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# Pollution Prevention by Utilizing Green Chemistry

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.

**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

## Substitution Opportunities

Carbon dioxide ($CO_2$) substitution represents a significant opportunity to substitute an existing benign substance for a wide variety of more toxic substances. The recyclability and reuse of $CO_2$ in many processes can make closed-loop systems possible.

*Solvent Substitution*
When $CO_2$ 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

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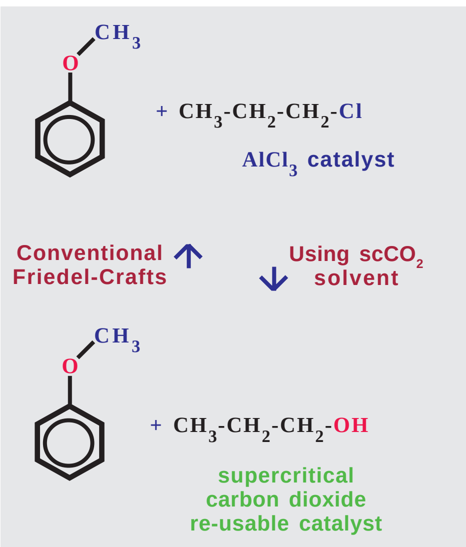
desired level for application. Because of its solvent-like properties, $CO_2$ can replace hazardous hydrocarbon solvents. Solvent use can be reduced by 50 to 85 percent; and use of hazardous air pollutants (HAPs), such as xylene and toluene, can be completely eliminated in some cases.

*Catalyst*
Utilizing $CO_2$ to replace traditional reaction catalysts can eliminate hazardous by-products and create closed-loop processes.




Comparing Friedel-Crafts products

**$CO_2$ case study**
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

*Bio-based materials*
Bio-based 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 non-renewable and sometimes hazardous materials. Many biological synthesis processes are replacing conventional refining or hazardous polymerization processes.

## Renewable Feedstocks

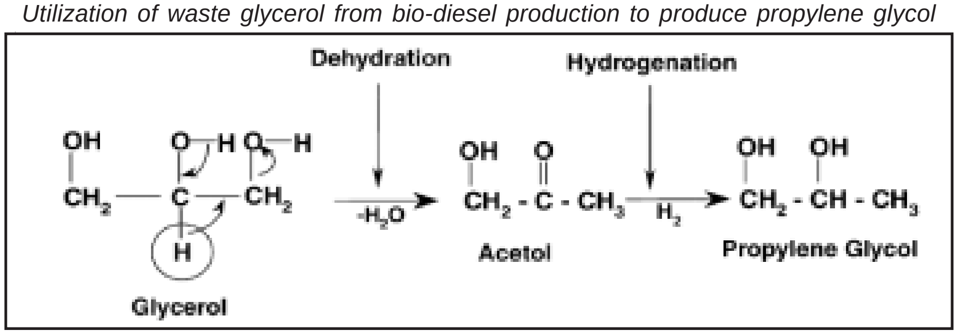
This alternative produces propylene glycol from waste glycerol more economically and efficiently than from petroleum. This boosts the biodiesel market by giving value to the glycerine co-product and provides a cheaper, less toxic antifreeze option to ethylene glycol.

*Enzymatic Reactions*
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.

## 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.

**Renewable Feedstocks**
*Utilization of waste glycerol from bio-diesel production to produce propylene glycol*



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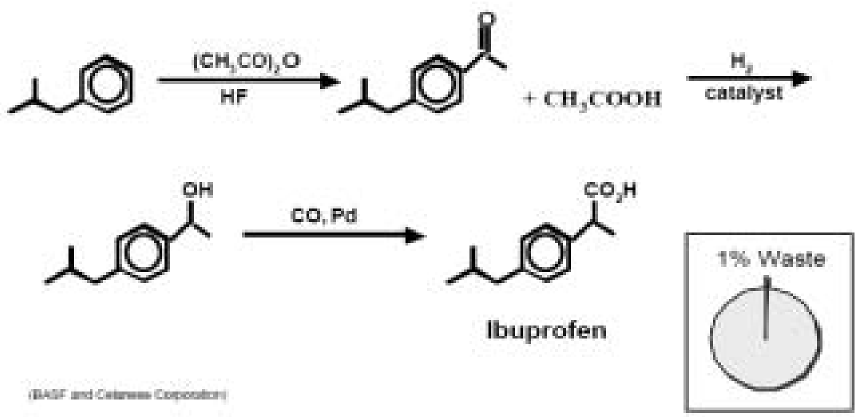
The Boots Company of England developed and patented the traditional industrial synthesis of ibuprofen in the 1960s (U.S. Patent 3,385,886). This synthesis is a six-step process and results in large quantities of waste chemical byproducts that must be disposed of or otherwise managed. Much of the waste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

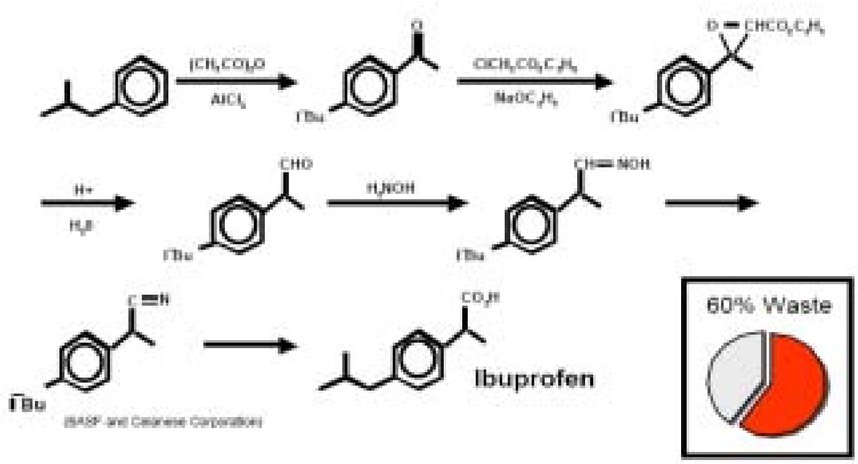
*BHC Alternative*

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 byproducts are reduced four to 10 times and the need for disposal and mediation of waste decreases.

**Green Chemistry Alternative Synthesis of Ibuprofen**




**Traditional Synthesis of Ibuprofen**




## 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.

## Green Chemistry Resources and References

*Presidential Green Chemistry Challenge Awards*
www.epa.gov/greenchemistry/pubs/pgcc/presgcc.html
www.epa.gov/greenchemistry/pubs/pgcc/winners/aa06.html

*Kenneth G. Hancock Memorial Award*
www.chemistry.org/portal/a/c/s/1/acsdisplay.html?DOC=greenchemistryinstitute%5Chancock.html

*Joseph Breen Awards*
www.chemistry.org/portal/resources/?id=43966216e85b11d6fc136ed9fe800100

*Green Chemistry Institute Sabbatical/Fellow Program*
www.acs.org/portal/resources/ACS/ACSContent/greenchemistryinstitute/PDF/gci_sabbatical.pdf

*Online Green Chemistry Training*
www.epa.state.oh.us/ocapp/p2/onlinep2training/onlinep2training.html

*Green Chemistry: Theory and Practice*, Paul Anastas and John Warner, Oxford University Press: Oxford UK, 1998. www.epa.gov/greenchemistry/pubs/principles.html

*Friedel-Crafts Reactions*, The Greener Industry Web site
www.greener-industry.org/pages/superCO2/4superCO2_friedel.htm

*Biochemicals for the Automotive Industry*, The Carbohydrate Economy. Institute for Local Self-Reliance. 1997.
www.carbohydrateeconomy.org/library/admin/uploadedfiles/Biochemicals_for_the_Automotive_Industry.pdf

*Biobased Propylene Glycol and Monomers from Natural Glycerin*, Professor Galen J. Suppes, University of Missouri-Columbia.
www.epa.gov/greenchemistry/pubs/pgcc/winners/aa06.html

Presidential Green Chemistry Challenge, 2005 Award Recipients.  Alternative Synthetic Pathways Category, Archer Daniels Midland Company.
www.epa.gov/greenchemistry/pubs/docs/award_recipients_2005.pdf

*Green Chemistry - Pollution Prevention by Design,* Zero Waste Alliance.
www.zerowaste.org/publications/gc_pres/index.html