

Pollution Prevention by Utilizing Green Chemistry

Introduction

Many of the basic concepts of green chemistry are familiar to pollution prevention practitioners. The concepts of substituting less hazardous materials into chemical formulations and reducing wastes have been around for many years. Green chemistry has taken these concepts and expanded the scope of possibilities by fully evaluating all aspects of chemical reactions, processes and formulations. This fact sheet is intended to introduce the concept of green chemistry to industry, academia and consumers and outline the positive environmental and economic benefits that result from implementation.

The term green chemistry can be contributed to a number of individuals, but is formally recognized by principles detailed in *Green Chemistry: Theory and Practice* by Paul Anastas and John Warner.

Substitution Opportunities

Carbon dioxide substitution

Carbon dioxide (CO₂) substitution represents a significant opportunity to substitute an existing benign substance for a wide variety of more toxic substances. The recyclability and reuse of CO₂ in many processes can make closed-loop systems possible.

The 12 Principles of Green Chemistry

(from *Green Chemistry: Theory and Practice* by Paul Anastas and John Warner, Oxford University Press, 1998)

- 1) **Prevention** - It is better to prevent waste than to treat or clean up waste after it has been created.
- 2) **Atom Economy** - Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- 3) **Less Hazardous Chemical Syntheses** - Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- 4) **Designing Safer Chemicals** - Chemical products should be designed to effect their desired function while minimizing their toxicity.
- 5) **Safer Solvents and Auxiliaries** - The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- 6) **Design for Energy Efficiency** - Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- 7) **Use of Renewable Feedstocks** - A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- 8) **Reduce Derivatives** - Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/ chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- 9) **Catalysis** - Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- 10) **Design for Degradation** - Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- 11) **Real-time Analysis for Pollution Prevention** - Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- 12) **Inherently Safer Chemistry for Accident Prevention** - Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires. www.epa.gov/greenchemistry/pubs/principles.html

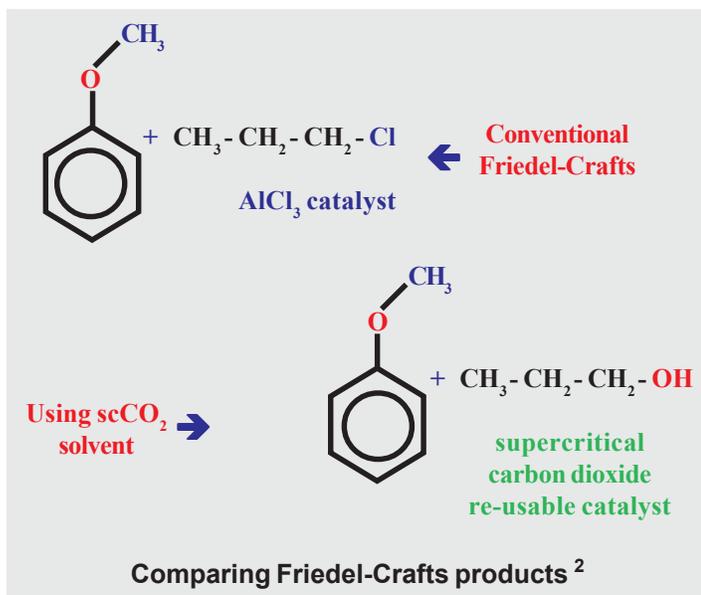
Pollution Prevention by Utilizing Green Chemistry

Solvent Substitution

When CO₂ is heated to 88°F and compressed to 1,100 psi, it acts like a solvent and can be used for thinning viscous coatings to the desired level for application. Because of its solvent-like properties, CO₂ can replace hazardous hydrocarbon solvents. Solvent use can be reduced by 50 to 85 percent; and use of hazardous air pollutants (HAPs), such as xylene and toluene, can be completely eliminated in some cases.¹

Catalyst

Utilizing CO₂ to replace traditional reaction catalysts can eliminate hazardous by-products and create closed-loop processes.



CO₂ case study¹

One automotive company used the Unicarb® system to apply a thin adhesion-promoter primer layer to automotive components made of thermoplastic polyolefin (TPO). Because TPO is made primarily of polypropylene, it does not adhere well to polyurethane coatings and traditionally requires the use of adhesion promoters. However, using the supercritical process, the company increased transfer efficiency from 28 percent to 38 percent. Coating coverage quadrupled, from nine parts per gallon (conventional coating) to 36 parts per gallon. With an annual spray line of 1.8 million parts, the company saved \$2.5 million in coating application costs alone.

Emerging Technologies

Biobased materials

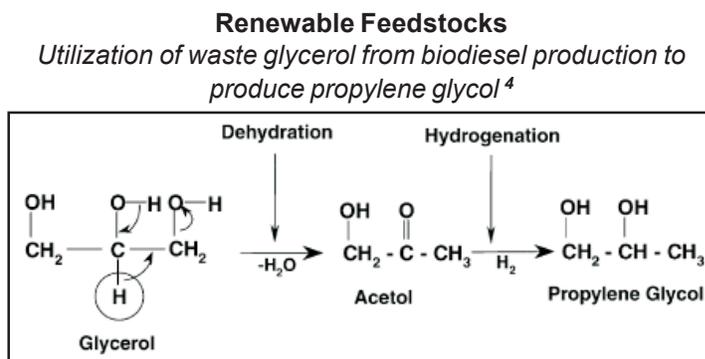
Biobased products are inherently less toxic and promote the principles of green chemistry by expanding opportunities to develop possible closed-loop processes utilizing renewable resources. Ultimately, renewable resources may produce a

significant amount of manufacturing, pharmaceutical and consumer materials which are currently produced with nonrenewable and sometimes hazardous materials. Many biological synthesis processes are replacing conventional refining or hazardous polymerization processes.

Renewable Feedstocks

Biobased feedstock for propylene glycol³

This alternative process produces propylene glycol from waste glycerol more economically and efficiently than from petroleum. This boosts the biodiesel market by giving value to the glycerine co-product and provides a cheaper, less toxic antifreeze option to ethylene glycol.



Enzymatic Reactions⁵

Important breakthroughs have occurred in using natural processes such as enzymatic action to create substances that previously required hazardous materials. For instance, Archer Daniels Midland Company (ADM) changed from a chemical intensive process to a natural enzymatic process to produce triglycerides that are free of any trans fatty acids. The ADM/ Novozymes process has the potential to save 400 million pounds of soy bean oil and eliminate 20 million pounds of sodium methoxide, 116 million pounds of soaps, 50 million pounds of bleaching clay and 60 million gallons of water each year.

Biobased feedstock for resins⁶

Dow has a new process to produce liquid epoxy resins (LER) which are used in marine protective, automotive, can coatings and many other applications. This process involves making a key raw material for LER resins, epichlorohydrin, from glycerine, a renewable-based feedstock.

The glycerine is a by-product of biodiesel production, which is made from renewable vegetable oil feedstocks. This will reduce waste water generation from the production facility by more than 90 percent compared to the conventional technology, and will almost completely avoid organic by-product formation. The process will significantly reduce the environmental footprint by consuming 30 percent less energy.

Pollution Prevention by Utilizing Green Chemistry

Alternative Synthesis Pathways

Another important aspect of green chemistry is the discovery of alternative synthesis pathways. A classic example of this is the traditional synthesis of ibuprofen which previously produced large quantities of hazardous waste and had a relatively low product yield.

The Boots Company of England developed and patented the traditional industrial synthesis of ibuprofen in the 1960s (U.S. Patent 3,385,886). This synthesis is a six-step process and results in large quantities of waste chemical byproducts that must be disposed of or otherwise managed. Much of the waste is created because atoms of reactants are not incorporated into the desired product (ibuprofen) but into unwanted byproducts.

BHC Alternative ⁷

The BHC Company has developed and implemented a new three-step greener industrial synthesis of ibuprofen (U.S. Patents 4,981,995 and 5,068,448, both issued in 1991). In this process, most of the atoms of the reactants are incorporated into the desired product (ibuprofen). Because the

process has very good atom economy/atom utilization, unwanted by-products are reduced four to 10 times and the need for disposal and mediation of waste decreases.

Production of Propylene Oxide via Hydrogen Peroxide ⁹

Propylene oxide (PO) is one of the biggest volume industrial chemicals in the world. It is a chemical building block for a vast array of products including detergents, polyurethanes, de-icers, food additives and personal care items. Its manufacture creates by-products, including a significant amount of waste. Dow and BASF have jointly developed a new route to make PO with hydrogen peroxide that eliminates most of the waste and greatly reduces water and energy use.

Production facilities are up to 25 percent cheaper to build because there is no need for equipment to collect and purify the co-product. The new process reduces the production of wastewater by as much as 80 percent and the use of energy by 35 percent over traditional technologies.

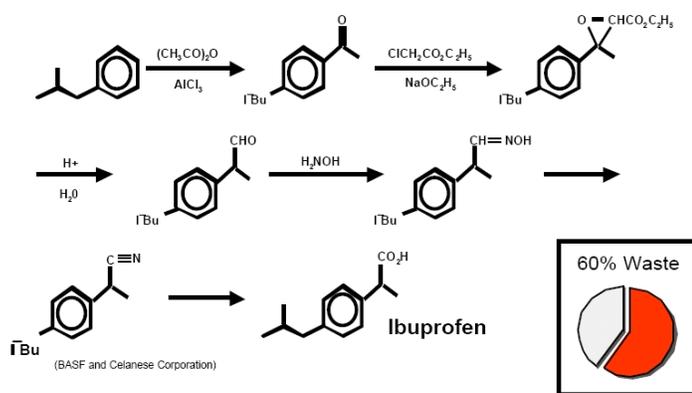
Supramolecular Chemistry

Concepts such as supramolecular chemistry achieve reactions in a solid state without the use of any solvents and achieve up to 100 percent yields. Supramolecular chemistry and self-assembly processes in particular have been applied to the development of new materials. Large structures can be readily accessed using bottom-up synthesis as they are composed of small molecules requiring fewer steps to synthesize. Thus most of the bottom-up approaches to nanotechnology are based on supramolecular chemistry.

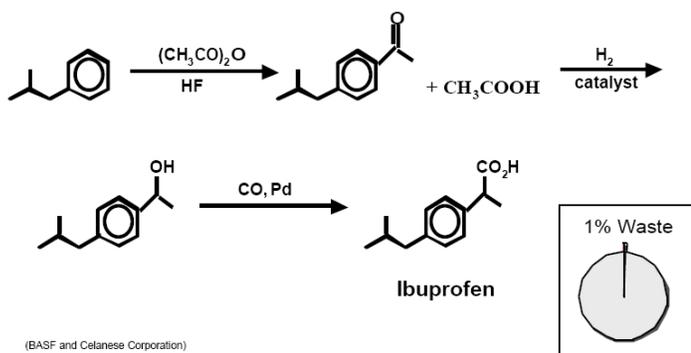
Supramolecular chemistry is often pursued to develop new functions that cannot appear from a single molecule. These functions include magnetic properties, light responsiveness, catalytic activity, self-healing polymers, chemical sensors, etc. Supramolecular research has been applied to develop high-tech sensors, processes to treat radioactive waste, compact information storage devices for computers, high-performance catalysts for industrial processes and contrast agents for CAT scans.

Supramolecular chemistry is also important to the development of new pharmaceutical therapies by understanding the interactions at a drug binding site. In addition, supramolecular systems have been designed to disrupt protein-protein interactions that are important to cellular function.

Traditional Synthesis of Ibuprofen ⁸



Green Chemistry Alternative Synthesis of Ibuprofen ⁸



Pollution Prevention by Utilizing Green Chemistry

References

¹ *Biochemicals for the Automotive Industry*, The Carbohydrate Economy. Institute for Local Self-Reliance.

www.epa.ohio.gov/portals/41/p2/biochemicalsautomotiveindustry.pdf

² *Friedel-Crafts Reactions*, The Greener Industry website.

www.greener-industry.org.uk/

³ *Biobased Propylene Glycol and Monomers from Natural Glycerin*, Professor Galen J. Suppes, University of Missouri-Columbia.

www.epa.gov/gcc/pubs/pgcc/winners/aa06.html

⁴ *Low-Pressure Hydrogenolysis of Glycerol to Propylene Glycol*

www.epa.ohio.gov/portals/41/p2/wasteglycerol.pdf

⁵ *NovaLipid™: Low Trans Fats and Oils Produced by Enzymatic Interesterification of Vegetable Oils Using Lipozyme®*, Archer Daniels Midland Company.

www.epa.gov/gcc/pubs/pgcc/winners/gspa05.html

⁶ *Dow Advances Sustainable Chemistry with Epichlorohydrin Made from Renewable Glycerine*

www.dow.com/commitments/studies/glycerine.htm

⁷ *Synthesis of Ibuprofen: A Greener Synthesis of Ibuprofen Which Creates Less Waste and Fewer Byproducts*

www.epa.ohio.gov/portals/41/p2/ibuprofencasestudy.pdf

⁸ *Green Chemistry - Pollution Prevention by Design*, Zero Waste Alliance.

www.epa.ohio.gov/portals/41/p2/zerowastegreenchemistry.pdf

⁹ *Innovative, Environmentally Benign Production of Propylene Oxide via Hydrogen Peroxide*

www.epa.gov/gcc/pubs/pgcc/winners/gspa10.html

Green Chemistry: Theory and Practice, Paul Anastas and John Warner, Oxford University Press: Oxford UK, 1998.

www.epa.gov/greenchemistry/pubs/principles.html

Green Chemistry Resources

U.S. EPA Presidential Green Chemistry Challenge Awards
www.epa.gov/greenchemistry/pubs/pgcc/presgcc.html

Warner Babcock Institute for Green Chemistry

www.warnerbabcock.com/

iSUSTAIN™ Green Chemistry Index

www.isustain.com/

Certification Cradle to Cradle® Certification

www.mbd.com/

Center for Green Chemistry & Green Engineering at Yale

www.greenchemistry.yale.edu/

Greener Educational Materials for Chemists. University of Oregon. <http://greenchem.uoregon.edu/gems.html>

Michigan Green Chemistry Program

www.michigan.gov/greenchemistry

California's Green Chemistry Initiative

www.dtsc.ca.gov/PollutionPrevention/GreenChemistryInitiative/index.cfm

American Chemical Society Green Chemistry Institute®

www.acs.org/greenchemistry

Online Green Chemistry Training from Ohio EPA

www.epa.ohio.gov/ocapp/p2/onlinep2training/onlinep2training.aspx