the 1970s scientists defined the term "Sustainability" in order to describe an economy "in equilibrium with basic ecological support systems”. Sustainability can be subdivided in environmental, economic and social/political.[15]

The European Union (U) for decades has changed its position on environmental issues and formulates all aspects of legislation with emphasis on “sustainable development” .The EU first formulated its sustainable development strategy during the 2001 Gothenburg European Council. Although sustainable development is enshrined in the EU Treaty, its implementation remains a problem. In 2005, the European Commission confirmed that a number of unsustainable trends. One controversial issue was the relationship with the Lisbon reform agenda for growth and jobs. In 2006 the European Council adopted a revised strategy.

In 2009 the European Commission adopted the 2009 Review of EU SDS. The review underlined that in recent years the EU has mainstreamed Sustainable Development into a broad range of its policies. The EU has taken the lead in the fight against climate change and the promotion of a low-carbon economy. At the same time, unsustainable trends persist in many areas and the efforts need to be intensified. The review takes stock of EU policy measures in the areas covered by the EU SDS and launches a reflection on the future of the EU SDS and its relation to the Lisbon strategy. The review is complemented by Eurostat's bi-annual monitoring report on sustainable development.[26]

Similar plans and legislation on Sustainable Development exist in most developed industrial countries and in some developing countries. In recent years the emphasis on SD is very obvious because it covers fundamental principles and coordinates efforts on a broad spectrum of activities for conservation and survival.

1.6. Sustainable Development and the Need for Green Chemistry and Green Engineering Principles

Green Chemistry and Green Engineering are an integral part of new thinking (we can called it new philosophy) which is needed to advance the goals of sustainability. The chemical Industry and synthetic chemical production is now the most important economic form in producing thousands of chemical products, consumer goods and materials. So, the goal for changes in the design, production and use of chemicals will contribute to sustainability. From the beginning the GC advances were focusing in feedstocks, reagents, solvents and syntheses.

The term “**Green Chemistry**” was proposed for the first time in 1991 from the chemist Paul T. Anastas working on a specialized programme commissioned by the Environmental Protection Agency (EPA). Green chemistry (which is also known as **sustainable chemistry**) is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry (GC) applies across the life cycle of a chemical product, including its design, manufacture, and use.[26]

Green chemistry wants to change how things were working until now. Green Chemistry demands new standards for chemicals and chemical processes. GC demands changes in the decisions made by chemists when are designing the industrial production. GC provides new techniques to reduce or eliminate negative environmental impacts. The use and production of these chemicals may involve reduced waste products, non-toxic components, and improved efficiency. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations.

Figure 1.5. Environmental Protection Agency (EPA) advanced the idea and applications of Green Chemistry from the beginning of the 1990s.

In 1996, the organization **International Union of Applied and Pure Chemistry (IUPAC)** (Zürich, Switzerland, known as the "IUPAC Secretariat") established a working group of scientists from various fields for Green Chemistry (Working Party on Green Chemistry).

In 1997, the **Green Chemistry Institute** was established by the biggest chemical society of the world, the **American Chemical Society**. The institute has great influence, initiatives and research applications on GC. After planning by individuals from industry, government, and academia, the Green Chemistry Institute (GCI) was incorporated in 1997 as a not-for-profit corporation. The GCI is devoted to promote and advance Green Chemistry in chemical industries, universities, research institutes and in the design and use of chemicals.

Also, in 1997 the first international conference on Green Chemistry took place in Washington DC, sponsored by IUPAC and the ACS (First International Green Chemistry Conference).

In the last decade various scientific journals started covering all issues related to green chemistry, clean processes and products and green engineering
i) Journal of Clean Processes and Products (Springer-Verlag) ,
ii) Green Chemistry (Royal Society of Chemistry and the University of York).
iii) Green Chemistry for Sustainability (Open Access, Springer),

iv) The *Green and Sustainable Chemistry* is an international open access journal dedicated to reporting on the latest advances in Green and Sustainable Chemistry. Published by Scientific Research Publishing, Irvine, California, USA

v) Journal of Green Engineering (River Publishers, October 2010, Aalborg, Denmark)

Also, scientific paper with green chemistry and engineering appeared in the last years in journals, such as **Environmental Science and Technology (USA)** and in the **Journal of Chemical Education** (USA)**.**

Another interesting initiative for Green Chemistry was undertaken in Italy. In 1993 a consortium was established among Italian universities, the **Interuniversity Consortium Chemistry for the Environment** (INCA). The purpose was to develop cooperative themes among chemists of various universities for environmental, technological and green chemistry issues. In 1993 the first meeting took place in Venice under the title "*Processi Chimici Innovativie Tutela dell' Ambiente*".

Another very active group of scientists on green chemistry and green engineering for sustainable development developed in England. The **Green Chemistry Network** (GCN) aims to promote awareness and facilitate education, training and practice of Green Chemistry in industry, commerce, central, regional and local government, academia and schools. The network was initially launched in 1998 with funding from the Royal Society of Chemistry and is now funded on a project-by-project basis. The GCN is a not-for-profit Company Limited by Guarantee. The centre of GCN is in the Chemistry Department of the University of York.

Similar organizations and initiatives on green chemistry and engineering were initiated in the last decade in Japan, Sweden, Denmark, Australia, Canada, South Korea and other developed industrial countries.

1.7. Green Chemistry Awards for Innovative Projects and Discoveries

In 1995 EPA established the special awards for innovative projects and discoveries for scientists, research institutes and chemical industries on Green Chemistry. The **Presidential Green Chemistry Challenge Awards** which are presented by the President of the USA.[27]

There are 5 different types of awards:

1. Greener Synthetic Pathway Award**,**
2. Greener Reaction Conditions Award,
3. Designing Greener Chemicals Award,
4. Small Business Award
5. Academic Award).

The Presidential Green Chemistry Challenge was established to recognize and promote innovative chemical technologies that prevent pollution and have broad applicability in industry. The Challenge is sponsored by the Office of Chemical Safety and Pollution Prevention of the United States Environmental

Protection Agency (EPA) in partnership with the American Chemical Society Green Chemistry Institute and other members of the chemical community

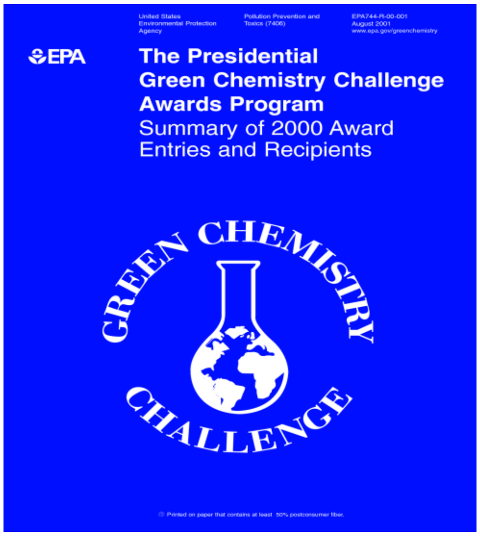


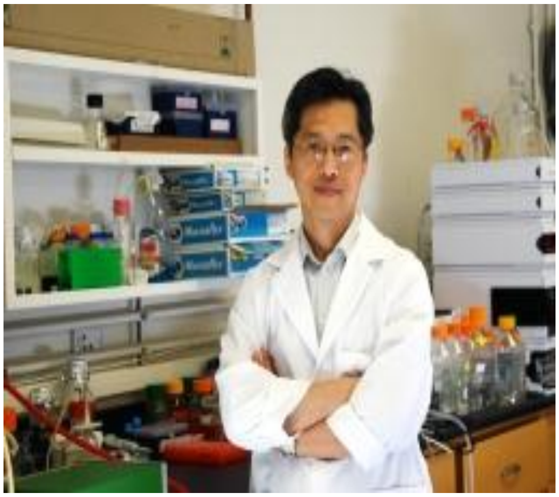
Figure 1. 6. The Presidential Green Chemistry Challenge Awards are recognized internationally for their positive contribution to the cause of sustainability.

The Presidential GCC Awards in the last two years are presented below.2010 Award Recipients

- **Greener Synthetic Pathways Award.** The Dow Chemical Company BASF Innovative, Environmentally Benign Production of Propylene Oxide via Hydrogen Peroxide
- **Greener Reaction Conditions Award.** Merck & Co., Inc. Codexis, Inc. Greener Manufacturing of Sitagliptin Enabled by an Evolved Transaminase (summary / podcast)
- **Designing Greener Chemicals Award.** Clarke Natular^{TM} Larvicide: Adapting Spinosad for Next-Generation Mosquito Control (summary / podcast)
- **Small Business Award.** LS9, Inc. Microbial Production of Renewable Petroleum^{TM} Fuels and Chemicals
- **Academic Award.** James C. Liao, Ph.D. University of California, Los Angeles Recycling Carbon Dioxide to Biosynthesize Higher Alcohols

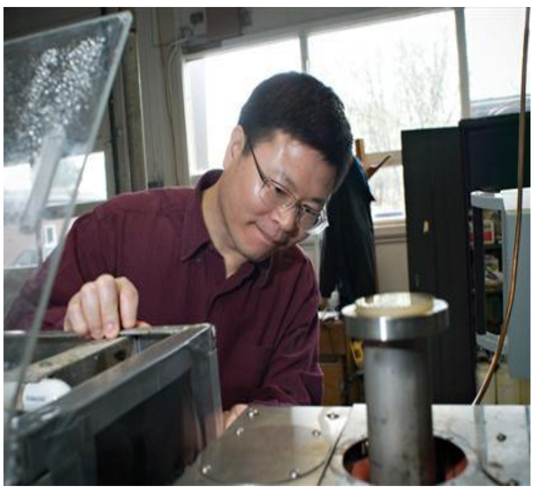
2011 Award Recipients

- **Greener Synthetic Pathways Award.** Genomatica Production of Basic Chemicals from Renewable Feedstocks at Lower Cost
- **Greener Reaction Conditions Award**. Kraton Performance Polymers, Inc. NEXAR^{TM} Polymer Membrane Technology
- **Designing Greener Chemicals Award.** The Sherwin-Williams Company Water-based Acrylic Alkyd Technology
- **Small Business Award.** BioAmber, Inc. Integrated Production and Downstream Applications of Biobased Succinic Acid
- **Academic Award.** Professor Bruce H. Lipshutz, University of California, Santa Barbara, Towards Ending Our Dependence on Organic Solvents



Dr James C. Liao, Presidential G.C. C. Award , UCLA (2010)

Professor Krzysztof Matyjaszewski Carnegie Mellon University (2009)



Professor Kaichang Li , winner of 2007 presidential GCC Award, Oregon State University, vegetable based pressure sensitive glue that is environmentally benign, cheap and is produced from vegetables

Presidential Green Chemistry Challenge Award for 2008. Οι ερευνητές Rob Maleczka **and** Mitch Smith και οι φοιτητές τους, Michigan State University

Figure 1.7. Various researchers and academics who won the Presidential Green Chemistry Challenge Awards in the USA

1.8. Green Chemistry Awards in Developed Industrial Countries

Green Chemistry Awards were established also in other countries to recognize the discoveries and scientific projects on green chemistry and green engineering and promote the sustainable development of chemical industries.

a) In Australia, the **Royal Australian Chemical Institute** (RACI) presents awards, in the same spirit with the American awards on green chemistry innovations and green chemistry educational projects.
b) In Canada there is the annual ceremony for **The Canadian Green Chemistry Medal** awarded to persons or groups of scientists who contributed with their research to innovations on Green Chemistry.
c) In Italy the awards for Green Chemistry are given by INCA, the **Interuniversity Consortium Chemistry for the Environment**) on Green Chemistry innovations, discoveries and applications for sustainable development. It started in 1999 and INCA gives three awards annually to industry for applications of green chemistry.
d) In Japan the awards are given by **The Green & Sustainable Chemistry Network,** (established in 1999). The network is a cooperation of chemical industries and research chemists. It started in 2001 and every year the importance of the event is emphasized by the presence of ministers of industry and leaders of established state scientific institutes.
e) In Great Britain (or United Kingdom), the annual Green Chemistry awards are given by **the Crystal Faraday Partnership**, a non-profit organization which was established in 2001. from chemical industry representatives and research chemists. **The Green Chemical Technology Awards** are presented by the Crystal Faraday from 2004 and there is substantial publicity through the publications of the **Royal Society of Chemistry**.
f) **The Nobel Prize Committee** recognised the great importance of the Green Chemistry and in 2005 the Nobel Prize on Chemistry was awarded to three scientists, Yves Chauvin, Robert H. Grubbs and R.R. Schrock for "the development of the metathesis method in organic synthesis.". The Nobel Prize Committee stated in its explanatory comment, "this represents a great step forward for 'green chemistry', reducing potentially hazardous waste through smarter production. Metathesis is an example of how important basic science has been applied for the benefit of man, society and the environment”.

All these developments in the last thirty years and the establishment of annual awards in various developed countries showed that Green Chemistry and Green Engineering are very important for sustainability. The old ways of producing chemical materials and introducing new materials for industry and consumers is inadequate and can be changed. Already there are numerous examples of Green Chemistry innovations, as we can see in the next chapters of the book that promote the meaning of sustainable development. Green Chemistry is an important new development in science, from theory to practice and at the same time promoting the education of the next generation of new scientists and technologists. Here we selected some recent papers describing the pioneers of Green Chemistry: towards meeting the grand challenges for sustainability in research and development and manufacturing. The future of Sustainable Development can be part of the goals of Green Chemistry.[28-37]

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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 of 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.

California Green Chemistry

Green Chemistry Network, University of York, England

Pfizer Green Chemistry Programme

American Chemical Society

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 CO_2 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:

(Risk = f(Hazard X 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.

In1997 **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.

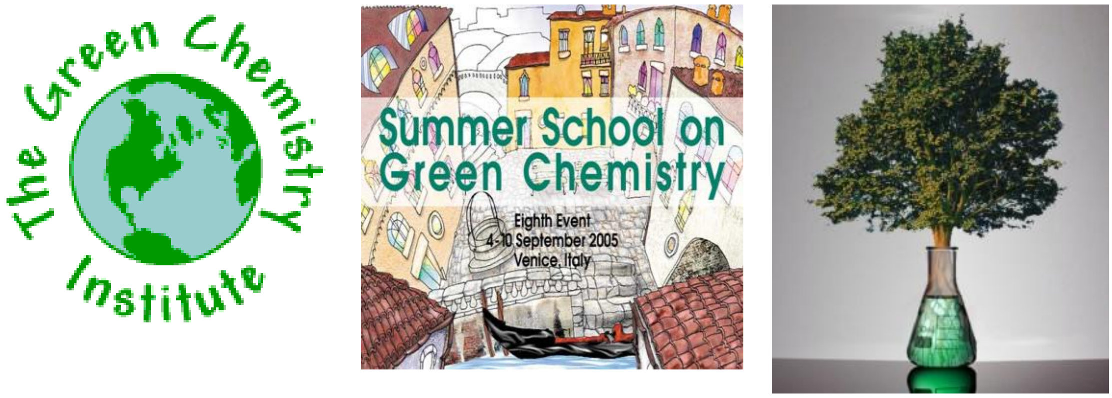


Figure 2.3. The Green Chemistry Institute (USA), the Summer School of Green Chemistry (University of Venice, Prof. P. Tundo) and other organizations all over the world promote the aims of Green Chemistry.

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).

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)

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.

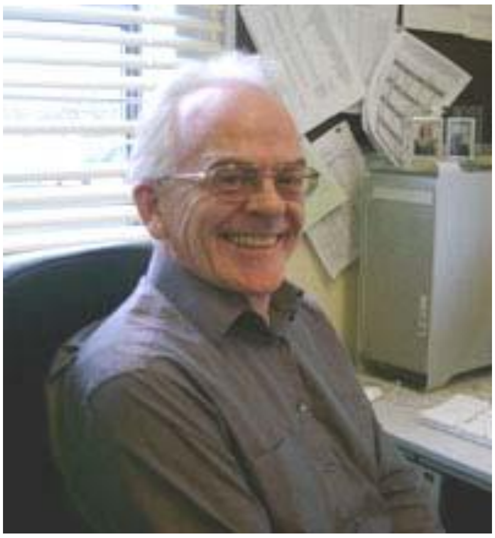
The Centre offers the postgraduate degree MSc Green Chemistry and Sustainable Industrial Technology . The Centre is involved with a number of green chemistry activities in the areas of research, industrial collaboration, the development of educational and promotional materials and networking both with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

Professor Paul Anastas (Yale)



Professor James Clark (York)

Professor Pietro Tundo (Venice**)**

Professor Michael Braungart (Germany)

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 porjetcs 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.

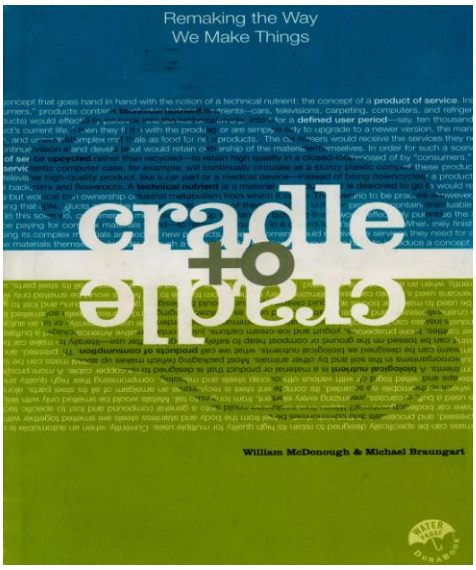
The “**Cradle-to-cradle**” design (it appears also under other names, such as C2C, or cradle 2 cradle, or is referred as regenerative design) is a new philosophy of how to make green things without pollution and waste. It is a biomimetic approach to the design of systems. Its basic idea is to model human 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).

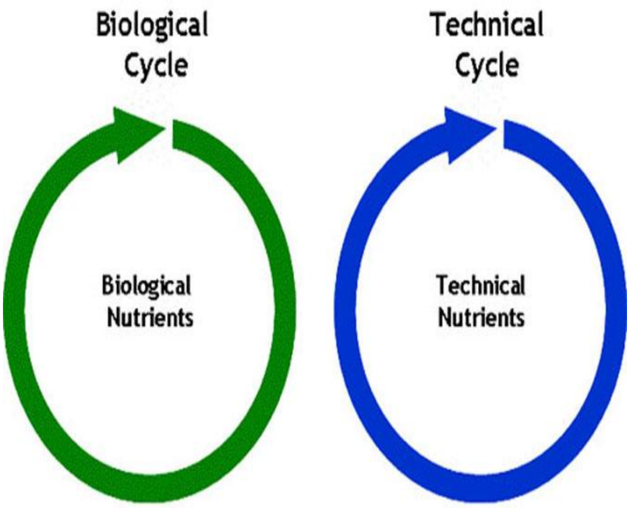
The phrase "Cradle-to-Cradle" was first used by the architect Walter Stahel in the 1970s but it was made more known by the American architect William McDonough and the German chemist , Professor. Michael Braungart. In 2002 they published the book "***Cradle-to-Cradle: Remaking the Way We Make Things***", 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.



"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. 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.

Figure 2.7. The picture of a typical chemical laboratory in a university or research institute. Green Chemistry strives for health and safety regulations in the working laboratories, less toxic solvents and minimum waste. The prudent management of dangerous chemicals is part of the efforts to reduce risk to humans and the environment.

2.7. Use of Alternative Basic Chemicals as Feedstocs 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 CO_2 per unit of product produced. Biomass may be an exception to higher energy and CO_2 emissions depending on how the CO_2 is accounted for. Planning for and developing new technologies to ease the eventual transition to alternatives and manage CO_2 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 photocatalyitic 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_2O_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

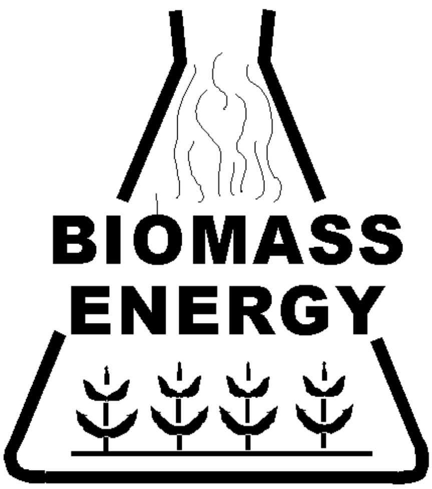


Figure 2.9. Biomass can become the starting material for the production of biofuel, biomaterials, biopolymers and for the production of engine fuels.

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 CO_2 emissions is considered by Green chemists a very important environmental problem. Any effort to reduce CO_2 emissions during the industrial processes is very important goal for GC. Also, any design in chemical process which sequester or capture or can use CO_2 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 CO_2 or with less toxic solvents and under room temperatures. The hydrogen peroxide (H_2O_2) 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 ^oC. 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, le4ss 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.

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3. Green Engineering: Fundamental Principles and Applications

3.1. Introduction to Green Engineering

In the last decades scientists in developed and developing human societies became aware that rapid economic growth and unrestrained use of natural resources caused substantial environmental problems and disrupted the future sustainability of many regions of the world. It has been recognised that pursuing high growth objectives without considerations of environmental degradation and natural resources depletion threatens sustainability.

The environmental movements of the 1960s and 1970s protested for the trends in economic growth and the inevitable environmental pollution on regional, national and global scale. Major environmental problems, like the ozone hole in the stratosphere, the global warming and the greenhouse effect, the spread of environmental pollution by polychlorinated compounds in remote places of the planet, plastic pollution of the oceans, the depletion of natural resources of fresh water, desertification, etc, are some of the problems causing international concern.

Green chemistry as a scientific movement of the 1990s for better design and innovations in the chemical industry was extended to “Green Engineering” which covers technological applications, engineering processes and products

According to Environmental Protection Agency (EPA): ”Green Engineering” embraces the concept that decisions to protect human health and the environment can have the greatest impact and cost effectiveness when applied early to the design and development phase of an industrial process or product. The goal of the Green Engineering is to incorporate risk related concepts into chemical processes and products designed by academia and industry..”.

Green Engineering is aiming to four major sections of the scientific and technological community : academia, university teachers (instructing students on new thinking in engineering processes and applications, through academic lectures and workshops that disseminate green engineering material), Software scientists (to provide engineers with integrated risk based tools for assessing hazards in process design and other programmes), industrial chemical engineers and other scientists (continuing education courses, providing new academic material, methodologies and case studies which illustrate green engineering alternatives in chemical process , new designs and technological innovations with green credentials for engineers), Continuous dissemination of sources and green engineering materials to academia and industry (continuous flow of information and ideas for new case studies and process design methodologies of green engineering).

The term Green Engineering in Greek has some problems in translation of the word “Engineering” In 2009 the (Πράσινη Μηχανική ή Τεχνολογία) which can mean also “technology”. The TEE (Τεχνικό Επιμελητήριο Ελλάδος, Technical Chamber of Greece) with more than 100.000 members encompassing all the engineering disciplines as well as architecture in Greece) in 2009 (1.4.2009) organized a series of lectures on the term of ”engineering”. The speakers though that the pest terminology was μηχανοτεχνία. The term for “Green Engineering” was proposed “Πράσινη Μηχανική“(“Μηχανοτεχνία”, or “Τεχνολογία”). In this chapter we use the term “Green engineering” in terms of technology (processes, products, design).[1-3]

Figure 3.1. Green Engineering is a substantial addition to Green Chemistry with very similar aims and principles which lead to sustainable developments through engineering and new design of processes and products.

In fact “Green Engineering” is the process and design of products aiming to conserve natural resources leading to sustainability goals. Also, green engineering aims to reduce the impact of processes and products to the natural environment. The term “green engineering” is applied to a variety of products, like houses, vehicles, consumer products (materials, electrical and electronic equipment) and devices that requires engineering technologies in the construction or making.

Green engineers can now graduate from various university engineering departments in developed industrialised countries. Other engineering graduates can have special training on various fields, attending special classes to understand how materials and other components can be made in an environmentally-friendly way. For example, engineers and architects concerned with home design may learn about the latest building materials and techniques. Green engineering and design is nowadays an important additional qualifications for every aspect of engineering.

3.2. The Twelve Principles of Green Engineering

Green Engineering (GE) focuses on how to achieve sustainability through science and technology. As in the case of Green Chemistry, Green Enginering are covered by 12 principles which were presented for the first time by Paul T. Anastas and Julie B. Zimmerman (*Environmental Science and Technology*, March 1, 95A-, 2003).[1]

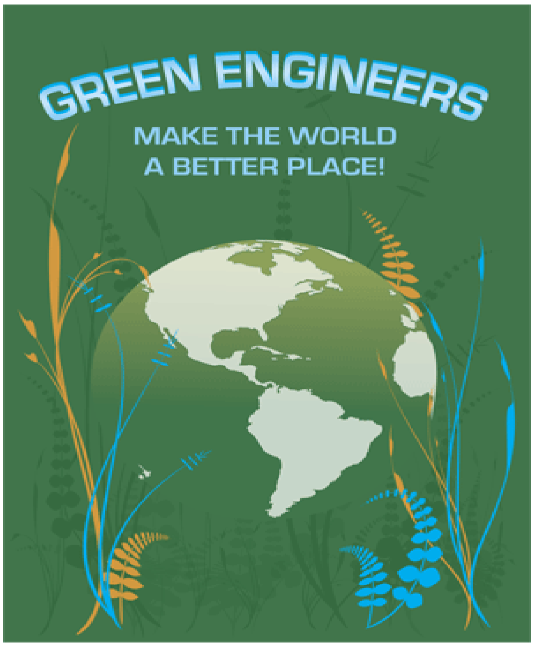
The 12 Principles of Green Engineering provide a framework for scientists and engineers to engage in when designing new materials, products, processes, and systems that are benign to human health and the environment. The breadth of the principles' applicability is important. The Green Engineering principles must be applicable, effective, and appropriate. Otherwise, these would not be principles but simply a list of useful techniques. It is also useful to view the 12 principles as parameters in a complex and integrated system. Just as every parameter in a system cannot be optimized at any one time, especially when they are interdependent, the same is true of these principles. There are cases of synergy in which the successful application of one principle advances one or more of the others. In other cases, a balancing of principles will be required to optimize the overall system solution.

The twelve principles of Green Chemistry cover the fundamental aspects of chemistry, chemical engineering and technology. In the case of Green Engineering the twelve principles are similar aspects of basic aims and goals for attaining sustainability through green engineering principles. The 12 Principles of Green Engineering have been implemented by scientists of American Chemical Society (ACS).

Table 3.1. The Twelve Principles of Green Engineering

Principle No. 1. Materials and energy must be Inherenttly non-hazardous, Rather Than Circumstantial Designers need to strive to ensure that all materials and energy inputs and outputs are as inherently nonhazardous as possible.
Principle No. 2. Prevention of Waste Instead of Treatment It is better to prevent waste than to treat or clean up waste after it is formed.
Principle No. 3. Design for Separation and Purification Processes Separation and purification operations should be designed to minimize energy consumption and materials use.
Principle N. 4. Maximize Efficiency in products and processes Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.
Principle No. 5. Output-Pulled Versus Input-Pushed Products, processes, and systems should be "output pulled" rather than "input pushed" through the use of energy and materials
Principle No. 6. Conserve Complexity Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.

Principle No. 7. Durability Rather than Immortality Targeted durability, not immortality, should be a design goal for products. After useful use of a product to disintegrate under natural conditions
Principle No. 8. Meet Need, Minimize Excess (Products) Design for unnecessary capacity or capability (e.g., "one size fits all") solutions should be considered a design flaw.
Principle No. 9. Minimize Material Diversity Material diversity in multicomponent products should be minimized to promote disassembly and value retention.
Principle No. 10. Integrate Material and Energy Flows Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows
Principle No. 11. Design for Commercial "Afterlife" Products, processes, and systems should be designed for performance in a commercial "afterlife."
Principle No. 12. Renewable Rather Than Depleting Material and energy inputs should be renewable rather than depleting



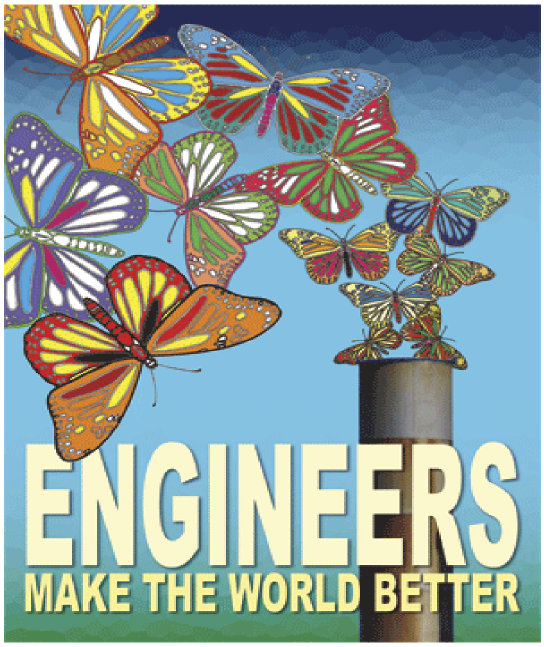


Figure 3.2. Green Engineering is an added qualification. Green Engineers design and apply green principles in their design of chemical processes and products to achieve sustainability and environmental protection.

Principle No. 1. Inherent rather than circumstantial. **There is a need for all materials and energy inputs to be Inherently non-hazardous as possible**

Many industrial starting materials are inherently hazardous from the beginning and their products inevitably will be toxic and cause environmental problems. Although the trend now is to minimise their negative aspects by investing in environmental mitigation processes, this is no an environmentally sustainable approach. The initial design of the products must evaluate the inherent nature of the selected material (toxicological and physicochemical properties) and calculate the energy inputs required. The first step must aim for a sustainable product and process with materials that are non-hazardous. Designers must developed methods and technological innovations to create inherently non-hazardous materials, for humans and the environment. If there is no alternative material, the design and the process must strive to remove the hazard in the final steps of the process. These can be achieved during purification or the cleanup steps of the product.[4-6]

The ideal case will be to use materials and inputs of energy and other reagents that are less hazardous, thus reducing the risks for environmental impacts and the cost to monitor, control and contain the environmental pollution caused by the rejection of the product as waste.

Principle No. 2. Prevention is best than treatment. **Prevention of waste is better than to clean up afterwards**

The initial design of industrial processes and products contains the intention to produce minimum waste ("zero-waste") but the notion is criticised from other scientists as ignoring the laws of nature. These laws are the first and second thermodynamic axioms and rules of enthalpy in systems.

[* In order to remind the readers the thermodynamic laws, briefly "…*The first Law of thermodynamics distinguishes between two physical processes : energy transfer as work, and energy transfer as heat. It tells how this shows the existence of a mathematical quantity called the internal energy of a system. The internal energy obeys the principle of conservation. The first law of thermodynamics states that perpetual motion machines of the first kind are impossible. The second law of thermodynamics distinguishes between reversible and irreversible physical processes. It tells how this shows the existence of a mathematical quantity called the* ***entropy*** *of a system, and it expresses the irreversibility of actual physical processes by the statement that the entropy of an isolated macroscopic system never decreases….".*

Waste is assigned to material or energy that the present processes or systems are unable to effectively exploit for beneficial use. It is natural when we use energy in the production of products that this energy is absorbed and the entropy decreases. With the use of the products the "disturbance" increases (entropy) , the products disintegrates and is transformed into waste. The scientists of green chemistry indicate that the concept of waste is human. There are no inherent properties in energy or products which inevitably will transform them into waste. Waste generation can be avoided or prevented wherever possible.

PT. Anastas and JB. Zimmerman in their pioneering article (2003),[1] stated that "….Green chemistry scientists will like to redesign products and use of energy in industrial processes in such a way so that waste is minimized. The generation of waste and its handling costs efforts and money.

There are new technologies that aim towards waste-free design at any scale and are based on the same concept: inputs are designed to be part of the desired output. This concept at the molecular scale (chemical reactions) has been described as "**atom economy**" and can be extended across design scales as the "**material economy**"…". There are now many options for energy generation that do not produce waste, one of these systems is fusion energy which can lead us to energy sustainability. [8-12]

Principle No.3. Design strategy for separation and purification. Processes for products with minimum energy consumption and material use

The traditional methods of manufacturing processes until now consume vast amounts of energy for separation of the products and cleaning with toxic solvents. Heat and pressure is applied in most conventional processes which increase the demand for energy. Green technologists would like to change this trend and reduce the use of energy. This can be achieved by radical changes in the design of the process. Green technologies will like to take design decisions at the earliest stage of manufacturing process so that self-separation and purification will be included in the process.

Economic and technical limitations in separating materials and components are among the greatest obstacles to recovery, recycle and reuse of materials and reagents. Green engineers studied how these obstacles can be overcome. Avoiding permanent bonds between two different materials is one solution. Fasteners that are designed for disassembly can be incorporated into the design strategy. At the molecular level in the chemical industry and in the laboratory the separation and purification is performed with distillations and column chromatography. Both methods are energy intensive and consume large quantities of toxic solvents. Scientists should aim to reduce the need for these wasteful processes. Design of self-separation and purification of products from the reaction medium is s desired technology. Addition of polymers in the reaction medium can be very useful in this process. Designed polymers can control the solubility of the substrates, but also can be ligands and catalysts for separation and reuse.[13-15]

Principle No. 4. Maximize mass, energy, space and time efficiency. By better designing in chemical processes and systems

Efficiency in very important in every manufacturing process and makes economic sense. Materials, energy, time and space are important variables that green engineers can take into account when designing their alternative innovations in industrial processes. Large batch reactors in chemical manufacturing is a typical example of how things were made in the conventional way. These are considered now "old" technology. Microreactors that operate continuously at very low volume with efficient mixing, high productivity and digitalized information of the process are considered more efficient. The reduction in scale of the production can be applied also to other factors, such as eco-industrial plants in cities with easy access for the workers (less car dependency, less suburban sprawl, less time consuming).[16-18]

Figure 3.3. Green Engineering and its principles can maximize efficiency in manufacturing processes and minimize waste and environmental pollution. Designing in the early stages and alternative innovations for the conventional chemical processes can improve substantially their sustainability.

Principle No. 5. Output-pulled versus input-pushed.

More energy or material ("input-pushed") can increase output, but the same output can be achieved by new designing where chemical processes are "pulled" (e.g. removing products from reaction system) without additional energy or material

Chemists and chemical engineers know from experience that a chemical reaction or transformation under high temperature, pressure, and additional material, will "puss" the balance the reaction forward, i.e. produce higher output of a desired product. (Le Châtelier's Principle, system at equilibrium under stress). Chemical engineers in their desire to increase output of a manufacturing reaction were adding more energy (heat, pressure) or starting material to shift the equilibrium and get the desired output

An example at the molecular level which can describe the chemical transformation is condensation reactions with the production of water. In order to increased the yield the water was eliminated from the product stream and thus the reaction was "pulled" to completion without additional energy or material. This is the new thinking in green engineering processes, the transformations must be "pushed" without extra energy and material with planning in advance manufacturing systems.

Another important aspect of manufacturing processes is the "just-in-time" manufacturing, which means products can be produced to meet the demand of the end user (final purchaser of the product) for the on exact for timeliness, quantity and quality. The good planning of manufacturing systems for the final output of a product can overcome waste, which is associated with overproduction, waiting time, processing, inventory and resource inputs.[19-21]

Principle No. 6. Conserve complexity. Products with high complexity should correspond to reuse, products with minimal complexity are favoured for value-conserving recycling or beneficial disposition. .

This is another very important aspect of manufacturing products with in-build complexity. The higher the complexity of a product the higher the expenditure on materials, energy and time.

A good example is the computer chips that have a significant level of complexity invested in them. To recycle a silicon chip may not be efficient method for recovering the value of the starting material. Whereas , for the paper bag the complexity is very low, but in this respect the value of the product and its material do not warrant the energy for collection, recycling and remanufacturing of the same product. Green engineers must thing in the designing stage about the end-of-life of a product. How important are the decisions to recycle, reuse or have a beneficial disposal, based on the invested material and energy for the product and its complexity.[22,23]

Principle No. 7. Durability rather than immortality. Design goal for products that will last beyond their useful commercial life

It is desirable that products are well constructed and durable during their useful commercial life, but not to be persistent and result in environmental problems. These two properties, durability and persistence after use are two contrasting and must be balanced in the designing stages by green engineers. The design must aim at products that are durable enough to withstand operating conditions during their lifetime, and avoid premature disposal. Efficient maintenance and repair of a product without added material is an advantage. Immortality or persistence to environmental conditions after disposal are not desirable properties because through bioaccumulation can be dangerous to living organisms.

A very good example for this principle is the single-use disposable diapers. The durability is very important and manufacturers invest on several materials, especially non-biodegradable polymers (polystyrene). The disposal of diapers is now one of the most important environmental problems for landfills of municipal solid waste. Green chemists, after long research studies, have proposed the solution of starch-based packing material Eco-fill, that can be readily dissolved in water.[24,25] In the last few years there are in the market diapers which can be cleaned and reused many times.[26]

The case of disposable plastic bags that everybody uses now for carrying consumer goods has become an international environmental problems due to the persistence of plastic in the water. Polymers made from biologically based materials is a new green chemistry initiative which replaces the petroleum-based polyacrylic acid polymers. Polyactic acid or polylactide is a thermoplastic aliphatic polyester derived from renewable resources, such as corn starch, tapioca products (roots) or sugarcanes. Lactic acid id produced by bacterial fermentation of starch. Polyactic acid is a product of green chemistry, can biodegrade under certain conditions, such as the presence of oxygen, and is difficult to recycle.[27,28]

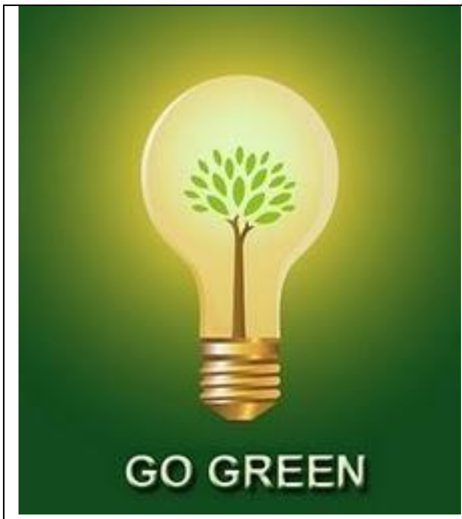


Figure 3.4. Go green has become a slogan. Green Engineering is applied to many aspects of chemical manufacturing and new electronic products. Green engineering concentrates on how to promote sustainability through science and technology. Green engineers are engaged in designing new materials, products, processes and systems.

Principle No 8. Green Engineering can meet needs and minimize excess.

The global economic competition of the last decades has changed dramatically the new technological advances in great variety of consumer products. Although new technology covered most of human consumer needs and social aspirations, it contributed also to many excesses, waste and environmental degradation, New materials, natural resources, energy and technology were wasted in many industrialised countries for overdesign and unusual capabilities of various products. Many products after their commercial life cycle cause increasing environmental problems as waste due to their complexity, extreme persistence and difficulty in recycling.

A good example is the disinfection of drinking water by chlorine. The technology is very useful to protect human life. The centralised location of disinfection causes excess chlorination in short distances and reduced disinfection in further distances. An alternative and sustainable policy will be to install actuator and control system to regulate the dose of chlorination. Chemical industry can apply a new strategy to limit material, energy and other reagents by introducing the use of enzymes as catalysts that operate at mild conditions.[29-31]

Principle No. 9. Minimize material diversity. **Reducing multiple components in products increases the possibility of useful reuse or recyclability**

Most of the consumer products of today (cars, electric and electronic equipments, food packaging, etc) are made in such a way that include multiple components. Even plastic materials contain a variety of other chemicals, such as plasticizers, dyes, stabilizers, flame –retardants. These added chemicals and in general material diversity increases the properties and useful function of products. But when these products come to the end of their life cycle they present a series of problems when considering disassembly, reuse and recyclability. Some products can be produced from one material than two or three. A good example is the new technology which is applied in plastics for cars. Different forms of polymer can have diverse properties and used for the construction of doors and instrument panels (metallocene and polyolefins have these properties and can be engineered to the different design properties). On the molecular level the example is the "one-pot" or cascading reactions that replace the multistep synthetic reaction in organic chemistry.[32-34]

Principle No. 10. Integrate local material and energy flows. Products and processes must integrate with available energy and materials flows, Industrial parks can take advantage of the existing framework of energy.

Industrial products and processes must take advantage of local and existing energy and material flows in the area where they operate, so that they can minimize the need for imports or transport from far away places of energy and raw materials. Also, at the local level they can exchange heat from other industrial units if there are exothermic operations. Byproducts from one industrial unit can become feedstocks for subsequent reaction processes in other industrial operations. In industrial parks, "waste" materials and energy can be captured throughout the production line and incorporated in other processes and other final products.[35-38]

Principle No. 11. Design for commercial "afterlife". Products and processes and components that remain functional can be recovered and reused.

Many commercial products, processes and systems after reaching their end of life become obsolete and have to be thrown away as waste. Green engineers have to take into account when designing these products. In order to reduce waste, some components or part of some processes as long As they remain functional can be reused or recovered as materials for another useful operation. Incorporating commercial "afterlife" properties into the initial design strategy of products and processes can save lots of material and energy with reuse and recovery of various parts. Mobile phones, computers, electrical equipment, printers, other commercial machines in offices or in the house become outmoded premature and had to be replaced with modern items. Designing products so that part of the components can be recovered would significantly reduce waste, and energy and materials for future products. Commercial "afterlife" is part of the green engineering design of new products.

There are many good examples of electrical machines and electronic products that have "end-of-life" design features so that can be disassembled into components, recycled, or reused with maintenance and easy repair. Xerox printers are designed so that after their commercial use, can be converted and be remanufactured. Various other big industrial companies have introduced green engineering design features in their products for easy repairs, recyclability or reuse after maintenance ((AT&T, General Electric, IBM, Procter & Gable, Whirlpool, etc). [39-41]

In the last decade there is a major shift in the way industrial manufacturers have changed the design of their products in order to reduce the end-of-life burdens to the environment. The **Product Life Cycle** (PLC) analysis has become a standard method following the various stages of a product's life. From starting materials, manufacture and final disposition the life of a product is analysed quantitatively from its environmental impact and natural resources use. It is represented with a cycle: Design—Manufacturing—Distribution—Customer—End-of-Life. Many software programmes have been developed recently dealing with PLC. The PLC is associated with engineering tasks, materials and energy, but also can involve marketing activities and new product development. [42,43]

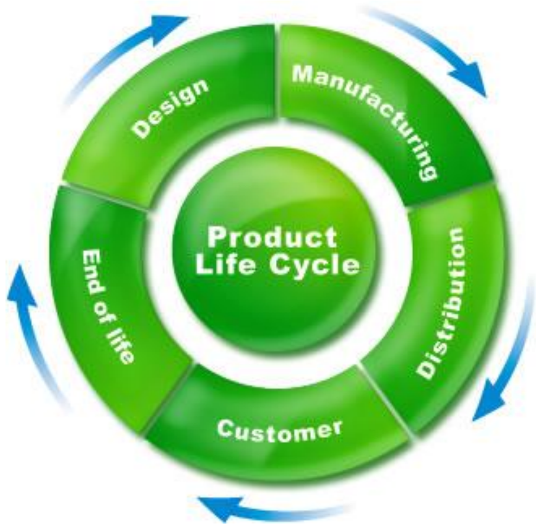


Figure 3.5. The Life Cycle of a product is considered a very valuable analysis of the manufacturing processes and the environmental problems which might be caused by the circulation of a certain product.

Principle No. 12. Renewable rather than depleting. **Materials and energy for manufacturing must be renewable for sustainable development**

The 20th century was characterized by a rapid economic growth that did not pay attention to natural resources and energy sources. This was the main cause for the extended environmental pollution and the depletion of valuable natural resources. Scientists and technologists agree that human civilization can not continue its path to material "prosperity" without renewable resources. Sustainability is in danger and societies can collapse from lack of natural resources. Renewable natural resources, that have the ability to be replaced through biological or other natural processes, can be used in sustainable cycles without damaging effects, but even in this situation there are limits. Renewable natural resources (material and energy) need to be managed carefully and to avoid exceeding their capacity to replenish. Renewability of natural resources and appropriate use is the key for sustainable development and protection of the environment.

Renewable natural resources are considered all biological materials, (biomass), solar energy, winds, geothermal energy, tides and any natural elements that are replenished with time. In the other end of the scale are depleting natural resources (which are cheaper and used extensively now), such as coal, natural gas, petroleum (fossil fuels), minerals, agricultural land, the seas, fresh water, etc.[44-46]

The framework of Green Engineering through its 12 principles covers some of the most important industrial processes and technological issues developed in the last decades. The 12 principles of Green Engineering are not a list of goals, but a set of the important methodologies that need changing in order o achieve these goals and promote sustainable development.

Education of engineers and changes in attitude and methods of the old professionals are the key components for green design and innovative alternatives. The new engineers have to be educated for the systematic integration of the 12 principles in molecular design, products, processes and manufacturing methods for the benefit of the society and the environment. The "old" ways of manufacturing have to be changed. We need to redefine the problems of sustainablity, renewable materials, new energy sources and strategies to meet needs but at the same time environmental protection.

The American Society for Engineering Education, for example, has establish a Green Engineering programme to teach and promote issues of green design in industrial processes and systems. But also, many universities offering engineering courses in industrialized countries started in recent years new courses for Green Engineering and "clean" or "green" production technologies.

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American Society for Engineering Education:
Green Engineering Program
(funded by EPA) (http://nebula.rowan.edu:82/home.asp)

Σχήμα 3.6. The American Society for Engineering Education for retraining engineers in the principles of GC.

Two new books of Allen and Shonnard for Green Engineering are thought to be very important for the teaching of Green Engineering principles and practices at university level.[47,48]

A new journal of Green Engineering that promotes innovative ideas and new research projects has started in October 2010 in Denmark (Journal of Green Engineering).[49]

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4. Green Chemistry: New Methods for Organic Synthesis and Applications

4.1. Organic Synthesis: Innovations and New Technology

Organic chemistry chemicals are some of the important starting materials for a great number of major chemical industries. The production of organic chemicals as raw materials or reagents for other applications is a major sector of manufacturing polymers, pharmaceuticals, pesticides, paints, artificial fibers, food additives, etc. Organic synthesis on a large scale, compared to the laboratory scale, involves the use of energy, basic chemical ingredients from the petrochemical sector, catalysts and after the end of the reaction, separation, purification, storage, packaging, distribution etc. During these processes there are many problems of health and safety for workers in addition to the environmental problems caused by their use and disposition as waste.

Green Chemistry with its 12 principles would like to see changes in the conventional ways that were used for decades to make synthetic organic chemical substances and the use of less toxic starting materials. Green Chemistry would like to increases the efficiency of synthetic methods, to use less toxic solvents, reduce the stages of the synthetic routes and minimize waste as far as practically possible. In this way, organic synthesis will be part of the effort for sustainable development.[1-3]

Green Chemistry is also interested for research and alternative innovations on many practical aspects of organic synthesis in the university and research laboratories of institutes. By changing the methodologies of organic synthesis health and safety will be advanced in the small scale laboratory level but also will be extended to the industrial large scale production processes through the new techniques. Another beneficiary of course will be the environment through the use of less toxic reagents, minimization of waste and more biodegradable by-products.[4-6]

4.2. Chemical Substances and Regulations

In the last decades various health and safety organizations (such as the NIOSH, OSHA, EPA in the USA and the European Chemicals Bureau and under the 1967 Directive on Chemicals) listed the number of chemical substances used for commercial reasons. In the beginning of the 1980s it was estimated that there were between 100-120.000 commercial chemicals identified by their CAS number, produced in quantities more than 100 kg.

The European Union in 1981 under the Dangerous Substances Directive (67/548/EEC) classified 100.000 existing chemicals which needed regulation, labeling and testing for their properties (except cosmetics, medicines, foodstuffs, pesticides, radioactive materials, etc). From 1981 onwards the European Chemicals Bureau (http://ecb.jrc.it, Ispra, Italy) gathered data for another 20-25.000 chemical substances. It is estimated that every year 600-800 new chemicals enter the international market. The health and safety authorities concentrate on the 2.500-3.000 high volume chemicals which are produced in million of tones every year.

But the new chemicals are covered by new more strict regulations and toxicity tests in order to be approved for commercial use. But the European system encountered many problems and in 2007 a new system REACH of registration and evaluation was established.

REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances) is the new European Community Regulation on chemicals and their safe use (EC 1907/2006). The aim of REACH is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. At the same time, REACH aims to enhance innovation and competitiveness of the European Union chemicals industry.

Statistics from the American Chemical Society (ACS) showed that the value of chemicals produced on a global scale in 2009 was in the order of 3.700 billion dollars ($). The countries with the highest production of chemicals were: USA (689 billions $), China (549 billions $), Germany (263 billions $), France (158 billions $), Brazil (126 billions $), Great Britain (123 billions $), Italy (122 billions $), Netherlands (81 billions $), Russia (77 billions $), etc. [7]

The biggest chemical industries in yearly sales at the international arena in 2007 [ICIS.com, The Top 100 global chemical companies, London, www.icis.com/home/)] were: BASF (Germany, 65 billions $, sales), Dow Chemicals (USA, 53 billions $, ΗΠΑ), INEOS (Great Britain, 43 billions. $), Lyondell Basell (Switzerland, 42 billions $), Formosa Plastics (32 billions $, South Korea), Du Pont (28 billions $, USA), BAYER (Germany), Mitsubishi (Japan), Akzo Nobel/Imperial Chemical Industries (ICI) (The Netherlands/ Great Britain), etc.

Chemical industry under the auspices of international organizations (such as OECD, Organization of Economic Co-operation and Development, UNEP, United Nations Environment Programme, etc) has complied with international standards on health and safety regulations and on safer chemical products and materials. Compared to the previous decades, all commercial chemical substances are classified, regulated and tested for their toxicity and their rate of biodegradation under environmental conditions. Some chemical substances, that are known for their high toxicity but are still in use for their properties and can not be replaced, are restricted in their use.

Chemical industries all over the world are competing for innovation and safer products. Green Chemistry and Green Engineering provide the tools and alternative materials, processes and systems which will change not only the sustainability of the production of chemical materials, but also their environmental credentials by reducing toxicity and increase recyclability.

4.3. Old and New Synthesis of Ibuprofen

Chemical industry is focusing from many years on some classic synthetic processes of important starting chemicals or crucial chemicals produced in high volume as intermediates in synthetic industrial reactions. The intention is to reduce the synthetic stages, to lower the energy use, to increase efficiency with higher yields and to minimize waste. Also, renewable starting chemicals away from the traditional petrochemical supplies of raw chemicals is another desired innovation.

Every Green Chemistry textbook describe the big successes of the last decades in the field of new synthetic routes for industrial chemicals. The first is the synthesis of **Ibuprofen**, the second is the synthesis of **Adipic acid** (important starting chemical substance for Nylon and catehole and the third is the synthesis of **Maleic anhydrite** (starting material for polyesters and dyes).

The pharmaceutical industry is considered now as the most dynamic sector of the chemical industry for the 21st century. Sales of medicines and other pharmaceutical products have increased fourfold from 1985. The analgetic and anti-inflammatory drugs is a category of medicines which are produced in vast amounts every year. Some of the most important are : **Aspirin** (acetylosalicilic acid), **Acetaminophen** (Tylenol, paracetamol) and **Ibuprofen.** Ibuprofen belongs to non-steroidal anti-inflammatory drugs with very high sales.

Ibuprofen was synthesized in 1960 by the pharmaceutical company Boot (England) and sold under the commercial name Aspro, Panadol and Nurofen. The synthesis of Ibuprofen was performed in six steps with the production of secondary by-products and waste. The main problem according to the scientists at the time was that this synthesis had a very “poor atom economy”. [8]

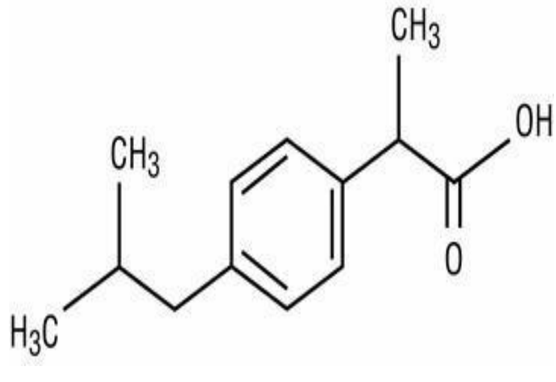


Figure 4.1. Ibuprofen as a non-steroid anti-inflammatory drug was very successful and its sales were increased substantially in the last decades.

The initial synthesis, observed under the “green” principles, had many disadvantages. The starting chemical could not be incorporated into the product, producing lots of by-products and waste. The six steps of the synthetic route was consuming chemicals and energy while lowering the yield of the final product.

In 1990 the company BHC after prolonged research on the subject discovered a new synthetic route with only three steps and increased efficiency. The atoms of the starting chemicals are incorporated into the products of the reactions and waste is minimised. In both synthetic routes the starting chemical is 2-methylpropylbenzene, which is produced from the petrochemical industry. The innovation in the new method was in the second step. A catalysts of Nickel (Raney nickel) was used thus decreasing substantially the steps of the synthesis.[9]

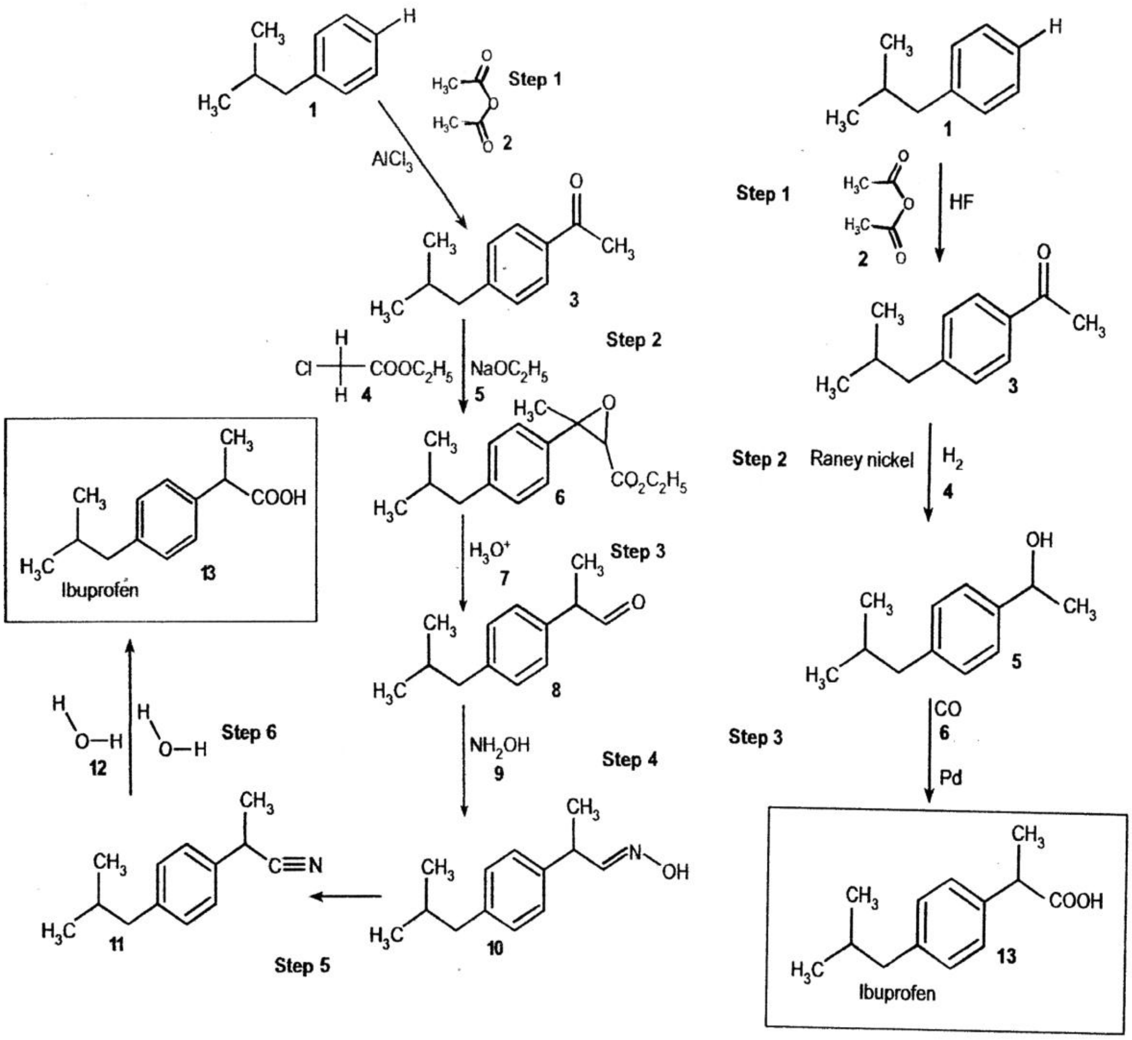


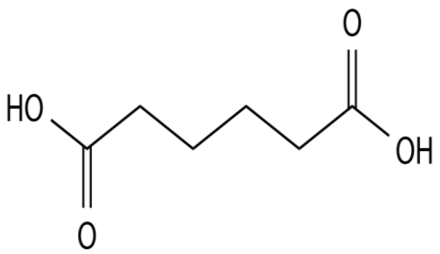
Figure 4.2. The two synthetic routes of Ibuprofen. In the old method the synthetic route comprised of six steps and in the second was reduced to three steps. The efficiency of the reaction increased substantially.

In the old synthetic route, each step had a yield of 90% so that the final product came to be 40% yield compared to the starting chemical. This resulted in the increased production of by-products as waste. The drug was produced annually (only in Great Britain) in 3.000 tones and we understand that substantial amounts of chemicals were lost as waste. Energy also was lost by the low efficiency of the reaction method. In the “greener’ method of three steps the final yield is 77%, whereas the Raney nickel catalyst (Nickel, CO/Pt) can be recycled and reused. In the old synthetic route, the $AlCl_3$ used as a catalyst had to be thrown away as waste. The energy requirements of the second method were much lower than the first.

The new synthetic route of Ibuprofen is a classic example of how Green Chemistry ideas can influence to the better the industrial synthetic methods, not only from the point of economic efficiency, but also from the point of more effective science and technology methods.

4.4. The new Synthesis of Adipic Acid. Differences and Comparisons among the Conventional and "Greener" Method

Adipic acid is a very important starting material for Nylon-6,6 and catehole (which is used in the pharmaceutical and pesticide industries). Adipic acid is produced annually in more than 2.000 million kg.



The molecular formula of Adipic acid

Figure 4.3. Adipic acid is produced annually as a starting material in 2.000 million Kg and any improvement in the initial synthetic conventional method will shave energy and materials for the chemical industry.

In the past, the industrial production of Adipic acid used benzene as a starting material. Benzene is one of the basic chemicals for industrial reactions and a solvent. It is known that derives mainly from the refining processes of the petrochemical industry. Be3nzene is also known for its carcinogenic properties (it causes leukemia to highly exposed workers). Afterwards the starting material became cyclohexanone or a mixture of cyclohexanone and cyclohexanol. For the oxidation process it was used nitric acid, producing toxic fumes of nitric oxides, NOx, which are also contributors to the greenhouse effect and the destruction of the ozone layer in the stratosphere. It was Inevitable that the method had to be changed again with more environmentally benign reactions.

. Finally, chemical engineers and synthetic organic chemists researched for alternatives. The "greener" method of adipic acid uses a new generation of catalysts. The starting chemical is cyclohexene and its oxidation is performed by 30% hydrogen peroxide (H_2O_2). The catalyst is dissolved in a special organic solvent (Aliquat 336). The catalyst is a salt of the metal

Volfram or Tungsten (W) [Tungsten catalysts (Na_2WO_4 /$KHSO_4$/ Aliquat 336].[10-12]

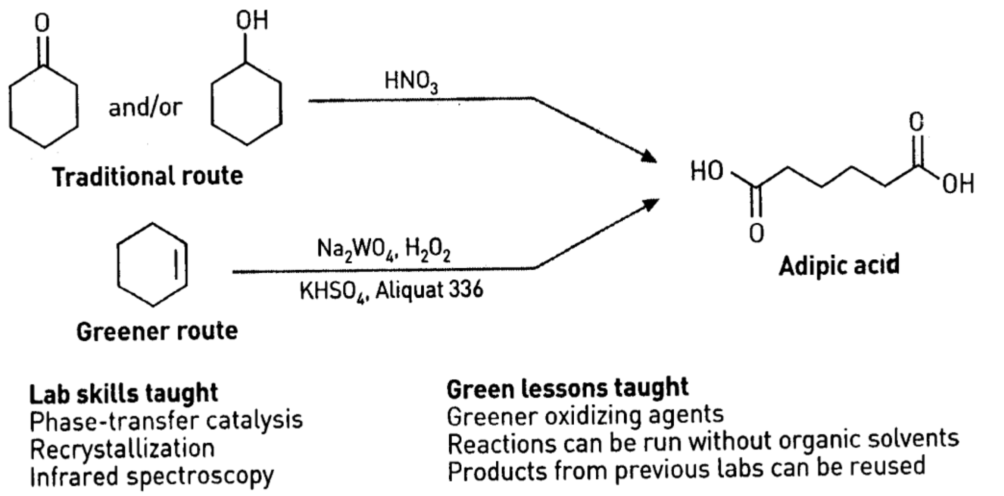


Figure 4.4. The "traditional route" for the synthesis of adipic acid and the new "greener" method, with less waste and recycling. In the second method W salts are used which can be recycled. [***Aliquat 336*** *(Stark's catalyst) is a mixture of octyl C8 and decyl C10* chains with C_8 predominating. It is a quaternary ammonium salt used as a phase transfer catalyst and metal extraction reagent *able to dissolve metal complexes].*

Although the oxidation with H_2O_2 is very effective and environmentally benign, scientists improved the reaction with new metal catalysts. They are using W as oxpoeroxo Tungten complexes and Molybdenium. With starting material cyclohexene or 1,2-cyclohexanediol the yield is 45-86%.[13]

Other scientists promoted the biocatalytic method of synthetic adipic acid from D-glucose. It is achieved with genetically transgenic bacteria *Klebsiella pneumoniae*, a non-toxic strain of *Escherichia coli, (Enterobactiriaceae).The scientist who researched and applied the new biocatalytic synthesis of adipic acid was awarded the* "Presidential Green Chemistry Challenge Awards Program" in 1998 in the USA.[14-17]

The new "greener" method of adipic acid from cyclohexene and H_2O_2 cab be easily set up in a school or university chemical laboratory and is used as a good example in teaching lessons and practical exercises of Green Chemistry.[18]

4.4.1. The "Green " Synthesis of Adipic Acid in a Chemical Laboratory

This is a brief description of the synthesis of Adipic acid in a conventional chemical laboratory where all chemical reagents are available.[18]

In a conical flask of 25 mL with screw cap a magnetic stirrer (Teflon) is place and then the reagents are added carefully:

i) 0.25 g sodium Tungstate dehydrate,

ii) 0.25 g of solvent Aliquat 336 (phase transfer catalyst), a thick liquid that can be added with a Pasteur pipette,

iii) 6.0 g (5.5 mL) solution 30% H_2O_2 (carefully because it can cause burns to the skin, wear gloves),
iv) 0.19 g $KHSO_4$ (potassium hydrogen sulphate),

The addition of the starting chemical cyclohexene (1.0 g) can be done after half minute of vigorous stirring to mix the reagents. A re4flux condenser is attached to the conical flask and the mixtures is stirred, slowly in the beginning (one minute) and more vigorously for 45 minutes. The reaction mixture is allowed to cool for 3 minutes and the milky liquid is warmed gently for few minutes. The tope layer is an aqueous mixture while the oily layer on the bottom is the Aliquat 336 solvent. With the help of the pipette we transfer carefully most of the top layer to a glass beaker and cool on ice for 10 minutes. The white liquid precipitates. Collect solid from the walls of the beaker with the help of a glass rod. The precipitate is separated and filtered under vacuum on a Buchner funnel. All solid crystals are collected in the centre and washed on the filter with 2-3 mL of cold water. Recrystallization is performed from water (1 mL for every 2.3 g of product). The mixture is boiled to 80-100 ^oC, more water is added to dissolve the solid crystals, The mixture is allowed to cool and the precipitate is filtered again on a Buchner funnel. The solid crystals can be washed with cold water The solid is dried in a furnace at 115 ^oC for 10-15 minutes. The melting point of the adipic acid can be determined at 151-152 ^oC. The yield can be between 90-95 %.

Figure 4.5. Preparation of adipic acid in a school's chemical laboratory. The white (milky) solid crystals can be easily separated and dried.

4.4.2. The Efficiency of the "Green" Method of Adipic Acid

The adipic acid synthesis by the two methods can be used as a good example for the "atom economy" (atom or mass efficiency) of reactions in synthetic routes.

A. The "old", traditional method for the adipic acid with cyclohexanone/cyclohexanol oxidation by Nitric acid. In the presence of catalyst copper/vanadium [Cu(0.1-05% & V (0.02-0.1%)] The reaction is:

$$\mathbf{C_6H_{12}O + 2\ HNO_3 + H_2O \rightarrow C_6H_{10}O_4 + NO_x\ (NO, NO_2, N_2O, N_2)}$$

In this method the negative aspect is the release of nitrogen oxides. The Yield is 93% If we take into account the mass of the atoms, for reactants and product, we can have the following calculations:
Product mass = (6C)(12) (10H)(1) (4O)(!6) = 146 g
Reactant mass = (6C)(12) (18H)(1) (9O)(16) (2N)(14) = 262 g
Yield or Mass efficiency of the reaction, is the ratio of product/reactants X 100 = 146/262 X 100 = 55,7%

*[**Reaction mass efficincy** takes into account atom economy, chemical yield and stoichiometry. The formula can take one of the two forms shown below: From a generic reaction where A + B → C Reaction mass efficiency = molecular weight of product C × yield m.w. A + (m.w. B × molar ratio B/A). Simply Reaction mass efficiency = mass of product C × 100 / mass of A + mass of B. Like **carbon efficiency**, this measure shows the "clean-ness" of a reaction but not of a process. These metrics can present a rearrangement as "very green" but they would fail to address any solvent, work-up and energy issues arising from the practical reaction].*

B. The new "greener" method.
The preparation from cyclohexene oxidized by H_2O_2 in the presence of the catalyst $N\alpha_2WO_4.2H_2O$ (1%) with solvent Aliquat 336 [$CH_3(v\text{-}C_8H_{17})_3N$] HSO_4 (1%)].
Reference: ¨Sato K, Aoki M, Noyori R. A "green" route to adipic acid: direct oxidation of cyclohexenes with 30 percent hydrogen peroxide. Science, 281: 1646-1647, 1998; Usui Y, Sato K. A green method of oxidation of cycloalkanones with 30% hydrogen peroxide. Green Chem 5: 373-375, 2003.

$$\mathbf{C_6H_{10} + 4\, H_2O_2 \rightarrow catalysts \rightarrow C_6H_{10}O_4 + 4\, H_2O}$$

The new "greener" method do no produce toxic waste and its yield is 90%.
Product mass =(6C)(12) (10H)(1) (4 O)(16) (2N)(14)=146 g
Reactant mass = (6C)(12) (18H)(1) (8 O)(16) = 218 g
Reaction Mass efficiency = 146/218 X 100 = 67%.
The reaction mass efficiency of the "greener" method is 11% higher than the first method.

4.5. The Synthesis of Maleic Anhydrite by Green chemistry Principles

Another very interesting organic synthesis that can be used in the teaching of "green" synthetic routes is the "old" and the new synthesis of Maleic anhydrite.

Maleic Anhydrite (MA) (or cis-butenediol acid) is a chemical substance of great industrial importance and is used as a starting material for the production of polyimides, polyester resins, surface coatings, lubrican additives, phthalic-type alkyd, plasticizers and copolymers. Also, is an important intermediate in the synthesis of 1,4-butanediol (in the industry of polyurethane and butyrolactone, solvent of dyes). Maleic anhydrite is produced annually in, approximately, one million tones.

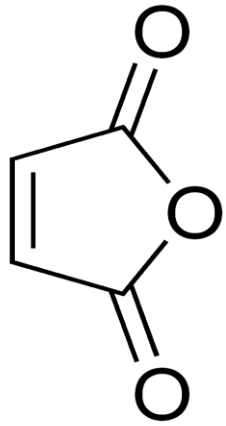
 

Figure 4.6. Maleic Anhydrite's molecular formula. It is a white crystalline substance produced annually in one million tones.

Traditionally, Maleic anhydrite was produced using benzene, butene or butane as a starting material and an oxidizing gas. Air was used as oxidizing agent and the catalyst Vanadium pentoxide under 3-5 bar pressure and 350-450 ^{o}C temperature.

In the 1970s the big energy crisis and the increase in petroleum products prices brought the first change in the industrial synthetic route. The starting chemical was exclusively n-butane. In the 1990s the method was changed to meet environmental criteria, stringent regulations of waste and better efficiency. Two very big industrial enterprises UCB Chemicals (Belgium) and BASF (Germany) started producing MA as a by-product of the oxidation of naphthalene into phthalic acid and phthalic anhydrite. The reaction is "greener" compared to the original which used benzene, and the "atom economy" of the reaction was better without much waste (decrease in CO2 emissions).[19.]

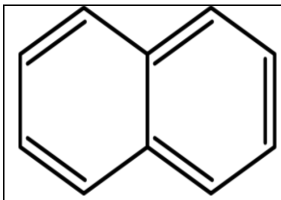
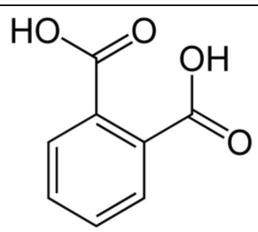
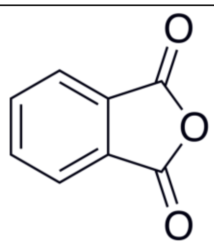
 Naphthalene	 Phthalic acid	 Phthalic anhydrite

Figure 4.7. Changing benzene as starting chemical into naphthalene made the production of Maleic acid more "greener' with greater efficiency and less waste.

4.5.1. Synthesis of Maleic anhydrite by the "old" and "new" Methods

A. **The "old" Method** used as a starting material **benzene** (C_6H_6) and a catalyst which was composed of oxides of Vanadium and Molybdenum , V_2O_5 and MoO_3 (fixed bed reactor)

$$\mathbf{2\ C_6H_6 + 9O_2\ (air) \rightarrow catalysts \rightarrow\ 2\ C_4H_2O_3 + H_2O + 4\ CO_2}$$

This oxidation reaction with air as an oxidizing agent has a yield of 95%
Product mass = 2(4)(12) 2(3)(16) 2(2)(1) = 196
Reactant mass =2(6)(12) 9(2)(16) 2(6)(1) = 444
Reaction Mass efficiency = 196/344 (X 100) = 196/444 (X100) = 44.4% .

B. **The "new greener" Method** with starting material **n-butane** and catalyst $(VO)_2P_2O_5$ (fixed bed reactor)

$$\mathbf{C_4H_{10} + 3.5\ O_2\ (air) \rightarrow catalyst \rightarrow C_4H_2O + 4H_2O}$$

The yield of the reaction is 6o%
Product mass = (4)(12) (3)(16) (2)(1) = 98
Reactant mass =(4)(12) 3.5(2)(16) (10)(1) = 170
Reaction Mass efficiency = 98/170 (X100) = 57,6%.

The industrial production of Maleic anhydrite was improved substantially in last decades by using new catalysts, such Vanadium-Phosphorous and special complexes of V-P in temperatures 0-200 ^oC without the use of solvent. This is a patented method of Standard Oil Company (Indiana).[20]

Also, the American industrial enterprise of [E.I du Pont de Nemours and Co (Wilmigton, Delaware, USA)], after 10 years of research developed a new synthetic route for MA by oxidizing n-butane with a circulating fluidized bed reactor.[21]

In Romania the Institute of Macromolecular Chemistry (Iasi, Romania) developed a new "greener" method for the synthesis of copolymers of MA with the use of microwaves. In this method free radicals are formed which advance the copolymerization of MA with vinyl monomers.[22]

4.6. Green Chemistry Metrics. The Environmental factor E for Waste in Chemical Reactions

Green Chemistry introduced various general metrics to give quantitative meaning of chemical processes. The environmental **E-factor** was established as the indicator of mass waste per unit of product in the chemical industry. The E-factor can be made as complex and thorough or as simple as required. Assumptions on solvent and other factors can be made or a total analysis can be performed. The E-factor calculation is defined by the ratio of the mass of waste (kg) per unit of product in kilograms:

E-factor = total waste (kg) / product (kg)

The Green Chemistry metric is very simple to understand and to use. It highlights the waste produced in the process as opposed to the reaction, thus helping those who try to fulfil one of the twelve principles of green chemistry to avoid waste production. The environmental E-factors ignores recyclable factors such as recycled solvents and re-used catalysts, which obviously increases the accuracy but ignores the energy involved in the recovery.

Roger A. Sheldon took his publications one stage further and produced the following Table for E-Factors across the chemical industry

Industry sector	*Annual production (t)*	*E-factor*	*Waste produced (t)*
Oil refining	10^6-10^8	Ca. 0.1	10^5-10^7
Bulk chemicals	10^4-10^6	<1–5	10^4-5×10^6
Fine chemicals	10^2-10^4	5–50	$5 \times 10^2-5 \times 10^5$
Pharmaceuticals	$10-10^3$	25–100	$2.5 \times 10^2-10^5$

Lapkin A, Constable D. Green Chemistry Metrics. Measuring and Monitoring Sustainable Processes, Wiley, West Sussex, UK, 2008.
Sheldon RA. Atom efficiency and catalysis in organic synthesis. Pure Appl Chem 72(7):1233-1246, 2000.
Sheldon Roger A.: ChemInform Abstract: Atom Efficiency and Catalysis in Organic Synthesis. ChemInform 32, 2001..
Sheldon Roger A.: Utilisation of biomass for sustainable fuels and chemicals: Molecules, methods and metrics. Catal Today 167,3, 2011..

4.7. New Methods in Organic Synthesis. Microwave Applications for Green Chemistry Synthesis

Microwave applications in organic synthesis is not something new. But it is interesting to realize the potential of this synthetic method with low energy requirements, less waste, no use of solvent. The principles of Green chemistry apply to most of the synthetic routes with microwave irradiation.

Figure 4.8. New equipment appeared in the market for microwave irradiation reactions with special reflux condensers and digital indicators.

Microwave-assisted eco-friendly organic synthesis have become a new trend with many applications in synthesising organic chemicals. Organic reactions under the microwave irradiation have many advantages compared to the conventional reactions which need very high temperatures. Microwave assisted reactions are "cleaner", last only very few minutes, have high yield and produce minimum waste.[23]

Microwave assisted organic synthesis has become an expanding field in synthetic research. New publications cover the many aspects of this "greener" technique and its practical applications.[24-29] The scientific literature is full of new research papers on microwave reaction mechanisms and applications.[30-34]

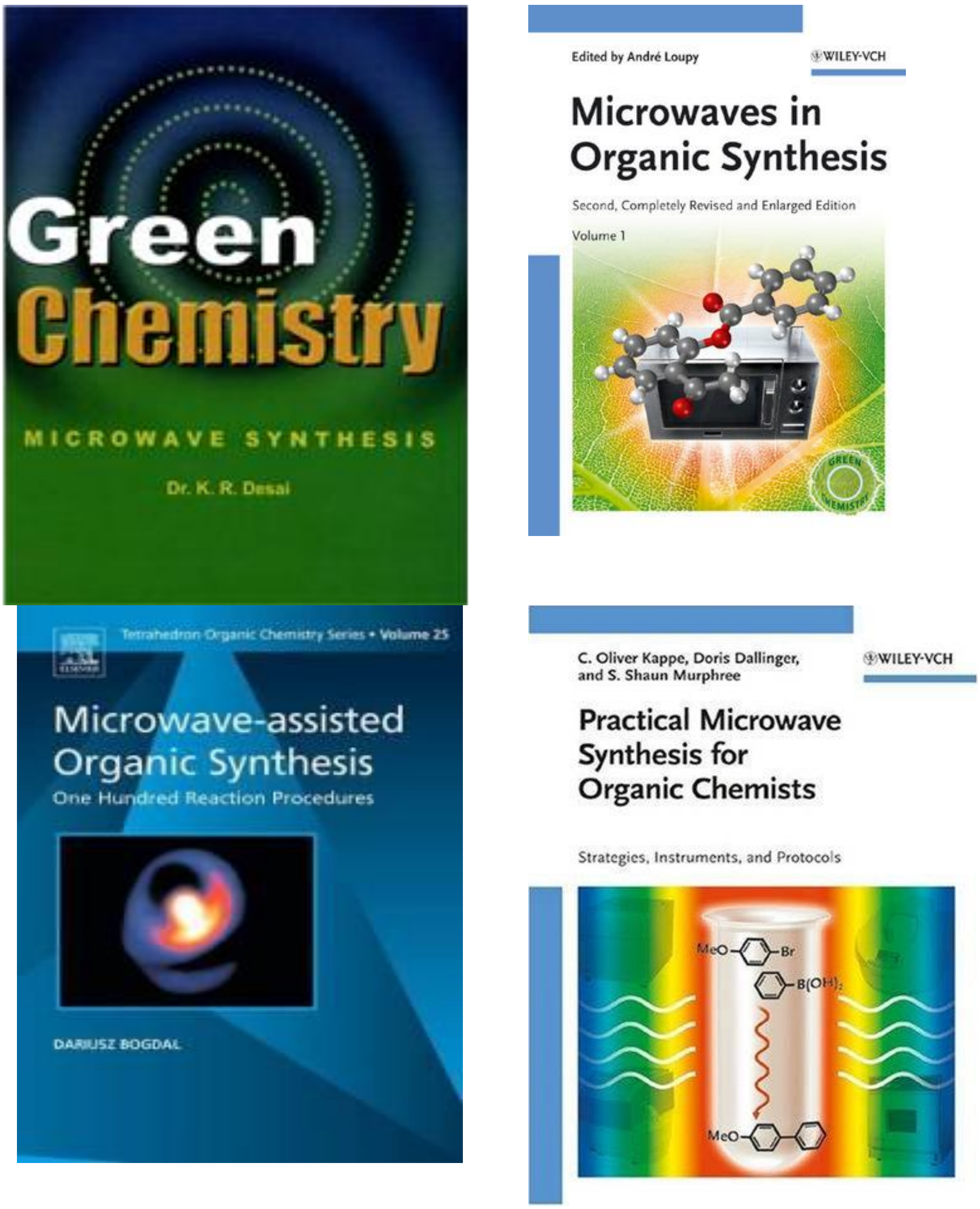


Figure 4.9. Numerous publications in the last years cover the multiplications of technical applications, research and methodologies in microwave assisted organic synthesis,

4.8. New “Green” Methods in Synthetic Organic Sonochemistry

. Ultrasound-assisted organic synthesis is another “green” methodology which is applied in many organic synthetic routes with great advantages for high efficiency, low waste, low energy requirements. **Sonochemistry** (in the region of 20 kHz to 1 MHz) has many applications due to its high energy and the ability to disperse reagent in small particles and accelerate reactions.

Irradiation with high intensity sound or ultrasound, acoustic cavitation usually occurs (growth, and implosive collapse of bubbles irradiated with sound). Experimental results have shown that these bubbles have temperatures around 5000 K, pressures of roughly 1000 atm. These cavitations can create extreme physical and chemical conditions in otherwise cold liquids.[35-37]

Also, Sonochemical engineering is a new field involving the application of sonic and ultrasonic waves to chemical processing. Sonochemistry enhances or promotes chemical reactions and mass transfer. It offers the potential for shorter reaction cycles, cheaper reagents, and less extreme physical conditions. Existing literature on sonochemical reacting systems is chemistry-intensive, and applications of this novel means of reaction in environmental remediation and pollution prevention seem almost unlimited and is rapidly growing area.[38]

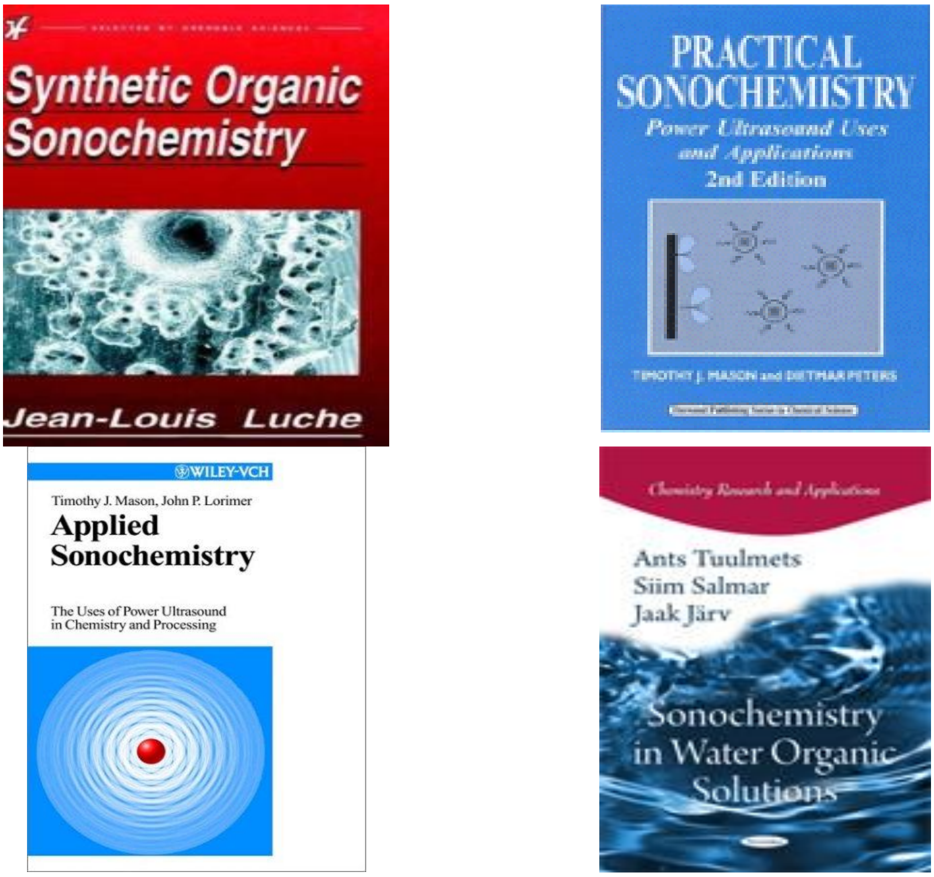


Figure 4.10. In the last decade there are many publications on Sonochemistry and its applications in organic synthetic routes

The scientific literature on sonochemistry research and applications is by now very extended and numerous books on the subject have been published in the last decade.[38-44]

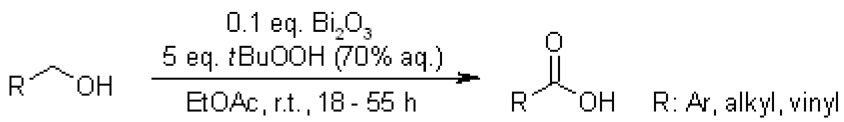
4.9. Bibliographical Sources: Examples of new "greener" synthetic methods with principles of Green Chemistry

The scientific literature is vast and contains a great number of research publications on the principles of Green Chemistry and how these can be applied to organic synthetic routes for "old" and conventional methods. The subjects of Green Chemistry are covered by various internet sites and networks which publish continuously new research.

URL:http://www.organic-chemistry.org/topics/greenchemistry.shtm

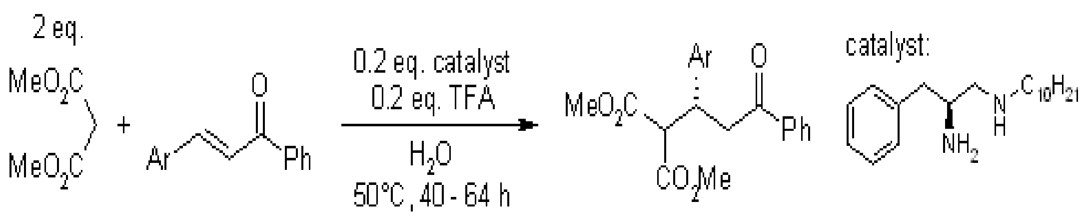
Recent research papers on Green Chemistry synthetic organic routes.

1. Transformation of aromatic and aliphatic alcohols in the equivalent carboxylic acids and ketones. Green synthetic method.



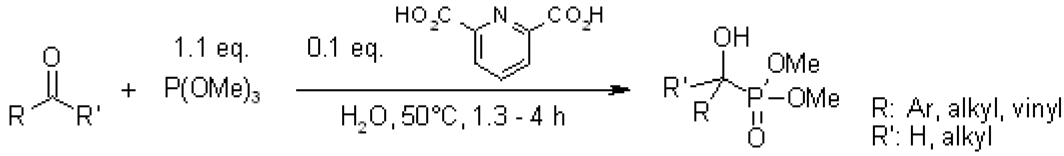
Various aromatic, aliphatic and conjugated alcohols were transformed into the corresponding carboxylic acids and ketones in good yields with aq 70% *t*-BuOOH in the presence of catalytic amounts of bismuth(III) oxide. This method possesses does not involve cumbersome work-up, exhibits chemoselectivity and proceeds under ambient conditions. is **The overall method green**.. Malik P., D. Chakraborty D. Bismuth (III) oxide catalyzed oxidation of alcohols with tert-butyl hydroperoxide. , *Synthesis*, **2010**, 3736-3740

2. Enantioselective Michaell addition



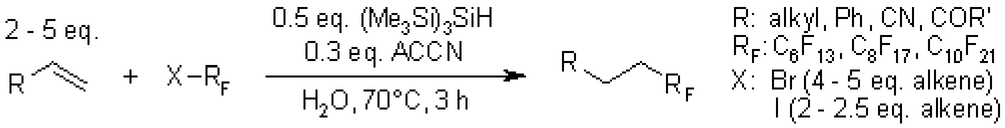
A highly enantioselective Michael addition of malonates to α,β-unsaturated ketones in water is catalyzed by a primary-secondary diamine catalyst containing a long alkyl chain. This asymmetric Michael addition process allows the conversion of various α,β-unsaturated ketones. Z. Mao, Y. Jia, W. Li, R. Wang, *J. Org. Chem.*, **2010**, *75*, 7428-7430.

3. Organocatalytic direct α-hydroxy phosphonate of aldehydes and ketones



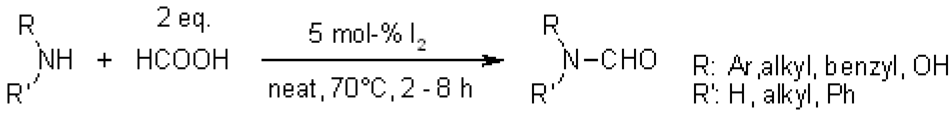
An organocatalytic, direct synthesis of α-hydroxy phosphonates via reaction of aldehydes and ketones with trimethylphosphite in the presence of catalytic amounts of pyridine 2,6-dicarboxylic acid in water is simple, cost-effective and environmentally benign. F. Jahani, B. Zamenian, S. Khaksar, M. Taibakhsh, *Synthesis*, **2010**, 3315-3318.

4 Intermolecular addition of perfluoroalkyl radicals



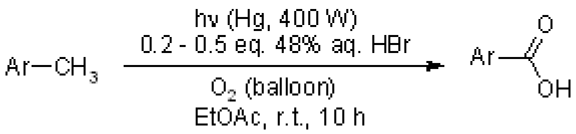
Intermolecular addition of perfluoroalkyl radicals on electron rich alkenes and alkenes with electron withdrawing groups in water, mediated by silyl radicals gives perfluoroalkyl-substituted compounds in good yields. The radical triggering events employed consist of thermal decomposition of 1,1′-azobis(cyclohexanecarbonitrile) (ACCN) or dioxygen initiation. S. Barata-Vallejo, A. Postigo, *J. Org. Chem.*, **2010**, *75*, 6141-6148.

5. Practical catalytic method for N-formylation



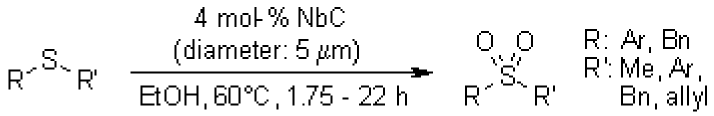
A simple, practical, and catalytic method for the N-formylation in the presence of molecular iodine as a catalyst under solvent-free conditions is applicable to a wide variety of amines. α-Amino acid esters can be converted without epimerization. J.-G. Kim, D. O. Jang, *Synlett*, **2010**, 2093-2096.

6. Direct oxidation of methyl group in aromatic nucleus



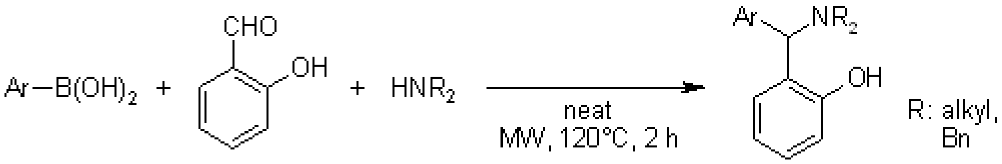
A methyl group at an aromatic nucleus is oxidized directly to the corresponding carboxylic acid in the presence of molecular oxygen and catalytic hydrobromic acid under photoirradiation. S.-I. Hirashima, A. Itoh, *Synthesis*, **2006**, 1757-1759.

7. Oxidation of sulfides with H_2O_2



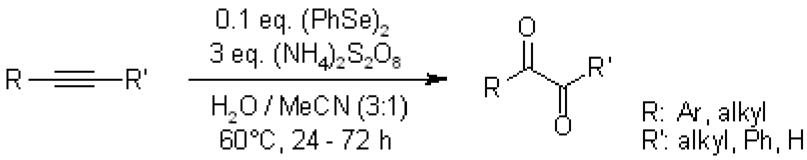
Oxidation of sulfides with 30% hydrogen peroxide catalyzed by tantalum carbide provides the corresponding sulfoxides in high yields, whereas niobium carbide as catalyst efficiently affords the corresponding sulfones. Both catalysts can easily be recovered and reused without losing their activity. M. Kirihara, A. Itou, T. Noguchi, J. Yamamoto, *Synlett*, **2010**, 1557-1561.

8. Borono-Mannich reactions in solvent-free conditions



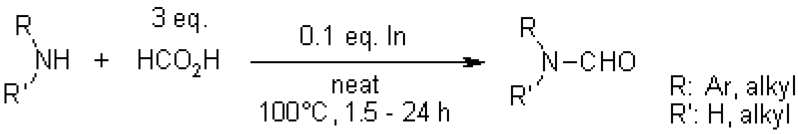
Borono-Mannich reactions can be performed in solvent-free conditions under microwave irradition with short reaction time. Full conversion of the starting materials towards the expected product was achieved, starting from stoichiometric quantities of reactants, avoiding column chromatography. No purification step other than an aqueous washing was required.P. Nun, J. Martinez, F. Lamaty, *Synthesis*, **2010**, 2063-2068.

9. Oxidation of alkynes in aqueous media



Oxidation of alkynes using ammonium persulfate and diphenyl diselenide as catalyst in aqueous media leads to 1,2-unprotected dicarbonyl derivatives or to hemiacetals starting from terminal alkynes. S. Santoro, B. Battistelli, B. Gjoka, C.-w. S. Si, L. Testaferri, M. Tiecco, C. Santi, *Synlett*, 2010, 1402-1406.

10. Mild method for N-formylation in the presence of Indium metal



A simple, mild method for *N*-formylation in the presence of indium metal as a catalyst under solvent-free conditions is applicable to the chemoselective reaction of amines and α-amino acid esters without epimerization.J.-G. Kima, D. O. Jang, *Synlett*, **2010**, 1231-1234.

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5. Green Chemistry and Hazardous Organic Solvents. Green Solvents, Replacement and Alternative Techniques

5.1. Introduction to Green Chemistry and Toxic Organic Solvents

The use of hazardous and toxic solvents in chemical laboratories and the chemical industry is considered a very important problem for the health and safety of workers and environmental pollution. Green Chemistry aims to change the use of toxic solvents with greener alternatives, with replacement and synthetic techniques, separation and purification which do not need the use of solvents.

Organic solvents are very important as liquid medium for reactions to take place, and after the synthesis of a chemical product for extraction, separation, purification and drying. Solvents are also very important in chemical analytical methodologies, spectrometry and measurements of physicochemical properties. The majority of solvents are organic chemicals with hazardous and toxic properties, costly (part of the petrochemical industry) and part of the large waste by-products of the chemical industry causing environmental problems. Although most of their toxic potential is known and there are safety rules for their use, prolonged and high concentration exposures can cause occupational diseases.[1,2]

The subject of toxicology of solvents and their occupational health and safety problems related to their use have been studied extensively. Some solvents were replaced of severely restricted due to their high toxicity or carcinogenicity. Many epidemiological studies with chemists and laboratory technicians in analytical chemical and biochemical laboratories showed that solvent exposure can cause adverse health effects. [3,4]

Aromatic solvents (benzene, toluene, etc), chlorinated and polychlorinated solvents (carbon tetrachloride, chloroform, dichloromethane, etc) and other organic solvents (DMSO, DMF, petroleum ether, diethyl ether, acetone, etc) are used in great quantities in many laboratory and analytical techniques. The persistent solvents (non-biodegradable) are difficult to recycle and their disposition is very expensive.[5,6]

One of principles of Green Chemistry is to promote the idea of “greener” solvents (non-toxic, benign to environment), replacement in cases that can be substituted with safer alternatives, or changes in the methodologies of organic synthesis, when solvents are not needed.[7,8]

Green Chemistry (GC) has placed the solvent issue of synthetic organic chemistry and practices in their use at the same level with alternative synthetic routes in chemical industry. “Green” solvents, replacement with other methods or recycling and reuse is at the core of GC goals.[9]

Figure 5.1. Organic solvents are a major part of chemical processes and research activities in chemical laboratories. The Green Chemistry is aiming to promote the use of "greener" solvents, solvent-free reactions or alternatives that can be benign to environment and human health.

5.2. Green Solvents and Alternative Methods

Green solvents have been characterised for their low toxicity, higher low solubility in water (low miscibility), easily biodegradable under environmental conditions, high boiling point (not very volatile, low odour, health problems to workers) and easy to recycle after use.

The well known monthly journal **Green Chemistry** has published a themed issue on **green solvents**- alternative fluids in science and application. This themed issue contains articles by world-leading chemists detailing the recent advances and challenges faced in this area.[10]

This issue promotes the innovative research towards the substitution of volatile organic solvents in solution phase synthesis. The series of articles are based on the keynote presentations at an international conference organised by Dechema, held in October 2010 in Berchtesgaden, Germany.

The topics are mainly based on the development and application of alternative solvents such as aqueous media, ionic liquids, supercritical phases, green organic solvents, soluble polymers, including phase-separable reagents or related separation strategies. There are increasing efforts from both academia and industry to develop cleaner and more sustainable processes and technologies. All the research work presented in this themed issue aims to reduce solvent-related environmental damage.

Articles are collated in a print and online issue of ***Green Chemistry*** (www.rsc.org/greenchem) published in June 2011 which is being widely promoted to inspire young chemists and generate enthusiasm for the future of green chemistry and sustainable technologies.[11]

A very interesting list of solvents, their toxic properties and the environmental impact have been listed by the American Chemical Society (ACS) . The solvent data *Green Solvents* is an app that provides a reference list of solvents. It contain information data (molecular formula, CAS No) and coded with numbers from 1 to 10 (the higher the number the higher the hazard or toxicity) for health and safety, and environmental hazards for air, water and waste. Solvents with greatest disposal/pollution problems are brown, and those that present less of a problem are green. For example, benzene presents a very serious health risk (red, 10), but it is relatively easy to dispose of (green, 2).

Green solvents is a list of solvents used for chemical reactions, which is annotated with information about its health and safety profile, and the environmental problems associated with its use and disposal. The list was composed by the American Chemical Society Pharmaceutical Roundtable. This web page is a technical demo of web-facing technology that is currently under development by Molecular Materials Informatics.
Internet site : Molsync.com/demo/greensolvents.php

Download Solvent Data

Substance Information				Use		Environment		
Category	**Structure**	**Name**	**CAS#**	**Safety**	**Health**	**Air**	**Water**	**Waste**
Acid solvents		Formic acid Download	64-18-6	2	6	5	4	7
		Acetic acid Download	64-19-7	3	6	6	3	6
		Propionic acid Download	79-09-4	2	5	6	4	6
		Acetic anhydride Download	108-24-7	3	6	6	2	7
		Methane sulphonic acid Download	75-75-2			6	6	10
Alcohol solvents		Methanol Download	67-56-1	3	5	6	3	6
		Ethanol Download	64-17-5	4	3	5	1	6
		1-Propanol Download	71-23-8	4	4	6	2	6
		2-Isopropanol Download	67-63-0	5	5	6	2	6
		1-Butanol Download	71-36-3	3	5	5	5	3
		2-Butanol Download	78-92-2	4	5	6	3	5
		Isobutanol Download	78-83-1	3	5	4	3	3
		t-Butanol Download	75-65-0	3	5	7	2	6

		Isoamyl alcohol Download	123-51-3	3	4	5	3	4
		Benzyl alcohol Download	100-51-6	4	3	4	2	4
		2-Methoxyethanol Download	109-86-4	4	9	5	3	7
		Ethylene glycol Download	107-21-1	3	3	5	1	7
Aromatic solvents		Benzene Download	71-43-2	5	10	6	6	2
		Toluene Download	108-88-3	5	7	6	6	2
		Xylenes Download	1330-20-7	4	4	4	7	3
Base solvents		Pyridine Download	110-86-1	3	6	7	7	6
		Triethylamine Download	121-44-8	4	7	5	7	4
Dipolar aprotic solvents		Acetonitrile Download	75-05-8	3	5	6	4	6
		Dimethyl formamide Download	68-12-2	3	7	3	2	7
		Dimethyl acetamide Download	127-19-5	2	7	3	7	7
		Dimethyl sulfoxide Download	67-68-5	3	4	4	4	8
		n-Methyl-2-pyrrolidone Download	872-50-4	3	6	6	2	7
		Sulfolane Download	126-33-0	2	3		5	8
Ester solvents		Methyl formate Download	107-31-3	5	7	7		6
		Methyl acetate Download	79-20-9	3	5	6	3	5
		Ethyl acetate Download	141-78-6	5	4	6	4	4
		Isopropyl acetate Download	108-21-4	3	4	6	3	3
		n-Butyl acetate Download	123-84-4	4	4	6	3	4

		Isobutyl acetate Download	110-19-0	5	3	5	2	2
		Dimethyl carbonate Download	616-38-6		3			5
		Amyl acetate Download	628-63-7	3	3	5	5	4
Ether solvents		Ethyl ether Download	60-29-7	9	5	7	4	4
		Methyl t-butyl ether Download	1634-04-4	6	5	8	5	2
		1,2-Dimethoxyethane Download	110-71-4		9		3	6
		Diglyme Download	111-96-6		8		3	7
		Tetrahydrofuran Download	109-99-9	5	6	5	4	5
		2-Methyl tetrahydrofuran Download	96-47-9	5	6			4
		Cyclopentyl methyl ether Download	5614-37-9	6			5	3
		Anisole Download	100-66-3	5	4		3	4
		1,4-Dioxane Download	123-91-1	8	7	4	4	6
Haloge-nated solvents		Dichloromethane Download	75-09-2	2	7	9	6	7
		Chloroform Download	67-66-3	2	9	7	7	6
		Carbon tetrachloride Download	56-23-5	3	8	8	5	7
		1,2-Dichloroethane Download	107-06-2	4	9	6	6	6
		Chlorobenzene Download	108-90-7	3	5	5	8	6
		Trifluoromethylbenzene Download	98-08-8		6	7	7	6
Hydrocarbon solvents		n-Hexane Download	110-54-3	6	7	5	8	1

		n-Heptane Download	142-82-5	6	4	4	7	2
		Isooctane Download	540-84-1	6	4	4		2
		Cyclohexane Download	110-82-7	6	5	4	7	2
		Methylcyclohexane Download	108-87-2	6	4	4		2
Ketone solvents		Acetone Download	67-64-1	4	4	7	1	5
		Methyl ethyl ketone Download	78-93-3	5	4	7	2	5
		Methyl isobutyl ketone Download	108-10-1	5	6	6	4	2
		Cyclohexanone Download	108-94-1	4	4	6	3	5

5.3. Green Chemistry, Green Solvents. Alternative Techniques in Organic Synthesis

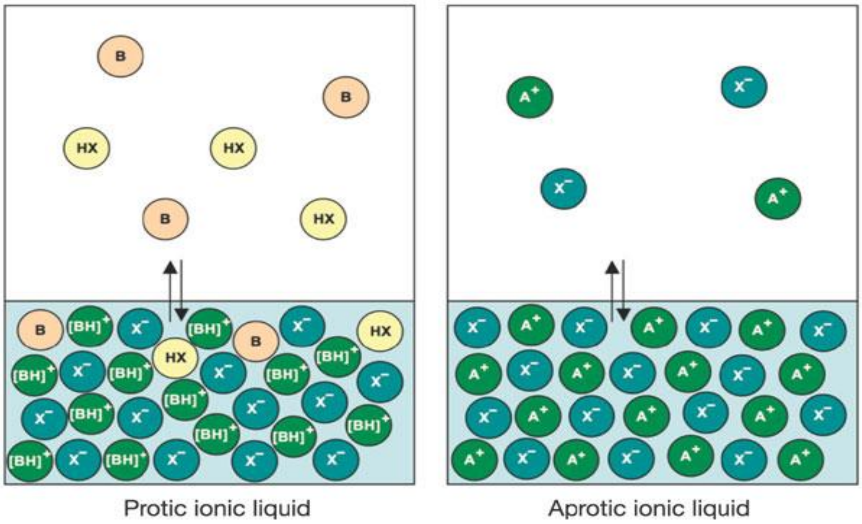
Green Chemistry aims for less toxic solvents but in recent years new methods have been developed where organic synthesis can be performed without solvents, mild conditions and low energy consumption.10 New conferences and symposia have promoted the use of alternative methods or “green” solvents.[12,13] The new field of “green” solvents in organic synthesis has been extended by research papers and publications.[14]

Some of these methods are presented below with a brief explanation of how they work and some references.

5.3.1. Ionic Liquids in Organic Synthesis. Are they Green Chemistry?

Ionic liquids are mixtures of anions and cations, molten salts, with melting point around 100 ^{o}C, which can be used as alternative solvents in organic synthesis. Although the ionic liquids do not comply full with green chemistry principles, they are very promising as alternatives to organic solvents.[15]

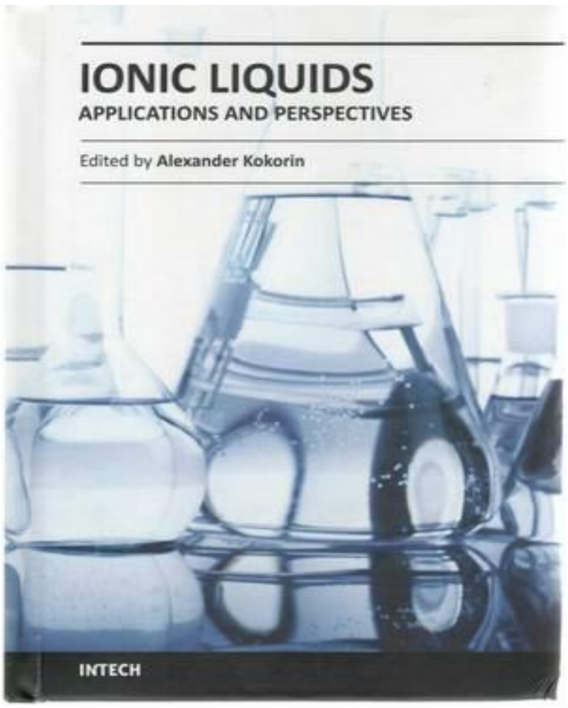
In the scientific literature there are a large number of research papers for the use of ionic liquids in synthetic routes and various applications.[16,17]



[For the protic ionic liquids there is a dynamic balance between the ionic form and the dissociated form $[BH]^+X^-(l) \leftrightarrows B(l) + HX(l) \leftrightarrows B(g) + HX(g)$.
The green circles represent cations, the bleu circles anions and the other colours neutral molecules. l=liquid phase, g=gaseous phase]

Figure 5.2. Schematic diagram of protic and aprotic ionic liquids in the liquid and gaseous phase.

Recent conferences and new books promote the methodologies of ionic liquids in organic synthesis.[18-21]



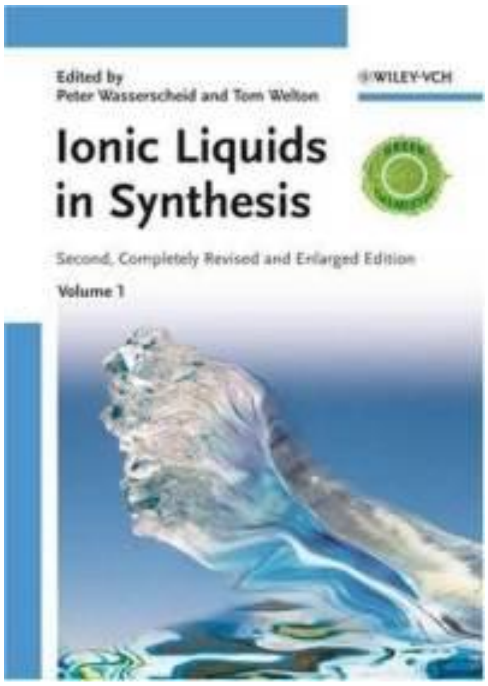
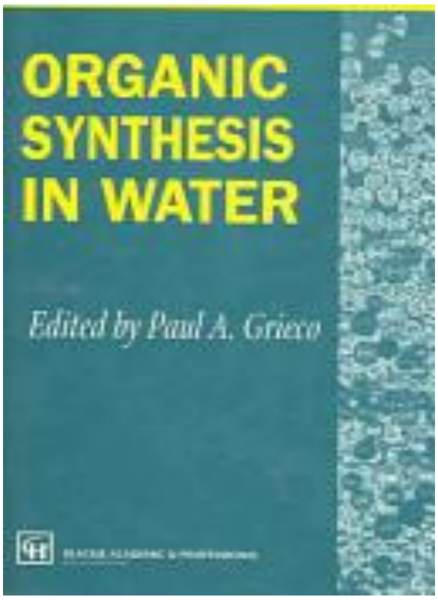


Figure 5.3. Books on Ionic Liquids and their applications to organic synthesis as alternative "green" solvents. Kokorin A (Ed). *Ionic Liquids. Applications and Perspectives* Intech, New York, 2011. . Wasserscheid P, Welton P (Eds).. *Ionic Liquids in Synthesis.* Volume 1. Wiley-VCH, West Sussex, UK, 2003

5.3.2. Organic Synthesis in Water

Although water is considered a problem for organic synthesis and the purification processes and drying in final products is very cumbersome, in recent years water is considered a good solvent for organic reactions. A good example id the synthetic routes of the Diels-Alder reactions in which the hydrophobic properties of some reagents makes water an ideal solvent. Water as a solvent accelerates some reactions because some reagent are not soluble and provides selectivity. The low solubility of Oxygen is also an advantage for some reactions where metal catalysts are used.[22-25]



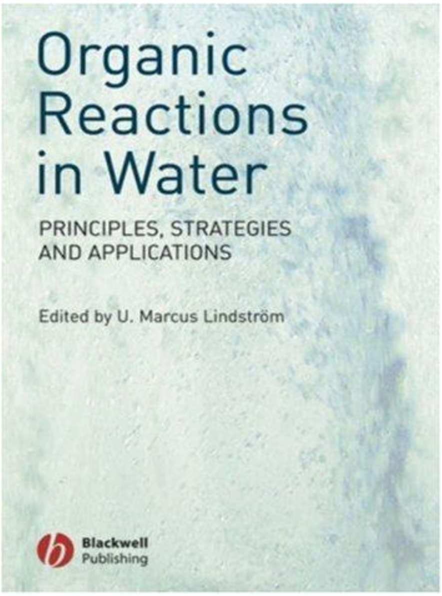


Figure 5.4. Books are published for organic reactions in water and the use of water as a solvent. In the last years water is used in many methods for organic reactions and the scientific literature has a large number of papers.

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5.3.3. Techniques for Organic Synthesis in Perfluorinated Phases

In some new methodologies chemists use perfluorinated diphasic solvents to dissolve a catalyst with very long perfuorinated chain. These catalysts can be very effective and provide high yields in some types of reactions where the catalysts play an important part. Another advantage is that after the reaction the catalyst can be separated and recycled.[26]

5.3.4. Supercritical carbon dioxide and supercritical water

A supercritical liquid is at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. The supercritical liquid 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 liquids 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.

Supercritical CO_2 and water are considered “green” solvents in many industrial processes, providing high yields in many reactions, and there are many examples of their use in the scientific literature.[26-29]

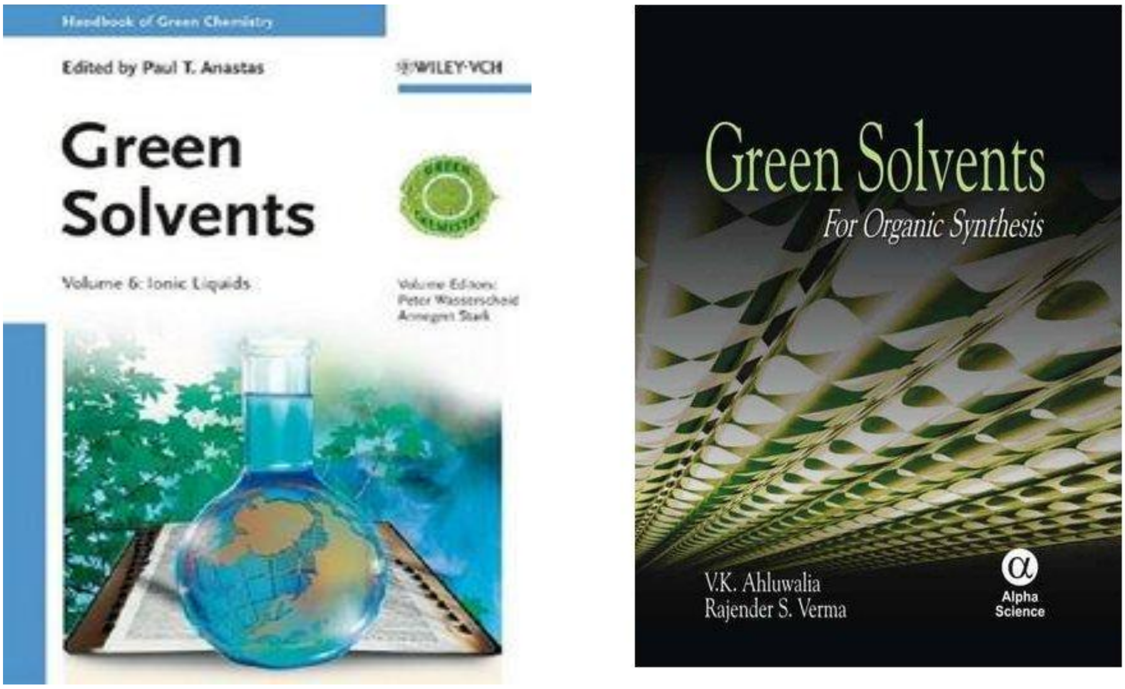
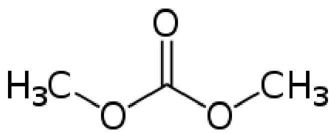


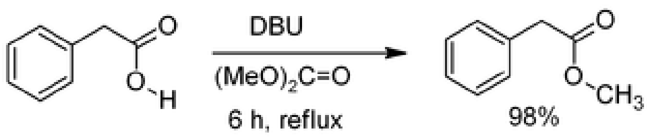
Figure 5.5. Many books have been published recently promoting the “Green solvents” as alternatives for organic synthetic routes in industrial processes and for research laboratory use.

5.3.5. Organic Synthesis with Carbonic esters

Carbonic esters, such as DMC, dimethyl carbonate ($CH_3OCOOCH_3$) are considered a new class of “green” solvents in many organic reaction processes. They can replace methychlorides and dimethyl sulphate esters which are toxic and hazardous.[30]



DMC can be used in methylation reactions of phenols, anilines and carboxylic acids. DBU is an alternative solvent that can be used for methylation reactions of phenols, indoles and benzimidazoles.[31,32]



5.3.6. "Green" Catalysis under the Green Chemistry Principles

It is not only the "green" solvents that will change the face of synthetic organic reactions, but also the use of "green catalysts" will improve substantially the efficiency of many industrial processes. The use of catalysts is one of the principles of Green Chemistry. Catalysis is considered a cornerstone for innovative changes in chemical processes. Catalysts will affect energy use and reaction time, will increase yield, reduce use of solvents, and lower production of by-products and waste.[33-35]

Figure 5.6. Catalysis with "green" catalysts (which can be recycled) is considered a very important step in the direction of Green Chemistry for many industrial processes. (Wiley-VCH has published in the last decade many books on Green Chemistry and Green Engineering)

5.3.7. Replacement of Toxic Solvents with Less Toxic Ones

The replacement of toxic or hazardous organic solvents in industrial processes and systems has been initiated long time ago. Examples, like replacement of benzene with toluene, cyclohexane instead of carbon tetrachloride, dichloromethane instead of chloroform etc. The scientific literature contains many examples and practices with replacement of the most toxic and hazardous solvents.[36,37]

5.3.8. Microwaves in Organic Synthesis, without Solvents

We examined in the previous chapters the use of microwave furnaces for organic reactions. These techniques do not require solvents and are considered "greener" than the conventional methods. The wide range of applications of microwave chemistry has been extended recently to many aspects of organic synthesis.[36-40]

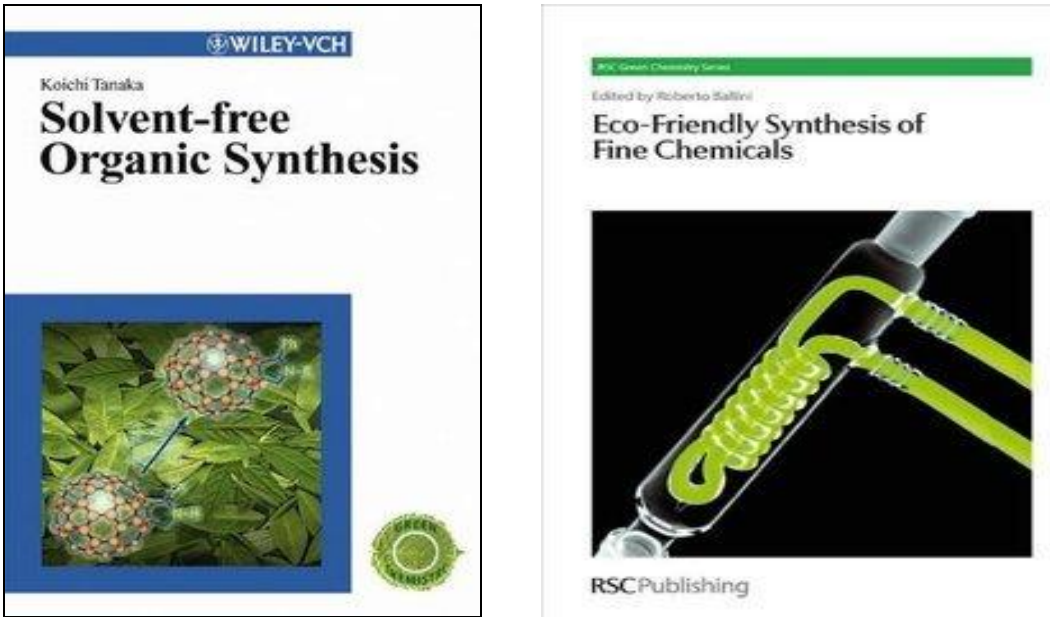


Figure 5.7. Catalysis under the Principles of Green Chemistry and Eco-friendly Synthesis are new innovative trends with substantial applications.

5.3.9. Sonochemistry in Organic Synthesis, without Solvents

Sonochemistry is also considered a methodology of organic reactions without solvents. Their use has been described before and it is obvious that their applications in organic chemistry will be extended further. High yields, low energy requirements, low waste, no use of solvents are some of the fundamental advantages of these sonochemical techniques.[41-43]

5.3.10. Other "Greener" Techniques

In addition to the above methodologies which do not require solvents or use less solvents than the conventional methods, there are are techniques of biocatalysis, self-thermo-regulated systems, soluble polymers, etc which are considered "green methodologies". Green Chemistry covers all these aspects of eco-friendly methods and promotes their use in research laboratories and in industrial organic synthesis processes. [44-46]

5.4. "Green Solvents" from Plants

Plants are considered a renewable sources of energy but also a resource for various materials. Plant oils or vegetable oils derive from plant sources. Unlike petroleum which is the main source of chemicals in the petrochemical industry they are renewable sources. There are three primary types of plant oil, differing both by the means of extraction and by the nature of the resulting oil:

Vegetable oils can replace petroleum derived organic solvents, with better properties and more eco-friendly conditions as waste. Chemists have advanced recently techniques so that some vegetable oils to become solvents and replace hazardous organic solvents.

As an example of plant-based oils we selected the research project by Spear et al. on soybean oils and their esters , [Spear SK, Griffin ST, Granger KS, et al. "Renewable plant-based soybean oil methyl esters as alternatives to organic solvents". *Green Chemistry* 9:1008-1015, 2007.

Figure 5.8. Vegetable oils can become a starting material for the production of eco-friendly solvents which are less toxic than the petrochemical industry's organic solvents

In the last decade, scientists are researching the use of "green" solvents in polymerization methods, since the polymer and plastics industries are using vast amounts of solvents. There have been some successful uses of alternative solvents in polymerization under the principles of Green Chemistry [Erdmenger T, Guerrero-Sanchez C, Vitz J, et al. Recent developments in the utilization of green solvents in polymer chemistry. ***Chemical Society Reviews*** 39:3317-3333, **2010**].

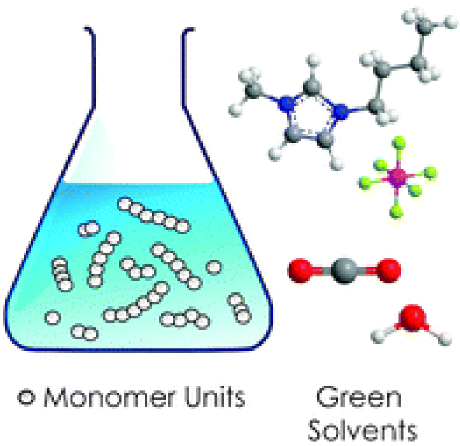


Figure 5. 9. Polymers can be prepared under industrial scale production with the use of eco-friendly solvents.

All these techniques aim at replacing toxic and hazardous solvents in many chemical processes in the synthetic laboratory and in the chemical industry.

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6. Life Cycle Analysis of Industrial Products. The Role of Green Chemistry and Green Engineering

6.1. Introduction: Life Cycle Analysis (LCA)

The Industrial Revolution of the 18th century resulted not only in a dramatic economic growth and the development of science and technology, but also promulgated the extended use of depleting natural resources. Chemical industry and Engineering were the cornerstones of this development which was not witnessed in the previous centuries of the history of human societies. Housing, transport, communications, pharmaceuticals, better food preservation, medical advances, universal education and other technological novelties improved substantially the quality of human life. The new technological advances provided food and shelter for the majority of 7 billion inhabitants of the planet, increased their standards of life and prolonged longevity without disabilities and infectious diseases. These are well known positive facts for developed and developing countries.

The Chemical Industry and Chemical Engineering played a very important role in all these advances. But at the same time in the pursuit to cover all these needs and aspirations the global situation worsened in other aspects. Environmental pollution got beyond repair, urbanization expanded dramatically, depletion of natural resources (including fresh water, minerals and fossil fuels) reached crisis levels and accumulation of industrial and urban waste threatens the quality of life achieved.

Green Chemistry and Green Engineering are involved to promote alternative innovations for some of these negative effects and attitudes. They aim towards renewable natural resources, new industrial processes and economic systems. The focus is now on new designs incorporating health and safety issues, renewable raw materials, alternative processes, innovative methodologies, energy conservation, recycling and better use of science and technology. Goals are to reverse, according to “green” chemists, the trend and bring back the ideas of Sustainable Development.

Industrial chemical products and machinery are part of the technology that is causing major environmental problems. Their assessment at all stages, from raw materials acquisition, to manufacture and disposal need to be evaluated and quantified. For an holistic approach of the subject scientists established the scientific method called **Life Cycle Analysis** (**LCA**). LCA is also known as life-cycle eco-balance. It is a technique to assess environmental impacts associated with all the stages of a product's life, from-cradle-to-grave (i.e., from raw material extraction, manufacture, distribution, use, repair, disposal or recycling).[1]

According to U.S. EPA, the LCA definition is: a technique to assess the environmental aspects and potential impacts associated with a product, process, or service, by compiling an inventory of relevant energy and material inputs and environmental releases;, evaluating the potential environmental impacts associated with identified inputs and releases; and interpreting the results to help you make a more informed decision.

The procedures of **life cycle Analysis or Assessment** (LCA) are part of the **ISO 14000** environmental management standards: in ISO 14040:2006 and 14044:2006. (ISO 14044 replaced versions of ISO 14041 to ISO 14043).

The classical definition of LCA is, "***Life Cycle Analysis is a procedure registering and analysing environmental impacts during the production of a product at all stages of its production and useful life cycle. The raw materials, the energy associated for extraction and manufacturing, the environmental pollution caused by its production and its whole life cycle until it was disposed or recycled as waste".***

The definition uses the term "product" in the broader meaning, because the life cycle comprises of many and different "services" and activities of our meta-industrial society. Modern man and woman are responsible and during his/her life use various modern material consumer products and products of information and communication for his/her practical aspects of life and work; In daily activities man is also the recipient of economic, social and cultural activities which influence his/her product acquisition and use.

The life cycle of a product involves many changes which can result in various types of environmental pollution. In the past, products that were looked as ideal for their properties proved to have multiple effects with time (e.g. chlorofluorocarbons, chlorinated pesticides, metals as catalysts, medicines, etc). Scientists initiated the LCA in order to assess in advance the effect of a product and design appropriately during its production and use.

According to the Society for Environmental Toxicology and Chemistry **(SETAC)**, LCA is a very important method for assessing the environmental impacts of a product during its whole life cycle or service (the so called "cradle-to-cradle" process). The methodology followed has a scientific basis and can be proved very useful for the design of new products and services.[2-4]

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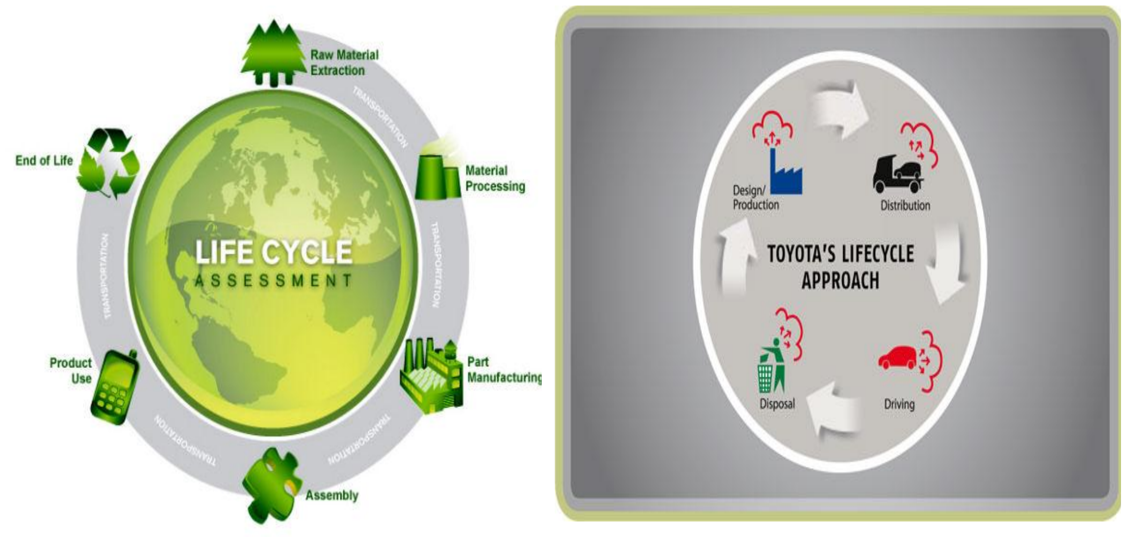

Figure 6.1. Schematic diagrams of the life cycle analysis (LCA) of a product.

6.2. What Are the Benefits from the Analysis or Assessment of the Life Cycle of Products?

The global economy is at present very competitive, the production of consumer products and services is influenced by many variables of quality, price and long term use of products. At the same time natural resources are depleting. Excessive energy use and hazardous products cause local and global environmental problems. The LCA assessment is a timely method to reduce the most important side effects of the manufacturing processes and help in the design of innovative materials. The most important benefits deriving from LCA are listed below:

a) Economic benefits. The LCA can help scientists and manufacturing engineers to pinpoint failures and environmental negative effects from the production and distribution of a certain product. These indicators can induce the manufacturer to be more affective, have higher productivity and produce better products. The economic rewards are obvious, as well as energy and material efficiency can be improved.

b) Benefits from the Design of the Product. The LCA can be introduced in the design stages to improve endogenous manufacturing problems and materials. It can lead to redesign changes and can indicate the advantages and disadvantages for the various methods of production.

c) LCA Can Increase Competitiveness and Innovation. The LCA can help manufacturers to improve distribution, use and quality of their products and promote competitiveness and innovative changes for a product and support advances in advertising claims of a product.[5]

Figure 6.2. Life cycle Analysis (or Assessment) can improve competitiveness of a product, its quality and can provide economic benefits to the manufacturer, to the consumer and to the environment.

6.3. The Process of Life Cycle Analysis of Products

The process of LCA of a product is a systematic process which take into account all the stages in the making of a product. It starts from the raw materials, the step by step industrial processes, the useful life as a consumer product and its final stages through maintenance, recycling or disposal.

The U.S. EPA (National Risk Management Laboratory, Cincinnati, Ohio, in the: *Life Cycle Assessment. Principles and Practices*, EPA/600/R-06/060, May 2006, Report by Scientific Applications International Corporation) states that: "…The LCA process is a systematic, phased approach and consists of four components: goal definition and scoping, inventory analysis, impact assessment, and interpretation of the results.."

a) **Goal Definition** and **Scoping** - Define and describe the product, process or activity. Establish the context in which the assessment is to be made and identify the boundaries and environmental effects to be reviewed for the assessment. Defining boundaries of the analysis is very important.

b) **Inventory Analysis** - Identify and quantify energy, water and materials usage and environmental releases (e.g., air emissions, solid waste disposal, waste water discharges). Simulation techniques and programming for environmental results (for similar or equivalent products) through computer programming is an important part of the analysis.

c) **Impact Assessment** - Assess the potential human and ecological effects of energy, water, and material usage and the environmental releases identified in the inventory analysis.

d) **Interpretation-Evaluate the results** of the inventory analysis and impact assessment to select the preferred product, process or service with a clear understanding of the uncertainty and the assumptions used to generate the results.

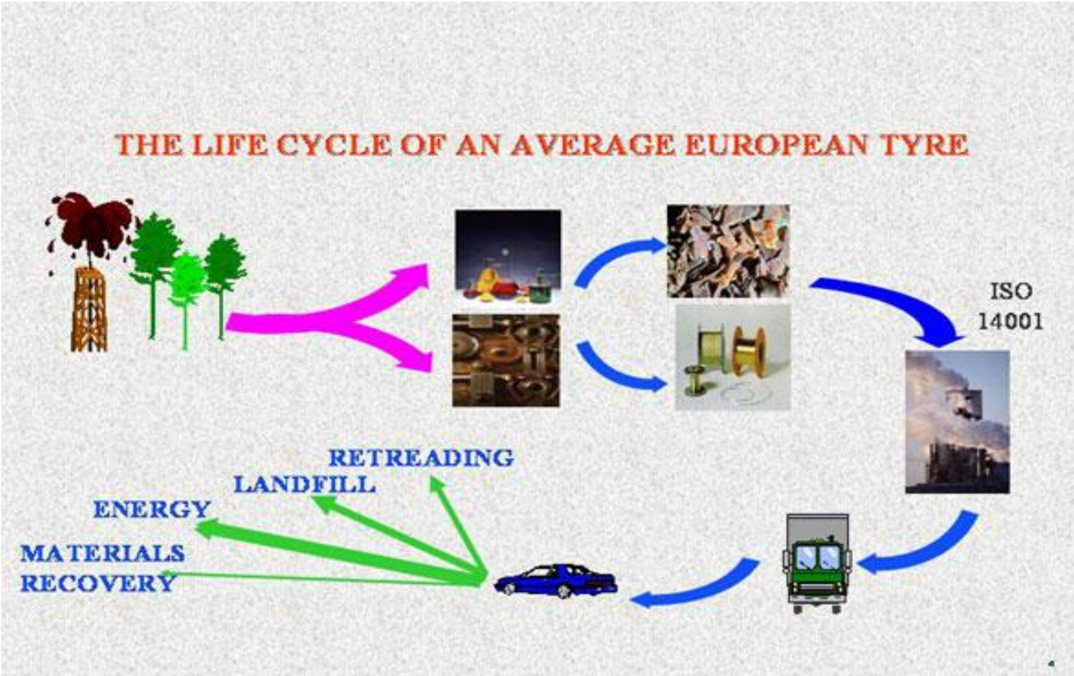

Figure 6.3. Life Cycle Analysis of an average European tyre. A typical example for raw materials, energy, rethreading, manufacturing, waste. .

The LCA sets new priorities for manufacturing and products. It gives emphasis on safety and health issues, environmental pollution, sustainability and renewable resources.[6]

Studies of LCA of some products with complicated function, composite materials and uncertainties in their environmental impact (air, water, soil, indoor environment, occupational setting, etc) can be very costly and can take a lot of time to collect data and interpret the results.[7]

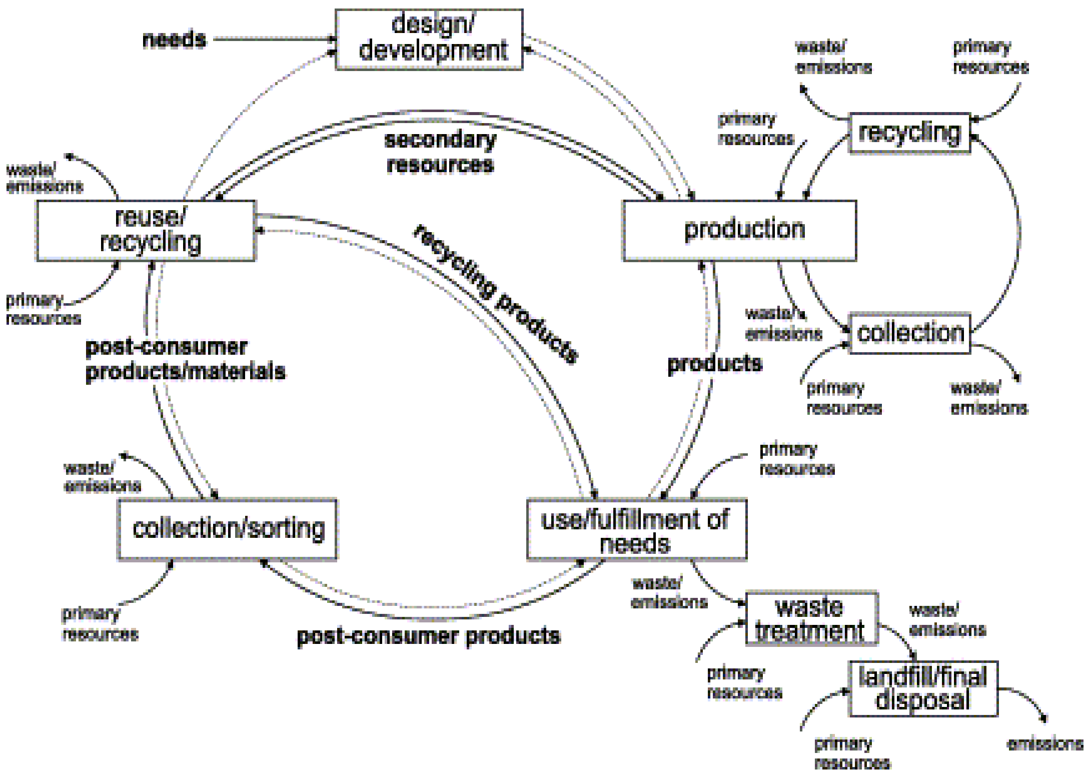

Figure 6.4. Schematic diagram of the LCA of a product. The Cycle starts from Needs ⇨ design development ⇨ manufacturing, production ⇨ use/fulfilment of needs ⇨ collection/sorting ⇨ reuse/recycling. Every stage has its own cycles, waste treatment, landfill disposal, primary resources, secondary resources, recycling products,

6.4. Quantitative Assessment of Various Impacts from the Life Cycle of a Product

Scientists analysing the LCA of a product have to collect quantitative data concerning raw materials (origin and environmental impact from extraction techniques, manufacturing of starting materials, etc). The next step is to collect data on environmental variables during the manufacturing processes (emissions, use of toxic solvents, by-products, waste0. Avery product during its life cycle can have some effects to the consumer and to the environment, but when reaches its end-of-life stage there are other environmental effects concerning its recycling, disposal, waste, incineration, etc. This process is called Life Cycle Inventory (LCI). The whole process with calculations, assessment, discussion and uncertainties is called Life Cycle Impact assessment (LCIA).[8]

The LCA assessment can be summarized in the Table 6.1. It contains various analyses: LCA, Cost Benefit analysis, Eco-balance analysis, Environmental analysis, Life Cycle Inventory, Product Line analysis and finally Resource and environmental profile analysis.

Table 6.1. The variety of analysis procedures that compose the LCA of a product (in three languages)

Ελληνική (Greek)	English	French
Ανάλυση Κύκλου Ζωής (ΑΚΖ)	**Life Cycle Analysis (LCA)**	**Analyse du Cycle de Vie**
Ανάλυση Κόστους Ωφέλειας	**Cost Benefit Analysis**	**Analyse Cout Benefice**
Οικολογικό Ισοζύγιο	**Eco-Balance**	**Ecobilan**
Ανάλυση Περιβαλλοντικών Επιπτώσεων Προϊόντων	**Environmental Impact Analysis for Products (EIA, P)**	**Analyse des impacts environment produits**
Καταγραφή Κύκλου Ζωής	**Life Cycle Inventory (LCI)**	**Comptabilite du cycle de vie**
Ισοζύγιο Υλικών και Ενέργειας	**Material and Energy Accounts (MEA)**	**Bilans matiere et energie**
Ανάλυση Γραμμής Προϊόντος	**Product Line Analysis (PLA)**	**Analyse de ligne produit**
Ανάλυση Αξίας Χρήσης	**Use Value Analysis**	**Analyse de la valeur d' usage**
Ανάλυση οικολογικού «προφίλ» φυσικών πόρων	**Resource & Environmental Profile Analysis (REPA)**	**Analyse des impacts environment d'utilisation des resources**

The analyst of LCA can compare other similar products and techniques of assessment. LCA can compare environmental impact (energy, pollution) assessments by using diagrams and tables with quantitative data.

Table 6.2 is an example of comparative LCA assessment. It represents a characteristic framework for the various studies and can be marked with parameters from 1 to 8 with qualitative symbols □ and ■ for representing total study or partial study of the variable. Table 6.2 can give the main characteristics of the study during the various stages of the production of products..

The questionnaire includes data on raw material, energy consumption of materials and energy for the manufacturing, production of waste (distributed in air, water and soil),and finally impact on ecosystems. The stages are: type and renewability of starting material, type of energy and use, production, distribution, transport, uses of product, recycling, reuse after maintenance or repair, type of waste. The profile of the LCA can be shown on Table 6. 2.

Table 6.2. Comparative environmental impact assessment by using 1-8 variables which represent eight different parameters of a study.
*****1** *= ecological label (οικολογικό σήμα),* **2***= ecological study (οικολογική εξέταση),* **3***= environmental impact assessment (εκτίμηση περιβαλλοντικών. Επιπτώσεων),* **4** *= Life Cycle Analysis (ανάλυση κύκλου ζωής),* **5***= Balance of Material & Energy (ισοζύγιο υλικών & ενέργειας),* **6***= technological Assessment (εκτίμηση τεχνολογίας),* **7***= Line product analysis (ανάλυση γραμμής προϊόντος),* **8***= ecological logistics (οικολογική λογιστική).* ***Symbols****: ■ full application, □ partial application of the study.*

Type of Study (Είδος μελέτης)	**Characteristics** (Χαρακτηριστικά)	**1 ****	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Subject of the Study (Αντικείμενο μελέτης)	**Technical Material & product Construction, enterprise** (Τεχνολ. Υλικό & προϊόν Κατασκευαστικό έργο Επιχείρηση)								
Boundaries of Study (Εμβέλεια)	**Partial Life Cycle** (Μερική Κύκλος ζωής)								
Impact assessment Επιπτώσεις (εκτίμηση)	**Environmental Social Economic** (Περιβαλλοντικές Κοινωνικές Οικονομικές)								
Results assessment Εκτίμηση αποτελεσμάτων	**Unidimensional (natural) Unidimensional (economic) Multidimensional** [Μονοδιάστατη Μονοδιάστατη (οικονομική) Πολυδιάστατη]								
Final parame-ters of results Τελικέςπαράμετροι	**One, Many, Multiple** (Μια, αρκετες, πολλές)								
Involved organizations (Εμπλεκόμενοι φορείς)	**Private office State institution** Μελετητικό γραφείο Κρατική Υπηρεσία								
Time of Study (Χρόνος μελέτης)	**Before, after** Εκ των Υστέρων Εκ των προτέρων								
Responsible Scientists of the Study (Υπεύθυνοιμελέτης)	**Scientists, State institutions** Επιστήμονες, κρατικές υπηρεσίες								
Recipient of Study (Αποδέκτες μελέτης)	**NGOs, citizens, institutions, Media** (ΜΜΕ, Ελεγκτικοί φορείς, πολίτες, ένωση καταναλωτ.								

Table 6.3. Life Cycle Analysis of Product (simplified matrix of the stages of LCA). In the squares the scientist add the qualitative and qualitative characteristics of the production process and life cycle environmental impacts

Environmental variables	**Stages in the Life Cycle of a Product** **1. Acquisition of raw materials, 2. Manufacturing, 3. Distribution , 4. Use, 5. final disposal, 6. Recycling, 7. Reuse** Στάδια της πορείας του Κύκλου Ζωής Προϊόντος (Απόκτηση πρώτων υλών) Παραγωγή Διανομή Χρήση Τελική Διάθεση Ανακύκλωση Επαναχρησιμοποίηση)

Acquisition of raw materials	1	2	3	4	5	6	7
Use of energy							
Production of waste							
Water pollution							
Soil and Air pollution							
Impact on ecosystems							

6.4.1. Application of LCA to Plastic and Glass Water Bottles

A classic example of LCA assessment is the plastic water bottle. In the last decades millions of plastic water bottles and no-alcoholic beverages are distributed worldwide. The plastic bottle has a very short LCA after use and can be discarded easily because of its low cost. It is well known from studies that plastic water bottle use energy and petrochemical raw material for its manufacturing and after use millions of rejected bottles pollute the environment or accumulate in congested landfills with substantial environmental problems. Plastic litter in oceans is considered very important.

Figure 6.5. Plastic and glass bottles of water and non-alcoholic beverages as waste are hazardous and have high environmental impact

Life Cycle Analysis of plastic water bottles is a very interesting example of a typical consumer society product which has very low cost but immense environmental impact of the polymer and plastics industry. It gas been estimated from production figures but also from landfills all over the world that plastic materials constitute 40-50% of the municipal solid waste. Millions of plastic bottle and plastic bags are the two most important consumer products that cause such a large environmental impact.

While glass bottles can be reused or recycled up to 95% with substantial retrieval of starting material and energy (manufacturing), plastic bottles can not be recycled efficiently. Glass bottle in some developed countries (Scandinavian countries) are recycled up to 95% because of special regulations and obligatory recycling on purchase. In other developed countries is around 60%. Green chemists and engineers would like to improve the recyclability of plastic bottles and their characteristic for biodegradation under environmental conditions.

Table 6.4. Life Cycle Analysis of glass bottles (water, refreshments or alcoholic drinks). The LCA can be applied for the number of returns (after cleaning and reuse). The quantitative data are indicative. The results can differ from country to country and any particular manufacturer.

Percentage (%) of Reuse	0	50	80	90	95	96	98	100
Number of Returns	1	2	3	5	10	15	25	30
Energy use (MJ/1000 L, Water use in kg/1000 L								
Energy and water	36656/644 *	21810/322	---	---	---	--	--	---
Emissions of gas pollutants								
CO_2/CO								
HC (hydrocarbons)/ Nitrogen oxides, NO_x								
SO_2/VOCs								
Particular matter (PM)								
Liquid production (cm^3/1000 L) & solid waste (g/1000 L)								
Suspended particulates								
Dissolved particulates								
Biological Oxygen Demand (BOD)								
Chemical oxygen demand (COD)								
Solid waste								

*** The numbers are indicative of the qualitative and quantitative differences in various LCA studies for glass bottle. Emissions, energy, materials can differ from country to country and to manufacturing technology.**

.**Table 6.5.** Inputs and outputs for the manufacture of white glass bottles (empty, 2L, ~395 g) (simapro.emit.edu.au/….Hand-outs effective LCA with SimaPro7)

		Use process in SimaPro
Inputs from nature	2 L water	Water, unspecified natural origin
	53 g Dolomite	Dolomite in ground
	23 g Feldspar	Feldspar in ground
Materials/fuels /Electricity for the mining activities	73 g Soda	Soda, powder, at plant/RER S
	42 g Limestone	Limestone, milled, loose, at plant/CH S
	248 g Silica sand	Silica sand
	0,244 kWh Electricity	Electricity, medium voltage, production UCTE, at grid/UCTE S
	3,57 MJ Natural gas	Natural gas, high pressure, at consumer/RER S
Emissions to Air		**Compartment**
	0,473 kg Carbon dioxide, fossil	high. pop.
	4,97E-05 kg Hydrogen chloride	high. pop.
	0,000018 kg Hydrogen fluoride	high. pop.
	7,72E-07 kg Lead	high. pop.
	0,0021 kg Nitrogen oxides	high. pop.
	0,000252 kg Particulates, < 2.5 um	high. pop.
	0,000016 kg Particulates, > 10 um	high. pop.
	0,000013 kg Particulates, > 2.5 um, and < 10um	high. pop.
	0,00344 kg Sulfur dioxide	high. pop.

The LCA assessment can take into account Advantages of Glass Bottles*. The main benefit in terms of public health is that glass is inert and impermeable. This means that substances cannot enter the product through the glass or leach into the product from the glass.*

*For this reason, glass is the only primary packaging material given GRAS (Generally Regarded As Safe) status by the US Food and Drug Administration (FDA). It has recently been exempted by the EU from REACH – the new chemicals legislation and, unlike other materials, is automatically considered as inert in European waste law. The inertness and impermeability also helps glass to preserve the freshness of products longer than other materials. Food and drinks packed in glass will always retain their original taste and smell because there is no interaction with the packaging. It is also the preferred packaging material for consumers – 74% of consumers prefer glass. Glass is 100% recyclable and infinitely so. Three usual negatives for glass is that it is heavier than other materials, it breaks and it uses a lot of energy. G*lass is considered as a sustainable product.

Glass bottles for mineral drinking water, non-alcoholic refreshment and alcoholic beverages have been replaced throughout the years by cans and plastics bottles (PET) because of cost, weight and reliability. Plastic bottles are using petrochemical starting materials (monomers) and their manufacturing is causing environmental problems. It is estimated globally that in 2007, the distribution of plastic bottled water was in the range of 200 billion litres. In the USA are consumed annually 1.5 million barrels of petroleum for the manufacturing of plastic water bottles. Also, their distribution consumes vast amounts of fossil fuels for trucks, vans and vehicles. In t56he period 1990-2005 the consumption of bottled water was increased fourfold. Data from the USA shows that 27% of plastic bottles are recycled (approximately 1.2 billion of kg of plastic, 2008). In European countries 30-40% of plastic bottles are recycled. More than 50% of the plastic bottles are sent as solid waste to landfills polluting extensively the oceans.[9,10]

Figure 6.6. Plastic bottle and containers are now predominant in the vast consumer market. Many food and beverage companies change into plastic (especially PET and paper cartons) for fresh beverages and water. Plastics constitute now 40-50% of municipal solid waste.

6.5. Other Types of Life Cycle Analysis

There are now many types of Life Cycle Analysis and assessment which promote the various interests of manufacturers, industries, consumers, Non-Governmental Organizations (NGOs) and state institutions. Some of them are very important from the economic and ecological perspective.

a) Economic input–output life cycle assessment

The Economic input–output LCA (EIOLCA) involves use of aggregate sector-level data on how much environmental impact can be attributed to each sector of the economy and how much each sector purchases from other sectors. This type of analysis can account for long chains (for example, building an automobile requires energy, but producing energy requires vehicles, and building those vehicles requires energy, etc.), which somewhat alleviates the scoping problem of process LCA.

EIOLCA relies on sector-level averages that may or may not be representative of the specific subset of the sector relevant to a particular product and therefore is not suitable for evaluating the environmental impacts of products. Additionally the translation of economic quantities into environmental impacts is not validated.

b) Ecologically-based Life Cycle Analysis

Most conventional Life Cycle Analyses use many of the same approaches and strategies as an Eco-LCA, the latter considers a much broader range of ecological impacts. It was designed to provide a guide to wise management of human activities by understanding the direct and indirect impacts on ecological resources and surrounding ecosystems.

6.6. Analysis and Assessment of Life Cycle of Products and International Networks of Standardization

The scientific assessment of the life cycle of products has become a very important features of many manufacturing products, processes and systems. The standardization of these analytical tools and assessment with similar qualitative and quantitative was the next movement by international organizations. The International Organization for Standardization (ISO) in Geneva of Switzerland undertook to standardize the procedure of various Life Cycle Analysis and Assessements.[11]

Figure 6.7. The International Organization for Standardization (ISO) has developed over 18 500 International Standards on a variety of subjects.

The International Organization for Standardization (ISO) is a global network with national offices with experts for standardization in 162 countries. The headquarters are in Geneva of Switzerland which coordinates the system. ISO is non-governmental organization which builds bridges between the state and private sections of the economy.

The equivalent organization in Greece is the **Ελληνικός Οργανισμός Τυποποίησης** (**ΕΛΟΤ**) [Hellenicos Organismos Tipopiesis, Greek Organization of Standardization], established in 1976, under the auspices of Ministry of Industry and Development, as a Anonymous Company under the title «ΕΛΟΤ Α.Ε.».The basic functions of GOS is the translation and dissemination of standards, the certification and validation of labels to various industries, workshops and services for the standardization, the follow up on standards, testing and research and the arrangement for educational material and educational lectures on standardization (ΕΛΟΤ, 50, Kifisou Street, GR-12133, Peristeri, E-mail: info@elot.gr ,Web: www.elot.gr/)].

6.6.1. Various Standards on Life Cycle Analysis and Environmental Management

There is a great variety of standards for life cycle analysis or assessment of products, environmental management, eco-labels, environmental principles and procedures eco management, etc.

a. The series ISO 14000 is the best known environmental management standards. ISO 14000 can help organizations to (i) minimize how their operations and processes negatively affect the environment, (ii) for organizations to comply with applicable laws, regulations, and other environmentally oriented requirements, and (iii) continually improve in their installations, processes and conservation activities. Standard ISO 14000 is similar to ISO 9000 quality management in that both pertain to the process of how a product is produced, rather than to the product itself. ISO 9000, certification is performed by third-party organizations rather than being awarded by ISO directly.

b) ISO 14001 Standards. The standard 14001 is not an environmental management system as such and therefore does not dictate environmental performance requirements, but serves instead as a **framework** to assist organizations in developing their own environmental management system. ISO 14001 can be integrated with other management functions and assists companies in meeting their environmental and economic goals.

c) Various ISO 14000 Standards (selection)

ISO 14001 Environmental management systems—Requirements

ISO 14004 Environmental management systems—General guidelines on principles, systems and support techniques

ISO 14020 series (14020 to 14025) Environmental labels and declarations

ISO 14031 Environmental performance evaluation—Guidelines

ISO 14040 series (14040 to 14049), Life Cycle Assessment, LCA, regulates pre-production planning and environment goal setting.

ISO 14062 guidelines, making improvements to environmental impact goals.

ISO 14063 Environmental communication—Guidelines and examples

ISO 14064 Measuring, quantifying, and reducing Greenhouse Gas emissions.

From the various international standards the most important for the life cycle pf products and their environmental credentials are:
ISO 14021 (1999) environmental labels, declarations, ISO 14024 (1999) environmental labeling-principles & procedures, ISO/TR 14025 (2000), Type III, environmental declarations-guiding principles and procedures.

The standards related to LCA are: 14040 (1997) “on goal and scope definition and inventory analysis”, ISO 1402 (2000) “on life cycle impact assessment”, ISO 14043 (2000) “on life cycle interpretation”. Also, standardization of methods and applications on LCA (LCA, International Standard/TR ISO TR 14062 (2000), and ISO 14040 (1997) on improvements of LCA and assessment, ISO/TR 14062 (2000).

The regulation of the European Union for the ecological management and system of auditing environmental impacts is very important: **Eco Management and Audit Scheme, EMAS, 1993 (EK 1836/93).** This is voluntarily accepted procedures in order for companies and enterprises to manage their products and industrial manufacturing processes. In the EU from 1992 there is the (EC 880/92) Regulation for **Eco Label Scheme.** Products with low environmental impact and friendly to water, and air and soil and with not toxic substances are given the Eco Label indicating to the consumer their superior quality and environmental credentials.

EU Ecolabel
www.ecolabel.eu

Figure 6.8. The Eco Label logo which can be added to products which have been verified by certified environmental organizations in the European Union.

LCA

Figure 6.9. Life Cycle Analysis of Lewis trousers and for other products has become a standard procedure now.

6.7. Data Banks on Information and LCA of Industrial Products

Prior to the development of the ISO 14000 series, organizations voluntarily constructed their own Environmental Management Systems, but this made comparisons of environmental effects between companies difficult and therefore the universal ISO 14000 series was developed (2004). An EMS is defined by ISO as: "part of the overall management system, that includes organizational structure, planning activities, responsibilities, practices, procedures, processes and resources for developing, implementing, achieving and maintaining the environmental policy' (ISO 1996 cited in Federal Facilities Council Report 1999). The standards ISO 14001 (2004) is implemented by more than 200.000 organizations in 155 countries worldwide.

Many industrial enterprises and companies have developed their own data banks for the Life Cycle Analysis or Assessment of their products (LCAs) giving the opportunity for inspection of their methodology by other researchers and for comparison with similar products.

For example, The Association of Plastics Manufacturers in Europe, APME, (www.apme.org) has been in the forefront of publishing electronically their LCA methods in data banks for their products. Other associations are [12]
The European Aluminium Association, (www.aluminium.org),
The European database, Europe for Corrugated Board - live cycle studies, (www.fefco.org),
International Nickel Products, LCAs (www.nidi.org),
The Steel Industry , LCA (www.worldsteel.org/env_lca.hp) ., etc.

Most researchers and analysts used specialised computer software (dedicated software) for the needs of Life Cycle analysis or Assessment of industrial products, or services or processes.

There are mainly three types of software for LCAs:[13]

a) Generic LCA software, typically intended for use by researchers, consultants and other LCA specialists,

b) Specialized LCA-based software of various types for specific decision makers, typically intended for use by designers in engineering or construction, the purchasing department, or environmental and,

c) Tailor-made Software for LCA, special software for particular customer and product (tailor made/ custom software**)**, The globalization of big industries and commercial enterprises, covering 5 continents and a great number of countries has made the standardization of Life Cycle Analysis (LCA) and other environmental legislation very difficult to implement. There are multiple regulations, different environmental standards and differences in working conditions and health and safety laws.

International organizations have special departments dealing with the specialized problems and different standards all over the world. With time most of these standards have become international.[14]

Motor vehicle manufacturers have extensive research departments dealing with Life Cycle Analysis and quantitative assessment studies and associated problems of their products under various environmental conditions in various continents and countries.[15-18]

. Although every industrial product is accepted to have different durability and life cycle in hot temperatures and cold climatic conditions, some parameters of LCAs remain constant and change only marginally.[19]

. The European Union, has promulgated various studies for LCA of industrial products.[20-22] Also, the UNEP (United Nations Environment Programme) in cooperation with SETAC (Society for Environmental Toxicology and Chemistry, USA) in 2002 initiated a programme for the scientific basis of assessments on the life cycle of industrial products.[23-26]

Some useful information and data banks on LCAs can be found in the following organization

The European Commission's Directory of LCA services, tools, databases, and provider,

The European Commission's LCA database ELCD (free of charge)

UNEP/SETAC Life Cycle Initiative; a stakeholder financed project

Department Life Cycle Engineering – LBP – University of Stuttgart.

Embodied Energy: Life Cycle Assessment*.* Your Home Technical Manual. A joint initiative of the Australian Government and the design and construction industries

LCA research at the Centre *for Environmental Sciences, Leiden University*

***American* Chemical Council,** Explanations on LCAs by the ACC

The National Risk Management Research Laboratory's LCA website

Life Cycle Analysis of industrial products has become an international responsibility for the majority of industrial manufacturers and can provide beneficial insights for the quality of various materials and equipments, their efficiency under environmental conditions, recycling and disposal.

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7. Green Chemistry and the Pharmaceutical Industry

7.1. Pharmaceutical and Drug Manufacturers. Can the Pharmaceutical Industry Embrace Green Chemistry?

Green Chemistry and Green Engineering have influenced in recent years the most important chemical industries and inevitably the Pharmaceutical industry is in the forefront for big changes towards ”greener” feedstocks, safer solvents, alternative processes and innovative ideas. All these changes will increase the environmental credentials of the pharmaceutical and at the same time the cost of the operations.[1,2]

. The pharmaceutical industry is embracing more and more “green” processes and technology operations. The research departments of many big drug manufacturers in the developed countries are advancing new methodologies, better biocatalysis reactions, less solvents and cuts in waste production. At the same time the pharmaceutical industry introduce safety and health regulations to protect the workers and environmental criteria for their products. Safety, Efficiency, Reliability and Economy are the four pillars of change and their promotion is considered as a competitive advantage, better environmental credentials and economical benefits.[3]

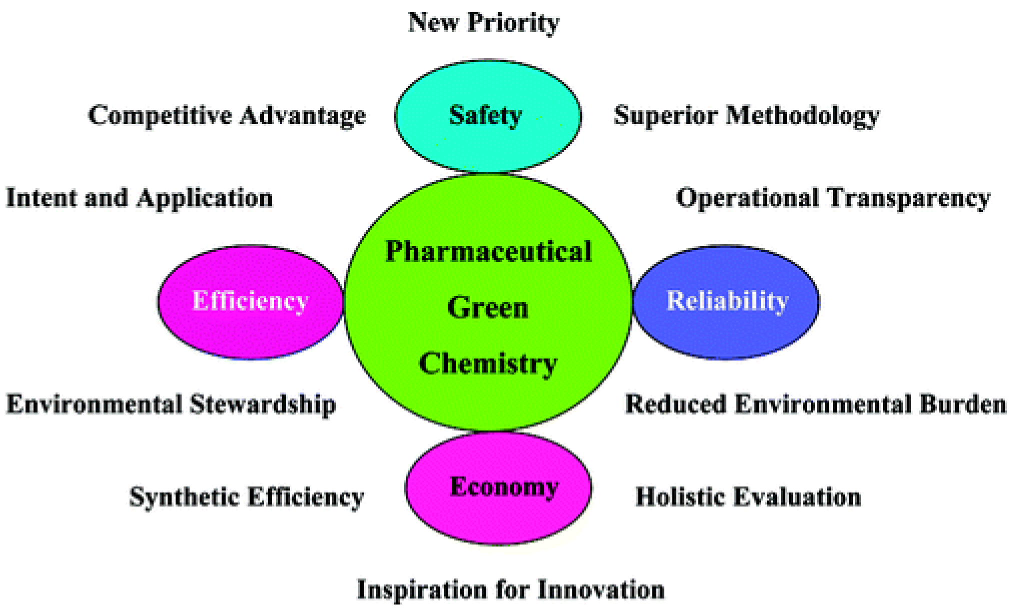

Figure 7.1. Schematic representation of the activities of pharmaceutical industries towards green chemistry principles and better applications of green engineering methodologies.

The pharmaceutical industry is well known for its intensive use of many petrochemical starting materials, conventional synthetic routes with conventional techniques, high energy requirements for industrial processes, high use of organic solvents for separation and purification, and production of high volume waste.

The Pharmaceutical industry is the most profitable of the chemical industries and its growth increases by 5-6% every year. On the global scale the Pharmaceutical industry produced drugs (2008) with the value of ~740 billion $. Half of these drugs (market sales) are produced in USA (53.5%), EU countries 28% and Asia-Pacific (Japan, Australia) 18.5% of drugs value. The five countries with most pharmaceutical industries are USA, Germany, UK, Japan and France (global pharmaceutical, www.pharma-mag.com)..

It is known that the Pharmaceutical industry produces more waste per Kg of product than other chemical industries (petrochemical, bulk & fine chemicals, polymer, etc). The pharmaceutical industry produces, for 6-8 steps organic synthetic routes, 25-100 kg of waste for every one Kg of product.[4,5]

The pharmaceutical industry depends on organic synthetic processes for its manufacturing of drugs and uses a variety of organic solvents for separation and purification of their products. Organic solvents are known for their toxic properties and the cost of their waste. It has been estimated that the big pharmaceutical company **GlaxoSmithKline** (GSK, UK) uses in its manufacturing large amounts of solvents and its non-water liquid waste contain 85-90% organic solvents.[8,7]

In the last decade pharmaceutical manufacturers embraced green chemistry ideas to promote their environmental credentials and increase the efficiency of their manufacturing processes. The Research and Development (R&D) departments of most pharmaceutical companies use a large percentage of their capital for investment in research for new drugs and innovative "green" synthetic routes. It is estimated that the discovery, research, clinical trials and distribution of a new drug is valued at 70 million $. It is inevitable that pharmaceutical companies would like to invest also in better efficiency, less toxic reagents and solvents, and environmental protection.[8]

An additional problem with the pharmaceutical companies are the new regulations for environmental pollution of water sources, not only from industrial waste, but also from traces of the drugs and medicinal products produced. It has been found that low concentrations of drugs and their metabolites were found in rivers, lakes and in coastal regions, affecting aquatic organisms (fish, benthic organisms). There is great need for pharmaceutical manufacturers to change into "greener" methods, less toxic reagents and solvents and to minimize their effluents and solid waste.[9-11]

7.2. Pharmaceutical Industry, Green Chemistry and Use of Solvents

The USA has the biggest pharmaceutical companies in the world and produces more than 50% of drugs and medicinal products. Studies showed that U.S. pharmaceutical processes use large amounts of organic solvents and their liquid waste is 85% non aqueous. The reduction in the use of organic solvents is an important issue in the pharmaceutical industry. New organic synthetic routes with minimum of “zero” solvents are in the research stage.[12]

The solvents which are lately more acceptable for organic synthetic processes have low toxicity: acetone (CH_3COCH_3), ethanol (CH_3CH_2OH), methanol (CH_3OH), 2-propanol ($CH_3CH(OH)CH_3$), ethyl acetate (EtOAc), isopropyl acetate, methyl ethyl ketone ($CH_3COCH_2CH_3$), 1-butanol and tert-butanol.

Solvents that are used for their ability to dissolve other chemicals, despite their toxicity, are: cyclohexane, n-heptane, toluene, methylhexane, methyl t-butyl ether, isooctane, acetonitrile, tetrahydrofuran (THF), 2-methylTHF, dimethylsulfoxide (DMSO), acetic acid and ethylene glycol .

Solvents that are been replaced in organic syntheses because of their high toxicity are: pentane, bis-isopropyl ether, diethyl ether, dichloromethane, chloroform, dimethyl formamide (DMF), N-methyl-2-pyrrolidone Pyridine, dimethyl acetate, 1,4-dioxane, benzene, carbon tetrachloride, trichloroethylene (TCE).[13]

The pharmaceutical industry has initiated many studies on the replacement of toxic solvents with solvents that are benign to human health (especially to their neurotoxicity and skin effects) and the environment.[14,15]

The **E factor** is a simple metric of Green Chemistry which can measure the efficiency of an industry concerning solvents and waste (defined and introduced by Roger A. Sheldon).. The E-factor calculation is defined by the ratio of the mass of waste per unit of product:

E-factor = total waste (kg) / product (kg)

The Green Chemistry metric is very simple to understand and to use. It highlights quantitatively the waste produced in the process as opposed to the reaction. It is one the 12 Principles of GC that measures the waste production. The E-factors ignore recyclable factors such as recycled solvents and re-used catalysts, which obviously increases the accuracy but ignores the energy involved in the recovery. It is well known from industrial data that the Pharmaceutical industry produces 25-100 kg of waste per kg of products, compared to 0.1 kg for the industry of oil refining, 1-5 kg in bulk chemicals industry and 5-50 kg in fine chemicals industry. [16]

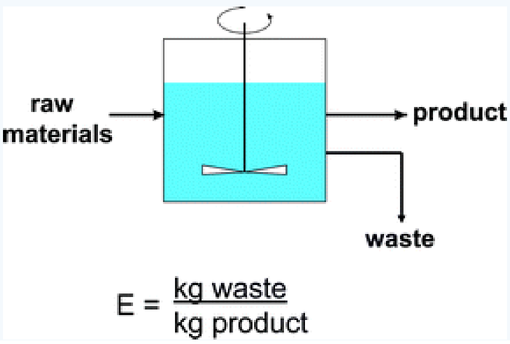

Figure 7.2. The E factor is a simple Green Chemistry parameter which can estimate the waste produced per kg of product and promote minimization of waste and solvent used.

Pharmaceutical industries are in the forefront of industrial enterprises which try to modernise their manufacturing operations and reduce their waste production. New and innovative techniques are developed for chemical synthesis at room temperature, with ionic liquids, with the use of microwave and sonochemical techniques, supercritical CO_2 and biocatalysis. Also, the pharmaceutical industries promote research in “green solvents” for more than a decade.[17-20]

7.3. Biocatalysis and its applications in the Pharmaceutical Industry

For many decades enzymes were used in food industries and in various organic synthetic routes. New catalytic synthetic methods in organic chemistry that satisfy increasingly stringent environmental constraints are in great demand by the pharmaceutical and chemical industries. In addition, novel catalytic procedures are necessary to produce the emerging classes of organic compounds that are becoming the targets of molecular and biomedical research. Enzyme-catalysed chemical transformations are now widely recognized as practical alternatives to traditional (non-biological) organic synthesis, and as convenient solutions to certain intractable synthetic problems. After many years of research the application of enzymes and biological materials in the pharmaceutical manufacturing has come to fruition and has become widespread in many organic synthetic methods. [21,22]

Biocatalysis has become a central issue of Green Chemistry and the application in chemical manufacturing can become very promising. Enzymes (proteins) can accelerate a reaction, lower the use of energy, use alternative starting materials, reduce the use of solvents and the production of waste. Enzymes are biomaterials that can biodegrade under environmental conditions. They are considered alternative and renewable chemicals and their cost is very low for application in the pharmaceutical industries. The enzymes have the advantage to cut down the number of steps in an organic reaction and can produce clean products with no need for purification.[22-25]

The well known pharmaceutical industry **Pfizer** has been experimenting for years with biocatalytic reactions in their manufacturing processes of drugs. Pfizer changed the process of an active substance, called pregabalin, in their drug manufacturing. Is the active ingredient of the medicine Lyrica (trade name). Pregabalin (2003) is an anticonvulsant drug used for neuropathic pain and as an adjunct therapy for partial seizures.

The drug has annual sales of approximately, 1.8 billion $ (2007). The synthetic route was conventional and used organic solvents. After many years of research, in 2007 Pfizer used enzymes for biocatalysis of the basic steps in the synthesis, reducing by 90% the use of solvents and by 50% the starting material. The E factor of the synthesis was reduced from 86 to 9. It is estimated that the company will reduce its industrial waste by 200.000 metric tones, compared to the old method, in the period 2007-2020.[26]

There are many successful examples of biocatalysis in the pharmaceutical industry for drug manufacturing. Pfizer synthesized the antiparasitic drug Doramectin (under commercial, trade name Dectomax).

Changing into biocatalysis in the synthesis increased efficiency of the reaction by 40% and reduced the by-products.

Another successful introduction of biocatalysis by the same company was for the synthesis of the drug **atorvasratin**, and the synthesis of artemisinic acid for the antimalaria drud **artemisinin**. Pfizer did some thorough research for the improvements of the yeast *Saccharomyces cerevisiae* in biocatalytic mechanisms.[27] Biocatalysis improved the efficiency of synthetic routes for the industrial production operation of the drugs **Oselravimit** and **Pelitrexol**.[28,29]

Another well known pharmaceutical industry that applied Green Chemistry principles and biocatalytic methods in the drug manufacturing is **Merck**. These changes brought substantial reductions in the use of solvents and increased efficiency. A success story is the synthetic biocatalysis of the antibiotic drug Gemifloxacin.[30,31] Similar success was achieved in the asymmetric hydrogenation reaction for the synthesis of the drug Taranabant.[32] A second generation synthetic route of the drug pregabalin in water has been published recently by Pfizer researchers.[33]

The other well known chemical and pharmaceutical companies **BASF** and **DSM Pharmaceuticals** (New Jersey) have advanced their research into biocatalysis and applied the method for the synthesis of their drugs. At **BASF** they used biocatalysis primarily for the production of chiral chemical intermediates required for the production of medicines. Enzymes in living organisms quite selectively prefer one form over the other of chiral compounds in the biological conversion process. BASF takes advantage of this principle in the biocatalytic manufacture of substances in technical plants. The chemical industry **Johnson Matthey** recently bought the German research company X-Zyme (Dusseldorf) for its biocatalytic innovative methods. The company after years of research establish biocatalytic transformation of ketones and keto-esters in chiral amines. These are starting materials for the production of chemicals and drugs.[34]

An interesting success story of the pharmaceutical industry is the enzymatic catalysis of one of the active subsytance in the famous medicine Lipitor (reduction of cholesterol). The synthetic route is considered a representative “green” synthesis of an intermediary (key component) for the active compound atorvastatin.[35]

Figure 7.3. The company **Codexis** won the Presidential Green Chemistry Challenge Award (2006) for the “green” biocatalytic synthesis of the active substances of Lipitor.

The Codexis (Redwood City, CA, USA) is an international company that markets enzymes and intermediates to global pharmaceutical manufacturers. Codexis biosolutions improve product purity and yields, reducing production process steps, eliminating toxic substances from the manufacturing process. Tailored enzymes enable targeted chemical processes to manufacture the specific pharmaceutical product with efficient manufacturing, lower costs and greater profitability. Merck and Codexis have jointly developed a new manufacturing process for **sitagliptin**, the active ingredient in Januvia (Type 2 diabetes). Merck and Codexis reported a 10-13% increase in overall yield, a 53% increase in productivity. Codexis is supplying pharmaceutical intermediates for the cholesterol-reducing drug Lipitor from Pfizer. Codexis won the US EPA Presidential Green Chemistry Challenge Award in 2006 (www.codexis.com/pharmaceuticals)..

These examples are some of the applications of biocatalytic methods in the pharmaceutical industry which support at the same time Green Chemistry principles and work for the sustainable future of the chemical industry. Enzymes frequently display exquisite selectivity, particularly chemo-, enantio- and regioselectivity, making them attractive catalysts for a wide range of chemical transformations. Also, enzymes operate under mild conditions of pH and temperature leading to the formation of products of high purity. Modern tools of protein discovery and engineering aid the development of novel biocatalysts and their tailor-designed implementation into industrial processes. Consequently, they find wide application in the production of pharmaceutical intermediates, fine chemicals, agrochemicals, novel materials, diagnostics, biofuels and performance chemicals.[34,36]

7.4. Green Chemistry and Pharmaceutical Industry

All these new developments in the pharmaceutical industries and other changes which are not been described for lack of space in this book, showed that Green Chemistry and Green Engineering principles are spreading to the most efficient chemical industry.

Figure 7.4. The Pharmaceutical industries have successfully applied the lessons of Green Chemistry and Engineering for the production of drugs.

The new methods of Green Chemistry have positive results in the pharmaceutical industry because their R & D investment is very robust and can cover research expenses and support innovative ideas. By applying Green Chemistry methods the pharmaceutical industries have better efficiency and lower cost for their operations, lower solvent use, less waste and improvement in the "green" credentials of the industry.[37-39]

In the last decade the pharmaceutical industry encounters some intractable problems with the disposition of large amounts of their products in landfills. There are no solution "cradle-to-cradle" and some products after their expiring date have to be destroyed (by incineration). Also, the environmental pollution of water sources from rejected medicines, metabolites and medical products is a serious problem.[40,41]

An article in Chemistry World (monthly magazine of Royal Society of Chemistry, July, 2008) describes the attractive combination of Green Chemistry principles and the economic benefits in the pharmaceutical industry at a period that patent expiries of bestselling drugs are in the near future and companies must meet the cut of costs.

"…The pharmaceutical industry's current drive to curb spending is helping to speed the adoption of green chemistry, say experts in the industry. Faced with looming patent expiries of their big-selling blockbuster drugs, and a lack of candidates set to replace them, many companies in the industry are looking to dramatically cut their costs. But far from being driven off the agenda by core activities, the importance of green chemistry is growing in many companies. "There's clearly a lot more cost pressure in the pharmaceutical industry these days, especially as the cost of discovering and developing drugs continues to increase", Peter Dunn, green chemistry lead at Pfizer, told *Chemistry World*. "But green chemistry offers significant cost advantages and hence is part of the solution to the problem."

"…The savings come about because efficient syntheses that avoid exotic reagents, minimise energy use and replace organic solvents with water are invariably cheaper to perform. "Even at lab scale, cost savings can be realised, and manufacturing scale process changes can save millions of dollars," says James Long, who's also on Pfizer's green chemistry team.

In 2005, several firms, along with the American Chemical Society's Green Chemistry Institute (GCI), established the **GCI Pharmaceutical Roundtable**, to promote the integration of green chemistry and green engineering in the industry. Nine companies - including Pfizer, Johnson & Johnson, AstraZeneca and GlaxoSmithKline (GSK) - are now roundtable members. At GSK as at Pfizer, belt-tightening has led to an increased focus on Green chemistry. "Specifically for GSK, the appointment of Andrew Witty as CEO has shone a spotlight on manufacturing efficiencies, and green chemistry has received a great boost as a result," says David Constable, responsible for promoting sustainable practices in R&D and manufacturing through green chemistry and engineering at GSK. "Going green is cost beneficial; it just has the perception that it is more expensive to do. In every case I know, the green option is the low cost option".

The industry is also starting to analyse the green credentials of chemical feedstocks bought in from external suppliers - an important shift, given that increased outsourcing is another outcome of pharmaceuticals' cost-cutting drive. At the 2007 pharmaceutical roundtable meeting, members agreed to include outsourced feedstocks when calculating their total mass productivity - the number of kilograms of material used per kilogram of final product - as a metric to compare performance from company to company. This agreement forces us to engage with our suppliers, to come up with the best solution,' says Henderson. The roundtable was set up to share best practice, but we're also very competitive…." [42]

Scientists believe that Green Chemistry is going to transform the pharmaceutical industry and drug manufacturing in the future. Green Chemistry can deliver both environmental and economic benefit and the pharmaceutical industry is keen to adopt most of its principles. Although Green Chemistry philosophy has been generally accepted by the scientific community, technical Green Chemistry evolution through education, investment, and exemplification has yet to achieve the appropriate attention and effort.[43-46]

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8. Green Chemistry and Sustainable Agriculture

8.1. Population Growth and the Food Crisis

World resources and their sustainable use is the most important global issue of the last decades. Inefficient use and wasted or polluted natural resources for excessive demands of consumer products it will lead to disastrous results. Green Chemistry and Green Engineering are aiming to reverse this trend and promote sustainability.

In December 2011 the EU Commissioner for the Environment Janez Potocnik in his annual address for the economic crisis in the eurozone said : "….It is difficult to imagine lifting Europe (and for the rest of the world) out of recession without growth. It is very difficult to imagine growth without competitiveness, and very difficult to be competitive without resource efficiency. Unless consumers and businesses take action to use resources more efficiently (from energy and water to food and raw materials such as precious metals, fossil fuels, etc), then their increasing scarcity, rising prices and today's wasteful methods of using them, will drive up costs yet further and reduce Europe's standards of living..."

"….We have simply no choice. We have to use what we have more efficiently. Resource efficiency is a real competitiveness issue for us. The current economic models used have failed to take into account the rapid changes all over the world, and one of most associated problems is that cheap resources and an inefficient use of raw materials and energy is at the core of the problem. Resources use and inefficiency has become the "mainstream" issue of economics…." (newspapers, 27 December, 2011).

The World population on Earth for thousand of years remained very low due to parasitic and infectious diseases and epidemic which reduced life expectancy to around 35 years. In 1000 AD the population was 275 million and in 1850 reached 1.2 billion people. The Middle Ages (14th-16th century) show the spread of epidemic and famines which exterminated vast numbers of people. Life expectancy dropped to 30 years in the period of the Great Famine (startted1315) because of the death of most children. The Great Famine was the first of a series of large scale crises that struck Northern Europe. From the Pyrenees to Russia and from Scotland to Italy it caused millions of deaths over an extended number of years and marks a clear end to an earlier period of growth and prosperity during the eleventh to thirteenth centuries. Later, during the Black Death (1411) period which was one of the most devastating pandemics in human history life expectancy dropped to 17 years of age.

In 1900 the world population was 1.6 billions. But in the 20th century the world population has grown tremendously fast. In 1950, the population almost doubled (despite two world wars and deadly infectious diseases) reaching

2.55 billions. In 1999 passed 6 billion, in 2008 the population became 6.8 billion and in the end of 2011 it reached the 7 billion mark.

This dramatic increase of the world population inevitably demanded tremendous increases in food production, but at the same time agricultural land in the last 100 years increased only twofold. This is a big challenge for human civilization, to increase food production but in a sustainable way because of the negative effect on depleting natural resources.

Each day 200,000 more people are added to the world food demand. It took only 12 years for the last billion of people to be added. These people need housing, food and other natural resources. The largest population increase is projected to occur in Asia, particularly in China, India and Southeast Asia, accounting for about 60% and more of the world's population (UN Population Division, 2007).[1,2]

For most of history, humans hunted or grew food for their own consumption, and food travelled only short distances inside a country. In the past, droughts, invasions of devastating insects, lack of water for irrigation, degradation of top soil, floods and other large scale natural disasters, combined with rapid population growth caused many famines in various regions of the world. The range of famine prone regions in the world has been shrinking for centuries. Currently famine regions are mainly limited to sub-Sahara Africa. Yet the impact of endemic hunger has not declined and the early 21st century seems to be faced with a new threat: global subsistence crises. The food crisis is visible in many parts of the world, especially in Africa. Also, the distribution of the global food production is uneven and some regions produce excessive amounts of food.[3-5]

Worldwide enough food is produced to feed everyone, yet this food and the technology to produce it do not always reach those in need. As a result of food deficits, it is estimated that in the last decade of the 20th century, one billion people every year do not get enough food for their needs and 400 millions are chronically malnourished. Every year 11 million children (aged 1-5 years old) die from hunger or hunger-related diseases due to lack of food and infections related to starvation.[6-8]

In the other hand food production has increased substantially because of chemical fertilisers and pesticides and recently due to biotechnology . The question that challenges the whole scientific community is can food production keep pace with population growth for the next half-century? [9,10]

This is a very difficult problem and an issue of sustainable development. The production of food has to be increased in a sustainable way to feed the hunger of people in various regions of the Third World countries but instead it is wasted in countries with excess food production. The international food crisis is going to continue, unless new changes and better distribution is taken place in the next 50 years.

In recent decades there has been impressive growth in food production, which has been attributed to the development of improved, disease-resistant varieties of staple crops (transgenic plants); the increased use of chemical fertilizers and pesticides; and the expansion of irrigated cropland. Nevertheless, per capita food production actually declined in 51 developing countries while rising in only 43 between 1979-1981 and 1986-1987. Among the African countries, 25 experienced a drop in per capita cereal production. In Latin America, production was also disappointing: 17 countries suffered a decline. In Asia, food production has managed to keep slightly ahead of population growth largely because of new breeds of Asian rice and the use of tremendous amounts of agricultural chemicals. However, in some areas losses from poor land management have erased the benefits which had been gained. Consequently, developing countries' food imports are rising dramatically to compensate for local deficits.

The United Nations warns the world's farmers will have to double the amount of food they produce to keep up with a rapidly growing population. The U.N.'s latest World Economic and Social Survey indicated that global food production will need to jump by 70-100% by 2050 to feed an anticipated 9 billion people. The report says such a dramatic increase in food production will only happen if countries make a concerted effort to use production methods that are much less harmful to the environment. It says without making major changes, food production will suffer as a result of climate change and pollution [United Nations, World Economic & Social Survey 2011. *The Great Green Technological Transformation*. UN/DESA, New York, 2011, (www.un.org/en/development/desa/policy/wess/wess/current/2011wess.pdf)]

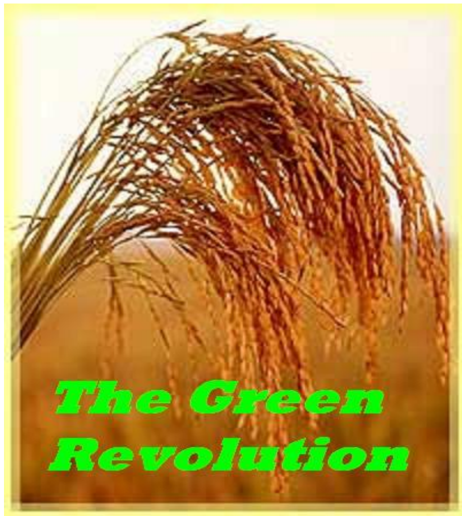


Figure 8.1. The “Green Revolution” (1960s) in various countries, especially in Asia, managed to increase the yields of many staple foods (cereal, rice) and stopped the food crisis which were endemic in the previous decades. But, the environmental pollution due to these increases was also an important negative factor to be taken into account.

In the last decades, starting form the 1940s and following the lead in the 1960s, research organizations produced interesting research developments called “**green revolution**:” . High-yielding varieties (hybrids) of cereal grains, rice and soy increased the agricultural production around the world. The initiatives, led by Norman Borlaug, the "Father of the Green Revolution" credited with saving over a billion people from starvation, involved the development of high-yielding varieties, expansion of irrigation infrastructure, modernization of management techniques, distribution of hybridized seeds, synthetic fertilizers, and pesticides to farmers.[11]

Despite the big changes in agricultural production and the substantial increase in food, chronic malnourished people exist in various countries of the planet. The opposite is happening in most countries of the developed world, with obesity and bad food consumption leading to a rapid increase in obesity. The obesity epidemic is a worldwide phenomenon. Obesity is not just a disease of developed nations. Obesity levels in some lower-income and transitional countries are as high as or higher than those reported for the United States and other developed countries. Shifts in diet and activity are consistent with these changes.[12,13]

In the other hand, increases in food production, intensification and mechanization of agricultural and husbandry processes resulted in desertification, degradation of the top soil, dramatic reduction of fresh water resources, environmental pollution by fertilisers and pesticides. These environmental impacts threatened to decrease the prospects for additional food production. Food security is at stake. It is estimated that lack of fresh water resources and degradation of farming soil will decrease production by 25% until the year 2050.[14]

Global Warming and the “Green House” effect is another threat to food production. Future changes in temperature in some regions will increase food prices. Also, increases in food prices in 2008 had a number if immediate factors, such droughts in major wheat-producing countries in 2005-06, low grain reserves, high oil prices, a doubling of per-capita meat consumption in some developing countries, and finally diversion of 5% of the world’s cereals to agrofuels. The above range of issues have been the subject of much mainstream media attention and there has been some debate as to how much of an impact the recent rise in biofuels has actually contributed to the rising prices. All these factors will be prominent in the future.

According to UNEP, the increases in food prices of 2008 resulted in an additional 110 million people worldwide to face poverty. It is considered that these trends might contribute to an increase in food prices by 50% in the next decades.[15,16] The problem of water resources for agriculture is very important. Studies showed that lack of fresh water in the future can decrease the cereal grain production by 12%. Other problems in agriculture, from loss of fertile top soil, pests and virus infections can decrease the arable land by 6% worldwide in the next 50 years.[17]

The production of the most important stable food products has increase dramatically in the last decades but also consumption. Global meat and dairy products is expected to increase form 225 million tones (1999-2001) to 465 million tones in 2050. In the same period production of milk from 580 million tones is expected to increase to 1043 million tones. But cereal production is expected to decrease by 5% and its consumption by 2%. Rice production increased substantially thanks to new hybrids to 456 million tones (2010). So, in the next 50 years the world is expecting increases but also decreases in food production due to climate change, desertification, decrease in fresh water resources and environmental pollution.[18-20]

8.2. Trends in Farming Practices and Sustainable Agriculture

Conventional agriculture (crops farming, livestock or husbandry, fish and forests) is a form of industrial production of food. Conventional or industrial agriculture relies on technology, agricultural machinery and intensified farming methods. The methods and techniques used in agriculture intend to achieve economies of scale in food production. These methods are widespread in developed nations and increasingly prevalent worldwide. Most of the meat, dairy, eggs, fruits, and vegetables available (estimated at over 90%) for consumers all over the world are produced using these methods of industrial agriculture.

In the last century the intensification and specialization of agriculture was inevitable. Agriculture relies on new technologies of agricultural chemicals (fertilizers and pesticides), mechanization, and plant breeding (hybrids and genetically modified organisms, GMO's). Conventional agriculture covered the human needs for food of an increasing population, but at the same time caused extensive environmental problems and wasted depleting fresh water resources. Also, agriculture increased the degradation rate of farming soil, caused extensive increase of nitrate pollution of water and various other types of environmental pollution. In this respect Green Chemistry would like to promote its expertise and innovative ideas as to what can be done to improve the environmental credentials of conventional agriculture and other types of farming. Green Chemistry would like to enhance the Sustainable Development of agriculture. [21]

In the last few decades new trends started to appear in the horizon with the intention to remedy some of these environmental impacts and make agriculture sustainable. The move towards **sustainability in agriculture** has developed by integrating ideas of socio-economic justice and conservation of resources and the environment within a farming system. This has led to the development of many responses to the conventional agriculture approach, including organic agriculture, urban agriculture, community supported agriculture, ecological or biological agriculture, integrated farming and holistic management, and increased trend towards agricultural diversification. The question is can Green Chemistry and Engineering achieve these changes.[21]

Organic agriculture is anew form of agriculture which gives emphasis to environmental conservation. Organic agriculture promotes the replacement of chemical fertilizers by compost and animal waste and the abandonment of chemical pesticides for the extermination of pests by biological means. The productivity of organic agriculture is much lower than the conventional and uses more land to produce equivalent amounts of food. It is performed mostly in small-scale farms for vegetables and fruit and at present covers up to 5-10% of the cultivated land and ~ 5% of livestock and poultry. The basic principles of organic agriculture are health (enhance the health of soil, plant and animal), ecology (help sustain ecologic systems, ecological cycles and biodiversity), fairness (ensure fairness to common environment), and care (responsible manner to protect health and well being of present and future generations).[22,23]

Another very promising methodology for agriculture is called **Good Agricultural Practices**, **GAP**). A “compromised” type of methodical agricultural practice which is supported by conventional technological advances and organic principles, high yields productivity and environmental protection with alternative innovations and strict management of adverse effects in farming and livestock production. It is an agricultural trend which support rational methods, low prices and health and safety for farmers.

GAP applies innovative or sustainable farming practices at different scales, such as integrated pest management, fertilizer management, conservation, surface tilling, crop rotation, limiting heavy tillage, use of green manure, avoid run-off of fertilizers, reduce erosion by wind through hedging and ditching, reduce soil salinization, etc. GAP relies on four principles: economical and efficient production of nutritious food (food security and food quality), sustainable use of natural resources (soil erosion) and minimum pollution (nitrate pollution, pesticide resistance, fertilizers when needed, etc), variability in farming and meeting cultural and social demands of society.[24-26]

Figure 8.2. Organic agriculture, Good Agricultural Practice, Integrated Pest Management, Sustainable or Ecological Agriculture are aiming to produce enough food for the increasing population but in sustainable way towards the depleting natural resources (farming soil, fresh water, biodiversity).

The international Food and Agricultural Organization (FAO, Rome) has issued guidelines for GAP. The European Union has established the European Protocol of certification for farmers who follow the GAP approach, the **EUREPGAP**, to verify consumers as to the quality of food products and the practices used for their production. (foodqualityschemes.jrc.ec.europa.en/eu/../6-Eurepgap_en.pdf). The commercial protocol of GAP is supported by a chains of shops in European countries with food. The U.S. Department of Agriculture operates an audit/certification programme to verify that farmers use GPA and Good Handling Practices.

Pesticide use in agriculture and pesticide residues in food products was always an important environmental and health issue. **Integrated Pest Management** (IPM) is a scientifically supported management plan for farmers which helps to reduce toxic pesticides. IPM is an ecological approach to agricultural pest control that integrates pesticides/herbicides into a management system incorporating a range of practices for economic control of a pest with minimized environmental impact.

In the EU countries, the IPM system is supported by the Directive EU 2009/128 which sets the rules and regulations for a scientific approach to pest control and prudent use of pesticides in various sectors of the agricultural operations. The IPM is covered in the developed countries by various rules and objectives which are part of common agricultural policies. At the same time the IPM plays an active role for farmers health and safety and minimization of pesticide residues in food. The pesticide residues issue is monitored extensively in the EU and the USA. The developed countries have started in the past decades to introduce restrictions in agricultural practices and to promote through subsidies alternative farming methods. Integrated Pest Management was one of them as well as monitoring and systematic analysis of pesticide residues in food and microbiological analysis of organic products.[27]

8.3. Quality of Soil, Conservation and Food Production

In the last century the area of farmland on a global scale increase by 2.5 times while food production multiplied tenfold. The conventional agricultural methods inevitable caused substantial erosion problems and soli conservation became an urgent environmental problem. FAO estimates that every year there a loss of around 50 million acres of agricultural land. The planet's total land area is 150 million km^2, but only 10% of the total is suitable for arable land. Permanent crops are 1%; meadows and pastures, 24%; forest and woodland, 31%. The remaining 34% is land surface that supports little or no vegetation:

Soil erosion and degradation of the top fertile part, overuse, acidification and salinization, are chronic problem and get worse with the years. Scientists and agronomists tried to promote various methods of agriculture in which the soil is conserved.

i) Crop rotation is a conventional alternation of crops to avoid nutrient depletion,
ii) Cover crops serve the function of protecting the soil from erosion,
iii) Windbreaks by trees or other means to protect soil erosion by winds,
iv) Contour plowing (or contour ploughing or counter farming) can increase crop yields from 10 to 50% partially as a result from greater soil retention ,
v) conservation tillage systems (No-till farming, also called zero tillage or direct planting or pasture cropping),
vi) Fallows called the temporary cessation of cultivation of the soil to regain productivity,

vii) Combination of cultivation of various plants to get rid of parasites and plant diseases

The retention of soil quality and conservation of its fertility has become a fundamental problem. Green Chemistry scientists have invested in researching and improving agricultural soils. They propose various also methods of integrated management of farmland, water resources, irrigation channels and biological composts.[28]

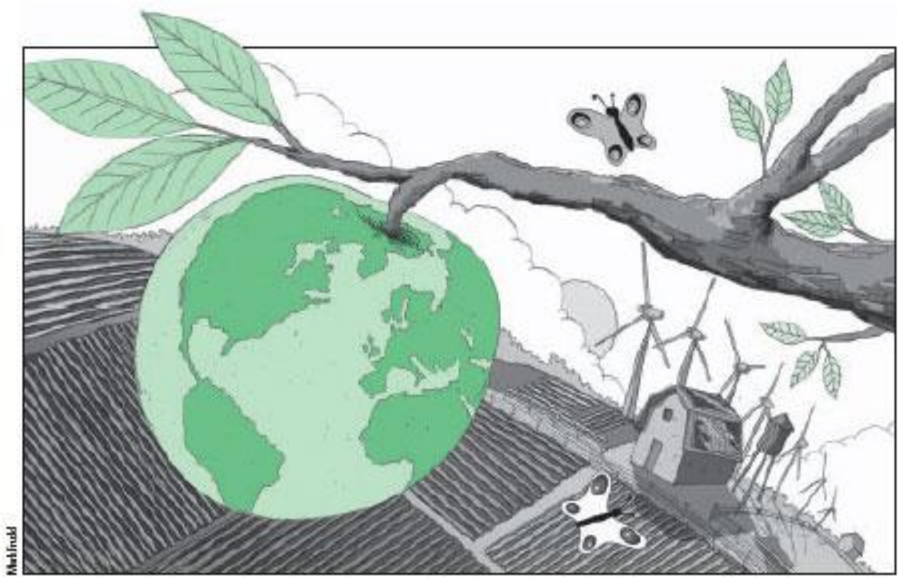


Figure 8.3. The Sustainability of agriculture and the conservation of soil and water resources has become a central issue in the Sustainable Development plans, with natural resources, ecosystem viability and biodiversity

In the European Union, the Directorate-General for Agriculture and Rural Development) has promoted extensive research on **the SoCo project** which supports sustainable methods in agriculture. (Joint Research Centre's, Ispra, Italy, http://soco.jrc.ec.europa.eu). The no-tillage system has been extended to various countries of the EU. In Finland and in Greece 10% of farmland is cultivated under the scheme. In Czech Republic Spain, Slovakia and UK is 5%. Reduced tillage is also applied to almost 25-50% of arable land of most of the European countries. Reduction in the use of fertilizers and pesticides is another aspect which is promoted through subsidies in the EU.

The latest trend in agriculture which was initiated a decade ago is the **Green Growth** policy from the UN. Green Growth is a policy focus for the Asia and Pacific region that emphasizes environmentally sustainable economic progress to foster low-carbon, socially inclusive development. Green Growth is a globally relevant approach to sustainable economic growth that was developed in Asia. The countries in the Asia and Pacific region must continue their economic growth to alleviate poverty, but at the same time must achieve social progress in combination with sustainable development. These countries with almost half of the planet's population meet their responsibilities for increased environmental degradation, climate change and diminishing natural resources.

The arable land on a global scale in the period 1985-2000 increased only by 5.5%, while the population increased by 24% (mostly in Asia and Africa). Developed countries managed to respond for the food demands but not in the developing and Third World countries. It is estimated that 30% of the food produced annually is wasted through collection, distribution and storage. Also, 50% of commercial food is wasted and it has to be diverted to landfills (supermarkets had to obey the law on dates of expiring use for fresh and dairy products). Scientists believe that this situation in the production and commercialization of food has to change. Achieving equitable distribution is not easy.[28-30]

UNESCAP's **Green Growth Programme** has evolved to emphasize the Sustainable Livelihoods Approach (SLA), a rights-based approach that recognizes the poor as a key stakeholder in the development process. Green Growth encourages the use of participatory assessments which identify the main constraints, opportunities and concerns faced by the poor and to include them into the policy planning and implementation cycle.

It is expected that global needs for food in 2050 will increase twofold from the present situation. But the preservation of natural resources and environmental protection are also very important issues. Sustainable Development in the only way to achieve these goals. The use of fresh water for agriculture from 40% which is now must be decreased, since around 50% (2050) of the population will live in areas with water shortages. Fish is covering a high percentage of the food needs of the population (around one billion). But an increase in global temperature by 3-5 ^{o}C will result in a decrease of the available fish and a substantial decrease in the production of wheat, corn, and meat (pork and cow).[31]

8.4. Can Green Chemistry Contribute to Innovative Solutions of Sustainable Agriculture?

Agriculture and conventional farm practices have substantial problems to resolve towards the road toy Sustainable Development. The question is, can Green Chemistry and its principles contribute to alleviate or minimize the most important problems of agriculture by offering innovative and sustainable solutions? Green Chemistry can contribute with innovative technology, "green" practices in water conservation and protection of the environment by promoting assessments of materials used and integrated programmes of conservation and eco-efficient approaches to land management.[32]

Improvement of farmland management and protection from erosion and salinization can be achieved with modern technological applications but the road to these applications are not easy to implement in large scale. Use of less fertilizers can be achieved with improvements in rate of absorption. New fertilizers with nutrient formulations (e.g. Next Fertizer System™) which are incorporated in complex compounds can be held in ready-to-absorb form. Nutrients can be incorporated in a proportion best suited for each crop type and soil situation, resulting in better Phosphorus and Nitrogen absorption. Formulation can be adjusted to required stability and release period according to need of the crop. New pesticides with lower toxicity and biodegradable metabolites are used already. Biological methods for pest control have been applied to a variety of crops with great efficiency and are environmental benign. The example of *Bacillus thuringensis* is a success story and it is used even in organic fruit and vegetables.

Biotechnology and genetically modified organisms is another scientific advancement towards sustainability. Despite the controversial dispute of their use, genetic plants can be very useful for increased efficiency. More and more scientists believe that technologies for genetically modifying foods offer dramatic promise for meeting some of the 21st century's greatest challenges. But like all new technologies, they also pose some risks, both known and unknown. Controversies surrounding GM foods and crops commonly focus on human and environmental safety, labelling and consumer choice, intellectual property rights, ethics, food security, poverty reduction, and environmental conservation. At present and after 20 years of controversies and regulations GM food and crops make a big difference towards sustainable agriculture. GM plants can be resistant to drought, increase their antioxidant nutrients and vitamins and resist virus and infectious diseases.

Genetically modified (GM) crops may contribute to increased productivity in sustainable agriculture, according to a groundbreaking study published in an article in the journal *Science* (8/7/2007). The study analyzes, for the first time, environmental impact data from field experiments all over the world, involving corn and cotton plants with a Bt gene inserted for its insecticidal properties.[33]

8.4.1. Improvements and management of soil quality in croplands.

Scientists for decades researched the issue of soil improvement and management for croplands. One very promising technology is the use of polyactylamide (PAM). A technological advancement which improves agricultural soil and cleans water. Polyacrylamide is a synthetic long-chain polymer designed to attract positively charged particles (organic material) or negatively charged particles (inert materials, such as sand or clay). PAM is a soil conditioner, stabilizes soil aggregates, reduces erosion and runoff while improving the quality of soil and water.[34]

Chemistry can offer various materials for the protection of the arable soil and improvements for the quality of soil in agricultural lands. Biotechnology also has to offer many solutions and technologies for soil erosion and management.[35,36]

Soil erosion of arable lands is a well known global phenomenon, especially in developing nations, because the need for food production is very important and the quality of cultivated lands very poor.[37] In the European Union for many years there is a dedicated **European Soil Bureau** that belongs to the Institute of Environment and Sustainability (Joint Research Centre, Ispra, Milan) and has accomplished extensive research on soil erosion and remediation techniques. Environmental remediation consists of the removal of pollution from soil, groundwater, sediment and surface water. Remediation is generally subject to an array of regulatory requirements.[38]

Also, there is an international network of scientific research institutes and laboratories (**Soil Erosion Network***)* which analyses data and do a lot of monitoring work and scientific studies on the issue. Some of the research results and their applications have been successful in improving soil quality and reduction of erosion.[39]

8.4.2. New pesticides. Biotechnological applications with biopesticides

Chemical pesticides played an important role in the last decades for the protection of crops from plant diseases and various pests. Despite the "bad" name that is connected with the extensive use of pesticides in the past (e.g. DDT, Rachel Carson's book "Silent Spring", 1962), pesticides had a serious role in increasing productivity. Some chemical pesticides are not biodegradable and their persistence (e.g. polychlorinated chemical pesticides) in the environment caused extensive pollution and adverse effects on certain animals and a decrease in biodiversity. Also, some pesticides were very toxic and caused extensive occupational diseases to farmers and pesticide applicators.

In the last two decades the scene in commercial chemical pesticides changed dramatically. Some persistent pesticides were banned, other were restricted and new pesticides with less toxicity and fast biodegradation were introduced. Green Chemistry and Green Engineering were involved in the innovative attempts to reduce pesticide toxicity and better techniques in their application. New pesticides, like pyrethroids, neonicotinoids and insect growth regulators, replaced old ones. Their properties were tested extensively before use for their benign environmental credentials and fast biodegradation. In addition, new biological pesticides found practical applications in agricultural crops, like the spinosyns, azadiractin and its analogues, and and *Bacillus thuringiensis.*[40-43]

Various natural pesticides were tested successfully in the protection of crops and agricultural products. The **Neonicotinoids** are a class of insecticides which act on the central nervous system of insects with lower toxicity to mammals. Neonicotinoids are among the most widely used insecticides worldwide, but recently the uses of some members of this class have been restricted in some countries due to a possible connection to honey-bee colony collapse disorder, though no scientific evidence has been established confirming that connection. Some of the most important insecticides of this category are acetamiprid, clothianiolin, dinotefuran, imidacloprid, thiacloprid and thiamethoxam. Several European countries suspended the use of certain neonicotinoid pesticides in response to incidents involving acute poisoning of honey bees. To EPA's knowledge, none of the incidents that led to suspensions have been associated with Colony Collapse Disorder.

Spinosyns is another form of new chemical class of insecticides used in crops. Spinosyns are secondary metabolites of the actinomycete (bacterium) *Saccharopolysporaspinosa*. The most important commercial spinosyn A and D, in the market they appear under the trade name spinosad. Spinosad has since been formulated into insecticides that combine the efficacy of a synthetic insecticide with the benefits of a biological pest control organism.

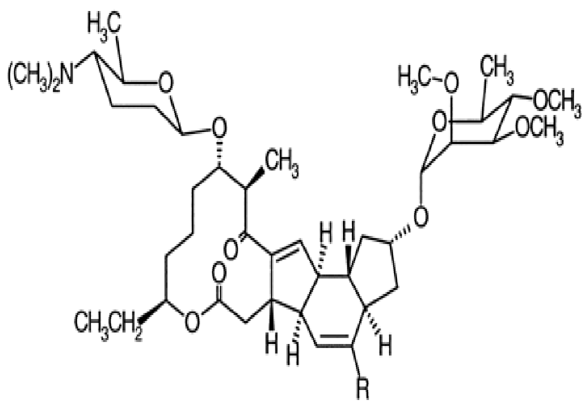
Avermectins (Αβερμεκτίνες) are natural products of the secondary metabolism of the bacterium *Streptomyce.* with potent anthelmintic and insecticidal properties. These naturally occurring compounds are generated as fermentation products by *Streptomyces avermitilis*, a soil actinomycete. Other anthelmintics derived from the avermectins include ivermectin, selamectin and abamectin. Synthetic analogues of avemectins are used as commercial pesticide products (emamectin και ivermectin).

Ryanoids are synthetic chemical insecticides with the same mode of action as the natural insecticide Ryanodine. This is an extract of alkaloids of the plant *Ryania speciosa* which is found as endemic plant in Latin America. The active substance is a mixture of ryanoidine (80%) and other ryanoids.

Pyrethroids are a group of synthetic pesticides similar to the natural pesticide **pyrethrum**, which is produced by chrysanthemum flowers. Althoug more than 1,000 pyrethroids have been made, only a few are used in the United States. These include permethrin (Biomist), resmethrin (Scourge) and sumithrin (Anvil). Pyrethroids are found in many commercial products used to control insects. Pyrethrum has been used for years as a natural insecticide.

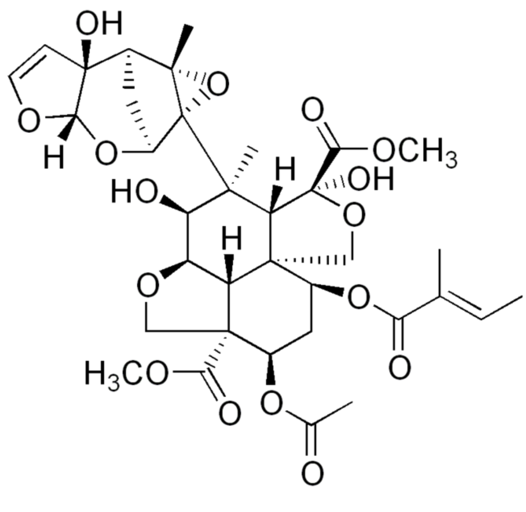
Azadirachtins another group of compounds that are use as natural pesticides. They are extracted from the seeds of the evergreen tropical tree Neem. The scientific name is *Azadirachta indica*. Scientists have synthesized analogues. Azadirachtin,is the active chemical compound, a highly oxidized tetranortriterpenoid. It is structurally similar to insect hormones called "ecdysones," which control the process of metamorphosis as the insects pass from larva to pupa to adult.

The bacterium ***Bacillus thuringiensis (Bt)*** is a Gram-positive soil-dwelling bacterium. It can be used as a biological pesticide and has been applied for years as an environmentally friendly biological pesticide for the extermination of caterpillars, moths and butterflies, and the green worms of tomato (*Heliothis armigena*). The bacillus is non toxic and can be used for its selective action against diptera (flies, mosquitoes) and Coleoptera (beetles) and nematodes. Fruit and vegetables can be collected 5 days after its application. In the market there are many commercial products.



Spinosad (Spinosyn A, R=H; Spinosyn D, R=CH_3)

Spinosyn



Azadiracthin

Figure 8.5. Spinosyn insecticide (natural product extracted from bacteria). Azadiracthin, extraction form the tree neem, is used a natural insecticide for various insects and mictobes. Azadiractin can be toxic to bees.[44,45] .

Green Chemistry is following all these developments in pesticide chemistry and their environmental criteria. Green Chemistry would like to direct research and development of new pesticides as long as they are effective, safe to farmers and the environment.

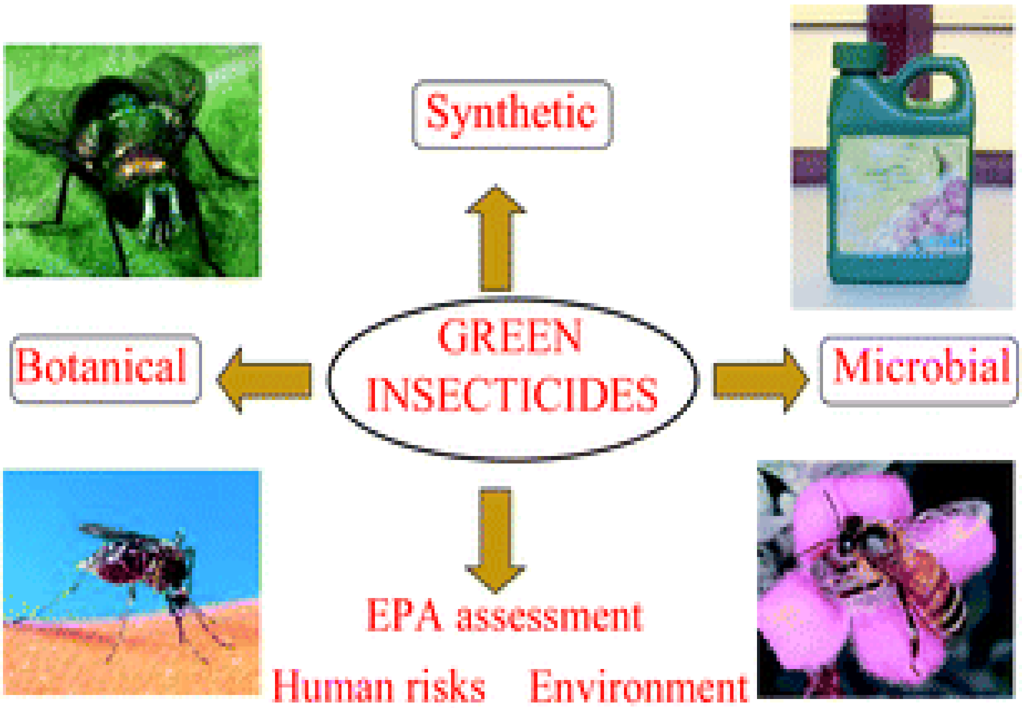


Figure 8.4. Green Chemistry is promoting the synthesis of new pesticides with less toxic ingredients, safer to farmers and the environment. Natural chemical molecules or their metabolites (extracts of microbial organisms or plants) with active substances can be the innovative ideas of the future.

Biopesticides use has been increased in the last decades in many countries. Already, a great variety of biopesticides are been synthesized or are extracted from plants and microorganisms and used as commercial products in agriculture and livestock. Canola oil, which is produced from seeds of rapeseed (*Brassica napus L.*) or field mustard (*Brassica campestris L)* with strong antioxidant properties and sodium carbonate can be used for the pesticidal properties. In the last decade almost 200 active bio-plant ingredients were patented as pesticides and more than 1000 commercial products appeared in the market.[46,47]

The basic categories of biopesticides are a) microbial pesticides (active ingredients from bacteria, protozoa and fungi), b) plant alkaloids or other plant compounds with strong insecticidal and pesticidal properties. Most of the new compounds and active metabolites are synthesized and molecular equivalents or analogues have been tested for their activity.[48,49]

Figure 8.5. Biopesticide use is increasing in the last decade and new products are introduced into the market every year. Their pesticide properties are not as strong as the chemical pesticides but their environmental criteria is an important advantage.

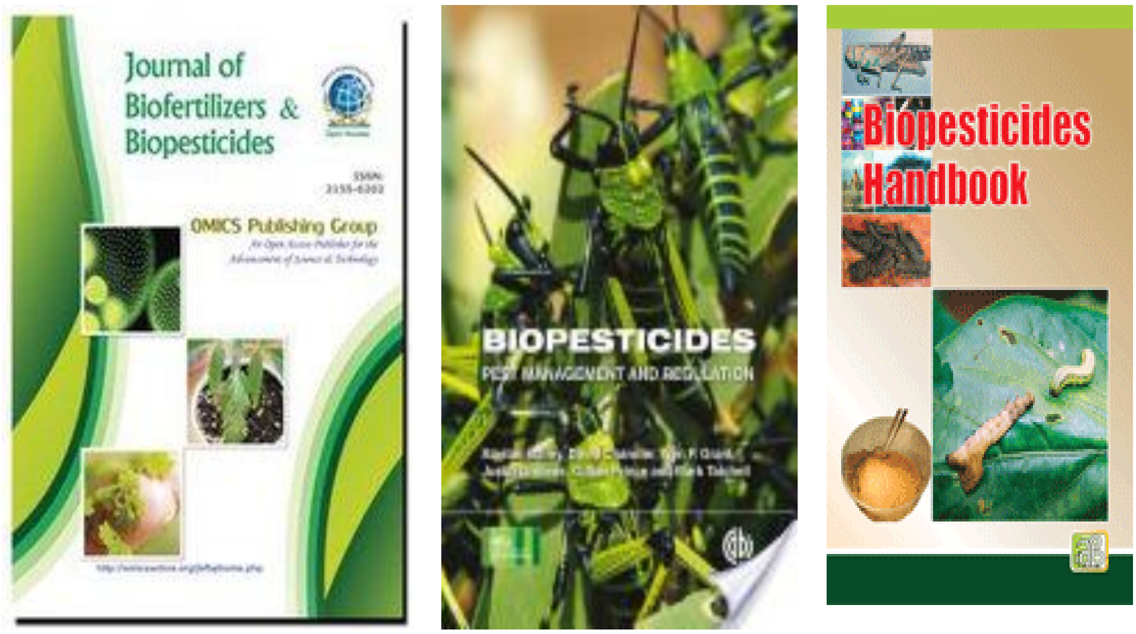


Figure 8.6. In the last decade many new magazines, scientific journals and reports are been published on biopesticides.

Another group of biological material that is used as pesticides are sexual pheromone traps. Pheromone traps utilize "bug hormones" or scents that stimulate the type of scent produced by the female insect to "seduce" or lure their male counterparts. Males lured into traps are prevented from mating.

These traps can be very beneficial for insect control and at the same time are non toxic and eco-friendly.[40,51]

Many publications, scientific reports and agricultural manuals promote the idea of biopesticides and their connection to the principles of Green Chemistry.[52-54]

8.4.3. Reduced use of fertilizers in agricultural practices

Fertilizer use was always very important for modern agricultural production and efficiency, but at the same time a cause of environmental concern. Fertilizers typically provide, in varying proportions: macronutrients: Nitrogen (N), Phosphorus (P), Potassium (K), Calcium (Ca), Magnesium (Mg), and Sulfur (S); and micronutrients: Boron (B), Chlorine (Cl), Copper (Cu), Iron (Fe), Manganese (Mn), Molybdenum (Mo), and Zinc (Zn).

The nitric and phosphate salts which are used as fertilizers have adverse environmental consequences (nitrates in soil and water, runoffs of extra fertilizers, desertification, phosporus can be washed into surface waters producing algae in slow moving water. These algae eventually decompose, remove oxygen and the process is called eutrophication). High nitrate levels in drinking water are considered to be dangerous to human health.

The global production of fertilizers was estimated at 206 million tones (2007=2008) and it was expected to increase at around 241 million tones in 2011-2012 at an annual increase of 5%. In the same period use of fertilizers was 197 million tones and expected to reach 216 million tones (2012), Of these fertilizers, 107 million tones are nitrogen fertilizers, 42 million tones of phosphorus and 29 million tones of Potassium fertilizers.[55]

Nitrogen fertilizers are predominantly urea (NH_2CONH_2). The advantage is that it is absorbed easily form the plants, but also it evaporates easily and can loose ~30% of its nitrogen. **Over-fertilization** of a vital nutrient can be a cause for environmental pollution. Fertilizer burn" can occur when too much fertilizer is applied, resulting in a drying out of the roots and damage or even death of the plant. The production of fertilizers is an big industrial process with large amounts of natural gas used.

Green Chemistry for many years tried to solve the problem of over-fertilization and other environmental parameters of fertilize use in agriculture. The nitrogen loss from nitrogenous fertilizers is considered big problem. The company IMC-Agrico Co developed the chemical N-(n-butyl thiophosphoric triamide), NBPT which is an inhibitor of the enzyme urease. In this way the hydrolysis of urea can be reduced as well as its release through evaporation.[56]

IMC AGRICO®

In 1996 the company Donlar Corporation (NanoChem Solutions, Inc) won the Presidential Green Chemistry Challenge Award for its invention of the biodegradable thermal polyaspartate (TPA). This compound when added to the soil in small quantities helps in the uptake of nutrients and fertilizers by plants. The easier uptake of fertilizers reduces the amounts needed and the cost.[57,58]

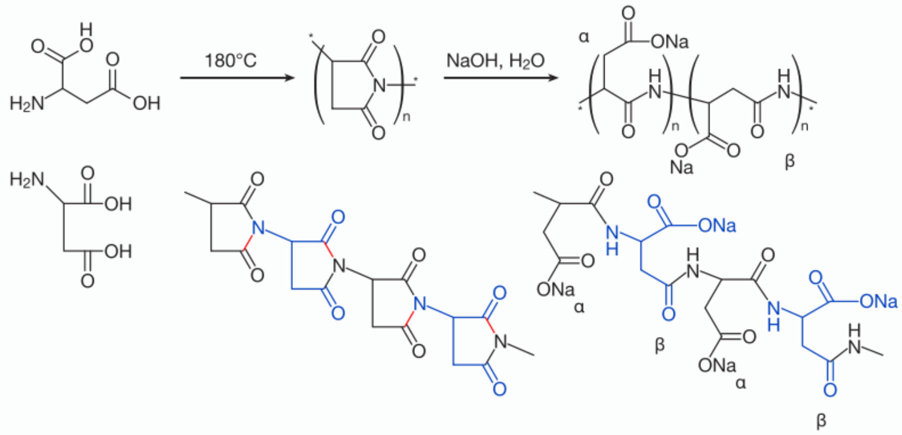


Figure 8.7. Thermal synthesis (180° C) of polyaspatic acid (salt with Sodium). It is a biodegradable polymer which can be used as a booster for the uptake of nutrients and fertilizers by plants.

Experiments with phosphorus fertilizers were contacted for many years in the Agricultural research centre of England, Rothamsted Experimental Station, for the production of phosphate organic manure and its application to farmalands with poor soil quality. The organic manure (Phosphate Rich Organic Manure, PROM) has some beneficial properties when mixed with soil form lands which are alkaline and have high content in salts. The manure also has very low residual properties.[59]

Some other examples of research activities and applications for new fertilizers, biomaterials, biopesticides and agricultural innovations can be found in the Presidential Green Chemistry Challenge Awards of the USA (EPA). In 2001 the award was presented to the company EDEN Bioscience Co for research and production of messenger proteins, non-toxic natural proteins, which are produced from fermentation. These proteins enhance the development of plants and protect them from diseases and parasites.

In 2001 the chemical company Bayer Corporation; Bayer AG (technology acquired by LANXESS) was awarded the PGCCA for the development of a chelatin agent (forms complexes). A biodegradable chelating agent [Baypure™ CX iminodisuccinate] which corrects and reduces the lack of mineral salts in plants.

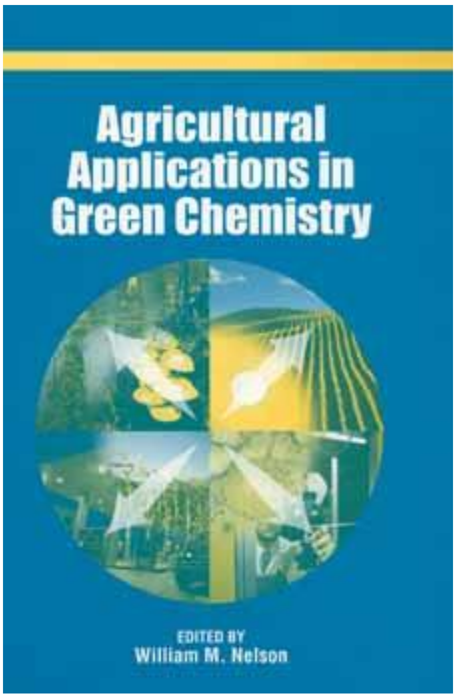
In 2004 the company Jeneil Biosurfactant Co won the PCCCA for its invention of a Rhamnolipid biosurfactant. The biodegradable surfactant increases the surface-activity and helps the uptake of fertilizers and the penetration (diffusion) of fertilizers and other nutrients from the soil to the plants. At the same time the compound is an active antifungal agents.[60]

8.5. Green Chemistry and Biotechnology

Green Chemistry has made many inroads into the technologies and methods of agricultural interest. The aims for a sustainable development with the help of science and technology is part of the Green Chemistry and Green Engineering strategy. In the 21st century science and technology must increase their innovative achievements with safer and environmentally friendly products. Agriculture and its related technological and environmental problems are obviously one of the targets of GC. Renewable materials and energy can come from agriculture, but at the same time there 7 million people to feed. Agriculture must increase efficiency and productivity with environmental credentials. The scientific community must tackle as one of the most urgent problems of sustainability for planet Earth.[61-63]

In 1/7/2010 the magazine Economist published an interesting article on the advances of biotechnology and Green Chemistry. Under the title Biotechnology : "Chemistry goes green" we can read :

"….Behind the scenes, industrial biotechnology is getting going at last.
IS GREEN chemistry ready for take-off? Delegates at a big conference on "industrial biotechnology" held near Washington, DC, this week by Bio, the industry's umbrella organisation, seemed to think so. Industrial biotech uses agricultural feedstocks, rather than petroleum-based ones, to produce chemicals, plastics and fuels. McKinsey, a consultancy, says global industry revenues will grow from €116 billion ($170 billion) in 2008 to as much as €450 billion by 2020. The World Economic Forum reckons the coming boom in "biorefineries" will create new markets worth almost $300 billion by 2020…"



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9. Green Chemistry and Its Role in the Energy Crisis. Biofuels and Biomaterials

9.1. Worldwide Energy Consumption, Energy Crisis, Fossil Fuels

The industrial civilization of the last 250 years was supported mainly by fossil fuels, especially coal in the beginning and petroleum and natural gas in the last 100 years. The Industrial Age was experienced as an energy revolution Despite the progress and use of renewable sources, fossil fuels monopolize in the last decade 85% of electricity production and most of the fuel transport needs. Petroleum and natural gas were exploited despite their depleting nature for the versatile and high quality energy products.

In the last decades the world recognized the dangers of unsustainable use of energy from fossil fuels and the climatic changes resulting in the greenhouse effect. The scientific community and environmental organizations have been alarmed by the consequences and depleting energy resources.

In response to the petroleum crises (mainly in the 1970s and later) and the dangers of global warming, the principles of “green energy” and sustainable development were supported worldwide. This has led to increasing interest in alternative energy and fuel research.

Statistical data for the energy resources and use at a global scale fossil fuels are covering most of the needs of industrial and post-industrial societies (electricity, transport and industrial processes). Petroleum covers 35% of energy needs, coal 27% and natural gas 23% (total 85%). The remaining 15% energy needs are covered by hydroelectric dams 6.3% and nuclear power 8.5%. Renewable energy sources (wind turbines, solar panels, etc) cover at present only 1% of energy needs of the post-industrial societies.

Scientists promoting Green Chemistry and Green Engineering are optimistic to the future outlook of alternative energy sources. It is believed that already new research and innovative applications will advance renewable energy resources. Geothermal energy, solar panels, wind power, tide and wave energy, biomass, can be improved and support cost effective schemes to produce technologically versatile energy with environmental criteria.[1,2]

Green Chemistry and Green Engineering overall target is to contribute to a paradigm shift in the world of fossil fuels by replacing petroleum-based energy products and the petrochemical industry with renewable sources. Science and technology is believed that can advance environmentally friendly resources which can be established on an industrial scale in an efficient and economical manner. Despite the many changes in recent years fossil fuels cover 85% of energy needs at global level. Biomass is plant matter used to generate electricity with steam turbines and gasifiers or produce heat, usually by direct combustion.

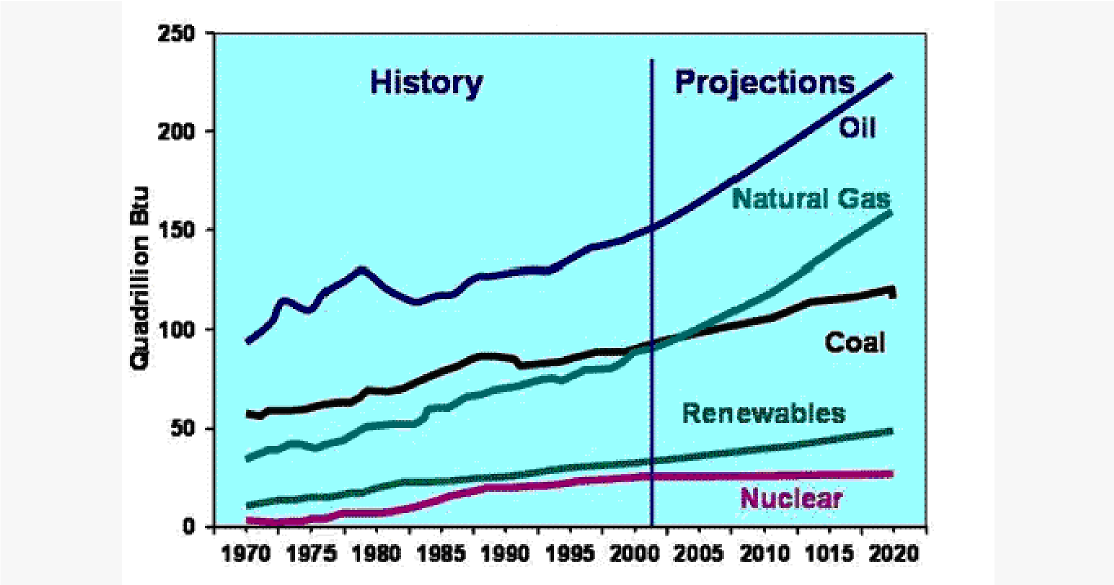


Figure 9.1. World Energy Consumption by Fuel Type in the period 1970 - 2020. [U.S. Department of Energy. Energy Information Administration. International Energy Outlook.. U.S. Energy Information Agency (EIA)]. One Barrel of oil = 5.8 million BTU (BTU =British thermal unit)].
(http://tonto.eia.doe.gov/FTPROOT/forecasting/o484(2002).pdf).

Renewable sources of energy (hydroelectric, wind, photovoltaic) produce only 2-3% and solid biomass at 10%. Some countries have invested heavily in some renewable sources (such as wind power). In the U.K. offshore wind power produced almost 12% of electricity in the year 2011 due to favourable conditions in winder 2011. Offshore wind farms could meet 25% of the UK's electricity needs (electricity to every house).

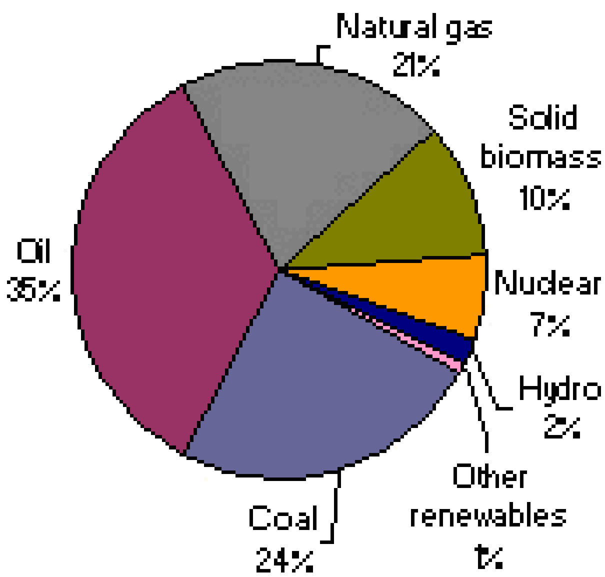


Figure 9.2. Global Energy Consumption by Source in 2007 (World Resources Institute, Earth Trends. Washington DC, 2008).

Fossil fuels are not renewable. It took many million years to be formed and their unrestricted use (3-5% trend in use every year) will exhaust them very soon. Although past predictions show the end of fossil fuels in the next few decades, new fossil fuels discoveries and better techniques of drilling extended their useful extraction until now. The other very important aspect is environmental pollution and large amounts of CO_2 emissions. In 2007 it was estimated that every year 21 million tones of CO_2 are produced from fossil fuels. Half of this amount is absorbed by the oceans, other water systems and the biosphere of the surface o the Earth. The other half of this polluting gas which is the most important factor in global warming remains in the atmosphere. Green Chemistry and Green Engineering are aiming to reduce the needs for energy sources that are depleting and contribute to global warming with renewable sources.

The principles of green energy and sustainable development has become the next goal of Green Chemistry movement. This has led to increasing interest in alternate power/fuel research such as fuel cell technology, liquid nitrogen economy, hydrogen fuel, methanol, solar energy, artificial photosynthesis, geothermal energy, tidal energy, wave power and wind energy. To date, only hydroelectricity and nuclear power have been significant alternatives to fossil fuel. But solar and wind power is in the forefront for electricity generation.[3-5]

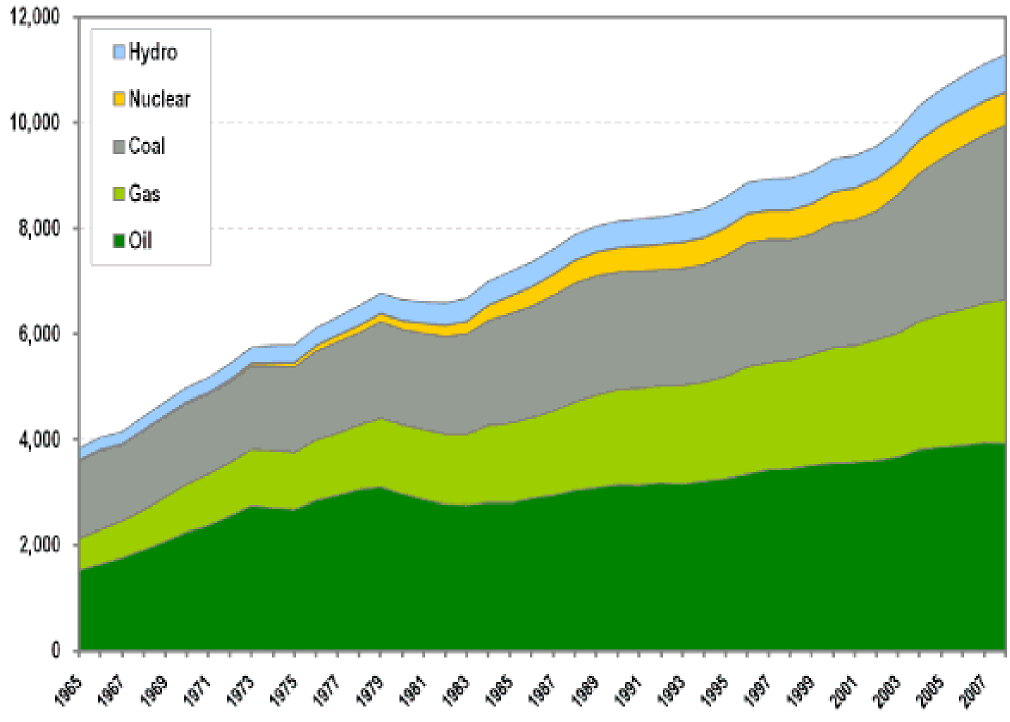


Figure 9.3. Time trends in energy consumption 1965-2008. The fuel consumption is in Mtoe = million tons oil equivalent. Coal from 39% in 1965 reduced to 29% in 2008, while petroleum from 40% was reduced in 35%. Gas increased from 15% to 21%. Small increases in Hydroelectric power (2%) and for nuclear power (7%).

There are various predictions (projections) for reserves of fossil fuels in various parts of the world. These estimates are not very accurate, only coal reserves are known with more precise figures, whereas gas and petroleum are estimates from surveys and geological forecasts In the year 2007 there were estimates of coal at about 905 billion tons, petroleum 1.119-1.317 billion barrels and natural gas 175-181 trillion cubic meters. [6-8]

The distribution of Electricity use by sectors of the economy in developed countries has been estimated in the last decades.

i) Industrial users (agriculture, mining, manufacturing, and construction) consume about 37% of the total,

ii) Personal and commercial transportation consumes 20%;

iii) Residential heating, lighting, and appliances use 11%; and

iv) Commercial uses (lighting, heating and cooling of commercial buildings, and provision of water and sewer services) amount to 5% of the total,

v) the other **27%** of the world's energy is lost in energy transmission and generation. Coal is the most common fuel for the world's electricity plants.[60]

Total world energy use by various sectors of the economy was (2008):[9] industry 28%, transport 27% and residential and services 36%.

In 2008, total worldwide energy consumption was 474 exajoules (474×10^{18} J=132,000 TWh). This is equivalent to an average energy consumption rate of 15 terawatts (1.504×10^{13} W).

The renewable energy sector has great potential and increased dramatically in the last decade worldwide. Estimates showed that the potential for renewable energy is: solar energy 1600 EJ (444,000 TWh), wind power 600 EJ (167,000 TWh), geothermal energy 500 EJ (139,000 TWh), biomass 250 EJ (70,000 TWh), hydropower 50 EJ (14,000 TWh) and ocean energy 1 EJ (280 TWh).[10]

In European Union (27 countries) the distribution of the energy consumption by sector of the economy was : Industry 28%, Transport 31%, residential 27%, agriculture 2%, Services 11% and other 1%. (www.kee.gr/perivalontiki/img/image53.jpg)

9.2. Biomass and Biofuels. How Green Are They?

Green Chemistry gave in the last decades numerous examples of research efforts for biofuels and their applications in viable energy production. Biofuels can be one form of renewable energy resources and in many cases can replace fossil fuels, since they can be come from biomass and are considered to be less polluting and they can reduce global warming by absorbing CO_2 during the growing of plants. In the last decade because of the increasing oil prices and energy crisis in the Middle East, biofuels are gaining increased public and scientific attention. There is a need for increased energy security, renewable energy sources and minimize greenhouse gas emissions

In the first few years of biofuel production there were some excesses and the use of useful stable plants (sugar, wheat and corn) resulted in the sudden increase of food prices worldwide. Inevitably, there were various social, economic, environmental and technical issues with biofuel production and use. The most important was: the effect of moderating oil prices, the "food vs fuel" debate. The other most important issue was the “sustainable” biofuel production, deforestation and soil erosion, loss of biodiversity and impact on water resources because of vast areas were cultivated for producing biofuels.

The issue of biofuels and their status as "green" fuels was the subject of an international study "*Towards Sustainable Production and Use of Resources. Assessment of Biofuels" (*UNEP. International Resource Panel, United Nations Environment Programme, New York, 2009). The study emphasized the many positives impacts on climate, energy security and biodiversity, but also some negatives, such as environmental and social effects. The first generation of biofuels was replaced very soon by the second generation which use more of non-food plants and animal fat waste. Second generation biofuels are biofuels produced from sustainable feedstock. Many second generation biofuels are under development such as cellulosic ethanol, algae fuel, biohydrogen, biomethanol, DMF, BioDME, Fischer-Tropsch diesel, biohydrogen diesel, mixed alcohols and wood diesel.[11-13]

In 2010 worldwide biofuel production reached 105 billion liters (L), up 17% from 2009, and biofuels provided 2.7% of the world's fuels for road transport, a contribution largely made up of ethanol and biodiesel.

The international and European strategy for the increased production of biofuels was dictated firstly from the effort to reduce the CO_2 emissions and secondly for energy security purposes and reduction of the monopoly of petroleum as basic energy source. Based on the broader European energy strategy, the EU through the Directive 2003/30/EC supported the biofuels with the intension to increase by 2010 their use to 5.7% in the transport sector. The main biofuels replacing petroleum products were bioethanol and biodiesel.[14,15]

In Greece, there is substantial progress in the production and use of biofuels fo transport. Statistical data in 2008 showed that consumption in Greece reached 2.750.000 million tons (MT) for diesel and 4.031.000 MT gasoline. In the same period there were 17 companies producing diesel (13 are Greek producers and 4 are importing biodiesel from Europe). For the production of biodiesel in Greece the raw material are oilseeds (sunflower, soya, cotton, rapeseed), vegetable oils (corn, sugar beets, small grain cereals). The Biofuels Directive 2003/30/EC has been adopted by the Greek government as Law3423/05].[16,17]

9.2.1. Types of Biofuels and "Green" Prospects for Renewable Fuels

Biofuels are liquids and gas fuels which are produced from different types of biomass. The term **biomass** according to scientists is every biological material from living organisms. Biomass can be used as an energy source directly (combustion) or be converted in to another biofuel. Examples of biomass can be forest residues (branches, tree stumps), wood chips, municipal solid waste, agricultural waste (cereal straw, hay) and other cellulogic material. Also, plant and animal matter that can be converted into fibers or other industrial chemicals by fermentation or distillation (biodiesel, bioethanol). Biomass can be grown from various plants and trees (cereal straw, switchgrass, hemp, corn, poplar, willow, palm trees, sugarcane etc).

The most important commercial types of biofuels are:[18]

a) Bioethanol. (CH_3CH_2OH).. Ethanol is produced by fermentation. This ethanol is mostly from carbohydrates, such as sugar or starch crops (corn or sugarcane). Cellulosic biomass, derived from non-food sources such as trees and grasses, is also being developed as a feedstock for ethanol production. Ethanol can be used as a fuel for vehicles in its pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions. Bioethanol is widely used in the USA and in Brazil.

b) Biodiesel. This is diesel fuel of biological origin and not from the usual petroleum refining. .Biodiesel is made from vegetable oils and animal fats and can be used as a fuel for vehicles in its pure form, but it is usually used as a diesel additive to reduce levels of particulates, carbon monoxide, and hydrocarbons from diesel-powered vehicles. Biodiesel is produced from oils or fats using transesterification and is the most common biofuel in Europe

c) Biogas. This gas is mainly Methane (CH_4) that is produced from biomass or as a biodegradation of organic matter, such as industrial and municipal waste in the absence of oxygen. The biogas can be cleaned sufficiently to become a good quality natural gas (~98% methane).. Biogas is produced by the anaerobic digestion or fermentation of biodegradable materials.

d) Biomethanol (CH_3OH). Is pure Methanol that is produced from various types of biomass by fermentation or special chemical process and can be used as a biofuel. Biomethanol is the simplest (and cheapest) of the alcohols. It is a versatile chemical that can produce a range of polymers and fuels. Its most immediate fuel use is to produce bio-methyl tertiary butyl ether (MTBE) to increase octane levels in petrol to prevent 'knocking'.

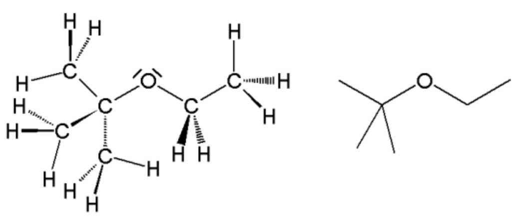
e) Biodimethylether . Dimethylether (CH_3-O-CH_3) is another type of biofuel that can be produced from biomass.

f) **Synthetic biofuels (or synfuel).** These fuels: are hydrocarbons or mixtures of synthetic hydrocarbons that can be produced from biomass. Common use of the term "synthetic fuel" is to describe fuels manufactured via Fischer-Tropsch conversion, methanol to gasoline conversion, or direct coal liquefaction. In 2009 on global scale the production of synthetic fuels were over 240.000 barrels per day.

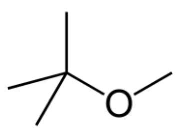
g) **Biohydrogen** This biofuel is hydrogen gas that is produced from biomass or by biodegradable fraction of industrial and municipal solid waste.

h) Clean Vegetable Oils. Vegetable oils that are produced from plants by extraction of crashed and pressurized vegetables or extracted from plants by dissolving parts of plants in water or another solvent. The mixture may also be separated by distilling the oil away from the plant material. These vegetables can be converted into biofuels.

i) Bio−ETBE:Ethyl *tert*-butyl ether, ETBE) can be produced from bioethanol and can be used as biofuel.



λ) **Bιo−MTBE**: [$C_5H_{12}O$, $(CH_3)_3$-C-O-CH_3)] that is produced from biomethanol..



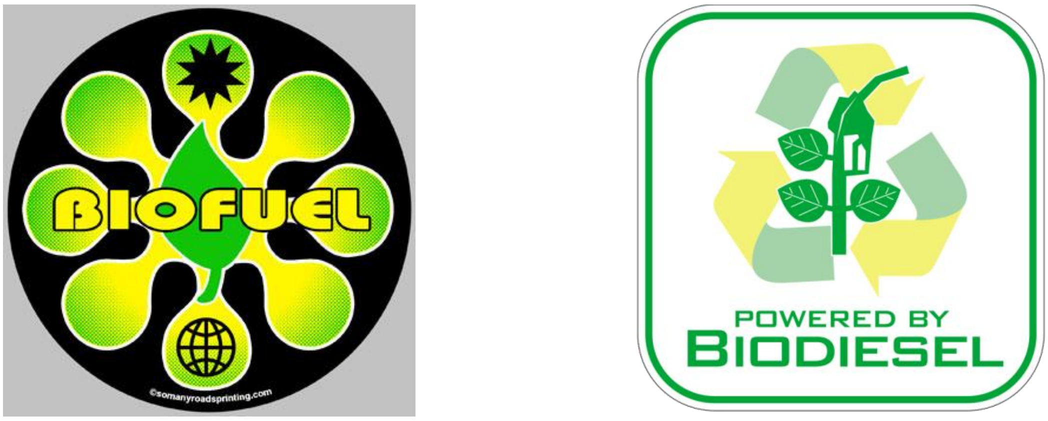


Figure 9.4. Biofuels can become important renewable sources of energy. Already, 9% of the fuels used in transport worldwide are from renewable biofuels (2005). Green Chemistry played an important part for the technological developments of biofuel production and the use of renewable raw materials.

The future of biomass as a renewable source of energy is very important in combination with other renewable sources (solar, wind, geothermal and wave energy). The planet Earth has vast amounts of biological material that are formed daily through the photosynthetic action of plants. This natural biomass can increase substantially with commercial plants cultivated in areas but with no interference with food crops and crucial dietary materials. Also, biomass can be produced from plant and animal natural waste and industrial and municipal solid waste. There are many types of biological and agricultural waste which can be converted by biochemical processes (enzymes and micro-organisms anaerobic ingestion, fermentation and composting) into gas or liquid biofuels Other chemical processes for converting waste and vegetable oils into biodiesel is transesterification or breaking down carbohydrates and simple sugars to make alcohols (ethanol, methanol). Research scientists are Scientists are still researching the effects of converting biomass.[19,20]

9.2.2. Advantages and Disadvantages of Biomass and Various Biofuels

Petroleum and its products from the 1960s were fundamental raw materials for many industrial products and fuel for transport at a global scale. The 1973 oil crisis caused a big blow to energy supplies and a major crisis. It started in October (and lasted until March 1974) when members of the OAPEC (Organization of Arab Petroleum Exporting Countries, consisting of OPEC plus Egypt, Syria and Tunisia) proclaiming an oil embargo and causing high oil prices. The proclamation disrupted supply and caused strong recession in many developed countries. This embargo was in response to the U.S. decision to re-supply the army of Israel during the Yom Kippur was with other Arab countries.

This oil crisis started a big discussion among scientists and economic analysts on the fate of future supplies of energy and forced many countries to look for alternatives. Biomass and the derived biofuels were available sources for alternative energy supplies that for a long period were neglected because petroleum was very cheap and easily available to be use as fuel and starting material for the chemical industry. Biofuels had another important advantage in the decrease of gases of greenhouse effect (especially CO_2).[22]

The main advantages of biofuels are:

i) **Cost**: Once the technology is widely available, biofuels can be significantly less expensive than gasoline and other fossil fuels, particularly as worldwide demand for oil increases. Energy security keeps cost of fuels very low.
ii) **Source Material**: Petroleum oil is a limited resource (depleting in the long term) that comes from specific materials, biofuels can be manufactured from a wide range of materials including crop waste, manure, and other byproducts, making it a efficient step in recycling.
iii) **Renewability**: Fossil fuels are depleting and at some stage will be very few sources left. In contrast, biofuels are much more easily renewable as new crops are grown and waste materials are collected every year.
iv) **Energy Security**: Dependency on foreign fuel sources is a very insecure prospect. Industrial developed countries can protect the integrity of their energy resources and make them safe from outside influences.
v) **Economic factors, employment**: Biofuels that are produced locally, and biofuel manufacturing plants can employ hundreds or thousands of workers, creating new jobs in rural areas. Biofuel production will also increase the demand for suitable biofuel crops, providing economic stimulation to the agriculture industry.
vi) **Environment. Biomaterials and biodegradability**: Biofuels are easily biodegradable and far safer to handle than traditional fuels, making spills less hazardous and much easier and less expensive to clean up. Environmental protection is more important.
vii) **Lower Carbon Emissions**: Burning biofuels produce significantly less carbon dioxide (CO_2) output and fewer pollutants making them a safer alternative to preserve atmospheric quality and lower air pollution. Growing plants absorb CO_2.

Despite the many positive characteristics of biofuels, there are also many disadvantages to these energy sources.

i) **Energy Output**: Biofuels have a lower energy output than traditional petroleum fuels, requiring greater quantities to be consumed in order to produce the same energy level.
ii) **Carbon Emissions**: Several studies analyzed the carbon footprint of biofuels, and while they may be cleaner to burn, there are strong indications that the process to produce the fuel (machinery necessary to cultivate the crops and the plants to produce the fuel) produces a large amount of carbon emissions.

iii) .**High Production Cost of Biofuel**: To refine biofuels to more efficient energy outputs and to build the necessary manufacturing plants to increase biofuel quantities will require a high initial investment.

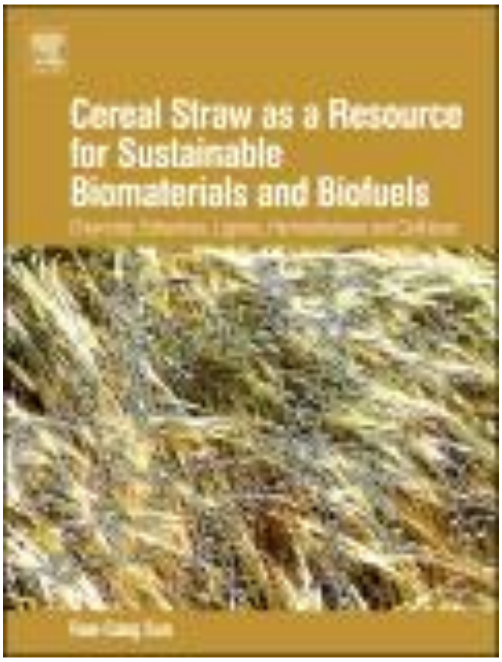
iv) **High Food Prices**: Some important food crops, such as corn and soybeans are grown for biofuel production. This will affect future prices of staple food crops.

v) **Crops Need Water**: Massive quantities of water are required for proper irrigation of biofuel crops as well as for the manufacture of the fuel, which could strain local and regional water resources.

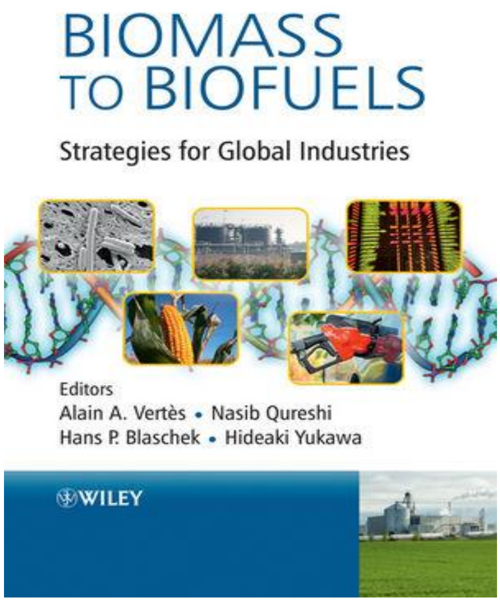
vi) **Availability**: Biofuels are not widely available for consumer purchase and most vehicles are not equipped to run on biofuel products. Limited availability reduces the desirability of biofuels as alternative energy sources.

vii) **Biofuel Smell**: Production of various biofuels produces heavy smells depending on the type of materials used, and those smells are generally undesirable near large communities..

If we balance advantages and disadvantages of biofuels there are more advantages for the future of biofuels. Biofuels are a reliable alternative energy resource but more development and research (Green Chemistry will play an important role in the future) is necessary to overcome the disadvantages of biofuels and make them suitable for widespread consumer use. Transport technology is already available for biofuels, but it needs more innovations and better strategies to increase consumer demands.[21-23]



Elsevier, Amsterdam, 2010



Wiley, Chichester, West Sussex, 2010

Figure 9.5. There are in recent years many new publications of research and development on biomass and new biofuels.
[Sun R-C. *Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels. Chemistry, Extractives, Lignins, Hemicelluloses and Cellulose*. Elsevier, Amsterdam, 2010.´Vertes AA, Qureshi N, Blaschek HP, Yukawa H (Eds). *Biomass to Biofuels. Strategies for Global Industries*. Wiley, Chichester, West Sussex, UK, 2010.]

In the first phase of the biodiesel production and other biofuels the increasing subsidies in various countries caused a diversion of some staple crops towards biofuel production and inevitable food prices increased. Particularly in some Asia countries food prices peaked causing problems in some areas and social problems. Also, in some countries, vast areas of farmland were planted with energy plants than staple crops causing increased food prices.[24, 25]

Green Chemistry and Green Engineering are striving to promote the alternative biofuels. Despite the disadvantages Green Chemistry is promoting the 3rd and 4th generation biofuels with decreases in cost, better energy efficiency and chemical processes that will transform biomass into biofuels.

There are mixed experiences in the last decade with biofuel use in industrial countries. The advantages were very obvious considering the energy security and the environmental problems. The disadvantages are also numerous and can be reduced with more technical innovations. Many scientists believe that there is scope for many improvements in the quality and the properties of biofuels. Environmental advantages can be multiplied substantially if industrial, agricultural and municipal waste will be converted in large amounts in biofuels.[26-29]

9.3. Green Chemistry and Energy Conversion of Biomass

Biomass was used for a long period of time by human civilization as a source of energy. Biomass burning and other low technology conversions were very low efficiency methods. In recent years the biofuel sector that is attracting many research projects and a great variety of innovative applications is transport and engines of internal combustion.The main question facing biofuels is not whether they can work, but how they might be developed further. There are many unresolved issues to proceed to large scale developments. OECD and its sister organization International Energy Agency (IEA) have defined several areas requiring extended research. All the indications are that biofuels represent a serious alternative to conventional fuels, although for the time being can compliment the existing transport fuels. The production potential, cost and the environmental impacts of producing ethanol, biodiesel and other liquid and gaseous fuels are still uncertain.

The research strategy used until now in developed countries combines the principles of Green Chemistry and Green Engineering for the conversion of various biomass materials into hydrocarbons with higher efficiency. The main goals in the chemical processes are to decrease the content in oxygen of the raw materials in order to achieve high density of energy, and to achieve formation of C—C bonds among the biomass and the intermediate products in order to increase the molecular weight of the final hydrocarbons.

Bioethanol and biodiesel are the two most important biofuels which are produced until now from starchy products and triglycerides raw materials (vegetable and animal lipids). These starting materials are connected with stable food (corn, sorghum, sugarcane, wheat, barley, straw). This is a great disadvantage because food prices increase substantially any time there are major disasters, floods or droughts and food production drops to low levels.

Scientists are trying to improve in the last decade the conversion efficiency of lignocellulogic starting materials into biofuels. Green Chemistry techniques and innovations improved substantially the conversion with thermochemical processes (vaporization, pyrolysis and liquefaction) of biomass. Researchers believe that many new advances in the conversion of biomass to biofuels can be achieved with the use of catalytic methodologies and preliminary processes such as hydrolysis of aqueous solutions of carbohydrates. Another great improvement in the process can be achieved with aldol condensation of ketones and oligomerization of alkenes to produce high quality bio-gasoline and biodiesel.[30]

Green Chemistry can play a vital role in the transformation of biomass through various chemical processes into useful and effective biofuels which will be at the same time environmentally benign. Also, Green Chemistry can be in the forefront of scientific research and applications for new biomaterials from biomass. The practical experience of technological development of the last 100 years was based on the petrochemical industry (crude oil, natural gas). The majority of starting chemical materials for synthetic routes are products petroleum refining. The most important petrochemical classes, produced by fluid catalytic cracking of petroleum fractions, were olefins (ethylene and propylene). Also, chemical plants produce olefins (ethane, propane) by steam cracking of natural gas. Aromatics (benzene, toluene and xylene) are produced by catalytic reforming of naphtha. Olefins and aromatics are the building-blocks for a wide range of materials such as solvents, detergents, and adhesives. Olefins are the basis for polymers and oligomers used in plastics, resins, fibers, elastomers, lubricants, etc..

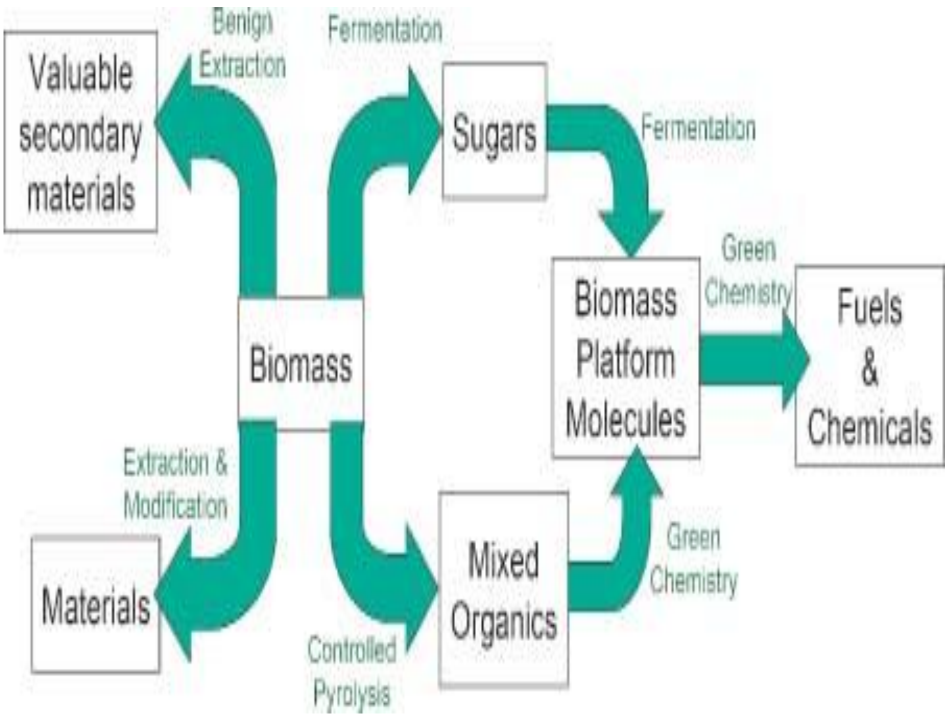


Figure 9.6. **Green Chemistry and Biorefineries**. A schematic diagram of Biomass in a network of production of fuels, chemicals, materials, sugars and valuable secondary molecules by Green Chemistry principles and benign chemical processes. (extraction, fermentation, pyrolysis, etc).

(Clark JH. Green chemistry for the second generation biorefinery, *J Chem Technol Biotechnol* 82(7):603-609, 2007)

Green Chemistry aims to replace the petrochemical industry with biorefineries. Green scientists envisaged various raw biomass materials and industrial or municipal solid waste playing a fundamental role. Biomass platform molecules to give fuels and chemicals. Biomass producing valuable secondary materials, sugars (by fermentation), mixed organics and others in a unified network biotransformations.[31]

The scientific literature in he last decade is full of new research, innovative ideas and environmentally friendly methods for applying the principles of Green Chemistry in biorefineries. These new processes presented alternative biomass material. A typical example is bana grass (*Pennisetum purpureum*), a very high tree-like grass and the oil from seeds of Jatropha curcas (non edible plant which produces vegetable oil, the plant is planted in India and Indonesia). These two plants from plantations can become raw materials for the production of biofuels. There are many advantages in the use of these plants because can be planted in poor quality soil, absorb CO_2, grow very fast and are not edible.[32,33]

There is extensive research for new types of biomass. Scientists are very careful about the type of plants which are going to grow for biofuels. The use of corn, sugar cane, soy and cereals (based on subsidies) for the production of biodiesel caused extensive increase of food prices. Also, scientists are researching methodically the chemical processes needed for their transformation (hydrogenation, condensation, gasification, extraction, etc) into biofuels. These processes have to be environmentally friendly (less toxic solvents, minimum energy use, atom economy synthesis, etc).[34-36]

Figure 9.7. The plant **Bana grass**, which looks like sugar cane and is used for elephants' food (India, Indonesis) is ideal for biomass material. ***Jatropha curcas*** (family *Euphorbiaceae*), is a species of flowering plant native of American tropics (Mexico). Produces flowers, its seeds are toxic and can reach a height of 6 m. It is poisonous semi-evergreen shrub. The seeds contain~30% oil that can be processed to produce a high quality biodiesel

Scientists devote extensive research efforts for the 3^{rd} and 4^{th} generation of biofuels. They are interested for the all types of waste (industrial, agricultural, animal waste, municipal, etc).They consider that conversion of waste into biofuels will be a very desirable and has great prospects to reduce the environmental burden of waste and at the same time increase their usefulness.[37-40]

9.4. Polymer Chemistry, Green Chemistry and Biomaterials

In the last 20 years there is a rapid progress of a great variety of polymeric materials produced from biomass. Also, a large number of biomaterials found successful commercial use. Although there are many research papers and report on the subject we summarise some of the most important aspects of biomaterials.

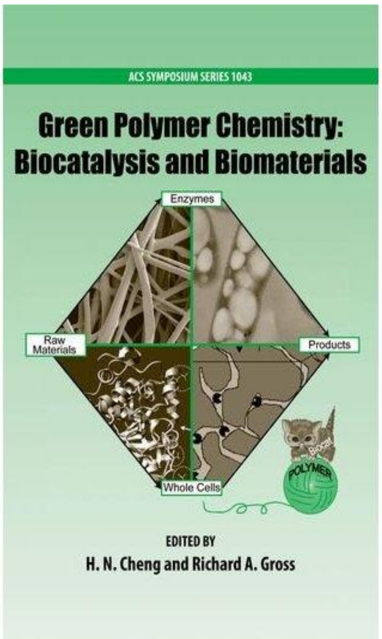
A very timely and important presentation and subsequent publication on the subject of polymers, biocatalysis and biomaterials was the American Chemical Society Symposium “Green Polymer Chemistry: Biocatalysis and Biomaterials” (ACS Symposium Series, Vol. 1043, ACS Publications, Washington DC, 2010).

Also, research and industrial applications in the last years are presented with valuable details in many publications, including the rising technological achievements in a great number of biomaterials and biomedical materials.[41-44]

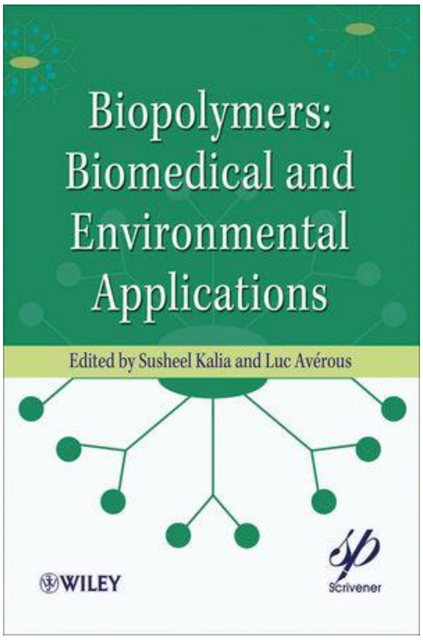
Chemical research on new polymers, biocatalytic processes and biomaterials were presented in the Symposium of the ACS (2010). Green Chemistry and Green Engineering principles and applications were involved in the majority of these new methodologies. Below, we present a series of subjects from the Symposium:

1) Green catalysts (e.g. biocatalysts, such as enzymes and whole cell of biological organisms)
2) Great variety of starting material from biomass (especially agricultural products and waste and basic chemical as feedstocks from biological substances).
3) Biodegradable polymers and biomaterials that will reduce the environmental impact and the formation of waste.
4) Recycling of polymer material and the catalysts used for their production (biological recycling).
5) Energy production from biomaterials, but also minimization of energy consumption for chemical processes’
6) Designing and production of commercial products that have the ability for improvements and better molecular design of their properties.
7) Use of less toxic solvents (e.g. aqueous solutions, ionic liquids, or reactions without solvents).
8) Scientific improvements in the organic synthesis and industrial processes (atom economy, high efficiency and yields, reduction of toxic properties of materials, etc)

Some recent publications on Green Polymer Chemistry, biocatalysis, biomaterials and biomedical applications indicate the great interest on these subjects in the scientific community and among industrial chemists.[45,46]



ACS Symposium , 2010



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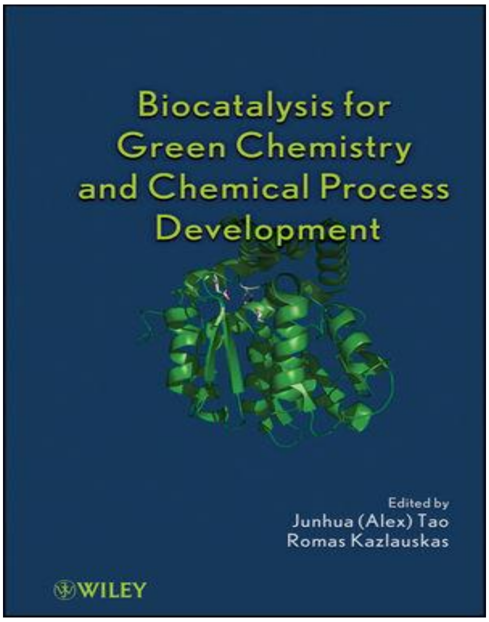

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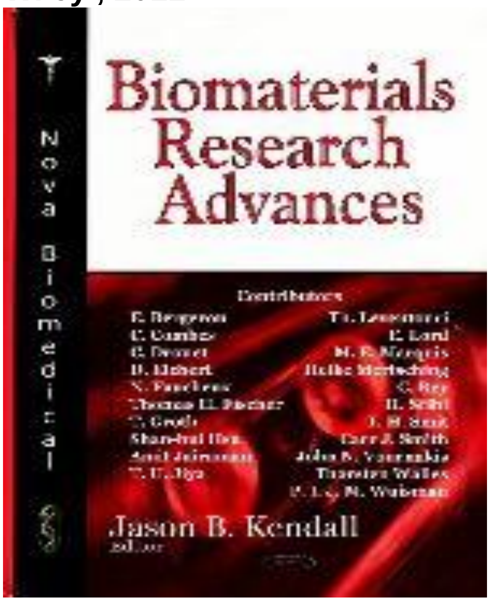
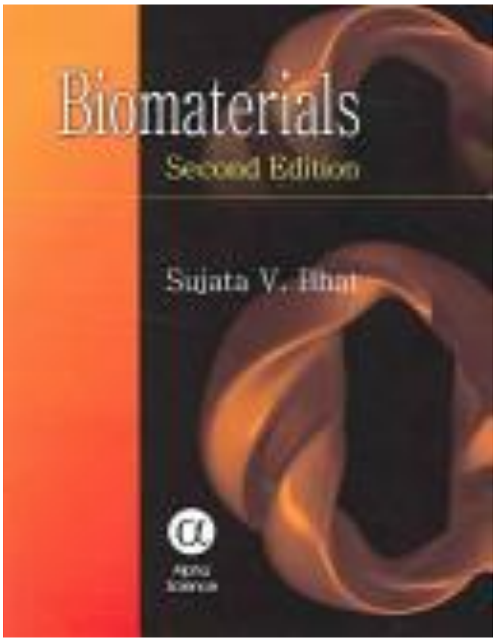


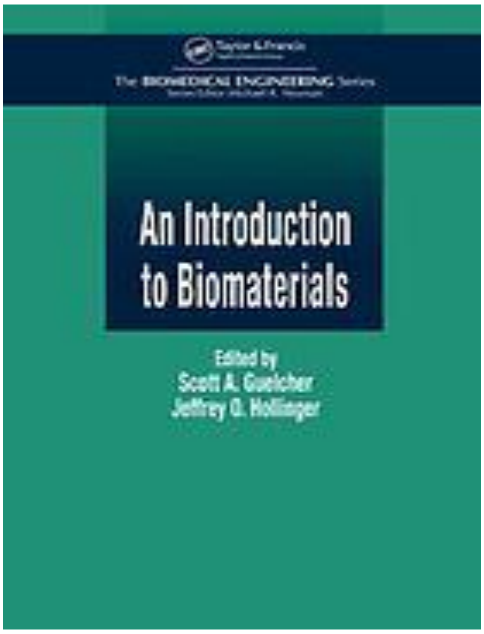
Nova Science Publishers, N.Y., 2008

Figure 9.8.. Various publications on biocatalysis, Green polymer chemistry, biomaterials and chemical processes showed the increasing interest of the scientific community and industrial chemists.

Biomaterials science and engineering is a highly interdisciplinary field intersecting medicine, biology, physics, chemistry, materials science, engineering and ethics. The subject of biomaterials and their applications has been covered by numerous publications.[47,48]



Alpha Science International, 2005



CRC/Taylor & Francis, 2006

Figure 9.9. Biomaterials have a great variety of applications for commercial products (biomedical items and equipment, electronic, etc).

9.5. Green Chemistry. New Scientific Perspectives in Biocatalysis and Biomaterials

Biocatalysts are becoming a very important scientific sector with great prospects for a variety of industrial applications. Biocatalysts achieve higher yields in chemical reactions and better efficiency in biotransformations with low energy demand for the chemical industry.[49,50]

Numerous biocatalytic methods are applied in the polymer chemistry and help in the production of a great number of biomaterils. With the increasing price of petroleum products and other fossil fuels, biomaterials that are produced from alternative and renewable energy and raw material sources are gaining ground.[51-53]

The most important advantage of biomaterials which are produced from vegetable starting materials is their biodegradability and their low impact on the environment when they become solid waste. At the same time there are financial advantages because the biocatalytic industrial process for their production uses less energy, with minimum waste and secondary intermediates. Recycling of these biomaterials is environmentally benign and can be achieved at low cost. Some new biocatalysts used in these processes are immobilized enzymes (*Novozyme-435-lipase, Novozymes A/S*).The well known chemical company.

Sigma has partnered with Novozymes™ to distribute the new enzymes. The world's largest manufacturer of high-quality industrial enzyme products, Novozymes was a 2001 recipient of the Presidential Green Chemistry Challenge Award for eco-friendly products. This partnership makes the Novo product line easily available to researchers through the Sigma-Aldrich Enzyme Explorer. Brand name of these enzymes include: Everlase™, Lipolase™, Pectinex™, Glucanex™. The commercialization of these enzymes has been very important for a series of industrial processes.[54-57]

Chemical industry and other sectors of the industries using chemicals have changed in the last few years the industrial production processes of their products. New designs, biocatalysis and biomaterials as starting chemicals increased efficiency and made "greener" methods more approachable. Designing new molecular models, with the help of electronic programmes, life cycle analysis and more innovative management of production steps gave the opportunity for reducing toxicity of chemicals and products. Biocatalysts reduced the need for organic solvents and some industrial processes can be performed in aqueous solutions.[58-60].

Green Chemistry and Green Engineering principles proved to be the catalysts for changing attitudes among chemical engineers and production practices. Biocatalysis was one part of these big changes towards sustainable methodologies. Microwave chemistry influenced many aspects of polymer chemistry and synthetic routes. Also, extraction, purification, separation and other techniques in polymer chemistry were improved by innovative advances.[61-66]

Recycling carbon dioxide has become a very important issue in chemical processes due to the pressing aspects of global warming. Green chemists would like to incorporate the CO_2 in chemical reactions as a starting material in synthetic reactions. The molecule of CO_2 is very stable (unreactive) and there great difficulty to break the double bond of carbon with the two oxygen atoms (O=C=O). The reaction with other organic molecules is available only with the use of very expensive metallic catalysts. Recently researchers Yu and Zhang achieved direct carboxylation of terminal alkynes. In this reaction the incorporation of CO_2 in phenyacetylenic molecule and the transformation of carboxylic acids in the presence of Caesium carbonate (Cs_2CO_3), under 2.5 atmospheres and 120oC temperature gave a yield of 90%. The same reaction was achieved with cheap catalysts (N-heterocyclic carbenes of Copper) at room temperature.[67]

$$\textbf{R-C}\equiv\textbf{C-R --}\rightarrow \textbf{Cs}_2\textbf{CO}_3\textbf{ / 2,5 atm/120 }^{o}\textbf{C --}\rightarrow\textbf{ R-C==C-COOH}$$

Scientists believe that the incorporation of CO_2 in chemical reactions will be a great step in reducing the emissions of carbon dioxide in the atmosphere. Chemical industries can turn their emissions in to useful chemical raw materials and with cheap catalysts incorporate CO2 into chemical processes.[67]

The great advantage of biomaterials is the fact that can be transformed into bio-products with exclusive properties and the assembly can be done into special forms. This has found many applications in biomedical products, such as synthetic tissue and bones. With very versatile properties resembling the biological organ.[68,69]

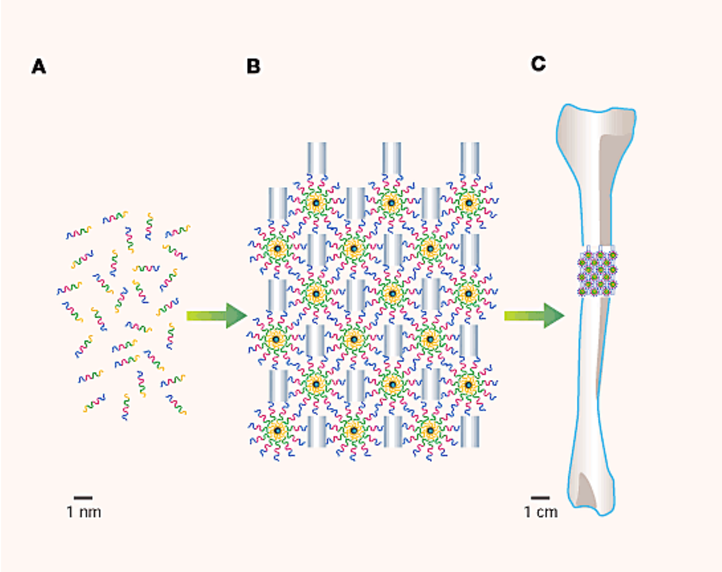


Figure 9.10. Many biomaterials can be designed in such a way that cam imitate natural tissues and bones. Designing their production process helps to assemble components in steps into the final product. This is called tissue engineering and finds many applications in biomedical products.

Tissue engineering is a newly emerging biomedical technology and methodology to assist the regeneration and repairing of defective and damaged tissues based on the natural healing potentials of patients themselves. Biomaterial technology plays an important role in the creation of this cell environment.[70,71]

Green Chemistry in the sector of polymer chemistry has been growing at a fast pace in recent years. Polymeric biomaterials with highly specialised properties and applications have been produced with Green Chemistry principlers and with the use of renewable materials. Additionally, they are easy to recycle and they are not toxic to the environment.

Polymer industry has changed dramatically.Polymers are produced : a) by new starting materials of biological origin, b) by innovative biocatalytic methods and enzymes, c) new synthetic routes of polyesters, polycarbonic polymers, polyamides and polysacharites, d) biocatalytic oxidation-reductions, e) reactions which are called grafting and functionalization (formation of new functional groups).[72-74]

In the last decade there are new polymer products and various applications. The trend is with synthetic proteins and polypeptides that have useful mechanical properties. These techniques use crosslinking and the products can have biomedical applications.[75-77] Another very important sector of biocatalytic polymers are polysaccharides with many applications.[78,79] and glycoaminoglycans.[80] Biomaterials are finding increasing applications in dentistry, medicine, cosmetics and skin products.[81.82]

Biomaterials and products of Green Chemistry have been advancing for many years. In the USA according to Pike Research, (www.innovativeindustry.net) the “green” chemistry products reached in 201 2.8 billion $. It is believed with the trends of recent years, by 2020 will reach 100 billion $.[83]

Biofuels are now a new and advancing technological and commercial enterprise which has to be regulated. New rules and restrictions have to apply for quality, properties and prices. The European Union recently 7 different certification schemes of biofuels (19/7/2011, MEMO 11/522). The EU decided that biofuels must not use for their production trees of forests not plantations but mainly plant debris and microalgae. The biofuels must produce at least 35% less CO_2 compared to conventional fuels and other gases that contriburte to global warming. In 2007 the EU countries were importing 26% of biodisel and 31% of bioethanol from USA and Brazil.[84]


GREEN CHEMISTRY NETWORK

Green Chemistry & the Consumer

Green Chemistry News, Views and Solutions for Sustainable Supply Chains

Newsletter

November 2008

Issue 32

EDITORIAL

In one of our "breakthroughs" we highlight an article from Japan which describes the efficient capture of phosphate pollutants in a way that enables easy recovery of the phosphate - a resource that is running out. We have been aware of the need to reduce pollution in chemical and related processes for a long time and more recently we have become aware of the finite quantities of many key substances in the virgin forms we have traditionally exploited. Our consumer society has been based on a consumption model which condemns resources to become, after a variable but sadly short period of time, waste. Inevitably in a limited system (the Earth) we will run out of virgin resources although the rates of depletion of them will vary depending on the (extractable) quantities available and our rate of consumption: for oil it seems likely to be later this century, for coal it may be longer (see the intriguing question posed by Bill Sanderson on page 13); for many metals we are apparently running out within 10 years or so (see Chemistry & Industry, Issue 16, 2008); for phosphates it is probably a few decades. For energy production, we are turning our attention to alternatives – wind, solar, wave – which are renewable and essentially unlimited; on biomass which is renewable but

(Continued on page 2)

CONTENTS

1

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10. The Role of Green Chemistry in the Improvement of Renewable Energy Sources and the Global Water Crisis

10.1. Sustainability and Renewable Energy Sources in the 21st Century

In the last 20 years developed countries faced major challenges in their economic and social development. The energy crises and rising oil prices forced critical thinking about the future. At the same time climatic changes and global warming continue to get worse due to increasing emissions of carbon dioxide (CO_2) and other gases of the green house effect.

The Earth's total endowment of fossil oil, before humans started using it, was roughly 2 trillion barrels of recoverable oil. Rising consumption has used already 50% of oil deposits. Consumption is currently at 31 billion barrels each year. And increasing because of China, India and other developing countries. There is no other solution than renewable energy sources and sustainable use of existing energy resources. Solar, wind, geothermal, and other environmentally friendly sources must replace the conventional fossil fuels and reduce emissions.

The global fresh water crisis is another serious problem in many developing countries and its sustainability threatens major areas of the planet. Green Chemistry and Green Engineering aiming to tackle these two problems by improving alternative and renewable energy sources, cutting emissions and use in a sustainable matter water resources.[1,2]

10.2. Renewable Energy Sources

The most renewable sources of energy on the planet are:[3,4]

1) **Wind power**: it can be used for the production of electricity and in many countries it can produce up to 5-10% of the electricity needs.
2) **Solar energy:** Solar panels were used initially for heating water in house roofs. The improved technology of photovoltaic panels is considered the future of electricity production in many countries. At the end of 2010, cumulative global photovoltaic (PV) installations production has been increasing by an average of more than 20% each year since 2002, making it a fast-growing energy technology. In 2010, cumulative global photovoltaic (PV) installations surpassed 40 GW.. Many solar photovoltaic power stations have been built, mainly in Europe
3) **Hydroelectricity**. There are many for decades large hydroelectric power dams. In the last decade small hydro stations proved to be more beneficial to the environment and use water power in a sustainable way.

4) **Geothermal energy**. It is produced in the interior of the Earth from physical radioactive decay of minerals and can be brought to the surface easily for electricity use and house heating.
5) **Tidal energy**. is a form of hydropower that converts the energy of tides into useful forms of power, mainly electricity. Although not yet widely used, tidal power has potential for substantial electricity generation. Tides are more predictable than wind energy and solar power. Tidal power has traditionally suffered from relatively high cost and limited availability of sites with sufficiently high tidal ranges or flow velocities,
6) **Wave energy**. Waves are caused by the wind blowing over the surface of the ocean. In many areas the wind blows with enough consistency and force to provide continuous waves. There is tremendous energy in the ocean waves. Wave power devices extract energy directly from the surface motion of ocean waves or from pressure fluctuations below the surface. Wave-power rich areas include the western coasts of Scotland, northern Canada, southern Africa, Australia, USA, etc.
7) **Oceanic energy**. Systems to harvest utility-scale electrical power from ocean waves have recently been gaining momentum as a viable technology. The potential for this technology is considered promising, especially on west-facing coasts.[
8) **Biomass**. Not only for heating but also from plant, industrial and municipal waste. Production of bioethanol, biodiesel and biogas.

Figure 10.1. Solar Thermal Power , PS20, Sanlúcar la Mayor, Sevilla, 20MWp, Open Apr 2009.

In 2010 about 16% of global final energy consumption comes from renewable energy sources. On a global scale, 10% of energy is coming from traditional biomass (heating), 3.5% from hydroelectricity and another 3% from wind, solar, geothermal, small hydro and biofuels. The share of renewable energy sources in electricity generation is around 19%. Wind power is growing at the rate of 30% annually, with a worldwide installed capacity of 198 gigawatts (GW) in 2010. Great Britain produced in 2011 almost 12% of its electricity by wind energy sources. These are major improvements in the production of energy by renewable energy sources.

Figure 10.2. Wind power turbines and photovoltaic panels are the.fastest-growing energy technologies in the last decade

A recent report of the United Nations (2011) on renewable energy sources found that at a global scale the investment flowing climbed from $80 billion (2005) to a record $100 billion in 2006. The trend continues in 2007 with another extra investments of $85 billion. In 2010 the investment on renewable energy increased by 32% and reached the level of $211 billion.[5]

Investments in renewable energy sources are fast growing in developed and developing countries and new more efficient methods appear on the horizon at a fast pace. China for example invested in renewable energy in 2010 $49 billion (28% increase compared to 2008). The same happened in the countries of Latin America, $13 billion in 2010 (39% increase compared to 2009). In Middle East $5 billion in 2010 (increase 104% compared to 2009) and in India $3.6 billion (increase 25%).[5]

In Europe the latest trend for investment in renewable energy sources was growing very fast. Although there was a decrease of 22% compared to the previous year in wind parks (wind turbine installations) the investment was $35 billion. Photovoltaic parks were the most fast growing sector for investment. In Germany $34 billion (increase 132$ compared to 2009), Italy $5.5 billion (59%), France $2.7 billion (increase 150%), etc.[5] Renewable energy sources now compete head-on with coal and gas in terms of new installed generating capacity and the % of world energy produced from renewable sources is sure to rise substantially as the tens of billions of new investment dollars bear fruit.

In the USA there is increasing investment trends for renewable energy sources but not to the same extend as in Europe. In 2009 renewable energy sources produced 8% of the total electricity in the USA. Solar and wind power constitute now 10% of various renewable energy producing sources.[6]

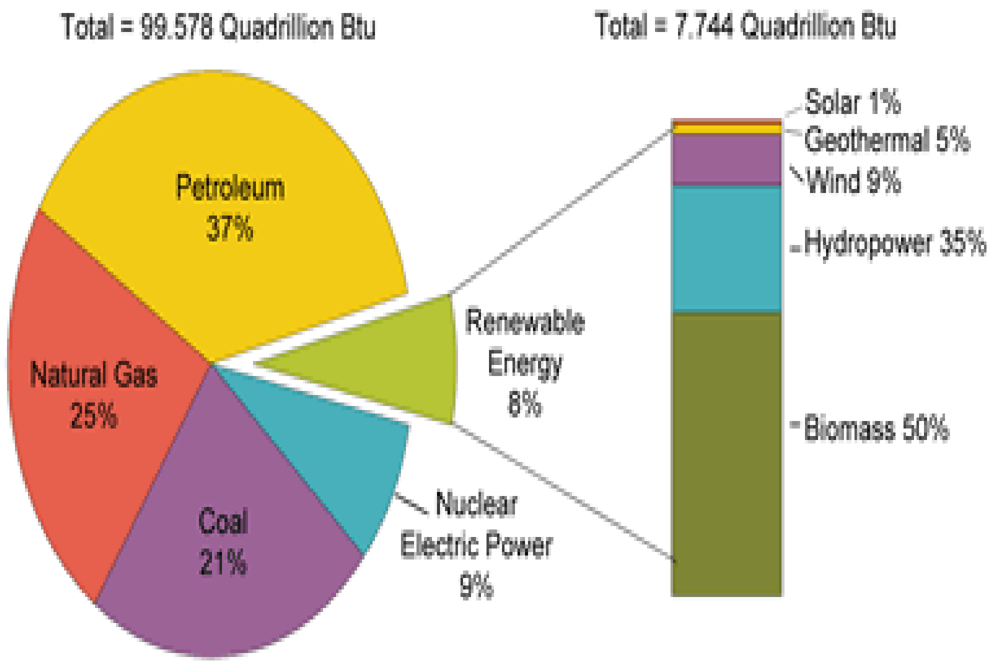


Figure 10.3. In 2009 the distribution of energy sources in U.S. Renewable energy sources cover 8% of the energy produced. Renewable energy sources are: biomass 50%, hydroelectric 35%, wind power 9%, geothermal 5%, solar (photovoltaic panels) ~1%.

Renewable energy sources in the countries of European Union (27 countries) in 2008 contributed to 10.3% of the total production of energy compared to 8.8% in 2006 and 9.7% in 2007. The EU in 2009 projected a new Directive on renewable energy sources and investments aiming to increase their use at a level 20% by 2020. These goals were the results of studies and statistical data of the conditions in various countries, the economic environment and investments in the last decade.[7]

Solar panel electricity systems, also known as **solar photovoltaic panels** (PV), capture the sun's energy using photovoltaic cells. These cells don't need direct sunlight to work - they can still generate some electricity on a cloudy day. The cells convert the sunlight into electricity, which can be used to run household appliances and lighting. The cost of photovoltaics is for the time being very expensive to compete with other systems of electricity generation

[*An average system is of 3 kWp costs around £10,000 (or $16.000, or 12.000 Euros). Most domestic PV systems cost around £3,000 to £3,500 per kWp* (kWp, *kilowatt-peak, a measure of electrical output commonly used for solar energy) devices installed, though small systems cost proportionately more. Costs vary between installers, so it is important to get several quotes. Other factors are: the more electricity the system can generate, the more it costs but the more it could save. Larger systems are usually more cost-effective than smaller systems (up to 4 kWp)]*

A study of the European Photovoltaic Industry Association) found that the production of 1kWh (kilowatt-hour, symbol kWh) cost in Germany 0.9 euro from coal, and from photovoltaics the cost is in the range of 16-0.35 euro, depending on the scale of the producing unit. Large systems are usually more effective and lower in cost. Many photovoltaic (PV) systems are at present supported by state subsidies (in Europe and in the USA). It is estimated that the cost of PV in 2020 will be much lower and able to compete with conventional and other renewable energy sources.[8]

Although the photovoltaic parks and PV panels are considered the most “greener” sources of energy, but there are for the time being many technological and methodological problems. It is hoped that new materials, lower cost and better management on green principles will promote this source of renewable energy in the future.[9,10]

10.3. Renewable Energy Sources: Advantages and Disadvantages

Conventional fossil sources of energy were for decades very cheap and effective in the production of electricity, in transport as fuels and for other uses. Renewable energy sources have the main advantage that they are sustainable, at least in our lifetimes. Also, renewable sources do not pollute the environment and can be extended without problems to the Earth ecosystems. Renewable sources of energy will reduce global warming and keep the atmosphere clean. Non-renewable resources such as fossil fuels are finite and their burning produces increasing amounts of pollutants.[11-13]

10.3.1. Advantages of Renewable Energy Resources

- Renewable energy sources are sustainable. Renewable energy sources are friendly to the environment (**zero emissions**). They do not produce waste (solid or liquid). Green Chemistry and Green Engineering aim to improve renewable methods of energy by providing low cost materials, better technological improvements and “greener” processes in their construction (such as and better materials and less toxic for photovoltaic panels).
- Renewable energy sources **are not finite** like fossil fuels.
- Renewable energy sources can help small countries for their energy security and provide alternative sources liberating their economies for petroleum and fossil fuel dependence. At the same time renewable energy offers economic independence from imports and materials
- Renewable energy sources offer **flexible applications** in the production of electricity for the needs of small areas, away from urban areas. Also, renewable energy can be produced at local level without need for transport of fuels in remote p-laces.
- Technological installations and equipment for renewable energy sources are very **simple to install and maintain** and they have long life compared to conventional energy sources, especially for electricity.
- Renewable energy sources are **subsidised** by state institutions and international energy programmes because in the long term will offer energy security and provide local population with employment and technical expertise. In this respect Green Chemistry and Green Engineering can offer innovative ideas and methodologies.

10.3.2. Disadvantages of Renewable Energy Sources

Renewable energy sources have also many disadvantages compared to conventional energy resources. Especially when compared to fossil fuels.

- In 2011, despite the rapid progress in the last decade, renewable energy sources cover only 10% of energy needs in most countries. **High cost**, technological problems and cheap fossil fuels hampered their applications or postponed research and development. Renewable sources need **better networks** and systematic management to become widespread.
- Renewable energy sources have very **low efficiency** (only 30%) compared to conventional energy sources.
- **Efficiency** of energy production by solar, hydroelectric and wind power is restricted by climate, seasons, temperature, lack of rain, cloudy atmosphere or lack of winds blowing in the area. These limitations need to be overcome with better planning, networks and connections to a larger energy system that uses also conventional means of energy production at times of high demand.
- **Wind turbines** are expensive. Wind doesn't blow all the time, so they have to be part of a larger plan. Wind turbines are causing problems with flying birds, they are noisy, and cause esthetic problems in some mountain areas of natural beauty. Wind turbines need more design and management in the areas of installation. Some offshore wind turbines have become very effective in the production of electricity but are very expensive and have maintenance problems. There is no 100% eco-environmentally “clean” technological solution, even with renewable energy sources..
- **River Dams** are expensive to build and disrupt the environment. They have also caused earthquakes. Smaller turbines are cheaper and easier to install
- **Energy for sea waves** -- different technologies are being tried around the world. They are very expensive.
- **Energy by tides** -- barrages (dams) across river mouths are expensive to build and disrupt shipping.
- Some hydroelectric dams cause the production of methane from the decomposition of plants below the water. There is need for better “greener” technological solutions.
- **Solar energy, photovoltaic panels**. Some materials are still very toxic. Solar panels are expensive. Not all climates are suitable for solar panels.
- **biofuel** -- Often uses crop lands and crops (like corn) to produce the bio-alcohol. This means that more land has to be cleared to grow crops, or there is not enough food, or that food becomes more expensive.

Figure 10.4. Renewable energy resources are sustainable sources and can be replace without harm to the environment. Also, renewable energy sources are eco-friendly.

In the last decade there is an increasing number of seminars and teaching courses (at undergraduate and postgraduate levels) by Green Chemistry organizations and Green Engineering institutions for scientists and engineers on renewable energy sources and latest applications in many developed countries.

Example, the **ACS Summer School on Green Chemistry and Sustainable Energy (2011, McGill University (Montreal, Canada).** Sponsored by various scientific organizations that provided funds for the fees and accommodation.

Figure 10.5. Sponsors of summer course on sustainable energy.

10.4. Renewable Energy Sources and the Role of Green Chemistry and Engineering

Renewable energy sources are established and their advancement in the production of energy is very rapid. But despite their eco-friendly nature and their sustainability there is a large scope for improvement and the use of better materials. New materials and innovative technologies appeared recently with the use of nanocatalysis and bio-interfaces. These surfaces achieved a forward leap in the transformation of simple material into energy.

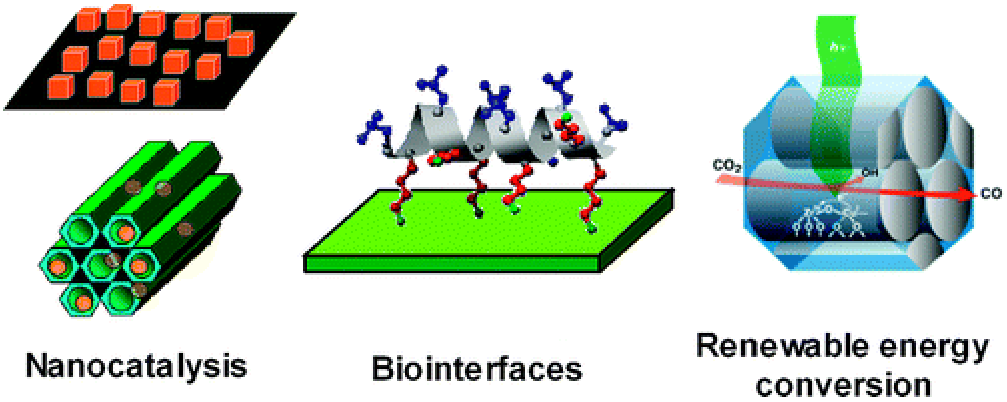


Figure 10.6. Nanocatalysis and bio-interfaces combined with other advances can be the new material for renewable energy production.

Recent research (Samorjai GA et al, JACS, 2009) advanced nanocatalysis and bio-interfaces in their role, as an innovative green chemistry application, for renewable energy conversion. Scientists used some of the most advance techniques in their study, such as scanning tunneling microscopy, sum frequency generation (SFG) vibrational spectroscopy, time-resolved Fourier transform infrared methods, and ambient pressure X-ray photoelectron spectroscopy. Nanocatalysis can form the platform for new arrangement of photosensitive materials. Innovative surface techniques can produce renewable energy through CO_2 to CO conversion.[14]

New technologies and new innovative materials for photovoltaic systems are improving every year through successive research applications. They have eco-friendly properties, their cost dropped substantially and their efficiency in the conversion of solar energy improved. Green Chemistry and Green Engineering played a substantial role in these innovations and the discovery of new materials (dye-sensitized photovoltaic cells, efficient solar cells).[15-20]

Technological advances have been achieved for of solar cells and electrochemical fuel cells, such as the hydrogen cell. These new technologies are the most efficient method for the hydrogen utilization in vehicles and its advancement has the “green” engineering prospects.[21]

Thousands of research institutes and industrial enterprises invested in innovative techniques and new materials for sustainable energy methods with eco-friendly outlook. The scientific literature is full of some innovative methods for renewable energy sources (hydrogen fuel, batteries, photosensitive materials, etc).[22-25].

At the same time analysts and technologists analyse trends and new applications. It is considered that of these methods will be very important in the future evolution of various sustainable techniques. Investment and competition, use of renewable materials, availability of raw materials and other factors will influence the future trends.[26,27]

The Green Chemistry Institute of the American Chemical Society organized in 2011 the 15th Conference of Green Chemistry and Green Engineering on the subject of renewable energy sources. Under the title "Annual Green Chemistry and Engineering Conference". Global Challenges, Greene Chemistry Solutions" there are various sessions that are going to be presented: "*Green Chemistry Approaches to Renewable Energy", "Green chemistry is having an impact on renewable energy including the use of earth, abundant materials and efficient catalyzed processes for energy storage, solar energy and fuels, and hydrogen storage, production and utilization".*
1) Biomass conversion to fuels;
2) Solar energy harvesting and conversion;
3) Energy storage in batteries, supercapacitors and chemical bonds;
4) Hydrogen production, storage and utilization.
As we can see the issue of renewable resources in at the top of interests of Green Chemistry

Figure 10.7. The 15th Conference (2011) of the Green Chemistry Institute of the American Chemical Society covers the subjects of sustainable energy sources and the role of Green Chemistry and Green Engineering.

10.5. Green Chemistry and Its Role in the Global Water Crisis. Water Shortages, Recycling and Reuse

The Planet Earth is facing one of the most urgent and serious problem of depleting natural resources. The global fresh water crisis. The problem of fresh water resources was from the past a critical factor in the development and collapse of civilizations. Water is also a factor for devastating infectious and parasitic diseases that exterminated large numbers of people in the Middle Ages. Global fresh water resources are threatened by rising demands from many quarters. Growing populations need ever more water for drinking, hygiene, sanitation, food production and industry. Climate change, meanwhile, is expected to contribute to droughts. The Organization of United Nations recognized the problem of fresh water and its international significance and promoted its sustainable use and conservation in developed and developing countries.[28-30]

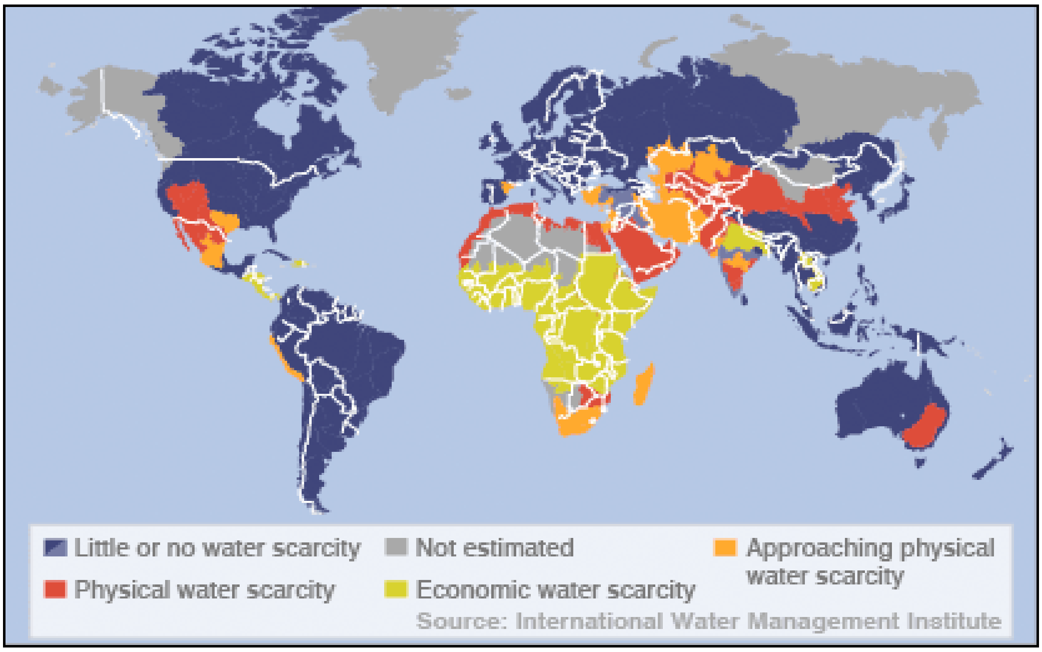
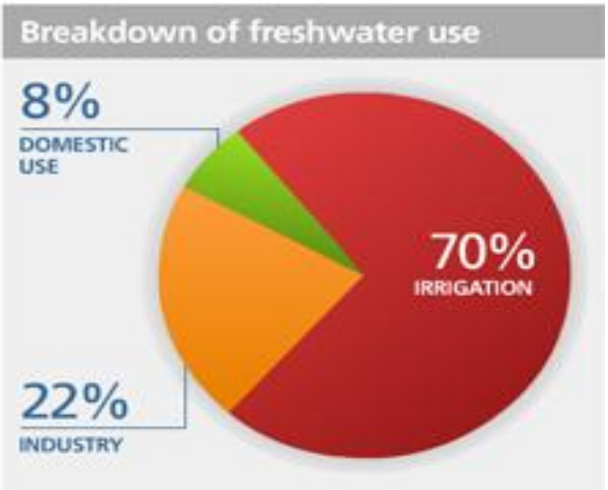


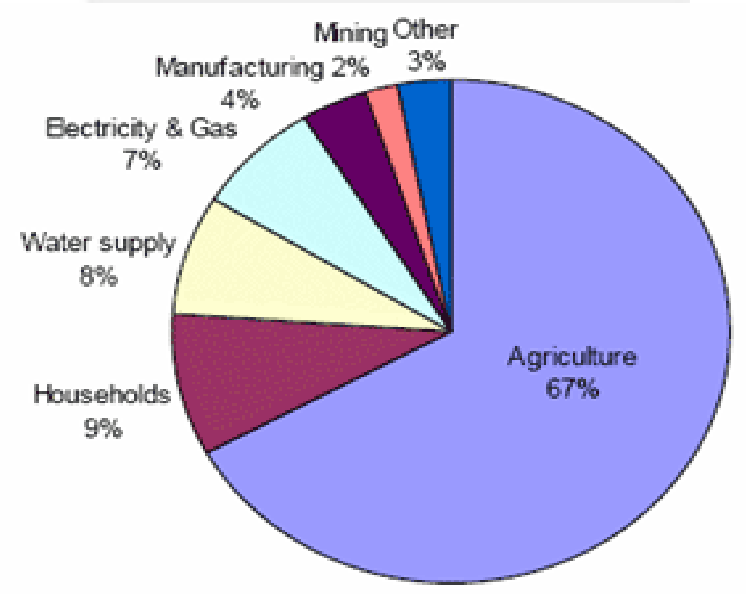
Figure 10.8. Global map of the areas that face acute shortages of fresh water. Africa countries, and especially the sub Saharan areas, are on the top list of acute shortages of fresh water (red colour). China, south Australia and India have also areas with high shortages of fresh water. (Source: International Water Management Institute, http://www.iwmi.cgiar.org/).

From 2001, OECD (Paris), the Organization for Economic Co-operation and Development which support the economic and developmental activities of the 34 most developed countries in the world, showed that agriculture and irrigation works consume between 56-75% of fresh water in most countries, while industry comes second with 20-22%. Among the various industrial sectors, the chemical industry is in the first position with 43% of the total water consumption by industry, in 2nd place with 26% is the metal processing industry and 3rd 11% is pulp and paper making.[31]

Agriculture is not only the major user of water resources but also contributes to water pollution from excess nutrients, pesticides and other pollutants. Sustainable management of water in agriculture is critical to increase agricultural production, ensure water can be shared with other users and maintain the environmental and social benefits of water systems. The OECD has been working for many years to address these challenges and to find “greener” solutions and technological innovations to reduce water use or to reuse and recycle waste water.

Green Chemistry and Green Engineering can play a very important role in all these innovations and technological advancements. Sharing water resources, sustainable use of water, recycling, advanced methods of treatments and reuse, and new more efficient methods of desalination. Green chemistry can provide tools to protect water quality in the face of increasing global pressures on water quantity. Green chemistry science and technology offers economically viable alternatives for water applications.[32]





Global water use in 2005

Figure 10.9. Consumption of fresh water in industrial and developing countries has increased substantially. Agriculture uses 67-70% (in Greece the 80-85%) of fresh water, industry 22% and households 9%.

Numerous research projects and technological solutions have been advanced in the last decades in order to minimise fresh water use and to find new methods for sustainable use. Green Engineering has offered many innovations and technological improvements for desalination, recycling and reuse of polluted water sources.[32-36]

In the last decades, the chemical industry invested heavily in plans to shave water and reduce consumption in various chemical processes. Water recycling, reuse and recovery in Industry: became a priority. Industrial wastewater treatment was another sect been researched and improved to a level that water can be reused again and again.[36-38]

The most important problem that chemical industry encounters with water is corrosion (it is used mainly for cooling industrial installations, metallic pipes and instruments, as well as in chemical reactions and as a solvent and for cleaning). Technological advances in this sector has been slow. Totytriazole (TTA) was used as anticorrosion chemical but had technical problems and was very toxic. Chemical industries needed technologies to treat suspended particulates and pollutants in their water systems. In the last decade many new anticorrosion materials appeared in the market, such as Bticorr-288 (Albright & Wilson American) and Stabrex (Nalco Chemical Co). These chemical highly anticorrosive but also less toxic and bidegradable.[32]

Pulp and paper industry and its associated technology was consuming vast amounts of water for many decades and its waste water was highly polluted. The composition of pollutants in waste water of paper industries, depend on the kind of raw material which was used. The oxidation and separation of lignin from cellulose was consuming vast amounts of water. Finally, the technological advances changed the process. Ozone, hydrogen peroxide and catalytic processes with polyoxometalates has reduced the use of water and waste water is not very toxic. Wood pulp paper bleaching is now performed by ozone or H_2O_2. The use of chlorine has been terminated, thus avoiding the production of highly dangerous dioxins and chlorophenols. Green Chemistry played an important role in these changes.[39-41]

Microelectronics and computer industries which produced semi-conductors and microchip were using millions of liters of ultrapure water. Also, these industries were using toxic chemical to scrub and prepared microchips. for the final steps of the industrial processes. The old methods of cleaning and in the final stages of the semi-conductors and chips were improved substantially. Supercrirtical CO_2 is used as a n eco-friendly technique.. Supercritical fluids have virtually no surface tension and a gas like viscosity, which enables them to clean these tiny spaces. The SCORR process has been shown to be effective at cleaning feature sizes down to the seven-micron level, which is the benchmark for the industry.[42-44]

During the last few years, carbon dioxide has also made inroads in the dry-cleaning industry, providing a safe cleaning alternative to the chemical perchloroethylene.

Another industrial sector which is using large amounts of water is textile and leather industry. Leather is usually tanned with chromium, or “chrome”: the chemical element used to coat other metals with a shiny finish that does not tarnish. Tanning hides with chromium salts produces soft, supple leather that can be dyed in a wide range of colours. By reducing the quantity of these salts to the precise amount required to maintain the quality consumers expect in a leather product, the discharge of chromium into the water used to process hides has been reduced by more than 90%. Large amount of water were once a significant part of many leather tanning processes. The leather industry has done its part to re-engineer its once-wasteful ways. For the past few decades, green science has helped the leather industry reduce its water consumption by more than 60% percent. This has been achieved by the development of new cleaning techniques, the use of batch processes instead of rinsing, and better water management.[46]

The pharmaceutical industry and film industry were using large amounts of water in their industrial processes. But in the last decades better design of industrial steps, innovations and better management reduced by 50% the use of water. The removal of silver (Ag) from the rinsing of films has been reduced substantially with a new photocatalytic method.[46,47.]

Metal processing industries is also another industrial sector that reduced the use of water with innovative changes in the chemical processes. Also, the recycling and management of aqueous waste haw been improved substantially.[32]

The chlorination of drinking water is a very important method for reducing microorganisms and infectious factors. In the last decades new disinfection methods have been advanced which are "greener", such as solar pasteurization, desalination with membranes, natural; filtration, and solar distillation.[48]

Green Chemistry and Green Engineering played a very important role in the innovative methods used today not only for the disinfection techniques of water, but in recycling, aqueous waste treatment, reuse, and sustainable management methods.[49,50]

Most of the North African and Mediterranean countries have an acute shortage of fresh water. At times of droughts some countries are suffering . In a recent conference in Athens, Greece, "*Advancing Non Conventional Water Resources Management in the Mediterranean*", (Athens 14-15/9/2011, Global Water Partnership Mediterranean) was very interesting in the innovative methods used by many countries and the sustainable use of water resources. Desalination, reverse osmosis, reuse of waste water after treatment, rainwater harvesting, recycling of agricultural water run off, inter-basin transfers were some the methods presented and were connected with sustainable water management.[51]

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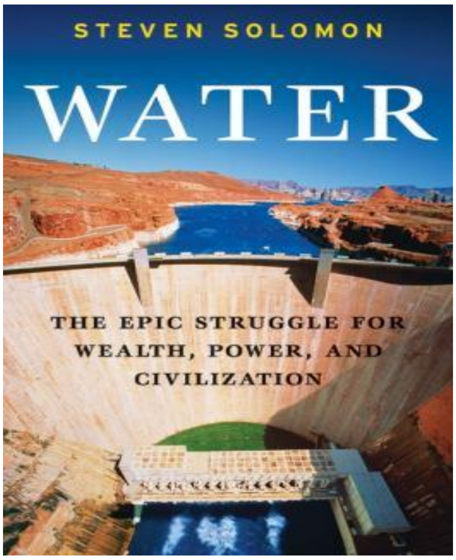
Books on the Global Water Crisis



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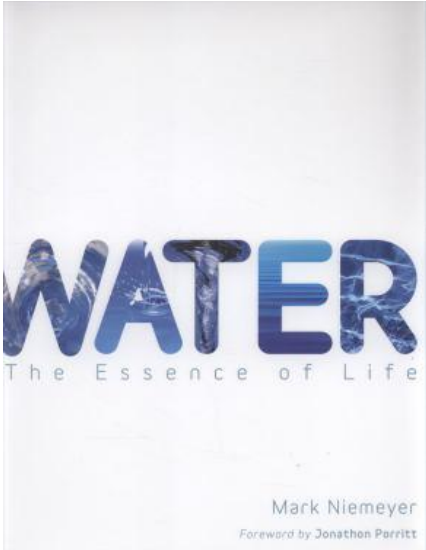

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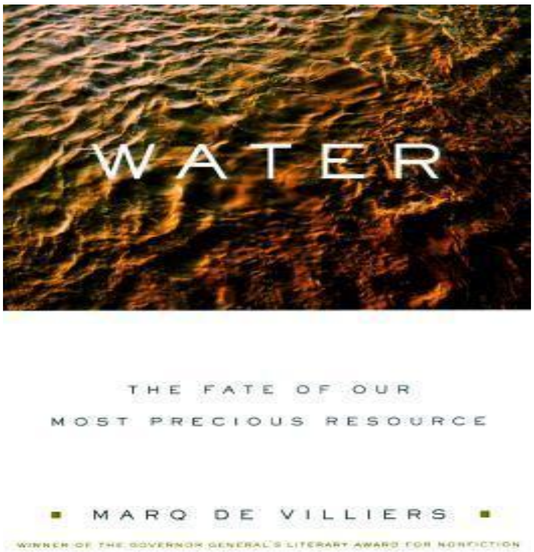

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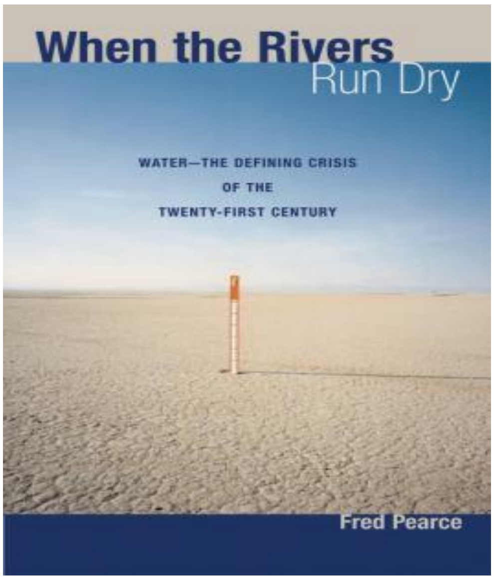

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11.Green Chemistry and Green Engineering. Eco-design and Recycling of Motor Vehicles, Electrical and Electronic Equipment

11.1. Global Production of Motor Vehicles, Electrical and Electronic Equipment

The Motor Vehicle, Electrical and Electronic Equipment Manufacturing advanced rapidly in the 21st century with innovative systems. Demand of these manufacturing products was very strong. In the past five years these industries had a very volatile market because of the economic crisis and the drop in demand of their products. Despite of the rising economies of China and India and other developing countries for motor vehicles, fridges, washing machines, computers and mobile phones, manufacturers showed a 4.3% drop in the product sales in the last five years.

These manufacturers use vast amounts of metals, plastic materials, electronic devices, paint and chemicals. At the same time they use high energy inputs, water and other natural resources and produce liquid and solid waste through their industrial processes. In the last decades all these industry have improved efficiency, introduced less toxic materials and reduce energy demand. Most of their products after their useful life cycle are designed for recycling of the most important parts and to minimize solid waste. Green Chemistry and Green Engineering have played an important role in all these changes of the last 20 years.

The Motor Vehicle manufacturers in the last decade produced more than 50 million vehicles per year. In 2010 the production reached 58 million vehicles and 19 million commercial vehicles of every type (total ~ 77 millions). China is at present the number one with 18 million vehicles annual production, Japan second with 9.5 million, USA third with 7.6 million. Germany 6, South Korea 4 and Brazil 3.5 million vehicles in 2010. Following the trends of motor vehicles demand and the increases of the market in the last years, it is evident that their production will increase 3-5 fold in the next 50 years.[1]

Electrical and electronic equipment manufacturing is another sector of economy that increased substantially with annual trends of 2-3%. Billions of electrical and electronic devices and equipments have become part of our modern life and improved substantially the quality of millions of people. These products consume large amounts of chemical materials, water, energy and produce in the end of the line vast number of liquid and solid waste.

The worldwide electrical and electronics industry is experiencing remarkable changes in the last decade. The worldwide electronics industry is distinguished by fast technological advances and has grown rapidly than most other industries over the past 30 years. Japan, Korea China, Taiwan, India and Singapore are the principal manufacturing hubs for electrical and electronics products. China very fast is becoming the manufacturing region of electronic products on the globe. The key electronics manufacturing in the USA are New York, Atlanta, Colorado, Detroit, New England, San Diego, San Francisco, and Texas. The electronic products manufacturing is expanding on an unprecedented scale in the Asian countries. In year 2002, Asia occupied 41% of total electronics market share, which has now risen to 56% in 2007.[2]

According to global statistical data the production of the Information Technology (IT), including electronic devices, computers, mobile phones, etc, in 2005 was a market of US $1.67 trillion (equipments) and $400 billions of services and programming, repairs etc. On a global scale, Japan is producing at present 24% of the electronic equipments and information products.[2]

International statistics of the last few years showed that electrical equipment and components accounted for a market of $285 billion (2008) and annual increases of 2-3% in the period 2004-2008. On a global scale, electronic equipment and instruments and electronic manufacturing services are estimated at US$ 626 billion and $106 billion respectively. The semiconductors manufacturing in 2009 was a market valued at $183 billion.[3]

In 2006, China became the largest producer of electronic products dominating the global electronics industry.

The increasing global production and demand for motor vehicles with conventional fuels is a very important environmental problem. It is estimated that 96% of cars use gasoline and diesel and consume 40% of the total petroleum products (approximately 75 million barrels). Atmospheric pollution by cars is a serious environmental problem in urban areas. In 1995 there were 500 million vehicles circulating on Earth. Today it is estimated that there are 1 billion vehicles and in 50 years 2-3.5 billion. In the USA (the highest ration in the world) there are 780 vehicles per 1000 population. International statistics showed that another grim statistical reminder is the 1.2 million deaths by car accidents (2.2% of all deaths).[4,5]

Figure 11.1. Motor vehicles, electrical and electronic equipments are causing major environmental problems by using depleting natural resources. After their useful life cycle both produce large volumes of toxic waste.

These global statistical data are presented to indicate the seriousness of the environmental problems and the inevitable use of natural resources for the industrial processes of millions of motor vehicle, electrical and electronic equipment every year. Waste and recycling of the vast volumes of these items is a daunting problems for all countries. China and India only, with their 2.5 billion population, have high demand for vehicles and electrical consumer products. Growth trends for motor vehicle and electrical consumer products in China and India for 2050.are very worrying. Projections showed that by 2030 China could have more highway vehicles than the U.S. has today. With the vehicle number projections and potential vehicle fuel economy data, it was projected that in 2050 China's on-road vehicles could consume approximately 614 million to 1,016 million metric tons of oil (or 12.4 million to 20.6 million barrels per day) and emit 1.9 to 3.2 billion metric tons (or 2.1 billion to 3.5 billion tons) of CO_2 each year. [Transportation Research Board of the national Academies, USA, Monograph, 2007. *Projection of Chinese motor vehicle growth, oil demand, and CO_2 emissions, through 2050*. (http://www.trb.org/news/blurb_detail.asp?id=8958)].

11.2. Recent Technological Improvements and Life Cycle of Motor Vehicles

The Life Cycle Analysis of motor vehicle, starting materials used, energy consumption, recycling and final waste have become important parameters in the design and processes for the manufacturers. All big motor vehicle manufacturers consider in the last decades the environmental impact of their products, the economy of fuel consumption, emissions of air pollutants, the type of polymeric and metal materials used, safety and efficiency in disassembly and recycling.

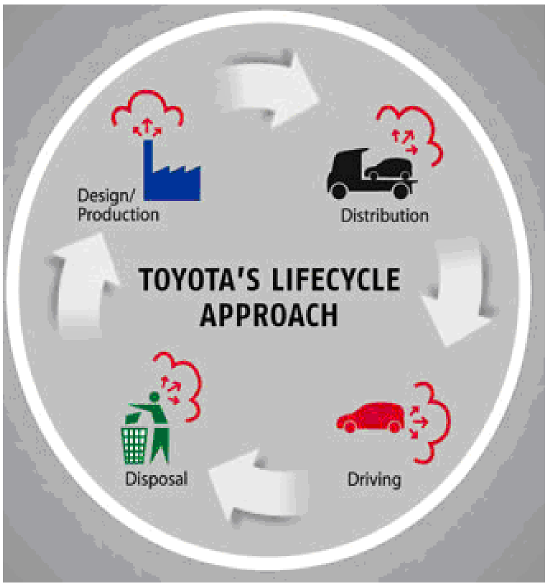


Figure 11.2. All big motor vehicle manufacturers consider seriously the environmental impact of their product. Designing, materials, emissions, safety and recycling are considered very important factors.

11.2.1. Improving Vehicle Fuel Efficiency

Controlling the energy demand from personal vehicles, and inevitable greenhouse gas (GHG) emissions, has become a major challenge for all countries. Curbing vehicle population growth, reducing travel demand and improving vehicle fuel efficiency are three key elements to reducing overall oil demand. A wide variety of approaches to address these three areas have been introduced in different parts of the world. Most industrialized countries have established programmes to address transportation related GHG emissions. Fuel economy programmes and GHG emission targets, either mandatory or voluntary, have proven to be among the most cost-effective tools in controlling oil demand and GHG emissions from motor vehicles.

The USA was the first country to establish fuel economy standards for passenger vehicles after the 1970's oil crisis (Energy Policy and Conservation Act, 1975). However, standards have remained unchanged for nearly a quarter century from the early 80s to late 2000s, while other countries especially European countries, Japan, and recently China, have moved forward, establishing or tightening GHG or fuel economy standards. In recent years, recognising the threat of climate change and potential oil shortages, efforts to further strengthen vehicle standards have been intensified globally. All major motor manufacturers have improved the efficiency of fuel economy of their vehicles [U.N. Commission on Sustainable Development (An F, Earley R, Green-Weiskel L, authors). *Global Overview of Fuel Efficiency and Motor Vehicle Emission Standards: Policy Options and Perspectives for International Cooperation*. 19th Session, New York, 2-13 May 2011].

The European Union from the 1980s had to endure the pressure of the strong lobby of motor manufacturers to undermine the EU fuel efficiency legislation and to avoid strict rules on fuel economy and emissions.[6-8]

Finally, the legislation imposed on passenger motor vehicles engines was 20 miles per gallon of petrol (mpg, 1 U.S. gallon =3.78 liters) established in 1985 and increased to 20 mpg recently and is hoped with the technological improvements to become 32.5 mpg in 2020.[5]

This reduction in the consumption of fuel in motor vehicles has been achieved by substantial improvements in the internal engines' technology. Vehicles and the automotive industry changed at an extremely fast pace from all perspectives, including technology innovation and deployment, the development and implementation of governmental standards and regulations, industry structural shifts and consumer choice.

Innovative technologies such as Battery Electric Vehicles (BEV) and Plug-in Hybrid Electric Vehicles (PHEV) pose new challenges when it comes to the quantification of fuel economy and fuel consumption. Some BEV manufactures have claimed that their vehicle achieve a fuel economies of up to 230 mpg a claim that caused controversy across the automotive industry. These substantial improvements were the result of "green" technologies and scientific innovations of the "green Engineering". Anastas and Zimmerman in their thoughtful article on the Principles of GE are indicating that "products, processes, space and time efficiency" is one principle that supports the big changes towards sustainable technologies in vehicles in the future.[9]

11.2.2. Reduction in Greenhouse Gas Emissions from Motor Exhaust

Under the pressure of environmental legislation and global warming, motor vehicle manufacturers were forced to redesign their vehicles for lower emissions. Especially in carbon dioxide (CO_2), nitrogen oxides (NO_x), carbon monoxide (CO) volatile organic compounds (VOCs) and suspended particulates (especially PM_{10}, 10 μm diameter). All modern motor vehicles are supplied with catalytic converters in their exhaust pipes. Air pollution from vehicles in urban areas in developed countries have been reduced substantially in recent years. Technological innovations minimize missions are because of environmental legislative restrictions.[10,11]

The European Union has its own set of emissions standards that all new vehicles must meet. Currently, standards are set for all road vehicles. Currently there are no standards for CO_2 emissions. The European Parliament has suggested introducing mandatory CO_2 emission standards to replace current voluntary commitments by the motor vehicle manufacturers. In late 2005, the European Commission started working on a proposal for a new law to limit CO_2 emissions from motor vehicles. In the USA, emissions standards are managed by EPA. The state of California has special dispensation to promulgate more stringent vehicle emissions standards, and other states may choose to follow either the national or California standards.

Although new vehicles are much “greener” than in the past, the rapid growth in the population of cars and the increasing fuel consumed remained around the same level. At present 1/3 of the fossil fuel energy on a global scale is consumed by various types of motor vehicles and transport and 50% of their emissions are toxic exhaust gases that are dangerous to human health and the atmospheric environment. Green Chemistry and Green Engineering are aiming to reduce further vehicle fuel efficiency, to introduce alternative energy sources (hydrogen, biofuel, electric cars, hybrids, etc) and through technological innovations to reduce vehicle emissions.[12,13]

11.2.3. EcoDesigning of Motor Vehicles, Electric and Hybrid Vehicles

For many decades the industrial strategy of motor vehicle manufacturers was to reduce the cost of industrial processes and lower the price of their vehicles. Other features that were strategic goals for the vehicle manufacturers were motor durability, easy maintenance, high speed and safety. Only in the last decade manufacturers added environmental impact, lower emissions, design for final disassembly and recycling.

Every year at global scale millions of motor vehicles are scrapped. The average lifespan of a car is 13-15 years. Also, the composition of a typical motor vehicle has changed substantially in recent years. Ferrous metal content has decreased significantly as lighter, more fuel-efficient materials such as plastics are incorporated into vehicle design. The recycling of parts and the reclamation of materials from motor vehicles is not a new industry. Metal parts in particular have for a long time had a value, either in terms of reuse or recycling. The dismantler will remove parts that can be sold for reuse. Also, dismantlers will remove the potentially environmentally polluting materials such as operating fluids and batteries (EC Directive 91/157/EEC), and then sell the hulk on to a shredding operation. Ferrous metals (by weight

~75%) are then removed by magnetic separation and non-ferrous metals are sorted both mechanically and by hand. Currently, the recycled vehicles in the developed countries is much greater than any other consumer product. But in the end of recycling million tones of remaining materials are buried in landfill sites each year. These materials are mainly made up of plastics, rubber, glass, dirt, carpet fibres and seat foam.

A typical family motor vehicle has a mean weight of 1500 kg (1998) and most of its body consisted of metallic items (75%) that were reduced and replaced with plastic. In 1977 plastics consisted of 4.6% and increased into 10-12% in 20 years. Aerodynamic design and new efficient rubber tyres improved fuel efficiency and there were many other improvements. The oil crisis, atmospheric pollution and global warming were the most important factors that influenced new legislation for small vehicles and stricter environmental standards.[14,15]

Figure 11.3. Hybrids and electrical vehicles is the new technological evolution in the motor vehicle manufacturing. It is considered that these changes will take many decades to establish.

The most important development in recent years was the **hybrid electric vehicle** (HEV). This motor vehicle combines a conventional internal combustion engine propulsion system with an electric propulsion system. The presence of the electric powertrain is intended to achieve either better fuel economy than a conventional vehicle and better eco-performance. Modern HEVs are much lighter and make use of efficiency-improving technologies (regenerative braking, which converts the vehicle's kinetic energy into electric energy).

Some varieties of HEVs use their internal combustion engine to generate electricity by spinning an electrical generator, while others reduce idle emissions by shutting down the internal combustion engine (minimizing urban pollution). The hybrid vehicles improve fuel efficiency by 20-40% compared to conventional vehicles. Under urban condition the hybrid vehicle can use its electric system improving fuel efficiency to 40%. Hybrid vehicles have all the characteristics of “green” design and “green” engineering but their prices remain much higher than conventional despite zero road tax for 5 years in many countries. There are also hybrids with fuel cells which use hydrogen and oxygen (air) to produce electricity.[16-18]

The Toyota hybrids combined with Lexus reached 1 million hybrids sold in the U.S. by 2009, and worldwide sales of hybrids by both brands totaled over 2 million vehicles by 2009. As the top selling hybrid in both the U.S. and Japanese markets, the Toyota Prius reached global cumulative sales of 2 million Prius in 2010. Worldwide, Toyota Motor Company is the leader with more than 3 million hybrids sold in 2011, followed by Honda Motor Co, and Ford Motor Corporation.

Research and developments of new technologies and innovations are continuing for improvements in motor vehicle performance and efficiency in fuel consumption. Despite these improvements, motor cars are a heavy burden for our meta-industrial civilization because they consume depleting natural resources and pollute the environment (emissions and waste). The population of motor vehicles is expected to reach one billion in 2020 worldwide, but it is hoped that new technological innovations, alternative fuels and recycling will make them “greener”. It is envisaged by Green Chemistry and Green Engineering principles that their industrial production will use “greener’ materials, better eco-design for easy disassembly and recycling of the majority of their parts and lower fuel consumption. These plans of course need more stringent legislation, investment in research and technologies in near future.[19, 20]

11.3. Improvements of End-of-Life Recycling of Motor Vehicles

Technical innovations and substantial improvements in the life cycle of motor vehicles, fuel economy and recycling were as a result of intense research and development in the last decades. New legislation, global warming, fossil fuel crisis and environmental concerns influenced these changes.

Despite all these changes road transport accounts for 20-25% of total emissions of carbon dioxide (CO_2) in most developed countries, contributing to climate change (greenhouse gases). Air pollutants from transport have adverse health effects to people and pollute the environment. Noise from road traffic affects large proportion of the urban population. The massive increase in vehicle numbers on a global scale have major impact on the natural resources through the use of depleting raw materials and the disposal as waste after end-of –life.

One of the most important problem is after the end-of-life vehicles are abandoned and are categorised as waste. Vehicles can go to special dismantler units and scrap dealers. All developed countries have very strict rules for end-of-life vehicles. Dismantlers strip the vehicles from anything recyclable and treat the rest as waste. It is estimated that on a global scale every year 40-50 million motor vehicle and trucks are in the end of their useful life and are becoming toxic waste. Vehicles must be processed to ensure that potential pollutants such as fuel, oils, brake fluids and other liquids are removed, collected and stored. Operators will need to ensure that de-pollution of vehicles is carried out in a manner that both controls environmental risk and the risks to the health and safety of those working in the industry. In the USA is estimated that 12 million vehicles every year are going for recycling. In the countries of the European Union recycled vehicles produce around 8-9 million tones of toxic waste. But despite strict legislation many countries have serious problems with old cars which are abandoned in urban areas. Recycling is a proper method to deal with the problem of old vehicles and million of tones of toxic waste can be useful for new materials.[21,22]

In the last decade motor vehicle manufacturers introduced Green Chemistry and Green Engineering principles in the motor industry aiming for alternative design and incorporation eco-features not only in the material used but also for easier disassembly and recycling. Environmentally benign manufacturing in the motor vehicle is intended to become one of industry's greatest strategic challenges, not only from an engineering perspective, but also from a business and marketing perspective. The new trends in the motor vehicle manufacturers are: lightweight, low/zero emissions, alternative propulsion systems, reduced vehicle energy consumption, weight reduction to improve fuel economy, renewable and sustainable raw materials,, increased recyclability and disposability after end-of-life. The motor vehicle is the world's most recycled consumer product.

In the USA and Canada 95% of old-retired cars are processed for recycling every year, at least 86% of a car's material content is recycled, reused and recovered. Recycling vehicles provides enough steel to produce almost 13 million new motor vehicles and saves ~85 million barrels of oil annually. New motor vehicles are expected to last more than 15 years.

All new motor vehicles are designed so that after retirement they can be easily disassembled into metals, plastics, oils, glass, rubber tyres, electronic items, batteries, electrical wires, etc. [23-25]

Figure 11.4. Recycling old motor vehicles is widespread in all developed countries. The motor vehicle is the world's most recycled consumer product.

In the countries of the European Union (EU) there are, around, 263 million motor vehicles (2006). In the last few years the motor vehicle market (annually) is around 15.7 million, while 13-14 million are retired as old or damaged. From the total number of motor vehicles only 7-8 million are recycled in dismantler operators and scrap merchants. 4-5 million retired motor vehicles are sold as second hand in other countries (Eastern Europe, Russia, Asia). Dismantling of motor vehicles has been covered in the EU with the 2000 Directive 2000/53/EC End-of-Life Vehicle (ELV). The EU has added technical improvements and the goals of the directive is for recycling 85-95% of old vehicles with environmental criteria.[26]

Motor vehicle recycling has become a very important issue in developed countries. Licensing and regulating operators for dismantling and scrap dealers has become a very profitable operation and million of useful materials are recovered. Rubber tyres, oils, batteries, metal, plastic, rare metals form catalytic converters (Pt, Pd), and electronic devices are recovered or used saving energy and raw materials.[27-31]

In the USA, the Society of Automobile Engineers (SAE International, Wareendale, PA, an association of 128.000 engineers, has produced very interesting materials for Green Chemistry and Engineering in the Automobile Sector.(Henry CJ. "*Environmental Sustainability for the Automotive Industry*: *Progress and Next Steps"*. Michigan GreenUp Conference, Ann Arbor, MI, October, 2011) [www.sae.org]

SAE J2960– "Implementation of Green Chemistry and Engineering within the Automotive Sector" under development, and SAE J2965 – "Terminology and Definitions for Green Innovation and Sustainable Practices in the Automotive Industry" under development Inventory of Green Chemistry & Engineering Case Studies from EPA Awards

Examples of Green Chemistry & Engineering Projects in the Auto Sector

Prevent Waste, . Design Less Hazardous Syntheses

- PPG'S Green Logic® Paint Detackifier: replaces petroleum-based and melamine-formaldehyde products.
- Zircobond Pretreatment: eliminates chrome, zinc, nickel, manganese,
- and phosphate from the metal pretreatment process

Example of Green Chemistry & Engineering Projects, Auto Sector-

Use Renewable Feedstocks, Biomaterials in Autos*,* Biopolymers

- Bio based resins: corn, castor beans, sugar cane
- Soy, soy oil: foams, thermoset resins, fillers, Fillers and Reinforcements
- Natural Fibers: hemp switch grass, flax, wheat straw, wood, kenaf, coconut
- One example of many products on the market: Biofoam soy seats
- In over 2 million Ford vehicles, in GM's Chevy Volt, and Nissan's Leaf

Elements in a "Green Car Factor" for Best Practices or Standards

- Direct vehicle emissions, Fuel/energy source/environmental impact
- Biofuels, Low carbon (e.g., natural gas)
- Environmentally friendly charging sources
- Materials: Components, panels, seats, electronics, power-train, tires
- Service: refrigerants, coolants, lubricants, hydraulics
- Impact on cabin air quality (chemical releases)
- Manufacturing processes: Waste produced, Resources (water, energy) consumed,
- Recyclability and disposability

(http://www.michigan.gov/documents/deq/deq-oea-chemistry-c3-henry_368244_7.pdf)

11.4. New Trends in "Green" Designing and Recycling of Electrical and Electronic Equipments

The energy crisis of the last decades, the depletion of natural resources, global warming and environmental pollution inevitably forced many engineers and manufacturers to think about green engineering in the electrical and electronic sectors of the economy.

Electrical and electronic manufacturing uses million of tones of metals (some of them very rare), plastics, energy, solvents and many depleting natural resources to manufacture, package and distribute their products. Conventional industrial methodologies, type of raw materials, designing and recycling were always part of the problem for many electrical and electronic devices. Electrical and electronic industries have changed drastically in the last decade with application of green chemistry and engineering principles, renewable and degradable starting materials, less toxic and dangerous chemicals, recyclable packaging plastic. Also, the new products have been ecodesigned for disassembly, recyclability and convenient disposal after the end-of-life. Eco-efficiency and ecodesign of their products are the most important issues now for electrical and electronic manufacturers .[32-34]

The European Union (EU) established special Directive for the ecodesign (2005/32/EC) and for recycling (2002/96/EC of electrical and electronic products and their components.[35,36] Companies producing a wide range of energy using products will have to comply with EcoDesign requirements in order to maintain their CE marking so that these products can continue to be sold in EU Member States. The EcoDesign Requirements for Energy Using Products (EuP) Directive became law in EU Member States in August 2007 and will set EcoDesign requirements for specific groups of products. The EcoDesign requirements will reduce the environmental impact of products across the life cycle, with a particular focus on energy.[35,36]

The electrical and electronic products targeted by the EcoDesign EU Directive are : Boilers, Water heaters (gas/oil/electric), Personal computers, Imaging equipment (copiers, faxes, printers, scanners), Consumer electronics (televisions), standby and off-mode losses of all electrically powered devices, Battery chargers, Office lighting, Public street lighting, Residential room conditioning appliances, Electric motors 1-150kW, Water pumps, Fans, Commercial refrigerators, Vending machines, Chillers, Domestic refrigerators, Freezers, Domestic dishwashers and Washing machines, Simple converter boxes for digital televisions

The WEEE Directive (Waste Electrical and Electronic Equipment directive 2002/96/EC). Producers of electrical and electronic equipment are facing strict new compliance rules for **collection, recycling and recovery** of waste equipment across ten broad categories, including IT and telecoms, electrical tools, medical electrical devices and control and monitoring equipment. WEEE compliance requirements are different in each EU Member State. But ENVIRON's web-based compliance systems enable manufacturers and importers of business products to have a single system for WEEE collection, recycling and reporting across Europe, see www.b2bweee.com for details.

RoHS Directive (Restriction of Hazardous Substances Directive, 2002/95/EC) The RoHS Directive requires that electrical and electronic equipment must not contain more than > 0.01% by weight of cadmium or > 0.1% by weight of lead, mercury, hexavalent chromium, PBB or PBDE in any single homogenous material. See b2bweee.com/legislation/rohs-obligations for further details

Manufacturers of refrigerators, washing machines and other electrical appliances) for years have complied with new legislation but also have changed drastically their practices to have "green" properties and ecodesign features of their products. They replace many toxic raw materials, upgraded the energy efficiency and introduced ways for easy disassembly, recycling and disposal.[37-41]

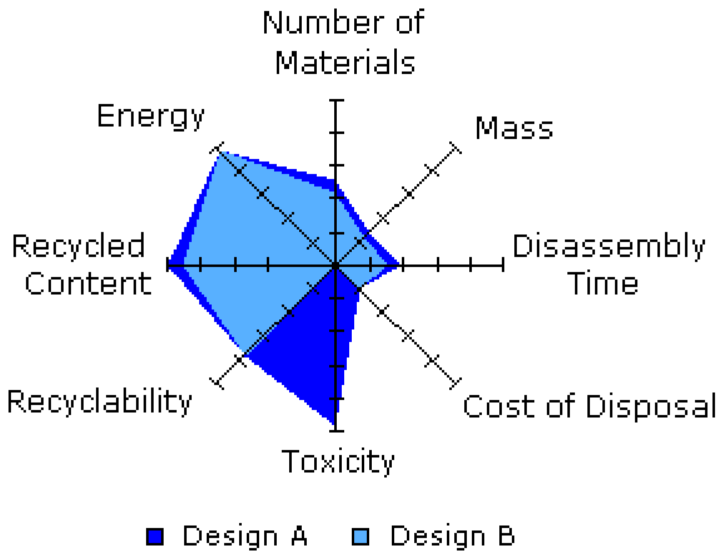
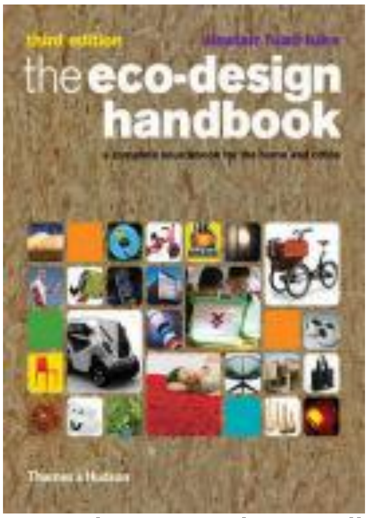


Figure 11.5. Schematic presentation for the "green" design for many appliances and products of Motorola from the University of Erlangen. The two colours show how product B has more environmental impact, higher toxicity, higher energy use, and cost for recycling in comparison with product A.
(Πηγή: http://www.motorola.com/EHS/environment/products/)

Electrical and electronic equipment and appliances that have been designed with the principles of Green Chemistry and Green Engineering have special codes and labels that inform the consumer about the materials of their components and ways of recycling (especially for plastics). In recent years recycling of electrical and electronic equipment have become a big industry and recovering rare metals and expensive materials is very profitable and can be used for new electrical and electronic systems.[42,43]

11.4.1. A Typical Example of Recycling a Washing Machine

Every year millions of washing machines (which has become a household appliance for all families in the developed and developing countries) come to the end of their useful life and have to be disposed and recycled. Dissasembly and recycling of a washing machine is a good example of an electrical appliance and its problems when the product has terminated its useful life. Washing machines contain a series of different materials, electric and electronic devices and composite materials.[44]



Alastair F-L. The Eco-Design Handbook. A Complete Sourcebook for the Home and Office. Thames & Hudson, London, 2009

Figure 11.6. The EcoDesign of electrical and electronic equipment and appliances has become the rule and by following the Green Chemistry and Green Engineering principles will save energy, depleting materials and protect the environment.

Disassembly of the various parts and separation of the components and composite materials is a highly specialized job and requires special instruments. The original design of the washing machines can help substantially in its separation into useful materials (metals, plastic, electronic, magnetic valves, compressors, thermal devices, electrical machine, etc).[45,46]

In many countries now there are special disassembly workshops that are sustainable because of the high price materials that can collect from the electrical machines and appliances. Some workshops can be connected with the manufacturers of electrical equipment and their contribution to environmental protection can be subsidized.[47,48]

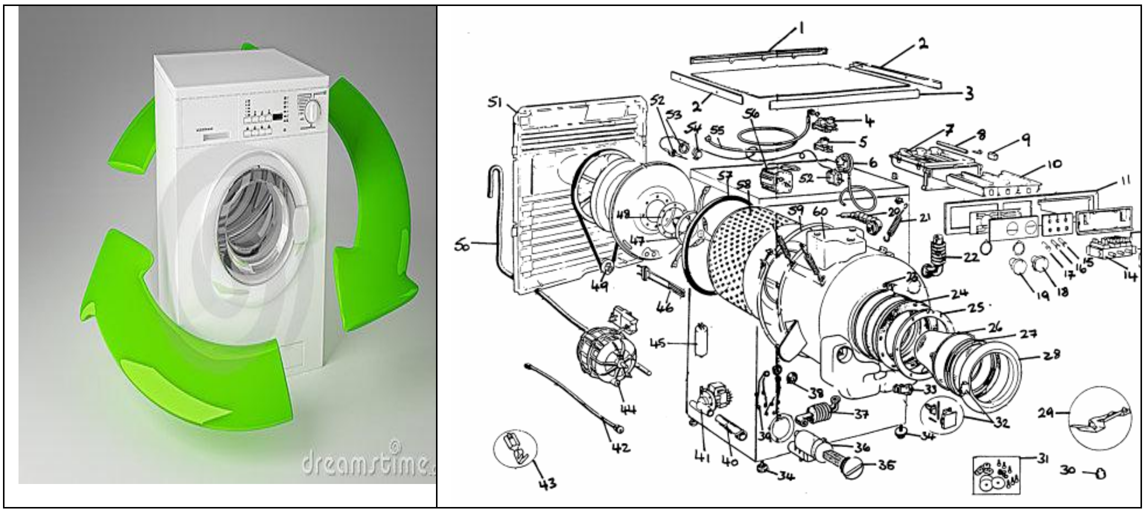


Figure 11.6. Disassembly and recycling of materials from electrical and electronic equipment can be a highly sustainable processes. EcoDesign can save depleting materials, energy and protect the environment. Green Chemistry and Engineering principles can apply to a great degree in all these processes and has economic and materials advantages.

11.4.2. Disassembly and Recycling of Mobile Phones

The first mobile cell phone appeared on the market in 1983 (Motorola, weight 800 g). Recent global statistics estimate that there are 3.5 billion mobile phones on the planet Earth. Mobile phone technology changes in the last 20 years every 2-3 years and approximately, 500 million mobile phones are sold every year. Inevitable million of mobile cell phones are thrown away. Mobile phones use some very expensive microprocessors and rare metals and manufacturers use large amounts of energy, solvents and water.[49,50]

Figure 11.7. Statistical data showed that there are 3.5 billion mobile phones circulating on a global scale. Mobile phone rejection is a serious environmental problem

The new generation mobile cell phones (3G, 4G) in the 21st century resulted in the explosive rise of mobile phone usage worldwide. Mobile phones use very important materials, such as copper, gold, palladium, silicon, intergrated circuits, etc. Also, the production of mobile cell phone requires considerable amounts of energy and water, and generates large amounts of pollution and waste. The massive rejection of obsolete or damaged mobile cell phones every year has become a very serious environmental issue and causes extensive damage to the aquatic environment, soil and the atmospheric air. Many studies in recent years found that disposal of used mobile cell phones produce toxic waste and numerous toxic pollutants [51-55]

Recycling of mobile cell phones has become obligatory in recent years in many countries and companies design their phones in such a way that can be recycled. In recent times more interest has been taken in the damage that is being done to our environment by mobile phones and other electronic devices. Many mobile phones contain a number of components which are potentially hazardous to the environment if not disposed of in the proper way. Recycling is actually becoming more important in the production of new mobile phones. The supply of raw materials used to create mobile phones will not last forever and so reusing the materials found in older models is becoming more necessary in order to produce new devices.[56,57]

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12. Green Chemistry and Green Engineering in Education

12.1. Sustainable Development and Green Chemistry

Our planer Earth showed from the 1980s serious and urgent problems of environmental pollution, an acute energy crisis and worrying depletion of natural resources. Sustainable development is a concept that at its core has a vision to balance different, and often competing, needs against an awareness of the environmental, social and economic limitations we face as a society. In the past economic development and particular needs of society were aiming for material consumption and a high level of life quality without considering the wider future implications

The longer human civilization pursue unsustainable development, the more frequent and severe its consequences are likely to become, which is why we need to take action now. Living within our environmental limits is one of the central principles of sustainable development. One implication of not doing so is climate change, the other is depletion of natural resources and environmental degradation of sensitive ecosystems, and biodiversity. Sustainable development is far broader than just environment, It is also about ensuring a strong, healthy and just society (social cohesion, equal opportunities).

The concept of sustainability or sustainable development received its first major international recognition at the **UN Conference on the Human Environment** (Stockholm, 1972). The term was popularized later (1987) by the World Commission on Environment and Development in their report “Our Common Future” (headed by the Norwegian prime minister, Brundtland Commission in the 1987 report). The “classic” definition is “***"development which meets the needs of the present without compromising the ability of future generations to meet their own needs".***

The Brundtland Report investigated the numerous concerns that had been raised in previous decades, that human activity was having severe and negative impacts on the planet, and that patterns of growth and development would be unsustainable if they continued unchecked. In the past some of these concerns were pressed through some important books, such as, Rachel Carson's *Silent Spring* (1962), Garret Hardin's *Tragedy of the Commons* (1968), *the Blueprint for Survival* by the Ecologist magazine (1972) and “The *Limits to Growth*” report by the Club of Rome (1972).

The concept of “sustainable development” (SD) formed the basis of the 1992 International Conference (or World Summit, held in Rio de Janeiro)) United Nations Conference on Environment and Development. The summit marked the first international attempt to draw up action plans and strategies for moving towards a more sustainable pattern of development.

The two key concepts of SD are: a) *the concept of **needs**, in particular the essential needs of the world's poor, to which overriding priority should be given; and b) the idea of **limitations** imposed by the state of technology and social organization on the environment's ability to meet present and future needs."* All definitions of sustainable development require that we see the world as a system—a system that connects space; and a system that connects time (International Institute for Sustainable Development, Canada).

Another definition of sustainable development as a result of various conferences and the urgent environmental problems of the planet. "*Sustainable development is maintaining a delicate balance between the improvement of the quality of life in the framework of carrying capacity of the supporting ecosystems*" [International Union of the Conservation of Nature (IUCN), United Nation Environmental Programme (UNEP) και (World Wildlife Fund, WWF), 1991].

There are over 100 definitions of sustainability and sustainable development. For example, a good definition of sustainable development is "maintaining a delicate balance between the human need to improve lifestyles and feeling of well-being on one hand, and preserving natural resources and ecosystems, on which we and future generations depend".

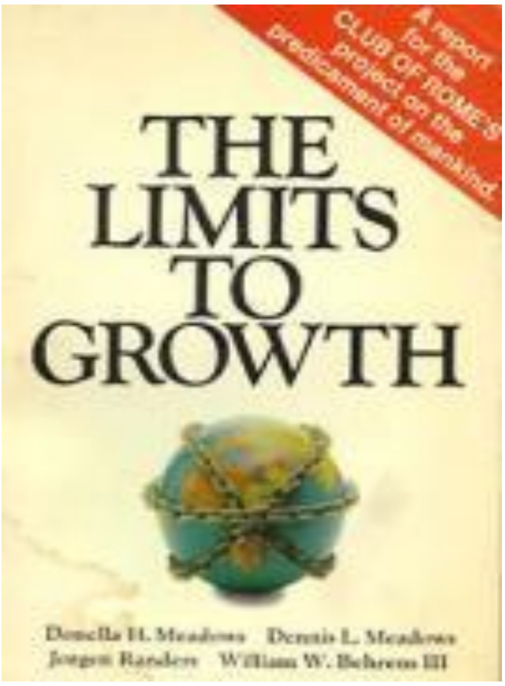
Another definition by the well known scientist Meadows (The Limits to Growth) "Sustainable is a society that can exist for generations and generations and can see in the future, a society that is flexible and wise so that do not undermine natural, social and supporting systems" (Meadows et al., 1992). The World Bank has its own definition of sustainable development "a process of managing a portfolio of assets to preserve and enhance the opportunities people face. Sustainable development includes economic, environmental, and social sustainability,which can be achieved by rationally managing physical, natural and human capital" (World Bank, 1992).

Figure 12. 1. Sustainability or Sustainable Development is a concept that has fundamental principles for the development of the human society on the planet Earth.

12.2. “Limits to Growth” and Its Relevance Today

From the 1970s a progressive group of scientists and industrialist concerned by the exploitation of natural resources and environmental pollution formed the Club of Rome and in 1972 published the book “***The Limits to Growth***”, a book that caused a stream of scientific discussions, programmes on TV and radio and many new paper on scientific journals. The book projected with scientific means the condition of the natural environment, the depletion of natural resources (metals, oil, water, soil) and the precarious situation for the future of human society. The central message of the book was that economic and industrial growth have restrictions because of the limited resources of the planet

“Limits to Growth” used the World3 model (computer programme) to simulate the consequence of interactions between the Earth's and human systems. The programme simulated the consequence of interactions between the Earth's and human systems. Five variables were examined in the original model, on the assumptions that exponential growth accurately described their patterns of increase, and that the ability of technology to increase the availability of resources grows only linearly. These variables are: world population, industrialization, pollution, food production and resource depletion. The authors intended to explore the possibility of a sustainable feedback pattern that would be achieved by altering growth trends. The purpose of the book was not to make specific predictions, but to explore how exponential growth interacts with finite resources.



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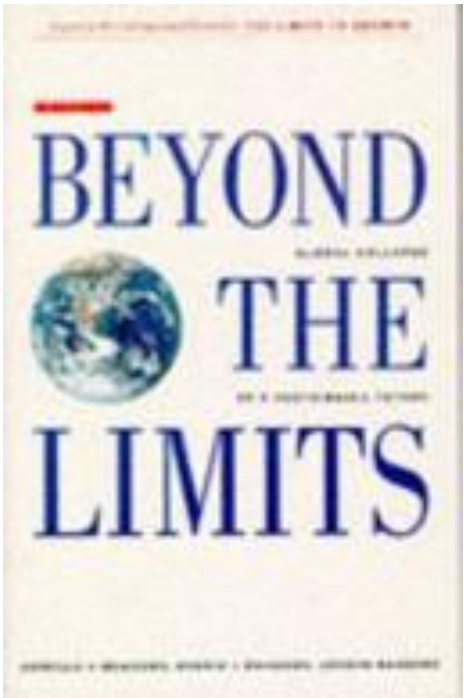

1992

Figure 12.2. Are they limits for the exponential growth of the human development? Earth’s resources are limited. The question is can human society grow without limits? Are these limits already reached?

“The Limits to Growth” was a milestone in attempts to model the future of our society, and it is vital today for both scientists and policy makers to understand its scientific basis, current relevance, and the social and political mechanisms that led to its rejection.[Bard U. *The Limits to Growth Revisited*. Springer, New York/Heidelberg, 2011].

In the 1968 Intergovermental Conference for Rational Use and Conservation of Biosphere (UNESCO), the issue of conservation of natural resources was very prominent. The same problem was emphasized in the thoughtful book of Rene Dubos and Barbara Ward “Only One Earth” (1972). In the 1972 Meeting of the International Union for Conservation of Nature and Natural Resources (IUCN), scientists put forward the critical problem of development and its connection to limited natural resources of the planet. From 1975 the United Nations Environment Programme (UNEP) and the World Wide Fund for Nature (WWF) published some studies for the strategic involvement in plans for sustainability and the future of the planet.[1-3]

All these events and studies paved the way for the successful 1972 first ***International Conference on the Human Environment*** (Stockholm) of the United Nations on Human Environment. It was the UN's first major conference on international environmental issues, and marked a turning point in the development of international environmental politics, attended by representatives of 113 countries and 400 governmental and non-govermental (NGOs) organizations. The meeting agreed upon a Declaration containing 26 principles concerning the environment and development; an Action Plan with 109 recommendations, and a Resolution. The conference paved the way for international actions (global warming, ozone layer, sustainable development, environmental education, etc). Sustainability or Sustainable Development became a concept of the future conferences, incorporating terms of environmental pollution, biodiversity, conservation of ecosystems, economic development, environmental education and others.

Environmental Education has been named as Education for Sustainable Development. Sustainability education (ES), Education for Sustainability (EfS), and **Education for Sustainable Development** (ESD) are interchangeable terms describing the practice of teaching for sustainability. ESD is the term most used internationally level and by the United Nations. **Agenda 21** was the first international document that identified education as an essential tool for achieving sustainable development and highlighted areas of action for education [books, Huckle, J, Sterling, S.R. (2006) *Education for Sustainability.* Earthscan, London, 2006; Tilbury, D Wortman, D. *Engaging People in Sustainability*. IUCN, Gland, Switzerland, 2004].

Green Chemistry and Green Engineering (Technology) have their roots in the fundamental principles of sustainable development (SD) . This was part of the United Nations Commission on Sustainable Development (CSD) that was established in 1992 by the General Assembly of the UN (UN Economic and Social Council). This was a global recommendation by the UN Earth Summit or Conference on Environmental Development (Rio de Janeiro, 1992).

Around the same period the term Green or Sustainable Chemistry was proposed for the first time in 1991 by the chemist Paul T. Anastas of the EPA as a new “philosophy” of chemical research and engineering that have environmental criteria, minimization of toxic substances and the use of renewable raw materials. Green Chemistry did not appeared out of the bleu but it was stimulated by changes in environmental laws and restrictions on industrial pollution. The USA Congress passed in 1990 the Pollution Prevention Act, an act that helped create a strong awareness on prevention of environmental pollution and emphasized the problems of sustainability.

The rest is history with fast developments in the world of green chemistry. In 1996 IUPAC (Paris established the Working Party on Green Chemistry), and in 1997 the Green Chemistry Institute, of the American Chemical Society, was formed. The GCI organized in 1997 the first International Conference on Green Chemistry of the IUPAC in Washington DC. In 1998 the first International Summer School on Green Chemistry started in Venice. Professor James Clark (York University, UK), after many years of research on GC, managed in 2001 to win a generous fund from the Engineering and Physical Sciences Research Council of UK to start the Green Chemistry Research Network, and an internationally well known Green Chemistry Centre of Excellence for research and higher education courses with the help of the Royal Society of Chemistry (RSC).[4,5]

In the last decades there are numerous new higher education courses and university department (chemistry, engineering) that are devoting their facilities and educational resources for Green Chemistry and Green Engineering in many countries. Research and industrial applications are increasing exponentially and many industrial enterprises and well known industrial companies are establishing new “greener” products.[6]

12.3. University Departments and Courses for Green Chemistry and Green Engineering

The educational and technological aspects of Green Chemistry and Green Engineering had a direct relevance to environmental sciences, applied organic and bioorganic chemistry, chemical, mechanical and electrical engineering courses with numerous applications, new materials, energy reduction and innovative chemical processes in industry. The prospect of new technologies and methodologies in the research laboratory and the manufacturing sector stimulated interests for new courses in research institutes and university department with sustainable development in mind.

Green Chemistry courses at university level were aiming, at undergraduate and postgraduate level. They are for chemists, biochemists, mechanical and electrical engineers to get new knowledge and skills required to design, synthesize and make materials in environmentally and eco-friendly ways. This aim can be achieved by using the 12 principles of GC and innovative research. At first, lessons will present the most important and urgent environmental problems of our planet, the depletion of natural resources and aspects of the conventional manufacturing technologies. Secondly, lessons will look at real world green chemistry and green engineering products. The emphasis will be on processes and manufacturing techniques dealing with starting materials (renewable and non-renewable), energy use, solvents, catalysis and bio-catalysis, and other methodologies. Lessons can deal with industrial case-studies, comparing the conventional “old” method and examples where green chemistry has been successfully implemented. The economic and environmental implications are obviously part of the “real” world manufacturing and students can get a thorough knowledge of how to study the problem and apply green chemistry solution through the 12 principles [*Center for Green Chemistry and Green Engineering at Yale, Introduction to Green Chemistry course*]

In the last decade new courses on Green Chemistry and Green Engineering, at undergraduate and postgraduate levels, started in many universities in USA, Great Britain, Italy, Spain, Australia, France etc. At the same time many conventional chemistry and engineering courses have introduced in their undergraduate and postgraduate curriculum subjects, additional lessons on Green Chemistry and Green Engineering, case-studies with eco-friendly designs, principles of GC and GE, energy minimization in chemical processes, renewable starting materials, bio-catalysis, etc.[7,8]

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12.3.1. Selected University Departments and Courses with Green Chemistry and Engineering in the USA and Other Countries

1. **University of Oregon (USA).** The University of Oregon has become the National Center on subjects of Green Chemistry and education ((http://greenchem.uoregon.edu/). In the undergraduate level there are laboratory exercises on Green Organic Chemistry: Undergraduate, Somophore Level: Green Laboratory Experiments, Organic Chemistry Laboratory . Hutchison JE. *Green Chemistry in Education*. (http://www.chemweb.com/alchem/articles/985883680896.html)
   In the USA some colleges and high schools are cooperating with university chemistry departments on lessons on Green Chemistry (that are subject to approval by the educational committees of the state). Example: University of Oregon/Worcester State College (College GC/GE, High School). Distance Education Green Chemistry Course..

2. **University of Scranton (USA**). The Chemistry Department of the university is very active for many years on undergraduate lessons on Green Chemistry with strong curriculum subjects on GC methodologies. Undergraduate “greening” courses with themes in Green Chemistry, environmental major, The main textbook (for many US schools) for educational programmes on Green Chemistry has been prepared by a professor of the university of Scranton. “*Real-World Cases in Green Chemistry”(2000).*

3. **University of Texas (Austin),** The university has an active department on GC with a well known and active undergraduate course on Green Chemistry. The title of the course: Undergraduate Green Chemical Engineering, Material Framework.

4. **University of Delaware (USA)** The university has an active department on GC studies and research activities . Undergraduate course: Senior undergraduate class. Green Chemistry course: Green Engineering –Out of this World CHEG. 667-Senior Undergraduate Class.

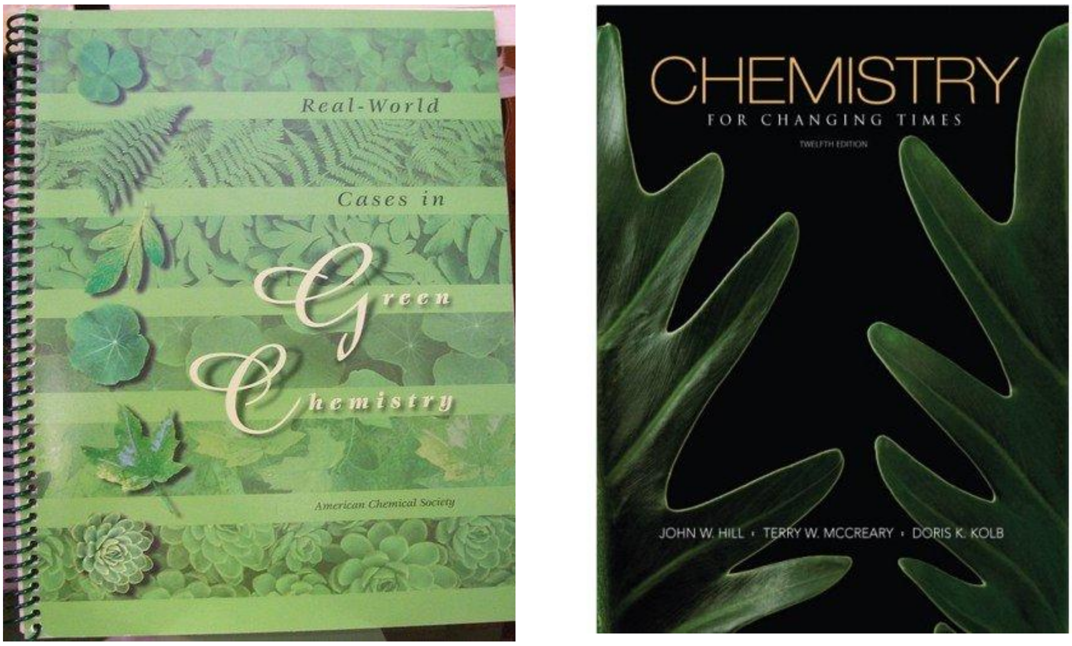


Figure 12.2. Textbooks of university courses on Green Chemistry in the USA. Cann CC. *Real-World Cases in Green Chemistry*. CAS publications, Washington DC, 2000. Hill JW, Kolb DK, McGreary TW. *Chemistry for Changing Times.* Prentice Hall, Upper Sadler River, NJ,, 2009 (12^{th} edition).

5. **University of Massachusets-Boston (UMB),** Postgraduate course for reasesarch in GC**.** Doctoral degrees in Green Chemistry (2001).

6. **Carnegie Mellon University (USA),** Undergraduate, Interdisciplinary Mutlilevel, Environment Across the Curriculum Multidisciplinary Programs, Educational Textbook: Nonchemistry Major, «Chemistry for Changing Times» (Chemistry Textbook)

THE INSTITUTE FOR GREEN SCIENCE
CARNEGIE MELLON UNIVERSITY

7. **University of North Carolina at Chapel.** NSF Science and Technology Center :

8. **Yale University: Center for Green Chemistry and Green Engineering in Yale.** Center activities are focused on educating undergraduate and graduate students in the principles and practice of GC & E. The Center also serves the wider academic community by providing opportunities for

faculty training and by developing and disseminating GC &E curriculum materials**.**

F&ES 885b/ENVE 360b/ENAS 660b/360b Green Engineering and Sustainable Design

Faculty: Matthew Eckelman, Julie Zimmerman : Subject of Instruction: Industrial Ecology, Scheduled for Spring 2012. This course focuses on a Green Engineering framework, the 12 Principles of GE, highlighting the key approaches to advancing sustainability through engineering design. Sustainablity, metrics, general design processes, challenges to sustainability.

F&ES 886a/FES 380 Greening Business Operations

Faculty: Marian Chertow, Thomas E. Graedel*, Julie Zimmerman Subject of Instruction: Industrial Ecology, Not Currently Offered...

The course examines various industries from engineering, environmental, financial perspectives, and emphasizes increasingly detailed analyses of corporate environmental performance. Methods are drawn from operations management, industrial ecology, and accounting and finance to investigate industrial processes, the potential to pollute, and the environmental and business implications of various sustainability approaches.

9. **University of Nottingham (UK),** Προπτυχιακό, Undergraduate, Multilevel Courses,. Green Chemistry for Process Engineering.

   In 2010 the well known pharmaceutical company GlaxoSmithKline (GSK) established in the University of Nottingham a research laboratory on “green” chemistry for the synthesis of drugs. The synthetic routes will be directed towards materials that are not connected with the petrochemical industry (“carbon neutral”, carbon neutral chemistry laboratory). The Dpt of Chemistry was selected because of its research experience and educational activities for many years in the subjects of Green Chemistry. The government in the UK has initiated a scheme for tax incentives for manufacturers that use “green” methodologies in the organic synthesis of their products.

12.3.2. Post Graduate Courses (MSc) in Green Chemistry

1. **University of York (UK)** Postagraduate course, MSc. Green Chemistry

   From the prospectus we read: «This masters module provides an introduction to the principles of green chemistry. There is increasing pressure from both society and governments for chemistry-based industries to become more sustainable through development of eco-friendly products and processes that both reduce waste and prevent toxic substances from entering the environment.»

   The curriculum of the course

   The costs of waste and the changing chemical industry , Green chemical technologies, life cycle considerations , Atom economy and experimental design , Use of renewable resources , Product and process design for sustainability; chemical product legislation

   Monitoring of Environmental Impact of Chemical Processes and Products

   National and transnational legislation reporting, waste and waste minimisation Recycling, reuse and recovery , Life cycle assessment , Measuring greenness

2. **MSc in Green Chemistry and Sustainable Industrial Technology**

   A one-year masters course offered by the **Department of Chemistry** at the **University of York** is run in collaboration with the Chemical, Pharmaceutical and related industries.

3. **Master en Quimica Sostenible** (Spain)
   This is a one-year course (60 ECTS credits) run at the **Faculty of Sciences** at the **University of Zaragoza**. It is run in Spanish by specialized lecturers from 9 Departments giving a multi-disciplinary approach (focusing on Chemistry, but also including Economics, Toxicology, Legislation, and Renewable Energies). The course is mainly directed at graduates in Chemistry or Chemical Engineering, though it is also open to other closely-related graduates.

4. **MSc in Green Chemistry: Energy and the Environment** (London)
   one-year course offered by **Imperial College London** and is designed to introduce postgraduate students to all aspects of sustainable chemical practices. Both the taught and research components will be multi-disciplinary in nature with input from several world class departments from Imperial (including Chemical Engineering, Biology and Environmental Policy), and the course content will include components as diverse as Green Chemistry, Renewable Energy, Biotechnology and Environmental Legislation.

5. **MSc Chemical Research in Green Chemistry (**University of Leicester**,** UK)**.** Applications are invited from outstanding students for a funded position on the MSc in Chemical Research (Green Chemistry with Industry). This course, which is funded through core CTA funding to the University of Leicester, provides masters-level training and includes industrial experience in the green chemistry sector.

6. **MSc in Green Chemistry (master de chimie verte) University Louis Pasteur** (Strasbourg I, France)
   Green chemistry is a chemistry for a sustainable global future. This new field includes applying a set of principles to reduce or eliminate the use or production of hazardous or toxic substances in the design, manufacture and use of products from the chemical industry (one year course).

7. **Master of Chemistry and EST (Universite de Savoie,** 73011 CHAMBERY CEDEX, France)
   The Specialty Chemicals, Environment, Sustainable Development (CESD Master of Chemistry and ESTs is for all students wishing to move to new careers in environmental and sustainable development. It aims to train senior managers and researchers.
8. **International Master in Molecular Catalysis and Green Chemistry**. (in English) Université de Rennes1. Campus de Beaulieu, 35042 Rennes Cedex, France
9. **Master en Quimica Sostenible**. University of Zaragoza, Dpt of Chemistry (Spain).

Postgraduate courses and PhD degrees in Green Chemistry and Green Engineering have been established in Australia, The Netherlands (Holland), Italy, Sweden, Spain, North Ireland, Wales, Brazil, Japan, etc.

Some indicative examples

- **PhD Position in Green Chemistry** and Catalysis at the Department of Biochemistry & Organic Chemistry, Uppsala University, Sweden.
- **Joint PhD Scholarship in Green Chemistry** (funded by the Italian Ministero dell' Universita) jointly by the Ca Foscari University of Venice and the University of Sydney (Australia).
- **PhD.** Dundalk Insitute of Technology (Dublin, Ireland) PhD Studentships "Green Chemistry" (Electrochemical Research Group)
- **PhDs studentships.** Centre for Green Chemistry, Monash Univetsity (Melbourne, Australia), funded by the Australian Research Council, 20 PhDs).

12.4. Educational Resources and Websites for Research Development in Green Chemistry

The subjects of Green Chemistry and Green Engineering, research and educational courses can be found in many information networks and websites.

1. Green Chemistry Network (Μ. Βρετανία)
(www.greenchemistrynetwork.org**/).**

This is a very informative and updated website. It was established in 1998 funded by the Royal Society of Chemistry. It is based in the Dpt of Chemistry of the University of York, UK.

The Green Chemistry Network (GCN) aims to promote awareness and facilitate education, training and practice of Green Chemistry in industry, commerce, central, regional and local government, academia and schools. The network was initially launched in 1998 with funding from the Royal Society of Chemistry and is now funded on a project-by- project basis. The GCN is a not-for-profit Company Limited by Guarantee. GCN aims at providing news and information about green chemistry via its website and newsletters. GCN aims at providing links to other organisations and government departments GCN aims at helping to organise and promote relevant conferences/workshops and training courses

2. Green Chemistry Institute-American Chemical Society (USA)
(http://portal.acs.org**)**

ACS Green Chemistry Institute®

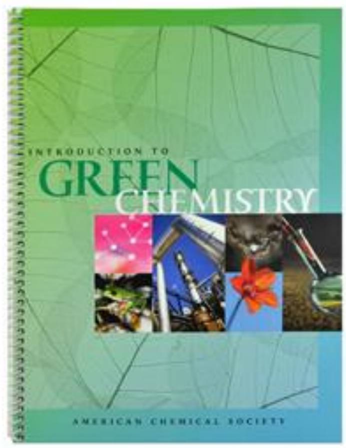
It is one of the updated website on Green Chemistry and Green Engineering, with rich educational programmes and information on research and developments in the fields of GC.

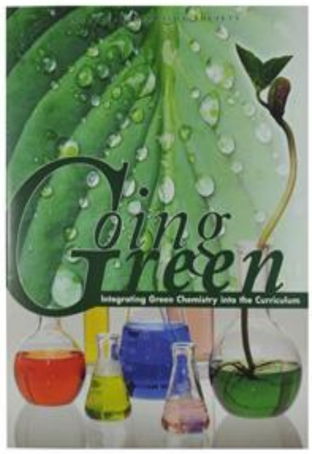
Educational Material and Books (Green Chemistry Educational Resources)

ACS aims to increase awareness and understanding of Green Chemistry principles, alternatives, practices, and benefits within traditional educational institutions and among practicing scientists.

BOOKS

- Real-World Cases in Green Chemistry, Volume I & II (ACS, 2000)
- Going Green: Integrating Green Chemistry into the Curriculum (2004)
- Introduction to Green Chemistry: Instructional Activities for Introductory Chemistry (ACS, 2002)
- Greener Approaches to Undergraduate Chemistry Experiments; en Español





ACS. Introduction to Green Chemistry: Instructional Activities for Introductory Chemistry HS25 (+CD-ROM). ACS publications, Washington DC, 2002 (20 $).
Parent KE, Kirchhoff M (Eds) *Going Green: Integrating Green Chemistry into the Curriculum*, American Chemical Society, Washington DC, 2004, τιμή $ 10)

ACS Green Chemistry Institute) (Online Resources)

- Green Chemistry Resource Exchange (developed by the ACS Green Chemistry Institute®)
- Greener Education Materials for Chemists (GEMs) (developed by the University of Oregon)
- University of Scranton's Teaching Green Chemistry Modules
- Certificate Program in the Essentials of Green Chemistry (offered by the University of California Berkeley Extension)
- Green Chemistry Network

3. Green Chemistry Educational Network (ΗΠΑ)

The Green Chemistry Education Network (GC Ed Net) serves as a catalyst for integrating green chemistry in chemical education at all levels. As a network of educators we support opportunities to research, develop, implement and disseminate green educational materials. The GC Ed Net reaches out to all chemistry educators through collaboration and mentoring, facilitating professional growth, and fostering the synergistic integration of green chemistry in education.

4. Greener Education Materials (GEMs)

Greener Education Materials (GEMs) is an interactive collection of chemistry education materials focused on green chemistry. Green Chemistry is the redesign of chemical transformations and processes to reduce or eliminate the use of materials that are hazardous to human health and the environment. The database is designed as a comprehensive resource of education materials including laboratory exercises, lecture materials, course syllabi and multimedia content that illustrate chemical concepts important for green chemistry.

5. IUPAC and OECD (Paris)

The International Union of Pure and Applied Chemistry (IUPAC, Paris) in cooperation with the OECD (Organisation for Economic Co-operation and Development, Paris, est. 1947) organize joint conferences on Green Chemistry and educational programmes on GC. (www.iupac.org/indexes/Conferences).´

6. Green Chemistry in Carolina (USA). Educational Programmes (www.carolina.com/category/teacher+resources/green+chemistry.do).

7. University of Oregon (USA).

The university of Oregon is in the forefront of Green Chemistry for many years and provides various educational programmes . Book, Haack, J. A. Greener Education Materials for Chemists. (http://greenchem.uoregon.edu/gems.html) .

8. Greening Schools, Illinois EPA & WMRC (USA)

(http://www.greeningschools.org)

There are many university departments that provide educational programmes, research projects and postgraduate degrees and informative websites on GC and GE, sustainability and sustainable development.

Australia •Centre for Green Chemistry •Royal Australian Chemistry Institute
Brazil •Química Verde no Brasil
Canada •Green Centre Canada • McGill University •Environment Canada
China •Chinese National Green Chemistry Conference
India •Green Chemistry Network Centre
Italy •Interuniversity Consortium — Chemistry for the Environment (INCA)
Japan •Green and Sustainable Chemistry Network
•Japan Chemical Innovation Institute
United Kingdom • University of Nottingham •York University
•Green Chemistry Network
Denmark. Center for Sustainable and Green Chemistry at the Technical University of Denmark.
Mediterranean (Basin) Countries Green Chemistry Network (MEGREC)
(Megrec.unitwin-network-731)
Mediterranean Basin UNITWIN Network for Green Chemistry (MEGREC UNITWIN Network) (731), established in 2006 at The Interuniversity Consortium Chemistry for the Environment –INCA, Venice (Italy).

12.5. Green Chemistry in Greece

In Greece there is the Hellenic Green Chemistry Network in the Department of Chemistry of the University of Patras. The Network coordinates educational and research projects in various Greek Universities. Professor K. Poulos is the coordinator. (Coordinator**,** Professor Constantine Poulos *PhD, CChem., FRSC* Department of Chemistry**,** University of Patras**,** 26500 Patras - Greece

"….Academic Members of the Department of Chemistry in the University of Patras unanimously decided to adopt and promote Green Chemistry as a means of Sustainable Development through a Green Chemistry Group that was created. Following the above decision the Department of Chemistry in the Aristotle University of Thessaloniki, the Department of Chemistry in the University of Ioannina and the Association of Greek Chemists were also established Green Chemistry Groups. All the above groups in close collaboration launched the Hellenic Network of Green Chemistry.

In academic year 2003-2004 the greening of the curriculum in the Department of Chemistry of the Univ. of Patras was based on a programme concerning reformation of the curriculum and which financially supported by the Ministry of Education It involved teaching for the 12 principles of Green chemistry, real-cases on green chemistry, microscale experiments, green Chemistry experiments in the courses of organic chemistry, polymer, catalysis and biotechnology. A summer school on GC took place for undergraduate and postgraduate students.

ΕΛΛΗΝΙΚΟ ΔΙΚΤΥΟ ΠΡΑΣΙΝΗΣ ΧΗΜΕΙΑΣ

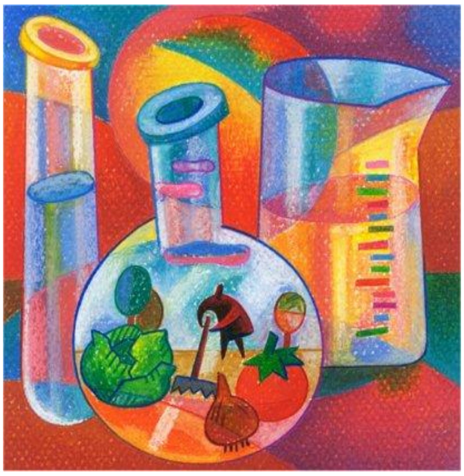
URL: www.chemistry.upatras.gr/hgcn

The Hellenic Green Chemistry Network organizes a Panellenic conference on Green Chemistry every two years in Greece

Figure **12.3**. The Hellenic Green Chemistry Network is based in Dpt of Chemistry of the University of Patras (Greece). Professor C. Poulos is the coordinator among the various Departments of Chemistry and researches that provide a platform for exchange of ideas and organize conferences.

In the last years in the Department of Chemistry of the University of Thessaloniki, Prof. Apostolos. Maroulis and Prof. Konstantina Hadjiantoniou-Maroulis are very active in research projects (undergraduate and postgraduate) and student thesis on Green Chemistry subjects

Translation of the book
Anastas PT & Warner JC. "Green Chemistry :Theory and Practice",(Oxford University Press, 2000),
By University Publications of Crete, Iraklion, 2007
Πανεπιστημιακές Εκδόσεις Κρήτης, 2007



An extensive article on Green Chemistry (in Greek) by Prof. A. Valavanidis and Th. Vlachogianni
"Green Chemistry and Technological Applications" (30.3.2011).
In the website of the Dpt of Chemistry, Univ. of Athens. Subject: Scientific Themes. (www.chem.uoa.gr)

Figure 12.4. The book by Anastas a& Warner "Green Chemistry: Theory and Practice", 2000 , was translated in Greek. There were 4 biannual conferences on Green Chemistry and Sustainable Development (2005-2011).

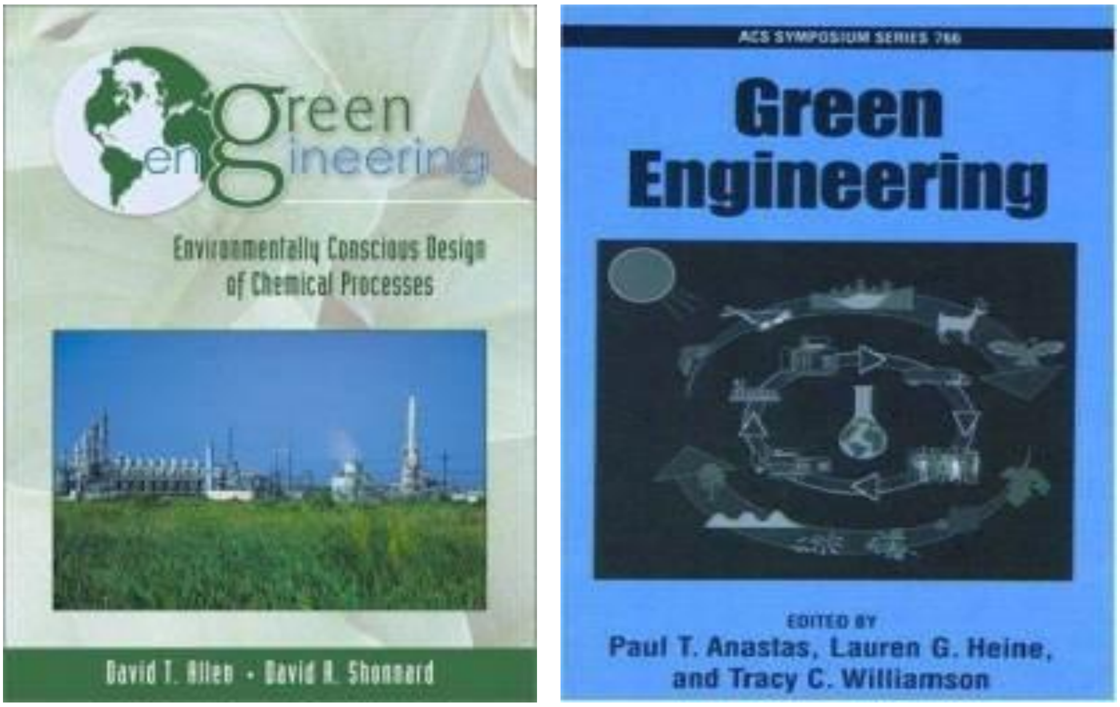
12.6. Green Chemistry and Green Engineering in the Educational Programmes of Engineers

Green Chemistry is connected with applied technologies and engineering through the 12 Principles of GC. Green Engineering covers every sector of engineering that is dealing with design, commercialization and use of processes and products in manufacturing and technical workshops. The aims of GE are to reduce, through design and innovative techniques pollution at the source, as well as health and safety to workers and consumers. Also, GE aims to be cost effective, minimize energy use and use as far as possible renewable materials. Green Engineers must apply the 12 principles of GE, use renewable starting materials that do not deplete natural resources, aim at life cycle analysis in all engineering activities, ensure that materials and energy inputs and outputs are non toxic and inherently safe, and have goals for reducing waste in engineering processes. In the last decade, many Engineering courses in most developed countries have introduced additional educational courses and technical expertise in Green Engineering subjects (mechanical engineering, electrical, civil, construction, energy, etc)..

In the USA the Environmental Protection Agency (EPA) developed many educational programmes of Green Engineering for engineers. The goal of the Green Engineering Programme is to incorporate risk related concepts into chemical processes and products designed by academia and industry.. The EPA programme targets four major sectors:[10,11]

a) **Educators**: A Green Engineering textbook, *Green Engineering: Environmentally Conscious Design of Chemical Processes* has been developed which can be used by educators for instructing "green" thinking in engineering processes and applications. Academic workshops for professors and students for green engineering materials and software.
b) **Software** - Provides chemical engineers with an integrated risk based suite of tools for assessing chemical hazards in process design.
c) **Industry** - Continuing education courses from the conversion of academic materials, methodologies, and case studies, to illustrate green engineering alternatives in chemical process design for new and practicing engineers.
d) **Outreach** - Sources, which promote and disseminate green engineering approaches to academia and industry facilitating a continuous flow of information and ideas for new and existing courses, case studies, and process design methodologies.

The strategy that is followed in the scheme of educational programmes have been promulgated and organised by various Institutes and Green Chemistry Centres (e.g. Green Chemistry Institute (ACS), Center for Green Chemistry & Green Engineering at Yale University). The educational programmes contain the fundamental principles of GE and their applications, thermodynamics parameters, the transport phenomena, control of chemical processes in industrial establishments, biotechnology, industrial ecology, environmental protection, life cycle assessment, renewable materials, energy minimization, nanotechnology, etc.[12]



Σχήμα 12.5. Green Engineering books are very important for the educational programmes of engineers at university level.

In the last decade there are many publications of books and educational materials on Green Engineering and the interconnection with sustainable development, renewable resources, alternative green energy sources, environmental protection, recycling, energy crisis and global warming, etc.[13-18]

Many Engineering Schools in the Universities and Technological Institutes in USA and Great Britain in the last decade have redesign their educational programmes to include the principles of Green Chemistry and Green Engineering at undergraduate and postgraduate levels. This is a selection of some universities.

University of Great Britain (selection))

- **University of Glamorgan**: MSc Renewable Energy and Resource Management, MSc Energy Systems Engineering
- **Glasgow Caledonian University**: BSc Environmental Civil Engineering, MSc Sustainable Energy Technology
- **University of Gloucestershire**: MSc European Rural Development, PhD Countryside and Community
- **Kingston University**: MSc Renewable Energy Engineering
- **University of Manchester**: MSc Environmental and Sustainable Technology
- **Newcastle University**: MSc Environmental Engineering, PhD Engineering and Science in the Marine Environment
- **University of Northampton**: MSc Wastes Management, BSc Wastes Management, BSc Wastes Management Pollution Control (distance learning), MSc International Environmental Management (distance learning)
- **University of Nottingham**: BEng Environmental Engineering, MSc Environmental and Resource Engineering
- **Queen Mary, University of London**: MSc in Sustainable Energy Systems, BEng/MEng Sustainable Energy Engineering

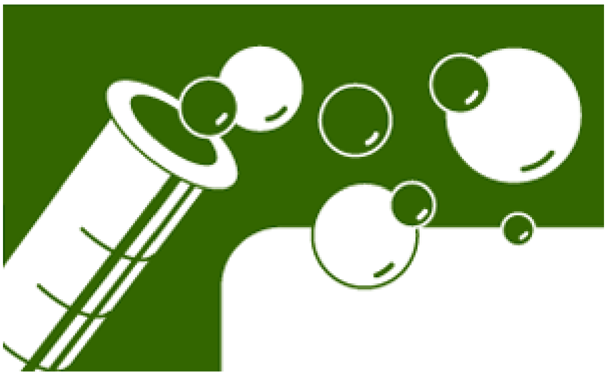
Universities and Colleges in the USA (selection
(www.ehow.com/info_7839751_green-engineering-colleges.html)

- Yale University. Center for Green Chemistry and Green Engineering
- University of Texas, Austin : Green Chemical Engineering-Material framework
- Rowan University : Green Engineering
- Carnegie Mellon University: Center for Sustainable Engineering
- Virginia Tech. Green Engineering.
- Western New England College. Green Engineering
- San Jose University. Green Engineering
- Stevens Institute of Technology. Green Engineering.

12.7. Green Chemistry and Laboratory Chemical Experiments

There are many books and websites with Green Chemistry experiments that can be performed in school and university chemistry laboratories.

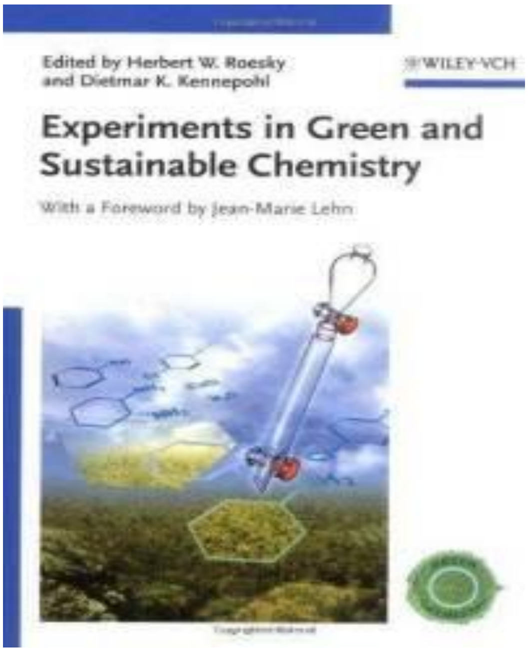
1. **Green Chemistry Labs (USA). (24 chemistry experiments)** (www.greenchemistrylabs.com/)



This is a manual containing twenty-four (24) experiments targeted at the high school level of education. It was developed by Dr. Sally Henrie, Kacey Fowler, Ruth Hall, and Kimberly Lindsey at Union University over multiple years. Dr. Marlyn Newhouse and Prof. Carol Leslie also contributed to the project.

2. **Monograph on Green Chemistry Laboratory Experiments. Green Chemistry** Task Force, Committee, Department of Science and Technology, New Delhi, India, 2000 (pp. 79, experiments in detail, comparison of conventional and green chemistry methods) (www.serc-dst.org/GC-monograph-final,pdf)

3. **BOOK. Roesky HW, Kennepohl D, Lehn J-M (Eds).** ***Experiments in Green and Sustainable Chemistry*****, Wiley-VCH, W. Sussex, 2009.**



The book avoids the trap of devoting many pages to educational theory or personal experiences of teachers - interesting though these are - but instead concentrates on what we really need, lots of good quality, proven case studies. Some **45 experiments written by 85 contributors from 15 different countries** are described in sufficient detail but are, mostly, thankfully concise, enabling the reader to judge quickly their suitability for a particular course.

4. BOOK. Doxsee K, Hutchison J. Green *Organic Chemistry: Strategies, Tools, and Laboratory Experiments*. Cengage Learning, New York, 2003.

There are numerous websites by universities , Green Chemistry Institutes, Chemical societies that provide educational materials and practical experiments for chemistry courses on Green Chemistry.

- American Chemical Society (*http://www.acs.org/education/greenchem),*
- *Green Chemistry Institute (http://www.acs.org/greenchemistryinstitute)*
- *Green Chemistry Network (http://www.chemsoc.org/networks/gcn/)*
- *University of Oregon (http://www.uoregon.edu/~hutchlab/greenchem/,)*
- *University of* Scranton (*http://www.academic.uofs.edu/faculty/CANNM1/greenchemistry.html)*

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8. American Chemical Society (ACS). American Chemical Society : Green Chemistry Education : Educational Resources , ACS Summer School on Green Chemistry and Sustainable Energy , Colleges and Universities with Green Chemistry Programs , Green Chemistry Student Chapter Awards , Green Chemistry Awards (http://portalacs.org/portal/acs/corg/content/...).
9. Green Chemistry Network. (www.greenchemistrynetwork.org) .
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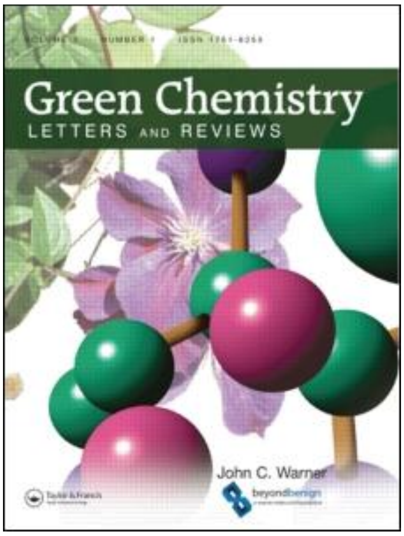

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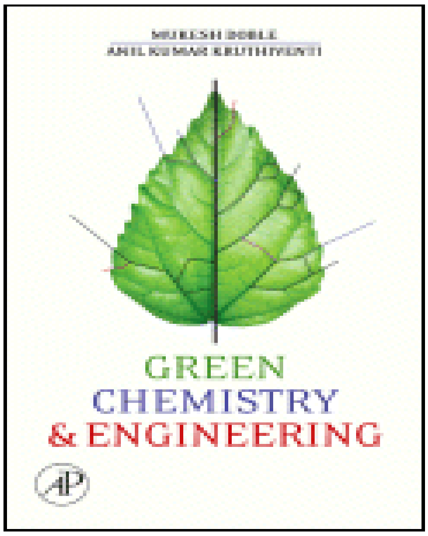

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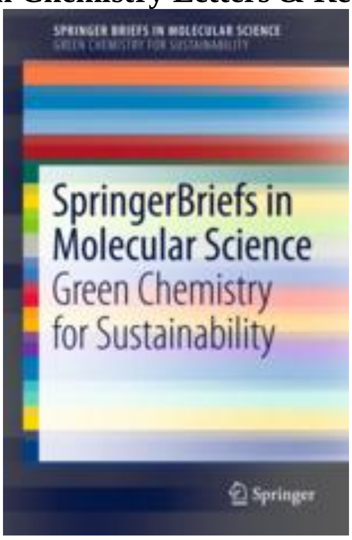

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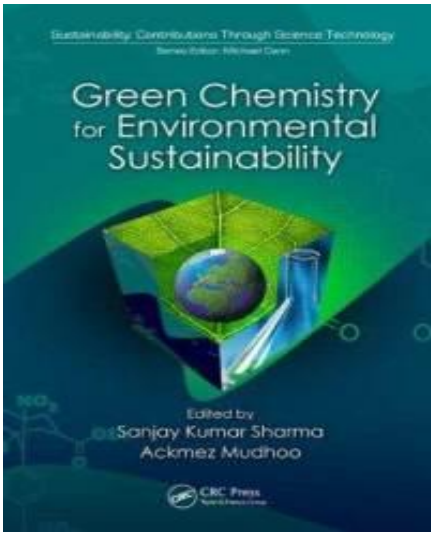

Sharma SK, Mudhoo A. Green Chemistry for Environmental Sustainability

APPENDICES

APPENDIX I.

Chemical Experiment:Biodiesel from vegetable oils
(For additional information on Green Chemistry and Greening Schools lessons from Illinois, Waste Management and Research Center, visit (www.greeningschools.org)

1. Measure 100 mL of vegetable oil., 2. Carefully add 15 mL of methanol.
3. Slowly add 1 mL of 9 M KOH., 4. Stir or swirl the mixture for 10 minutes.
5. Allow the mixture to sit and separate., 6. Carefully remove the top layer using a Beral pipette., 7. Wash the product using 10 mL of distilled water. Mix.
8. Allow the mixture to sit and separate., 9. Carefully remove the top layer using a Beral pipette., 10. Measure the amount of biodiesel you have collected and compare it to the amount of vegetable oil you started with.

Discussion Questions
1) What changes did you see between the characteristics of the starting materials (cooking oil, methanol, and potassium hydroxide solution) and the final products (biodiesel and glycerol)?, 2) Which did you have more at the end, the product or the waste?, 3) What signs did you observe that a chemical reaction had taken place? 4) What is the purpose of the washing step 7 above?, 5) In the commercial production of biodiesel, 1200 kg of vegetable oil produces 1100 kg of crude biodiesel. How does your yield compare to this?

Instructional notes " Making biodiesel"
In this activity, students make biodiesel from cooking oil. The cooking oil is mixed with methanol and a catalyst
(potassium hydroxide). Cooking oil is a lipid called a triglyceride or triacyglycerol. The structure of this type of lipid is
characteristic of all animal and plant fats. It consists of a glycerol attached to three fatty acids. Differences among the
fats are due to the different fatty acids connected to the glycerol.
In making biodiesel, the reaction breaks the bond between the glycerol and the fatty acids. A methyl group is added to
the end of the fatty acid, which is what we call biodiesel, and the other products are glycerol and the remaining
potassium hydroxide catalyst.

References

2. The National Biodiesel Board, www.biodiesel.org.
3. A comprehensive report on the economics and science of using soybeans to make biodiesel is presented at
www.mda.state.mn.us/ams/ soydieselreport.pdf.

Biodiesel—Using Renewable Resources

Objectives
1) Examine ways to use renewable resources to replace nonrenewable starting materials., 2) Examine characteristic properties of matter

Green Chemistry Principles
1) Safety first-and last., 2) Wastes? Why make them?, 3) Use renewable resources

Levels
High school (may be used as a demo for discussion in middle school classes)

APPENDIX II.

Summary of Green Chemistry and Green Engineering Education Efforts (USA)

PRE-COLLEGE GC/GE EDUCATION EFFORTS

Pre-College Level	**Educational Tool**	**Organization**	**Contact**
Elementary and above	Textbook: *Chemistry Experimentation for All Ages*		Ken Doxsee
Elementary/Middle School	Pollution workbooks & programs: Pollution Solutions, Pollution Prevention: A Story of Carbopond Cleanup	Suffolk University/Rohm & Haas	Pat Hogan
Middle School	Energy and Pollution Prevention Program	Michigan Technological University	James Mihelcic
Middle School	Green Chemistry and Environmental Sustainability: A Middle School Module	Pfizer	Berkeley Cue
High School	*Chemistry in the Community; Introduction to Green Chemistry*	American Chemical Society	Kathryn Parent
High School	Distance Education Green Chemistry Course	University of Oregon/Worcester State College	Julie Haack/ Margaret Kerr

UNDERGRADUATE GC/GE EDUCATION EFFORTS

Undergraduate Level	**Educational Tool**	**Organization**	**Contact**
Undergraduate	Green Chemical Engineering Material Framework	University of Texas, Austin	David Allen
Sophomore Level	Fall & Winter Term Green Laboratory Experiments Organic Chemistry Laboratory	University of Oregon	James Hutchison
Interdisciplinary Multilevel	Environment Across the Curriculum Multidisciplinary Programs	Carnegie Mellon University	Cliff Davidson
Nonchemistry Major	*Chemistry for Changing Times*, 10th ed., Chemistry Textbook for Nonmajors		John W. Hill, Doris K. Kolb
Multilevel Undergraduate Courses	Green Chemistry for Process Engineering	University of Nottingham	Steven Howdle
Advance Chemistry	Industrial and Applied Green	York University	John Andraos

Undergraduate Level	Educational Tool	Organization	Contact
Undergraduate Course	Chemistry		
Undergraduate	Textbooks: *Chemistry in Context, Real-world Cases in Green Chemistry, Greener Approaches to Undergraduate Laboratory Experiments*	American Chemical Society	Kathryn Parent
Undergraduate	Video: Green Chemistry – Innovations for a Cleaner World Companion	American Chemical Society	Kathryn Parent
Undergraduate	Textbook: *Environmental Chemistry*, 3rd Edition		Michael Cann
Senior Undergraduate Class	Green Engineering – Out of this World CHEG 667 – Senior Undergraduate Class	University of Delaware	Richard Wool
Senior/Grad students	National P3 Design Competition: People, Prosperity, and the Planet	EPA	Julie Zimmerman
Undergraduate	Green-Soil & Water Analysis at Toad Suck (GSWAT) Laboratory Course	Hendrix College	Liz Gron
Undergraduate Honors	Green Business Seminar	Suffolk University	Pat Hogan
Undergraduate	Green Engineering Freshmen Curriculum Module	Rowan University	David Shonnard
Undergraduate	NSF Grant – Sustainability Principles for Curriculum	Cal Poly, San Luis Obispo	Linda Vanasupa

GRADUATE GC/GE EDUCATION EFFORTS

Graduate Level	Educational Tool	Organization	Contact
Graduate	Ph.D. Chemistry Program	University Massachusetts Lowell	John Warner, Amy Cannon
Graduate, Postdoctoral	Sustainable Chemistry in the Pharmaceutical Industry Green Chemistry Workshop	Pfizer – Groton Labs	Berkeley Cue
Graduate, Postdoctoral	Green Chemistry & Business Case Studies, including contact with Campus Business Clubs	Cornell University	Tyler McQuade
Graduate, Postdoctoral	Partnership Program with Southern University Science Education Program with Peace Corps	Michigan Technological University	James Mihelcic

FACULTY GC/GE EDUCATION EFFORTS

Faculty Level	Educational Tool	Organization	Contact
Faculty	Sophomore Green Organic Laboratory Education & Training	University of Oregon	James Hutchison
Faculty	Green Chemistry Educational Ambassador Sites	University of Oregon	Julie Haack
Faculty	International Faculty Training	University of Oregon	Ken Doxsee
Faculty	Textbook: *Going Green – Integrating Green Chemistry into Curriculum*	American Chemical Society	Kathryn Parent
Faculty	Center for Sustainable Engineering (CSE) Workshop: Faculty training to develop and sustain environmental programs; Bookbuild Web site	Carnegie Mellon University	Cliff Davidson
Faculty	ASEE Green Engineering Web site	Rowan University	David Shonnard
Faculty	DICE Recruitment Program	Nottingham	Steve Howdle

INDUSTRY EDUCATION EFFORTS

Industry	Educational Tool	Organization	Contact
Internal (In-house)	Pfizer Green Chemistry Achievements	Pfizer	Berkeley Cue
Internal (In-house)	Process Position– Green link between Research & Manufacturing	Merck	John Leazer

GENERAL GC/GE EDUCATION EFFORTS

General	Educational Tool	Organization	Contact
Educational Materials	Frontiers in Chemical Engineering Education	MIT	Jeffrey Steinfeld
Chemistry Educational Material	GEMS – Green Education Materials for Chemists	University of Oregon	Julie Haack
Textbook	*Green Engineering: Environmentally Conscious Design of Chemical Processes*	Michigan Technological University	David Shonnard/David Allen
Business School Education	Business Case studies, Chemistry & Business School Collaborations	Green Chemistry Institute	Kathryn Parent
Electronic Tools	Green Chemistry Alternative Selection ProtocolNEMI Analytical Method Database	Green Chemistry Institute	Kathryn Parent
Web site	Joseph Breen Chemistry Awards	Green Chemistry	Paul Anastas

General	Educational Tool	Organization	Contact
		Institute	
Web site	Canadian Green Chemistry Network		John Andraos
DVD	Meeting Global Challenges	American Chemical Society	Kathryn Parent
Textbook	*Bio-based Polymers & Composites*	Academic Press	Richard Wool
Textbook	*Green Chemistry and the Ten Commandments of Sustainability*	ChemChar Research Inc.	Stanley E. Manahan
Book	*Sustainability in the Chemical Industry: Grand Challenges and Research Needs*	National Research Council	National Academies Board on Chemical Sciences and Technology

Exploring Opportunities in Green Chemistry and Engineering Education: A Workshop Summary to the Chemical Sciences Roundtable.
National Research Council (US) Chemical Sciences Roundtable; Anastas P, Wood-Black F, Masciangioli T, et al., editors.
Washington (DC): National Academies Press (USA); 2007.

APPENDIX III

Brief Guide of Universities with Educational Actions on Green Chemistry and Green Engineering

United States (USA))

Connecticut

- Yale University

Massachusetts

- Bridgewater State College
- Gordon College
- University of Massachusetts, Boston
- University of Massachusetts, Lowell: Center for Green Chemistry

Pennsylvania

- Carnegie Mellon Institute for Green Oxidation Chemistry
- University of Scranton

Mid-Western

Arkansas

- Hendrix College (green organic chemistry)

Illinois

- University of Illinois-Urbana-Champaign

Minnesota

- St. Olaf College

South

Alabama

- University of Alabama

Western
California

- Berkeley Center for Green Chemistry
- UC Berkeley Extension

Colorado

- Colorado School of Mines

Oregon

- University of Oregon

Other Countries

Australia

- Monash University Centre for Green Chemistry
- Murdoch University: Sustainable Chemistry/Green Chemistry

Eurtope
The Netherlands (Holland)

- Delft University of Technology: Biocatalysis and Organic Chemistry

Italy

- Interuniversity Consortium Chemistry for the Environment (INCA)

Northern Ireland (UK)

- Queen's University of Belfast: Ionic Liquid Laboratories

Spain

- Institute of Science and Technology (IUCT)
- Green Chemistry Network of Spain (REDQS - Red Española de Química Sostenible)

Sweden

- Centre for Environment and Sustainability - Chalmers University of Technology/Göteborg University

United Kingdom

- Green Chemistry Centre of Excellence at York
- University of Leicester Green Chemistry Group
- University of Nottingham Green and Analytical Chemistry

South America
Brazil

- Universidade do Vale do Itajaí: Center for Technological Earth and Sea Sciences

Chemistry for a Sustainable World

APPENDIX IV:

WEBSITES for GREEN CHEMISTRY and GREEN ENGINEERING

MVSSOLUTION INC. The Technology Realization Company

(http://www.mvssolutions.com/greenlinks.html)

Green Chemistry & Related Resources

- The Green Chemistry Institute - A partnership with the American Chemical Society
- EPA Green Chemistry - U.S. Environmental Protection Agency Green Chemistry
- Grüne Chemie - Green Chemistry Links
- Green Chemistry Network - Royal Society of Chemistry Green Chemistry Network
- GSCN - Green & Sustainable Chemistry Network - Japan Chemical Innovation Institute
- INCA- Consorzio Interuniversitario Chimica per l'Ambiente - Inter-University Consortium of Chemistry for the Environment
- NSF Science and Technology Center - Environmentally Responsible Solvents and Processes
- EPA Green Engineering - US Environmental Protection Agency Green Engineering
- Green Business Letter - Hands-On Journal for Environmentally Conscious Companies
- GreenBiz.com - Resource Center on Business, the Environment and the Bottom Line
- EnvironmentalChemistry.com - Environmental, Chemistry & Hazardous Materials Info & Resources
- Journal of Green Engineering – (River Oublishers, Aalborg, Denmark, October 2010)
- SustainableBusiness.com - Business, Environment, Green & Clean Technologies
- United Nations - Division for Sustainable Development
- BSDglobal - Business and Sustainable Development: A Global Guide
- National Renewable Energy Lab - The US Department of Energy's (DOE) laboratory for renewable energy research & development
- Energy Efficiency and Renewable Energy - The US DOE's energy information portal
- Biomass - Biobased Chemicals and Materials - Commercial or industrial products derived from biomass feedstocks
- REPP & CREST - Renewable Energy Policy Project & Center for Renewable Energy and Sustainable Technologies
- Solvent Alternatives for Green Chemistry - Solvent Substitution Resources on the Internet
- SAGE - Solvent Alternatives Guide
- Toxics Use Reduction Institute - Toxics Use Reduction Institute (TURI) at the University of Massachusetts Lowell

- Pollution Prevention - Pollution Prevention Info on the Internet
- Zero Waste Alliance - Nonprofit Partnership Working for the Elimination of Waste and Toxics
- Center for Remanufacturing and Resource Recovery - Technologies for a Sustainable Future
- IDSA Ecodesign - Green design topics for product designers
- Environmental Entrepreneurs - Professionals and business people who believe in protecting the environment while building economic prosperity

Visit the MVS Solutions Environmental Chemistry Resources page for information concerning chemistry and the environment.

Visit the MVS Solutions Green Chemistry Development page for information concerning green

ACS Webinars: Green Chemistry & Sustainability Series

(http://acswebinars.org/heben**)**

"**Green Chemistry and Renewable Energy** – Two Peas in a Pod" A short presentation followed by Q&A with speaker Michael Heben of the University of Toledo and Ohio's Wright Center Endowed Chair for Photovoltaics Innovation and Commercialization. Global demand and investment for renewable energy has been growing at a fast pace. However, many chemistry researchers are still uninformed about green chemistry principles and application in the developing technologies for the renewable energy sector. Join our speaker, Dr. Michael Heben from University of Toledo, as he discusses the symbiotic relationship between renewable and green energy. Learn how you can benefit from melding these sources to create sustainable solutions for the energy future.

Open access Journal for Green Chemistry and Sustainable Chemistry (2011)
(Springer Briefs in Molecular Sciences)
Green and Sustainable Chemistry
(Website: http://www.scirp.org/journal/gsc
[**Green and Sustainable Chemistry** (GSC) covers subjects relating to reducing the environmental impact of chemicals and fuels by developing alternative and sustainable technologies that are non-toxic to living things and the environment].
Scientific Research Publishing (SCIRP: http://www.scirp.org) is an academic publisher of open access journals. It also publishes academic books and conference proceedings. SCIRP currently has more than 150 open access journals in the areas of science, technology, and medicine.

GLOSSARY

USEFUL TERMS ON GREEN CHEMISTRY AND GREEN ENGINEERING

Green or Sustainable Chemistry *is the branch of chemistry concerned with developing processes and products to reduce or eliminate hazardous substances. One of the goals of green chemistry is to prevent pollution at its source, as opposed to dealing with pollution after it has occurred.*

Green Chemistry *is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products (PT. Anastas and J. Warner "Green Chemistry: Theory and Practice")*

Green Engineering is the design, commercialization and use of processes and products that are feasible and economical while reducing the generation of pollution at the source, minimizing the risk to human health and the environment" (Environmental Protection Agency, USA)

Green Engineering embraces the concept that decisions to protect human health and the environment. Also, it can have the greatest impact and cost effectiveness when applied early to the design and development phase of a process or product"

Green Engineering can be defined as environmentally conscious attitudes, values, and principles, combined with science, technology, and engineering practice, all directed toward improving local and global environmental quality"

Principles of Green Chemistry. The 12 Principles of Green Chemistry provide a framework for chemists to use when designing or improving materials, products, processes and systems. The principles focus on sustainable design and have been the backbone for a wide range of innovative solutions created over the past decade in chemical processes, in manufacturing of various products, in designing new less toxic materials, recycling and producing eco-friendly equipment .

Principles of green Engineering

These principles were developed by more than 65 engineers and scientists at the Green Engineering: Defining the Principles Conference (Sandestin, Florida in May of 2003). The preliminary principles forged at this multidisciplinary conference are intended for engineers to use as a guidance in the design or redesign of products and processes within the constraints dictated by business, government and society such as cost, safety, performance and environmental impact.

Sustainable Development (**SD**): a pattern of growth in which resource use aims to meet human needs while preserving the environment so that these needs can be met not only in the present, but also for generations to come The term Sustainable Development was used by the Brundtland Commission ("Our Common Future", United Nations World Commission on Environment and Development in the 1987) which coined what has become the most often-quoted definition of sustainable development as development that "**meets the needs of the present without compromising the ability of future generations to meet their own needs."**

Sustainable development combines the carrying capacity of natural systems with the social challenges facing humanity.

Sustainability was another term that was employed to describe an economy "in equilibrium with basic ecological support systems."
The concept of **sustainability** relates to the maintenance and enhancement of environmental, social and economic resources, in order to meet the needs of current and future generations. There are 3 different types of sustainablitiy.

- **Environmental sustainability** – requires that natural capital remains intact. The source and sink functions of the environment should not be degraded. Therefore, the extraction of renewable resources should not exceed the rate at which they are renewed, and the absorptive capacity to the environment to assimilate wastes should not be exceeded.
- **Social sustainability** – requires that the cohesion of society and its ability to work towards common goals be maintained. Individual needs, such (health and well-being, nutrition, shelter, education and cultural expression) should be met.
- **Economic sustainability** – which occurs when development, which moves towards social and environmental sustainability, is financially feasible.

Natural Resources. Natural resources are either renewable or non-renewable. Non-renewable natural resources are: fresh water, fossil fuels, oil, coal, metals or minerals (copper, iron ore, gold, silver, platinum, etc), natural gas. Once non-renewable resources are removed it will take a very long time, if ever, to replace them.

Renewable resources are natural resources that can be replaced in a relatively short period of time or used through conservation efforts without depleting the resource. We consider renewable natural resources to be: animals, insects, reptiles, plants, trees, water, grass, solar, wave, ocean and wind energy. The depletion of natural resources is caused by 'direct drivers of change such as mining, petroleum extraction, fishing and forestry as well as 'indirect drivers of change' such as demography, economy, society, politics and technology.

International Conferences on the Environment and Sustainable Development

i) 1972, Stockholm Conference on the Human Environment,
ii) 1980, World Conservation Strategy of the International Union for the Conservation of Nature (IUCN),
iii) 1992 Earth Summit in on Environment and Development Rio de Janeiro, Brazil in 1992
iv) 2002, third UN Conference on Environment and Development in Johannesburg, South Africa (credited with creating the most prevalent definition of sustainability).
v) 2012, "Rio+20", 4^{th} UN Conference on Sustainable Development , called historic opportunity to define "Green Economy:. This conference will be the 20 follow-up of the historic 1992 UN conference. The conference will be in Rio de Janeiro, Brazil (

INDEX

A

B

C

D

E

F

G

H

I

J

L

M

N

O

P

T

U

W