

A NEW ASPECT FOR OUR ENVIRONMENTAL IMPROVEMENTS

Emad S. Shaker* and Ahmed H. El-Sayed

Journal

J. Biol. Chem.
Environ. Sci., 2008,
Vol. 3(1): 377-388
www.acepsag.org

Agric. Chemistry Dept., Agriculture Faculty, Minia University

ABSTRACT

Use of chemistry for pollution prevention is called Green Chemistry. It is the design of chemical products and processes that are environmentally benign. Green chemistry encompasses all aspects and types of chemical processes that reduce negative impacts to human health and the environment. The importance of the new area is providing goods and services for growing population without sacrificing environmental quality.

The growth of the chemical industry is likely to take place in the developing world, coincident with the rising population. However, many of the global environmental impacts attributable to the population growth have ties to chemical processes or products: loss of biological species in forests and in waters, ozone depletion, downstream pollution from unsustainable agricultural practices, the pollution of fresh and marine waters, the persistent organic pollutants into the ecosystem, changing climate causing changes in the hydrologic cycle with manifestations in flood, drought, sea-level change, and the spread of infectious diseases.

INTRODUCTION

Recently, we can notice the increasing pressure from both developed societies 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 chemical industry is vitally important to the world economy; however the success of the industry has led to some environmental damage and a low public perception of the industry. In order to prevent further environmental

damage, adoption of the cleaner processes must be assured. Industry is making progress, but it is frequently commented that new graduates are not adequately equipped with the tools, techniques, and culture to ensure that they can rapidly make a positive impact on industry's increasing requirement for clean technology. Globally there is a growing requirement for cleaner processes, with many *third-world* countries now insisting that licensed technology is the cleanest available. So to ensure the future success of chemistry-based industries, it is vital to equip students with the requisite tools, knowledge and experience.

Green chemistry is defined as the use of chemistry for pollution prevention. More specifically, green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. The "*Green Chemistry Centre*" will have roles for education and research in clean chemical technology. The groups have excellent links with many organizations around the world. There are several research groups at York for example, are interested in aspects of Green Chemistry including catalysis, supported reagents, alternative solvents, environmental fate and sustainable development. Green Chemistry Centre for Industry provides as well links with many chemical and other companies.

"*The Pollution Prevention Act*" of 1990 established a national policy to prevent or reduce pollution at its source whenever feasible. *The Pollution Prevention Act* provided an opportunity to expand beyond traditional programs and devise creative strategies to protect human health and the environment. A highly effective approach to pollution prevention, green chemistry applies innovative scientific solutions to real-world environmental situations, all through voluntary partnership programs. This innovative approach to pollution prevention through the environmentally conscious design of chemical products and processes is the central focus of Green Chemistry Program, an initiative under the Design for the Environment Program.

Green chemistry is a highly effective approach to pollution prevention and it applies innovative scientific solutions to real-world environmental situations. The 12 Principles of Green Chemistry, originally published by *Paul Anastas* and *John Warner* in *Green Chemistry* (1998). They provided a road map for chemists to implement green chemistry. Promoting this new approach to pollution prevention through the environmentally conscious design of chemical

products and processes is the focus of Environmental Prevention Agency's (EPA) Green Chemistry Program.

The Twelve Principles of Green Chemistry

1. Prevent waste: Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.

2. Design safer chemicals and products: Design chemical products to be fully effective, yet have little or no toxicity.

3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to humans and the environment.

4. Use renewable feedstocks: Use *raw materials and feedstocks that are renewable* rather than depleting. *Renewable feedstocks* are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

5. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.

6. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

7. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.

8. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.

9. Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible.

10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

11. Analyze in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for

chemical accidents including explosions, fires, and releases to the environment.

So, we can define the chemicals that are less hazardous to human health and the environment as:

- Less toxic to organisms and ecosystems
- Not persistent or bioaccumulative in organisms or the environment
- Inherently safer with respect to handling and use

EPA's Green Chemistry Program promotes the research, development, and implementation of innovative chemical technologies that accomplish pollution prevention in a scientifically sound and cost-effective manner. To accomplish these goals, the Green Chemistry Program recognizes and supports chemical technologies that reduce or eliminate the use or generation of hazardous substances during the design, manufacture, and use of chemical products and processes. More specifically, the Green Chemistry Program supports fundamental research in the area of environmentally benign chemistry as well as a variety of educational activities, international activities, conferences and meetings, and tool development, all through voluntary partnerships with academia, industry, other government agencies, and non-government organizations.

In 1995, the Office of Pollution Prevention and Toxics (OPPT) launched the Presidential Green Chemistry Challenge, a voluntary partnership to support further green chemistry research and recognize outstanding examples of green chemistry. The Presidential Green Chemistry Challenge Awards highlight successes in research, development, and industrial implementation of technologies that prevent pollution at the source while contributing to the competitiveness of the innovators.

EPA's Green Chemistry Program works with many partners to promote pollution prevention through green chemistry. Partnering organizations represent academia, industry, other government agencies, scientific societies, trade organizations, national laboratories, and research centers. Specific partners of EPA's Green Chemistry Program in scientific organizations and industry are listed below.

Scientific Organizations:

- American Chemical Society (ACS)
- Green Chemistry and Engineering Subdivision

- Green Chemistry Education Resources
- Green Chemistry Institute (GCI)
- Green Chemistry Publications
- Council for Chemical Research (CCR)
- International Union of Pure and Applied Chemistry (IUPAC)
- National Research Council (NRC)
- National Science Foundation (NSF)
- Society for Environmental Toxicology and Chemistry (SETAC)

Industry

- The BF Goodrich Company
- The Dow Chemical Company
- Dow Corning Corporation
- E.I. DuPont de Nemours
- Eastman Kodak Company
- Monsanto
- Polaroid Corporation
- Rochester Midland Corporation
- Solutia
- Trade Associations
- American Chemistry Council
- American Petroleum Institute (API)
- Society of the Plastics Industry (SPI)

HISTORY

Shortly after the passage of the *Pollution Prevention Act* of 1990, 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 program called "*Alternative Synthetic Pathways for Pollution Prevention*". This program 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 Program has built collaborations with academia, industry, commerce, government agencies, and non-government organizations to promote the use of chemistry for *environmentally friendly chemical products and processes*.

By offering environmentally benign alternatives to the more hazardous chemicals and processes that are often used in both consumer and industrial applications, green chemistry is promoting pollution prevention at the molecular level. Green Chemistry Program supports basic research in green chemistry in order to provide the chemical tools and methods necessary to design and develop products and processes that are more environmentally benign.

Green Chemistry Education Activities

In order for green chemistry to be incorporated effectively into chemical product and process design, it first must be incorporated into the education system. For green chemistry to become widely adapted and practiced, chemists must be formally educated about green chemistry during both their academic and professional training. To accomplish this, Green Chemistry Program supports a variety of educational efforts that include the development of materials and courses to assist in the training of professional chemists in industry and education of students in academia.

Recent research trials from the green chemistry

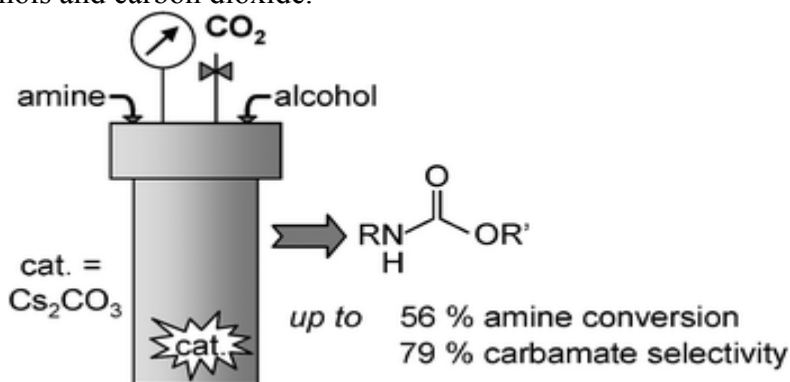
Marsden *et al.* (2008) established a green protocol for producing simple esters by selective oxidizing an aldehyde dissolved in a primary alcohol. They utilised air as the oxidant and supported gold nanoparticles as catalyst. The oxidative esterifications proceed with excellent selectivities at ambient conditions. In this protocol, benzaldehyde is oxidised at a reasonable rate below -70°C and acrolein is oxidized to methyl acrylate in high yield.

Green solvent combination in the biphasic system water/ CO_2 has been used as a reaction and extraction medium (Roosen *et al.*, 2007). The pH control in the aqueous phase is possible up to a pH of approximately 6 by means of buffer salts, and the resulting pH can be predicted by an algebraic equation.

In replacing the traditional volatile organic solvents in industrial processes, Kulacki and Lamberti (2008) used room-temperature ionic liquids. They studied effects of 1-butyl-, 1-hexyl- and 1-octyl-3-methylimidazolium bromide on the growth rates of freshwater algae in 96 h standard toxicity bioassays. Increases in alkyl chain length increased the toxicity of these ionic liquids to algae.

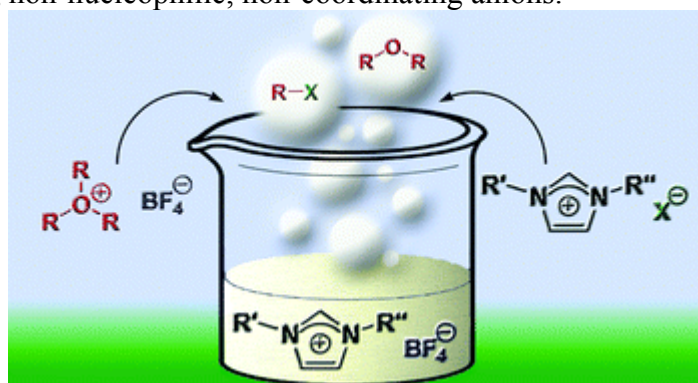
Zhang *et al.* (2007) esterified alcohols by carboxylic acids in a halogen-free Bronsted acidic ionic liquid, *N*-methyl-2-pyrrolidonium methyl sulfonate. Especially for esterification of ethanol by acetic acid, good conversion and high selectivity were obtained. The liquid esters formed a separate phase, and the ionic liquid could be reused after removal of water under vacuum.

Ion *et al.* (2008) prepared various carbamates in a halogen-free way starting from cheap and readily available reagents as amines, alcohols and carbon dioxide.

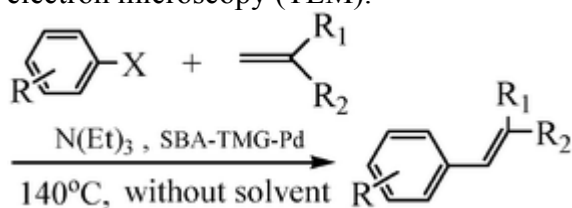


Basic catalysts were able to convert both linear and branched aliphatic amines to the corresponding carbamates with good yields, in mild reaction conditions and even in the absence of dehydrating agents.

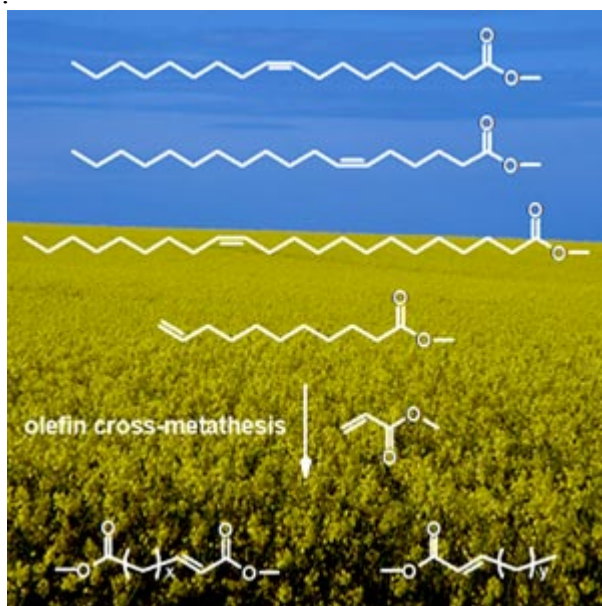
Vu *et al.* (2007) found a range of electrophilic reagents to facilitate simultaneous halide-trapping/anion metathesis of halide-containing salts in the absence of solvent to afford ionic liquids bearing non-nucleophilic, non-coordinating anions.



In solvent-free conditions, Ma *et al.* (2008) carried out Heck arylation of olefins with aryl halides. The reaction was done in the presence of Pd catalyst supported on 1,1,3,3-tetramethylguanidinium (TMG)-modified molecular sieve SBA-15. SBA-TMG-Pd was much more active and stable than a Pd catalyst supported on pristine SBA-15. The catalysts were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM).

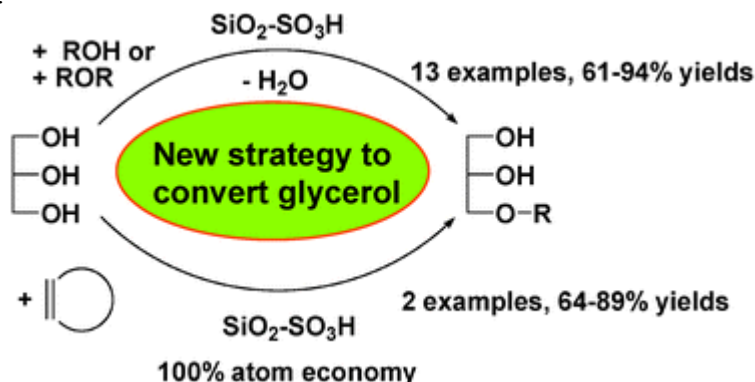


The magazine of *Chemical Science* (2007) published an efficient catalytic approach turns plant oils into precursors for polymers and detergents with very little waste. As renewable sources, plant oils attract chemical industry for the availability, price and environmental impact. Fatty acid derivatives from natural feedstocks as castor oil have been used to make *diesters monomers* for making polyesters and polyamides.



Simple cross-metathesis reaction was between fatty acid derivatives and the widely available compound methyl acrylate. The reaction was initiated by commercially available catalysts and cut down on the long reaction times. This reaction is efficient use for the synthetic potential of nature and hardly produces any waste. Beside, it is solvent free; selective for the cross-metathesis product and the by-product is a starting material for detergents.

Behr *et al.* (2008) utilized the glycerol as a by-product of biodiesel production in esters, oligomers, glycerol carbonate, telomers, branched alkyl ethers, propanediols and epoxides. Numerous addition, reduction and oxidation reactions *via* heterogeneous, homogeneous and biocatalysis have been presented. Gu *et al.* (2008) allowed the first catalytic access to valuable monoalkyl glyceryl ethers. Direct etherification of glycerol with alkyl alcohols, olefins and dibenzyl ethers was successfully catalyzed by acid functionalized silica.



In oil refinery, petroleum is converted into gasoline, oil, and monomers as ethylene and propylene. They produce high volume chemicals (such as gasoline and diesel), plus a number of low volume, high value materials. On the other hand, corn grain and soy biorefinery produce high volume fuels as ethanol or biodiesel; and high value products and chemicals. Soybean oil is converted into biodiesel by treating the oil with methanol and a recyclable catalyst. The by-product glycerol must be converted into higher-value chemicals (as 1, 3-propanediol, acrolein, and propylene glycol) that can replace petrochemicals.

Producing ethanol used to be from crude oil in a direct hydration process with high temperatures, pressures and large amounts of waste. In a conference held in York University (2006), research focused on producing ethanol from renewable resources such as; hydrolyzing starch and cellulose to simple sugars and followed by fermentation. The fermentation process takes place using enzymes and then the ethanol is recovered by fractional distillation. In biomass energy, America relies on corn while Brazil produces bioethanol from sugarcane.

Since the industrial revolution, the atmospheric CO_2 concentration has increased by 40%. As CO_2 is a greenhouse gas, the rise in atmospheric levels has been directly linked to global warming. In York conference, possibilities have been studied CO_2 capture through extracting it from the atmosphere or from large stationary sources. The purpose of CO_2 capture is to produce a concentrated stream of CO_2 at high pressure that can readily be transported to a storage site.

To the potential effect of nanotechnology on human health and environment, the developments have been with little regard. The only regulation for nanoparticles is the covering same material in bulk form by changing their size, shape and surface characteristics.

Green chemistry metrics incorporate into nanotechnology at the source for potential health effects and medical application. Nanoparticles can enter the human body through the lungs, the intestinal tract and to a lesser extent the skin. They can be modified to cross the brain blood barrier for medical applications (Albrecht *et al.*, 2006).



It has been found in conclusion the drivers for change toward the modern green chemistry for economic, societal and environmental reasons. These reasons should include increasing costs of energy,

petrochemical, waste disposal, storing hazardous substances. The reasons include also; increasing fines of pollutions, demands of emerging nations and producer responsibility. New legislation need for testing all the chemicals to diminish supplies of non-sustainable resources.

REFERENCES

- Albrecht, M.; Evans, C. and Raston, C. (2006) Green chemistry and the health implications of nanoparticles. *Green Chem.*, 8, 417-432.
- Anastas, P. and Warner, J. (1998) Green Chemistry; Theory and Practice. Oxford University Press, New York.
- Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J. and Lindner, F. (2008) Improved utilization of renewable resources: New important derivatives of glycerol. *Green Chem.*, 10.1039/b 710561d
- Gu, Y.; Azzouzi, A.; Pouilloux Y.; Jerome, F. And Barrault, J. (2008) Heterogeneously catalyzed etherification of glycerol: new pathways for transformation of glycerol to more valuable chemicals. *Green Chem.*, 10.1039/b 715802e
- Ion, A.; Doorslaer, Ch; Parvulescu, V.; Jacobs, P. and De Vos, D. (2008) Green synthesis of carbamates from CO₂, amines and alcohols. *Green Chem.*, 10.1039/b 711197e
- Kulacki, K. and Lamberti, G. (2008) Toxicity of imidazolium ionic liquids to freshwater algae. *Green Chem.*, 10.1039/b 709289j
- Ma, X.; Zhou, Y.; Zhang, J.; Zhu, A.; Jiang, T. and Han B. (2008) Solvent-free Heck reaction catalyzed by a recyclable Pd catalyst supported on SBA-15 *via* an ionic liquid. *Green Chem.*, 10.1039/b 712627a
- Marsden, Ch.; Taarning, E.; Hansen, D.; Johansen, L.; Klitgaard, S.; Egeblad, K. and Christensen, C. (2008) Aerobic oxidation of aldehydes under ambient conditions using supported gold nanoparticle catalysts. *Green Chem.*, 10. 1039/b 712171g.
- Meier, M.; Rybak, A. and Doll, K. (2007) From plant oils to polymers. *Chemical Science*, 12.
- Renewable resources & biorefineries conference 6th – 8th September, 2006. The University of York.
- Roosen Ch.; Schumacher, M.; Mang, Th.; Leitner, W. and Greiner, L. (2007) Gaining pH-control in water/carbon dioxide biphasic systems. *Green Chem.*, 9, 455-458.

- Vu, P.; Boydston, A. and Bielawski, Ch. (2007) Ionic liquids via efficient, solvent-free anion metathesis. *Green Chem.*, 9, 1158-1159.
- Zhang, H.; Xu, F.; Zhou, X.; Zhang, G. And Wang, C. (2007) A Bronsted acidic ionic liquid as an efficient and reusable catalyst system for esterification. *Green Chem.*, 9, 1208-1211.

رؤية جديدة لتطوير البيئة

عماد صبرى شاكى وأحمد حسن السيد

قسم الكيمياء الزراعية - كلية الزراعة - جامعة المنيا

يأخذ تطور الصناعة الكيميائية في دول العالم النامى صورة مرتبطة بالزيادة السكانية. حيث ترتبط الكثير من التأثيرات البيئية العالمية بالزيادة السكانية وطرق الصناعات الكيميائية أو نواتجها. ومن هذه التأثيرات البيئية فقد التنوع البيولوجى فى الغابات والمياه. وتقتب الأوزون وتلوث المجارى المائية الزراعية وتلوث المياه العذبة والمياه البحرية وعدم تحلل الملوثات العضوية فى النظام البيئى وكذلك التغير المناخى الذى يؤثر فى النظام المائى والذى يظهر فى العديد من الظواهر مثل الفيضانات والجفاف وتغير مستوى سطح البحار وسرعة انتشار الأمراض المعدية.

أنتشرت هذه الأيام العلوم الحديثة التى تهتم بالبيئة مثل الكيمياء الخضراء وهو ما يعنى أستعمال الكيمياء فى منع التلوث البيئى. والكيمياء الخضراء هى التى تهتم بالنواتج الكيميائية والطرق الحميدة بيئيا. وتشمل الكيمياء الخضراء كل الأنواع والطرق الكيميائية التى تقلل من السلبات على صحة الإنسان والبيئة. وأهمية هذه الوسائل الجديدة فى الأمداد بخدمات جديدة للنمو السكانى بدون المساس بسلامة البيئة.