La química verde y el desarrollo sustentable

Green chemistry and sustainable development

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Resumen

La química es indispensable para asegurar que las siguientes generaciones de productos químicos, materiales y energía sean sustentables. La química es también esencial para limpiar el planeta de contaminantes ya existentes. En este artículo se presenta una breve revisión del desarrollo de la Química Verde, enfatizando sus principios, así como citando ejemplos específicos de compuestos usados en procesos no contaminantes sustentables y de apoyos otorgados para motivar el desarrollo de procesos sustentables y Química Verde.

Palabras clave: ambiente, sustentable, incentivos para química verde.

Abstract

Chemistry is essential to ensure that the next generation of chemicals, materials and energy are sustainable. Chemistry is also essential to clean the planet of pollutants already existing. This article presents a brief review of the development of Green Chemistry, emphasizing its principles, as well as citing specific examples of compounds used in environmentally sustainable processes, as well as provided support to encourage the development of sustainable processes and Green Chemistry.

Key Words: environment, sustainable, incentives for green chemistry..

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Introduction

At the beginning of the seventies began the Association of the word Green with the environment, having as background the environmental philosophy conceived by Rachel Carson, who published his book Silent Spring in 1962 (Carson, 1962;) Carson, 2010), where he warned of the harmful effects of pesticides on the environment and attributed the increased pollution to the chemical industry. The title of the book was intended to emphasize that, keep on like this, we could live a spring without birds, "silent”. If we assume that the word "green" means environmentally safe, the question arises: is it possible that the chemistry is green? There are opinions opposite to this, some people think that chemistry is synonymous with pollution, toxicity and risk, others believe that the knowledge generated by this science will be enough to solve the environmental crisis that the world is living, specifically since the beginning of the industrialization era. The truth is that in many aspects of life, the study of chemistry has been used to solve problems, but its application, especially at industrial level, has also caused environmental problems. Chemistry plays an essential role since the formation of the Earth to virtually all aspects of daily life nowadays; it is involved in the air we breathe, the water we drink, the plastics we use, our meals, clothing and the buildings we inhabit. Chemistry is at the heart of the science in the sense that it is fundamental to create technologies on which you can build and develop a nation, is also essential to ensure that the next generation of chemicals, materials and energy are sustainable (Sanghi, 2012).

On the other hand, sustainable development was defined by the World Commission on Environment and Development in 1987, as development that meets the needs of present generations without compromising the ability of future generations to meet their own needs, as it appears in the Brundtland report "Our common future", commission headed by the Prime Minister of Norway, Gro Harlem Brundtland (World Commission on Environment and Development, 1987).

In the United States in 1990, the Pollution Prevention Act was passed in order to point out a line of conduct for American policy in the prevention or reduction of pollution from their sources whenever possible being human health and environmental protection the aim. In 1992, Mexico's National Institute of Ecology (INE) is created with technical and regulatory powers in ecology, which evolved in 2012 to the National Institute of Ecology and Climate Change (INECC) as an organization sectored in SEMARNAT whose some of its goals are: to coordinate and conduct studies and projects of scientific and technological research along with academic and research institutions, public or private, national or foreign, on climate change, environmental protection and preservation and restoration of ecological balance, and promoting and disseminate criteria, methodologies and technologies for the conservation and sustainable use of natural resources.

Before the "Green Chemistry" concept, chemists had valued the success of a reaction or process using almost exclusively the concept of "yield". A significant advance to quantify residual chemicals was the concept of "atom economy" introduced by Trost in 1991, as the number of atoms of the reagents which are incorporated in the product (Trost, 1991). For example, *addition reactions* are completely atomically economic, but *substitution reactions* necessarily result in partial loss of atoms due to the leaving group which is a residue. Because of the atom economy not consider the use of solvents and separation media, in 1992, Sheldon proposed the "E factor" which was defined as the mass ratio of waste and products (or amount in grams of waste per gram of product). Thus this way considers other complementary parameter that takes into account all materials consumed to obtain the pure product, but not incorporated in it (Sheldon, 1992; Sheldon, 2007). In particular, the manufacture of fine chemicals and pharmaceuticals have the highest values of the factor E.

The concept of "Green Chemistry" is related to the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. This definition was introduced by Paul Anastas, who along with John Warner wrote the book "Green Chemistry: Theory and Practice" in 1998 (Anastas, 1998) where emerge the 12 principles of Green Chemistry, as criteria that seek to assess how respectful a reaction, a process or a chemical is to the environment, figure 1. These principles have been widely disseminated by the same author, who was editor of the book of the ACS symposium on Green Chemistry in 1994 (Anastas, 2010; Horvath, 2007; Anastas, 1996).

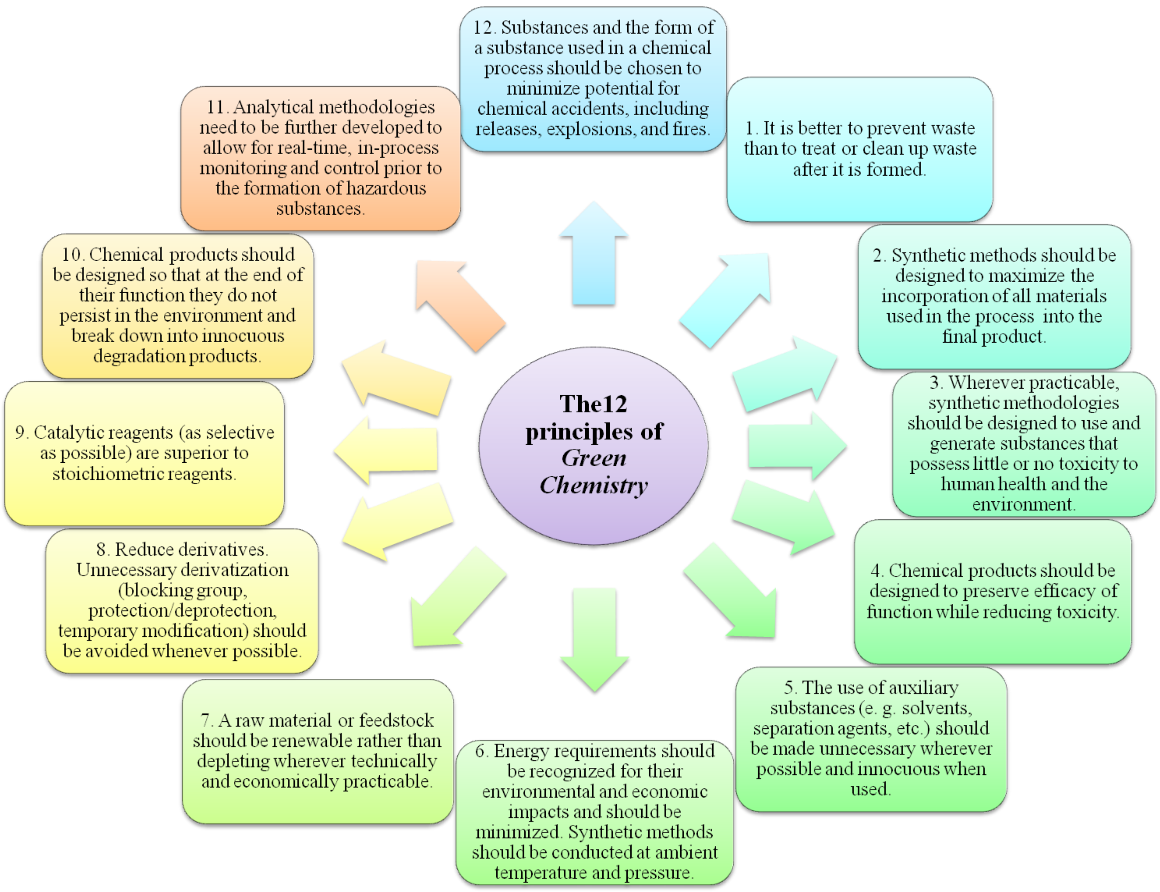


Figure 1 Principles of Green Chemistry.

For example, in some processes which involve materials in the production cycle which are not strictly converted into product. These materials are paid first as raw materials and then as waste to be treated. Moreover, because of many conventional solvents used in the industry are flammable, volatile, or have acute or chronic health effects, alternative solvents are sought to perform reactions and solvent free processes, conditions contributing to provide more safety for workers in the chemical industry. In this context, advances in catalysis using transition metal compounds are replacing traditional methods for reductions, oxidations, and other organic transformations involving the use of stoichiometric amounts of metals or metal hydrides, metal oxides, acids and hydroxides, generating stoichiometric amounts of inorganic wastes. Replacements of these reactions are catalytic hydrogenation with H_2, oxidations with O_2 or H_2O_2, carbonylations with CO, hydroformylations reactions with H_2 and CO, and C-C bond formation with residues ranging from low to zero. In these reactions the metal catalyst acts as a chemical machine that does its job many times without being consumed and therefore without generating the corresponding stoichiometric by-products (residues). In addition, alternative processes to the thermic ones, which look for save energy, are those using microwaves (microwave chemistry), high frequency sound waves (sonochemistry), and electromagnetic radiation (photochemistry).

Green or Sustainable Chemistry? Environmental Chemistry?

Green chemistry is focused on process design, preparation and use of chemicals with a lower potential risk of environmental pollution than traditional processes, based on different technologies. "Sustainable Chemistry" expands the definition to larger systems not only a reaction, provides a holistic approach in which the application of the philosophy of green chemistry includes the Green Engineering principles, and the establishment of a multidisciplinary program. The term "sustainable" is broader than "green" (Krähling, 1999). Environmental chemistry is the chemistry of the natural environment and pollutant chemicals in nature. Thus, green chemistry is responsible for the "environmental sustainability" addressing the subject at *molecular level*, focusing primarily on the design of low risk chemical products and processes, efficient use of materials and energy, and development of renewable resources. This is carried out through the *catalysis*, the use of *alternative solvents*, *analytical chemistry*, *polymer science* and *toxicology*, to name a few. In several cases it is necessary to "redesign" basic materials for our society looking to be benign to humans and the environment, preferably with economic and social benefits.

Green Chemistry Activities in the world

Some countries that encourage research in green chemistry and provide financing to projects and awards are mentioned below.

United States of America. The Green Chemistry Program of the Environmental Protection Agency of the United States (EPA) supports basic research in green chemistry, as well as a variety of educational activities to rise the public awareness on this issue. The Green

Chemistry Institute of the American Chemical Society recognizes outstanding contributions to green chemistry through the Presidential Green Chemistry Contest. President Clinton announced the prize (Presidential Green Chemistry Challenge Award) in March 1995, which was first awarded in 1996 in five categories. Some of the academic awards are: Year 2013, Prof. Richard P. Wool, University of Delaware, *Polymers and Sustainable-composites: Optimal Design.* Year 2012, Prof. Geoffrey W. Coates, Cornell University, *Synthesis of biodegradable polymers from* CO_2 *and CO.* Year 2011, Prof. Bruce H. Lipshutz, University of California, Santa Barbara, *Towards the end of our dependence on organic solvents.* Year 2010, Ph. D. James C. Liao, University of California and Easel Biotechnologies- LLC, *Recycling* CO_2 *to biosynthesize heavy alcohols*.

United Kingdom. The British Royal Society of Chemistry (RSC) established a Green Chemistry Network (GCN) based in the Department of Chemistry of the University of York, which provides education, training and practice on Green Chemistry for academy and industry. RSC publishes since 1999 an international scientific journal called Green Chemistry, one of the most important in the field worldwide. It also gives the Green Chemistry Award. Some of the awards are: Year 2014, Prof. Michael North, University of York, *Using* CO_2 *as a source to synthesize other chemicals*. Year 2012, Prof. Edman Tsang, University of Oxford, *Development of new catalytic nanoparticles that facilitate the replacement of hazardous substances in some chemical processes*. Year 2010, Prof. R. Sheldon, Delft University of Technology, *Development of clean catalytic technologies for the minimization of toxic waste*.

European Union. Awards for the Environment to European Companies (European Business Awards for the Environment, EBAE) was established in 1987 to recognize and promote innovation in sustainability. Companies must first succeed in their country (national competition) before they can participate in the biennial European competition, implying that the EBAE winners must be the best of the best from the member countries of the European Union and candidate countries. Some of the awards are: Year 2012, Umicore, Belgium, *Recycling of NiMH- and lithium ion-batteries: a new sustainable business* (the project involves recycling of valuable elements such as Co, Ni, Cu and rare earths). Year

2010, Zenergy Power GmbH and Bültmann GmbH, Germany, *Reduction in power consumption by using a heating magnetic switch*.

Japan. The Institute for Chemical Innovation of Japan is responsible for the research and development of Green and Sustainable Chemistry through the Green and Sustainable Chemistry Network (GSCN), which organizes international activities, exchange of information and proposal project financing. Some of the prizes awarded are: Year 2011, Akifumi Noujima (student), Osaka University, *Development of gold nanoparticles as catalyst for oxidation of alcohols*. Year 2010, Prof. Akihiko Kudo, Tokyo University of Science, *Development of powder photocatalysts for hydrogen production from water and sunlight*.

Australia. The Royal Australian Chemical Institute (RACI) inaugurated an annual award in 1999 (Green Chemistry Challenge Award) to prevent contamination and recognize the efforts in this field. Nominations for Technology in Green Chemistry must have achieved significant results in the last 5 years in Australia, in other words, technologies must have been researched, demonstrated, implemented, applied, patented, etc. It is noteworthy that the last prize was awarded in 2010 to Professor Milton Hearn from the Centre for Green Chemistry, Monash University, for his work in education and training in green chemistry at the graduate level, with above 535 scientific articles, several books, and 20 patents on developments in chemistry and biotechnology. The last three years there were no winners, and this year the call is open.

Mexico. Support for development of Green Chemistry in Mexico is based on financial funds provided mainly by the National Council of Science and Technology (CONACYT) to universities through projects generated by the initiative of researchers. These funds, although important, are still scarce, additionally, there is not a good synergy between academy and industry. In the case of Mexican industry, the activities of pollution prevention are as much focused on the monitoring of the rules, which are frequently below the standards of many developed countries, and it is necessary awareness of the problem. On the academic side, in some universities, gradually it has begun to encourage the development of projects that seek to find synthetic routes that reduce the use of harmful substances and hazardous waste generation. In 1993, by agreement of Lic. Luis Donaldo

Colosio, Secretary of Social Development, the annual "Ecological Merit Award" was established in order to recognize individuals, organizations and institutions who project or carry out important actions for the environment. Another annual award is the "AgroBio" which from 2003 awards bachelor thesis, master and doctoral degrees, as well as journalism and research work related to agricultural biotechnology. There is also the annual program of Volkswagen "love the planet" since 2006 in two categories: Award for Scientific Research in Biological Conservation and Supporting a Research Project in a Natural Protected Area. In 2010 the "Cleantech Challenge Mexico" was created as an annual contest of green businesses in Mexico to promote the development of the new Mexican green economy, with the opportunity to receive investment from private funds. For example, in 2012 one of the awards was for *Biofase*, a Mexican company dedicated to the design, development and commercialization of bioplastics produced from avocado bones; another in 2011 was given to *Ecoplant* for a process involving CO_2 capture and processing into industrial products with high quality, demand and economic value such as sodium, calcium, magnesium and lithium carbonates.

In addition, three Nobel prizes have been awarded for transcendent research in Green Chemistry. In 2010 to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki by the *cross-coupling reactions catalyzed by palladium in organic synthesis*. In 2005 to Yves Chauvin, Robert Grubbs and Richard Schrock for *the development of the metathesis reactions energetically favored and less dangerous in organic synthesis with various applications in the polymer industry, pharmaceuticals and biotechnology method*. In 2001 to William S. Knowles and Ryoji Noyori for their *catalytic hydrogenation reactions of chiral* and to K. Barry Sharpless for their *chiral catalytic oxidation reactions*. Figure 2 shows some of the important persons that have contributed significantly to the development of Green Chemistry.

Figure 2 Important persons who have contributed to the development of Green Chemistry.

Towards to sustainability

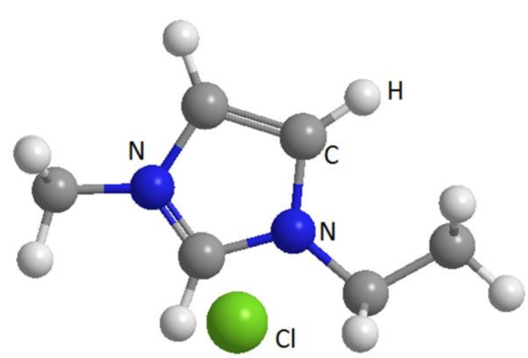
It is possible to achieve cost savings by reducing the generation of waste (whose treatment and disposal are becoming increasingly expensive, especially when dealing with hazardous waste) and energy use (since it is likely to represent the largest proportion of process costs in the present and future). These strategies involve not only economic benefits, but also the over-exploitation of natural resources and ecosystem disruption would be avoided. Furthermore, if renewable energy sources are used, the industry can be truly sustainable. In this way risk is reduced by the handling of hazardous substances, as well as accidents that impact both society and nature.

From thought to practice

In practice, a close collaboration between academia, industry and government sectors is required in order to synchronize the different ways of thinking, considering the environmental care and pursuing innovation for cleaner technologies. The use of "green" products has increased, not just for fashion but by necessity. Examples of specific cases of significant chemical alternatives in the fight against pollution are:

1. ***Use of green solvents: Ionic Liquids***

Ionic liquids are generally salts which melt at a temperature below 100 °C and are composed of a bulky organic cation and a smaller inorganic anion (example in Figure 3). Their best known advantages: They have a very low vapor pressure (they are not volatile), possess high thermal stability (they are not easily decomposed by raising temperature), they have high specific heat (they absorb large amount of heat rising very little their temperature), high solvating power (they dissolve a wide range of organic molecules such as plastics, dyes, petroleum, including DNA and inorganic molecules), and frequently they are excellent catalysts and easily reciclables (Handy, 2011; Wasserscheid, 2002). Robin Rogers, director of the University of Alabama and James Davis, a researcher at the University South Alabama, designed and synthesized several of them to remove cadmium and mercury from water, and CO_2 and H_2S from gas natural (Visser, 2002; Pan, 2012). Despite being called "green solvents" due to their almost zero volatility, it is necessary to take into account all the process from its synthesis to its recycling and disposal. Currently for obtaining and recycling ionic liquids are used volatile organic compounds VOCs or water. How "green" are ionic liquids depends on the environmental impact resulting from the production process, its toxicity and its application. It is clear that each "new" solvent generates benefits and problems, however, if we can find new clean and available synthesis and disposal routes, ionic liquids could represent an important alternative to various existing pollution problems of common solvents.



1-Ethyl-3-methylimidazolium chloride

Figure 3 Example of the molecular structure of an ionic liquid.

2. Use of catalysts: Fe-TAML Activators

Research of Professor Terrence J. Collins at Carnegie Mellon University have led to the creation of a new class of oxidizing activators catalysts. Such catalysts are iron complexes with macrocyclic tetraamido ligands, Fe-TAML (TAML = macrocyclic tetraamido ligand), figure 4, with comparable efficiencies to peroxidases. When these complexes activate *hydrogen peroxide* in water have major environmental implications, in particular, highlighting their purification efficiency of contaminated water with numerous persistent organic pollutants and pathogens difficult to eliminate. These complexes can be used in the delignification of paper, in the textile and laundry. The environmental benefits would result in a laundry that replace stoichiometric procedures by and catalytic ones requiring less water. Additionally, TAML peroxide activators have great potential in the purification of water from various industries, the destruction of pollutants and the remotion of sulfur from fuels. Oxidation processes using hydrogen peroxide activated by Fe-TAML compounds, instead of chlorinated compounds which produce highly toxic organochlorine compounds, can now be used to prevent and remove contaminants from these industries (Collins, 2002; Ghosh, 2003; Collins, 2011).

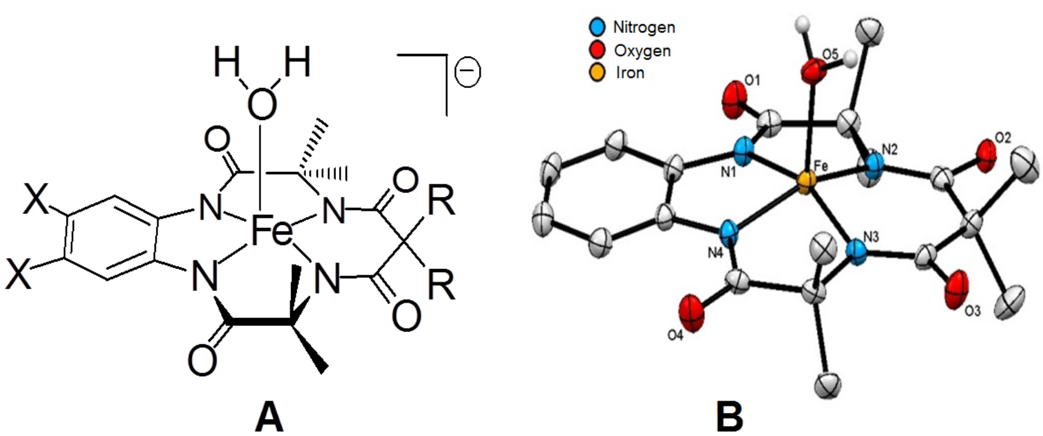


Figure 4 (A) Complexes Fe^{III}-TAMLs and (B) X-ray structure of the anionic part of the R = CH_3 Fe-TAML complex with X = H (hydrogen atoms are not shown for clarity).

3. Applications of supercritical fluids

Supercritical fluids have been used as extracting solvents. These fluids are above the critical point (Figure 5) in such state they diffuse as gases and dissolve as liquids, and small changes in pressure and temperature cause large changes in density (Gordon, 2006). Examples are water (H_2O) and carbon dioxide (CO_2). In this supercritical state, the CO_2 acquires great solvating power and can be used as a solvent of many substances, in fact, since the 70's it is used in the extraction of caffeine from green coffee seeds to obtain decaffeinated coffee, substituting a hazardous solvent such as dichloromethane or ethyl acetate (Ordóñez, 2006). It is also used in the extraction of fragrances, spice flavors and oils (Luque de Castro, 1993). Supercritical water is used for the destruction of organic waste under oxidizing conditions and as solvent in hydrolysis reactions as recycling of PET, to mention some of its applications (Gordon, 2006).

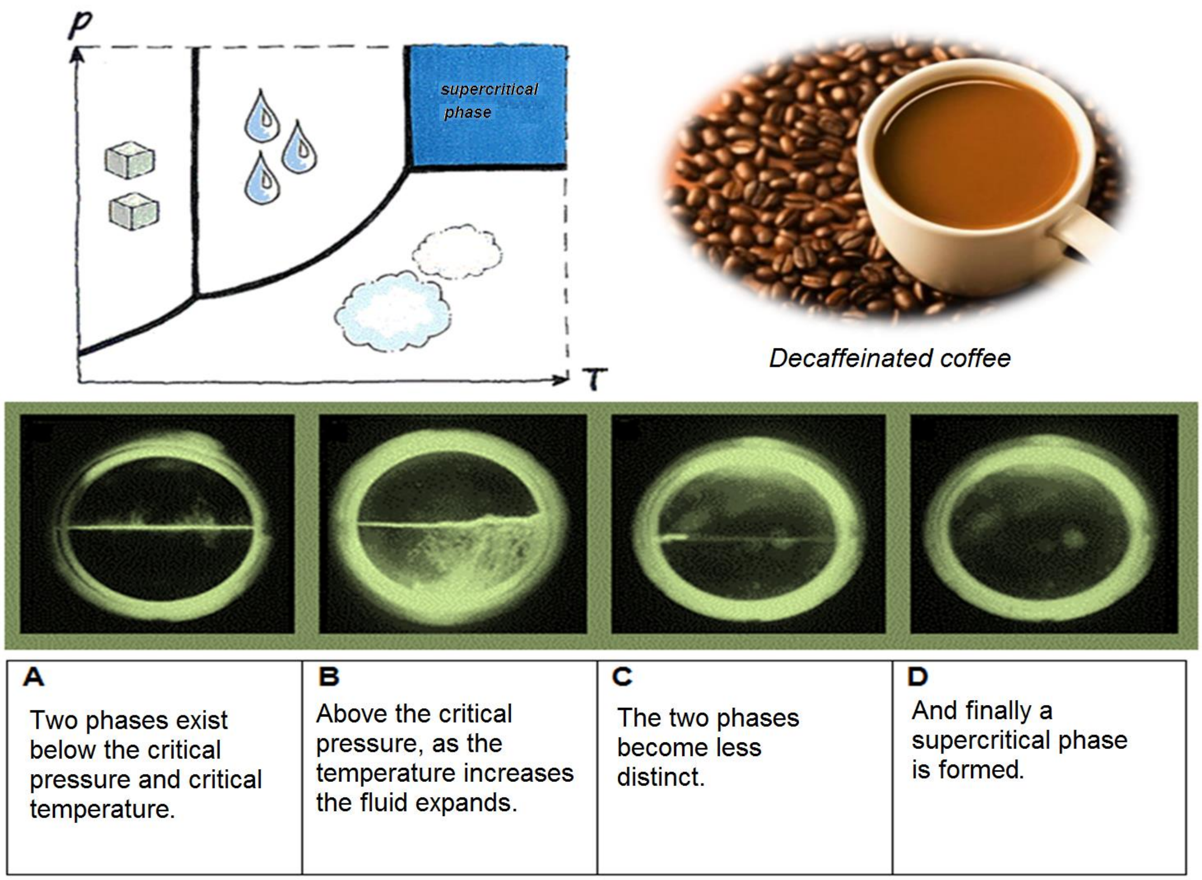


Figure 5 (top left) phase diagram. (down) stages forming a supercritical phase.

Future Actions

Authentic Green Chemistry is designed to eliminate or at least reduce the sources of pollution with the intention that the new products and processes do not endanger any life. However, nature is a system full of very sensitive balances often very complex, and it is necessary to achieve a comprehensive level of multidisciplinary knowledge. Combining science and technology along with the protection of nature, of which we are a part, is one of the many challenges that everyone must face. Chemistry plays a key role in the research and establishment of the necessary conditions to achieve sustainable development, achieve new holistic approaches in order to solve these problems and avoid causing new ones hitherto unknown. In the coming years, the Sustainable Development and Green Chemistry concepts will continue to take an increasingly important place in sectors such as industry, government and even the social, thus achieving more favorable decisions for the environment and the future of humanity. Unfortunately in our country and in many other countries, the main barriers are lack of information, causing insufficient development of environmental awareness, insufficient or inadequate investment and the slow transition between the academic and industrial sectors, although there are institutes, organizations and businesses looking for innovation and implementation of Green Chemistry. Most of the successes of the Green Chemistry in the past two decades are related to waste minimization and among the challenges of the future are that the green chemistry chemists achieve that molecular properties are sufficiently controllable to minimize risks of chemicals used. Other challenges are for alternative methods of synthesis to reduce energy consumption, to obtain materials that reduce dependence on fossil resources and a controlled use of raw materials based on biological sources. Moreover, the issue of environmental sustainability requires "scientific solutions" for research and development of more benign materials and processes for the environment, and "political solutions" for the regulation and control of the care of it.

"Green chemistry make our dreams come true in the XXI century"

– Green and Sustainable Chemistry Network of Japan–

"Green chemistry represents the pillars that support our sustainable future. It is imperative to teach the value of Green Chemistry to tomorrow´s chemists"

– Daryle Busch (President of the ACS, 1999-2001)–

"Green chemistry is more effective, more efficient, more elegant, is simply a better chemistry"

– Paul Anastas –

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