Pollution Prevention Via Green Chemistry

The key to green chemistry is that companies do it not because the government forces them to, but "because it's **more profitable**, **cheaper** and **customers like it**,"

-Paul Anastas, Director of the Green Chemistry Institute at the American Chemical Society.

Welcome to our presentation about opportunities to reduce pollution and increase profitability through the utilization of green chemistry principles.

12 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.

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

Green chemistry can be largely summarized by the first 2 of the above principles, with the following 10 being separate areas of emphasis. Generally speaking- designing efficient, effective, and environmentally benign chemicals and chemical processes largely captures the concept of green chemistry. The above principles were developed by Paul Anastas and J. C. Warner in Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30.

The Twelve 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. **http://www.epa.gov/greenchemistry/pubs/principles.html**

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Dynamic Field

In 2005 Ryoji Noyori* identified three key developments in green chemistry:

- use of supercritical carbon dioxide as a green solvent,
- aqueous hydrogen peroxide for clean oxidations and
- The use of hydrogen in asymmetric synthesis

Examples of applied green chemistry are supercritical water oxidation, on water reactions and dry media reactions.

- Bioengineering is also seen as a promising technique for achieving green chemistry goals. A number of important process chemicals can be synthesized in engineered organisms, such as shikimate, a Tamiflu precursor which is fermented by Roche in bacteria.

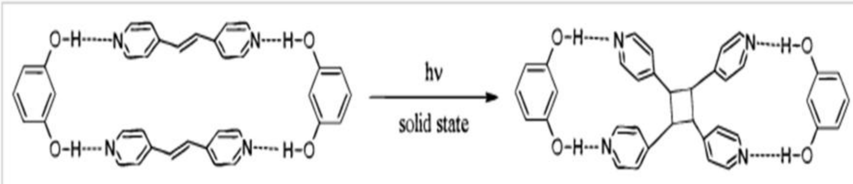
***Ryoji Noyori- The Nobel Prize in Chemistry 2001**

http://nobelprize.org/nobel_prizes/chemistry/laureates/2001/noyori-autobio.html

Unlike some reduction concepts that have been around for quite some time green chemistry is a rapidly expanding field with almost limitless possibilities for continuously improving chemicals and chemical processes.

Supramolecular Chemistry

Research is currently ongoing in the area of supramolecular chemistry to develop reactions which can proceed in the solid state without use of solvents. The cycloaddition of *trans*-1,2-bis(4-pyridyl)ethylene is directed by resorcinol in the solid state. This solid-state reaction proceeds in the presence of UV light in 100% yield.



Cycloaddition of *trans*-1,2-bis(4-pyridyl)ethylene

Concepts such as supramolecular chemistry achieve reactions in a solid state without the use of any solvents and achieve up to 100% 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.

The Nobel Prize in Chemistry 2005

For the development of the metathesis method in organic synthesis

In 1971 **Yves Chauvin** was able to explain in detail how metatheses reactions function and what types of metal compound act as catalysts in the reactions.

Richard Schrock was the first to produce an efficient metal-compound catalyst for methasesis. This was in 1990. Two years later **Robert Grubbs** developed an even better catalyst, stable in air, that has found many applications.

The word metathesis means 'change-places'. In metathesis reactions, double bonds are broken and made between carbon atoms in ways that cause atom groups to change places. This happens with the assistance of special catalyst molecules. Metathesis can be compared to a dance in which the couples change partners.

Metathesis is used daily in the chemical industry, mainly in the development of pharmaceuticals and of advanced plastic materials. Thanks to the Laureates' contributions, synthesis methods have been developed that are

more efficient (fewer reaction steps, fewer resources required, less wastage),

simpler to use (stable in air, at normal temperatures and pressures) and

environmentally friendlier (non-injurious solvents, less hazardous waste products).

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.

http://nobelprize.org/nobel_prizes/chemistry/laureates/2005/chemadv05.pdf

The Nobel Prize for Chemistry in 2005 was awarded based on advances in green chemistry, to reduce solvent use and produce more efficient processes with higher yields and less hazardous waste/intermediate materials.

Biobased Hazard Reduction for Workers & Capital

PETROCHEMICALS	HEALTH RATING	FLAMMABILITY RATING
Methyl Isobutyl Ketone (MIBK)	2	3
Methyl Ethyl Ketone (MEK)	1	3
Xylene	2	3
Toluene	2	3
Styrene	2	3

BIOCHEMICALS	HEALTH RATING	FLAMMABILITY RATING
Soybean Oil	0	1
Coconut Oil	0	1
Grain-derived alcohol	0	0
Rapeseed Oil	0	1
Terpene (pinene)	1	0

Note: Ratings from the NFPA and chemical manufacturers.

HEALTH RATING

0 = no hazard
1 = caution (may irritate)
2 = warning (if inhaled/absorbed)
3 = corrosive/toxic
4 = danger (possibly fatal)

FLAMMABILITY RATING

0 = not combustible
1 = combustible if heated
2 = combustible liquid
3 = warning (flammable liquid)
4 = danger (extremely flammable liquid/gas)

http://www.carbohydrateeconomy.org/library/admin/uploadedfiles/Biochemicals_for_the_Automotive_Industry.pdf

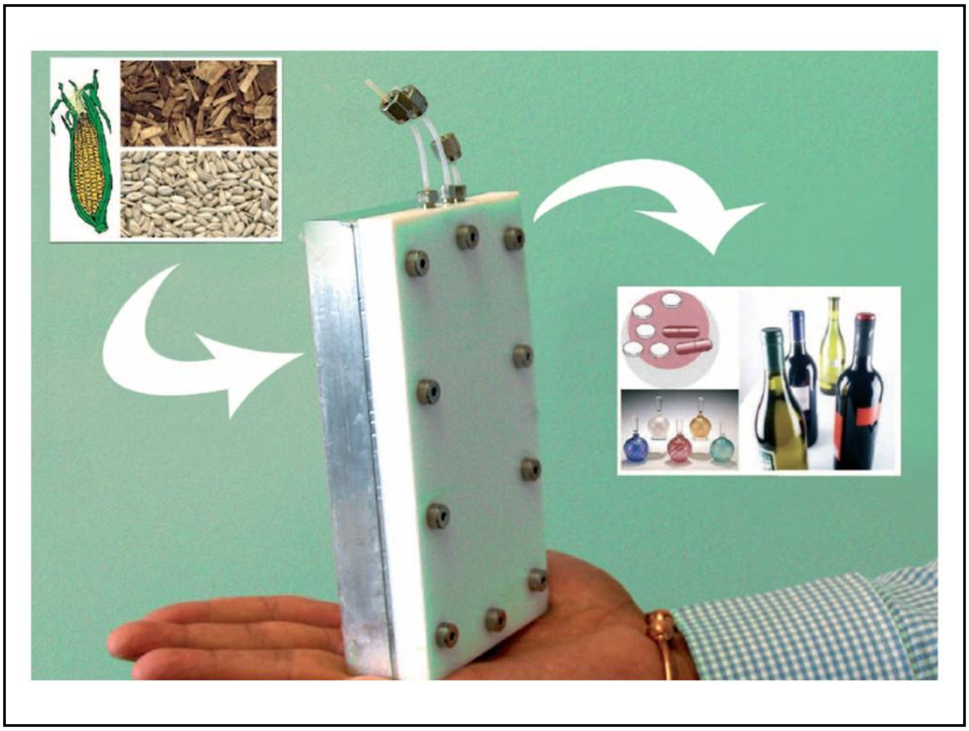
Green Chemistry yields additional savings for manufacturers by reducing risks to workers and consumers. More efficient processes that also limit a manufacturers liabilities are a double savings.

Biobased Alternatives for the Automotive Mfg. Sector

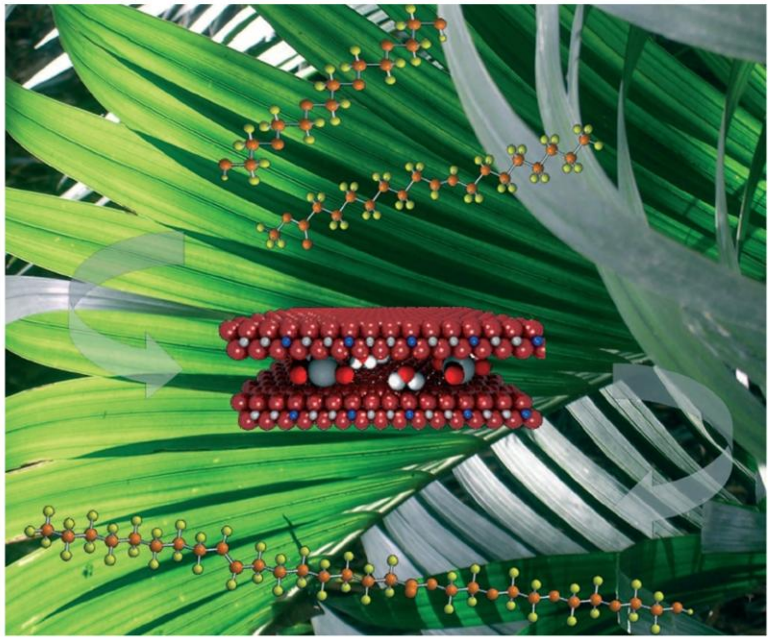
- Biochemical-Based Cleaning and Degreasing Operations
- Biochemical Alternatives for Paint Stripping Operations
- Biochemical Alternatives for Spray Paint Applications
- Biochemically-Derived Automotive Fluids
- Natural Fiber Substitutes for Automotive Components

http://www.carbohydrateeconomy.org/library/admin/uploadedfiles/Biochemicals_for_the_Automotive_Industry.pdf

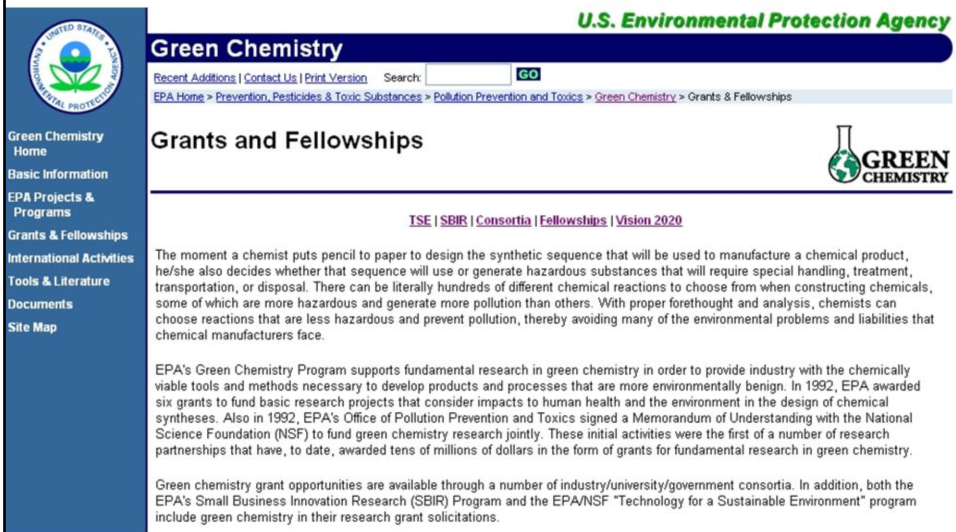
Biobased products open opportunities to not only utilize the principles of green chemistry but also be from renewable resources. Many biological synthesis processes are replacing conventional refining or hazardous polymerization processes.



Ultimately renewable resources may produce a significant amount manufacturing, pharmaceutical and consumer materials which are currently are produced with non-renewable and sometimes hazardous materials.



A significant component of utilizing green chemistry will be the synthesizing materials and being able to disassemble and re-synthesize the same or different materials, creating a truly closed-loop lifecycle process.


U.S. Environmental Protection Agency

Green Chemistry

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Grants and Fellowships

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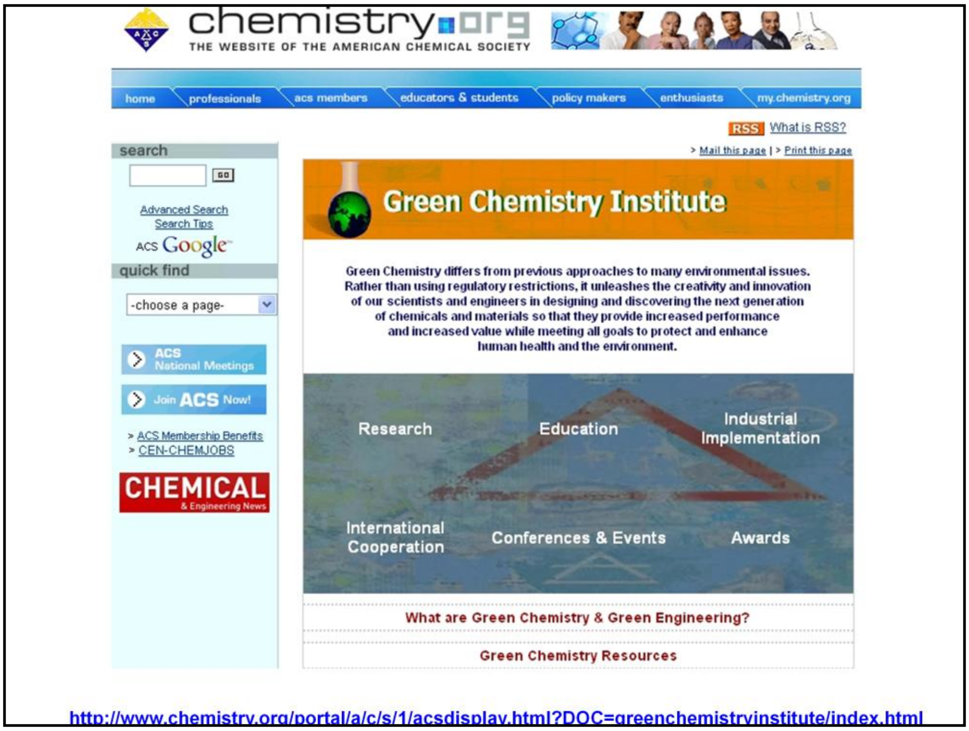
The moment a chemist puts pencil to paper to design the synthetic sequence that will be used to manufacture a chemical product, he/she also decides whether that sequence will use or generate hazardous substances that will require special handling, treatment, transportation, or disposal. There can be literally hundreds of different chemical reactions to choose from when constructing chemicals, some of which are more hazardous and generate more pollution than others. With proper forethought and analysis, chemists can choose reactions that are less hazardous and prevent pollution, thereby avoiding many of the environmental problems and liabilities that chemical manufacturers face.

EPA's Green Chemistry Program supports fundamental research in green chemistry in order to provide industry with the chemically viable tools and methods necessary to develop products and processes that are more environmentally benign. In 1992, EPA awarded six grants to fund basic research projects that consider impacts to human health and the environment in the design of chemical syntheses. Also in 1992, EPA's Office of Pollution Prevention and Toxics signed a Memorandum of Understanding with the National Science Foundation (NSF) to fund green chemistry research jointly. These initial activities were the first of a number of research partnerships that have, to date, awarded tens of millions of dollars in the form of grants for fundamental research in green chemistry.

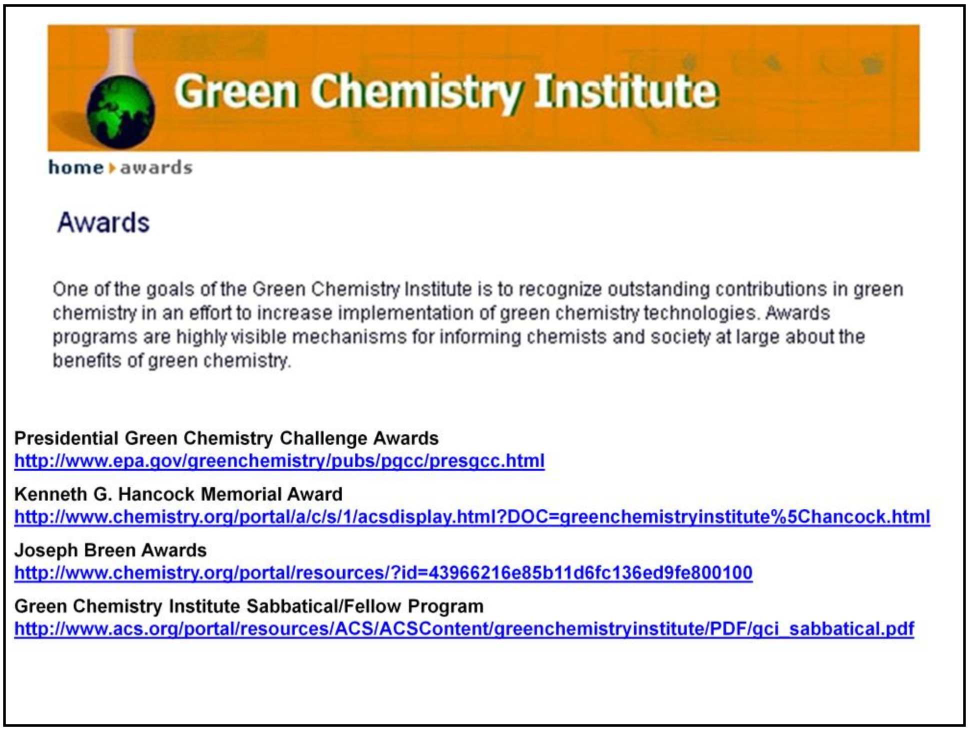
Green chemistry grant opportunities are available through a number of industry/university/government consortia. In addition, both the EPA's Small Business Innovation Research (SBIR) Program and the EPA/NSF "Technology for a Sustainable Environment" program include green chemistry in their research grant solicitations.

http://www.epa.gov/greenchemistry/pubs/grants.html

Green chemistry is being aggressively promoted on several fronts to advance this technology in the face of dwindling non-renewable resources and environmental health and safety considerations such as limiting toxic waste materials.



The American Chemical Society is an active proponent and information center for green chemistry & green engineering research/implementation.


Green Chemistry Institute

home ▸ awards

Awards

One of the goals of the Green Chemistry Institute is to recognize outstanding contributions in green chemistry in an effort to increase implementation of green chemistry technologies. Awards programs are highly visible mechanisms for informing chemists and society at large about the benefits of green chemistry.

Presidential Green Chemistry Challenge Awards
http://www.epa.gov/greenchemistry/pubs/pgcc/presgcc.html

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

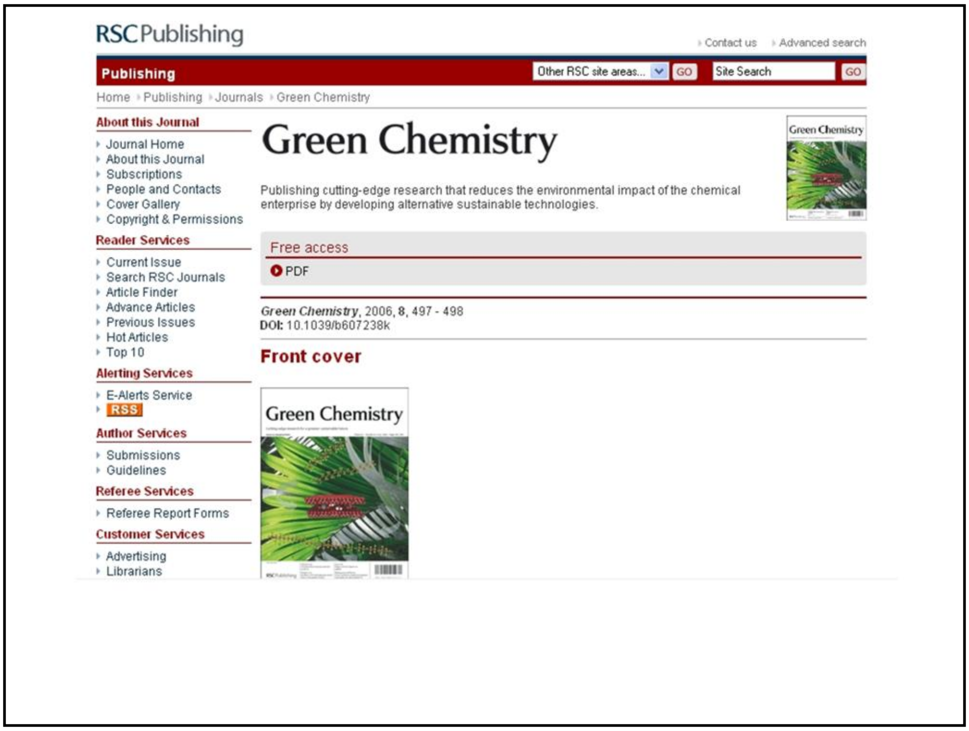
Joseph Breen Awards
http://www.chemistry.org/portal/resources/?id=43966216e85b11d6fc136ed9fe800100

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

Substantial opportunities exist for companies to achieve excellent branding and name recognition for advances in green chemistry. Most advances have also yielded significant cost savings and competitive manufacturing advantage to companies that have implemented green chemistry principles into their research and development of new products and processes. Excellent case study information can be found by referencing the above green chemistry award resources.

http://www.nsfstc.unc.edu/

The National Science Foundation is actively engaged in sponsoring and collaborating on research efforts in green chemistry. This center is an example of one promising area of replacing traditional solvents and solvent processes with benign solvents or alternative benign processes.



Green Chemistry magazine is another useful resource for tracking ongoing research and technology breakthroughs in the field of green chemistry. The ability to search for various types of research and implementation documents makes this a very significant resource.

For companies or researchers who are familiar with pollution prevention, the University of Massachussetts at Lowell has been a significant contributor to this field through such outstanding enterprises as the Toxic Use Reduction Institute (TURI). The Center for Green Chemistry has outstanding research ongoing in a number of green chemistry areas

2006 Gordon Research Conference
Green Chemistry

Sunday, August 27th - Friday, September 1st, 2006
Magdalen College, Oxford University, Oxford, UK

Emerging Issues in Green Chemistry- Terry Collins / Paul Anastas / Barry Trost

Fine Chemicals from Sustainable Raw Materials-Jeremy Tomkinson / Rawle Hollingsworth / James Clark

Photochemistry-TBA / TBA / Michael Oelgemoller

Design of Compounds for Lower Environmental Impact-Gillian Stephens / Larry Wackett / Anne-Marie Tillman

Green Process Design- Buzz Cue / Greg Whited / Eric Beckman

Greener Processes in Ionic Liquids- Robin Rogers / Chris Hardacre / Buxing Han

New Reaction Discovery- C-J. Li / Jae Sung Lee / Graham Hutchings

Greener Processes in Non-Traditional solvents- Joan Brennecke / Philip Jessop / Pete Licence

Oral Presentations of Selected Posters-Janet Scott / Jim Hutchinson

Chemical Impact on the Environment-Terry Collins / J. Peterson Myers / TBA

Metal Recovery and Reuse-TBA / Dave Bergbreiter / Martin Goosey

New Opportunities in Green Chemistry-Jim Bashkin / Wayne Garrison / John Warner

http://kazlauskas.cbs.umn.edu/GreenChem06.html

Green Chemistry is in no way limited to organizations within North America. Worldwide interest in this field has been significant for quite some time and international conferences on green chemistry research and technology have been frequent.

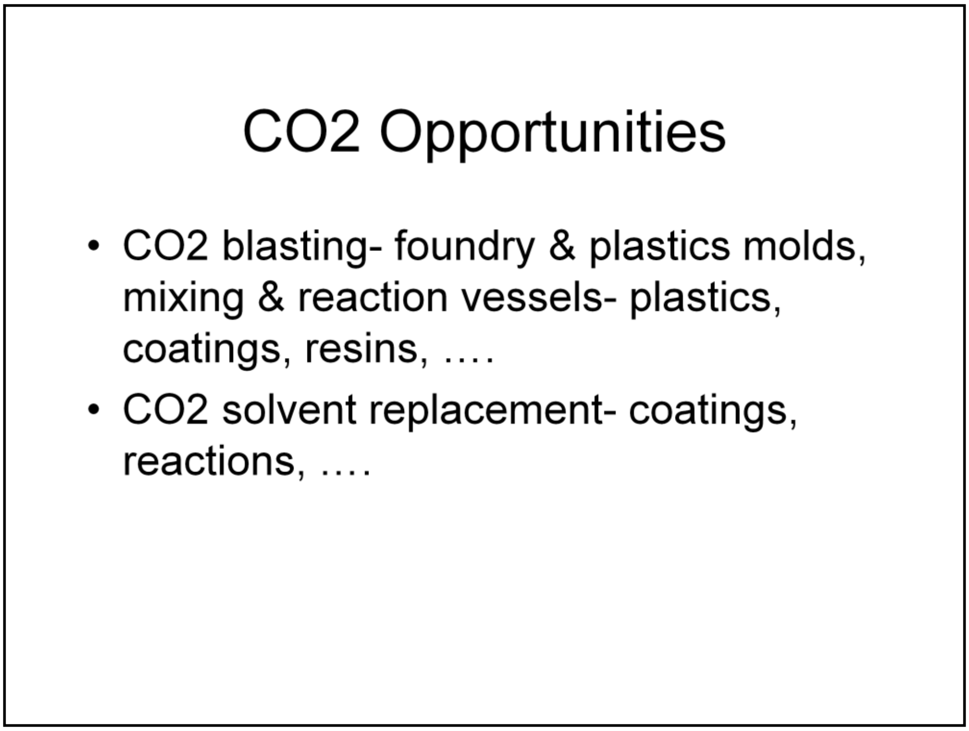
It is important to note that a major emphasis of green chemistry in the international community is the economic impacts of utilizing cheaper renewable inputs and reducing costs by eliminating hazardous materials management/treatment/disposal costs.

CO^2 Substitution for Conventional Solvents

Carbon Dioxide can replace conventional solvents in a wide variety of coating, cleaning and other processes.

Solvent use can be reduced by 50-85%; and use of hazardous air pollutants (HAPs), such as xylene and toluene, can be completely eliminated in some cases.

When CO_2 is heated to 88°F and compressed to 1100 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, CO_2 can replace hazardous hydrocarbon solvents. A conventional hydrocarbon based coating emits 4.0 pounds of VOCs per gallon, compared to a CO_2 coating, which emits less than 2.3 pounds of VOCs per gallon. Solvent use can be reduced by 50-85%; and use of hazardous air pollutants (HAPs), such as xylene and toluene, can be completely eliminated in some cases.



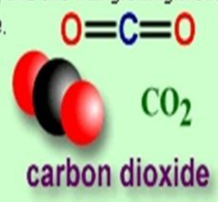
Carbon Dioxide substitution represents a significant opportunity to utilize an existing benign substance to replace a wide variety of more toxic and more damaging substances. The recyclability and reuse of CO2 in many processes can make closed loop systems possible.

Solvents

Solvents are used to dissolve reactants, and also to extract and purify products. For economic reasons, solvents are usually recycled.

Unfortunately many organic solvents are volatile, flammable and may pose a risk to health and the environment. All traces of these solvents must therefore be captured, as vapour cannot simply be vented to the atmosphere.

Alternative approaches are being developed, and one with growing areas of application is the use of supercritical fluids, of which the most common is carbon dioxide.



Solvents are critical for a multitude of industrial processes. The substitution of Carbon Dioxide CO2 represents a significant opportunity eliminate a wide variety of environmental, health and safety hazards.

CASE STUDIES

Case Study One

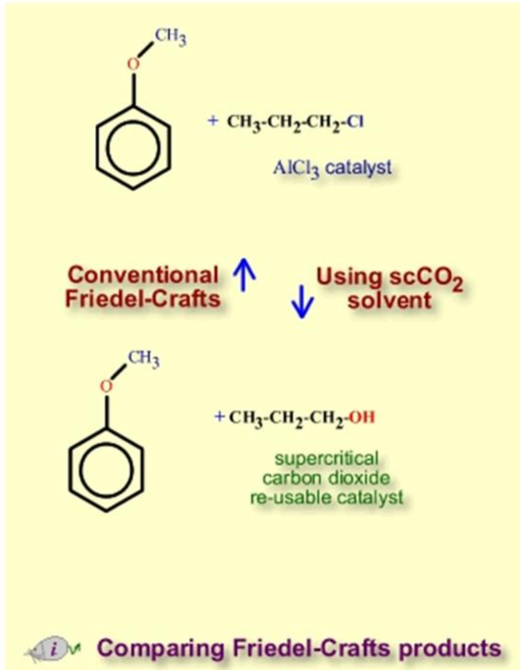
When an automotive company applied an acrylic lacquer clearcoat to automotive sport wheels with the Unicarb® system, it reduced solvent emissions by 75%. In addition, transfer efficiency of the coating was nearly doubled, from 30% to 54%, while maintaining film thickness and producing a high quality appearance. This resulted in a 42% reduction in material costs, and a 27% (per part) reduction in overall application costs. Unicarb® reduced the company's waste treatment and removal costs by 75%. Also, by reducing rejects by 25%, Unicarb® saved costly reworking expenses. Payback period for the installed system was less than six months.

Case Study Two

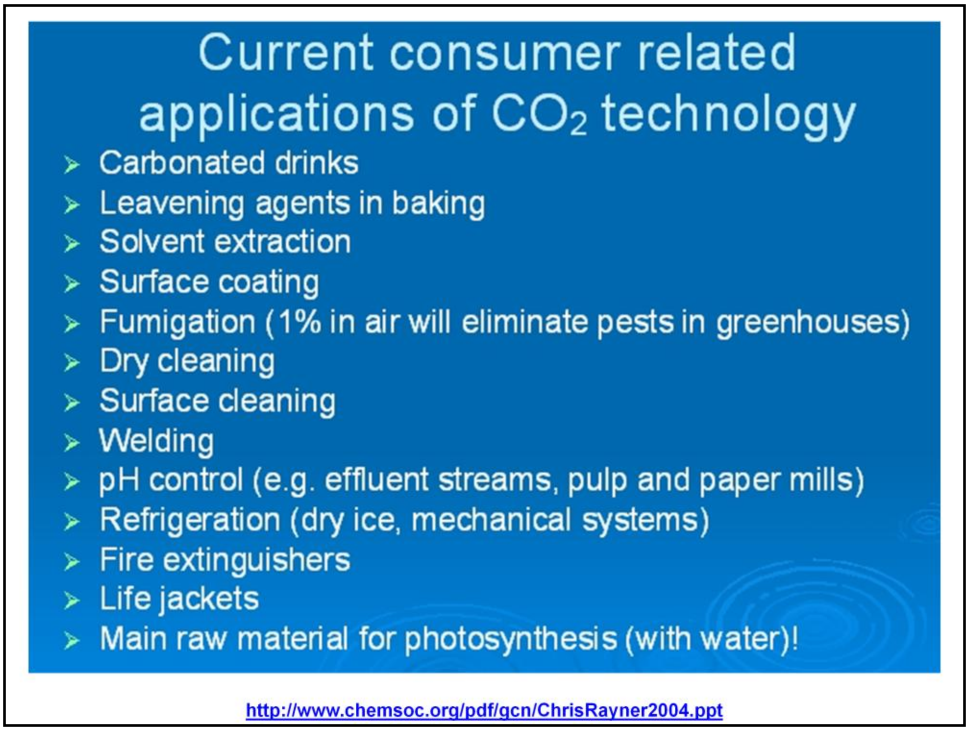
The Unicarb® system was used by one automotive company to apply a thin adhesion-promoter primer layer to automotive components made of thermoplastic polyolefin (TPO). Because TPO is made primarily of polypropylene, it is a difficult substrate for polyurethane coatings to adhere to, and traditionally requires the use of adhesion promoters. However, using the supercritical process, transfer efficiency was increased from 28% to 38%. Coating coverage quadrupled, from 9 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 reduced coating application costs alone.[16] ■

http://www.carbohydrateeconomy.org/library/admin/uploadedfiles/Biochemicals_for_the_Automotive_Industry.pdf

The utilization of CO_2 in these coating processes produced impressive cost and emission reductions. In this case transfer efficiency was increased from 28% to 38%. Coating coverage quadrupled, from 9 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 reduced coating application costs alone.



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



CO2 has been utilized in a wide range of consumer and industrial process for quite some time. Its everyday uses make it easy to overlook as a significant resource for additional utilization.

Carbon Dioxide Fumigation

Sealing of Welded-steel Hopper Bins for Fumigation of Stored Grain with Carbon Dioxide

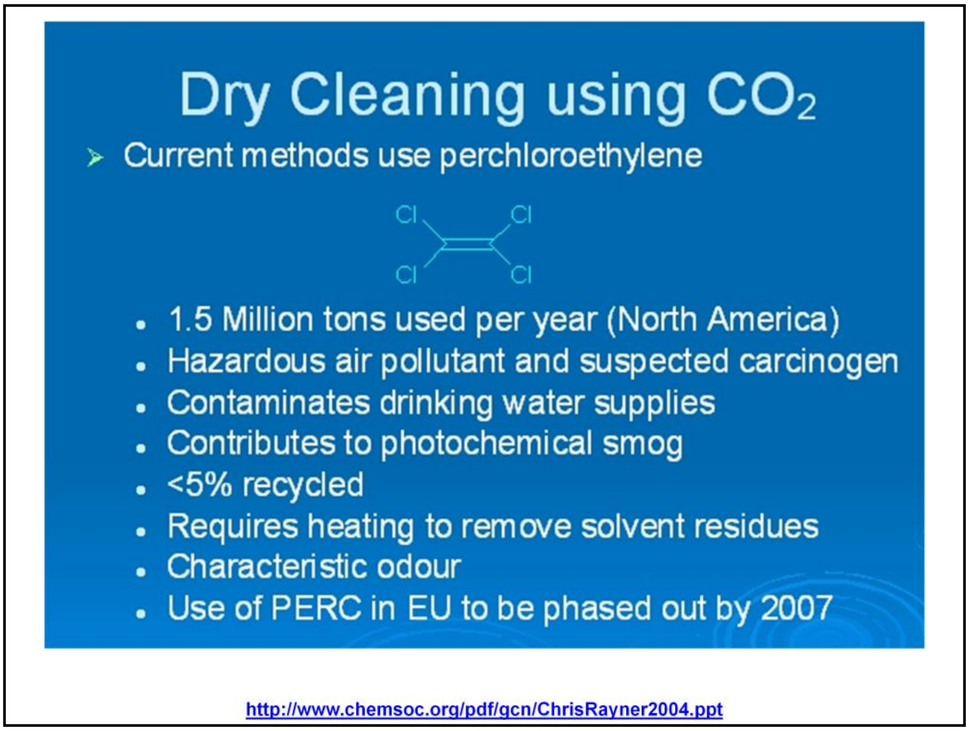
Researchers at the Agriculture & Agri-Food Canada Cereal Research Centre, Winnipeg and the Department of Biosystems Engineering, University of Manitoba, have developed and tested practical methods for sealing welded-steel hopper bins for effective use of carbon dioxide to kill insects in stored grain.

For many years, chemical insecticides and fumigants have been widely used to control or eradicate stored-product insects. In recent years, however, concerns about toxic residues in the grain and potential health hazards to applicators have encouraged the search for other solutions.

One alternative is to modify the atmosphere in the bin to create an environment lethal to insects. Researchers have found that an increased carbon dioxide concentration in a storage structure (60% volume in air) can kill rusty grain beetles, one of the most common stored grain pests in Western Canada. The main advantage of carbon dioxide is that it does not leave toxic residues on the grain; nor does an elevated carbon dioxide level affect seed germination or quality. Carbon dioxide is registered for use as a grain fumigant.

http://res2.agr.gc.ca/winnipeg/fs/fs08_e.htm

The use of carbon dioxide as a pesticide/fumigant for food grains represents a significant opportunity to reduce the risks to both workers and consumers from hazardous chemicals.



Carbon dioxide utilization in dry cleaning processes has the potential to dramatically reduce the exposure of workers in this industry to hazardous process chemicals.

Water-based vs. Waterborne Chemistries

In the case of a paint or coating formula, the binder may be dissolved in the solvent, as in a solvent-based gloss paint. The solvent may be an organic solvent or it may be water. Alternatively, the binder may be in the form of an emulsion suspended in water.

The terms solvent-based or water-based are not, strictly speaking, accurate. The coating is not `based' on water or solvent, but is either dissolved or suspended in it. The terms `water borne' and `solvent borne' are more accurate descriptions.

Solvent-borne decorative paints tend to have a slower drying time than water-borne due to the nature of the binder. This is usually based on natural oils, such as soybean oil, which reacts with the oxygen in the air to form a tough durable film.

In terms of paints and coatings, formulations that are dissolved in water are often referred to as water based. Formulations which are suspensions in water are often referred to as waterborne. Waterborne chemistries may be essentially the same as organic solvent based formulas with water serving as the “carrier” for the constituents.

The concept of replacing many hazardous solvents and cleaners with water based chemical formulations has been around for quite some time and produced significant environmental benefits and cost savings. Additional research to find even more environmentally benign formulations may yield even more desirable processes and products

Waterborne Chemistries
Aerospace Coatings Example

Coating	1-1-02	D45 AMS	% VOC
Chemical Agent Resistant	220gm/litre	<150gm/litre	46% less
Non Slip Walkway	220gm/litre	<150gm/litre	126% less
Low Anti Infrared Reflectant	340gm/litre	<150gm/litre	126% less
Primer – Internal / External	340gm/litre*	<150gm/litre	126% less
Top Coat	420gm/litre	<150gm/litre	180% less
Impact Resistant	420gm/litre	<150gm/litre	180% less
Clear Top Coat	520gm/litre	<190gm/litre	247% less
Fire Resistant - Civilian	650gm/litre	<150gm/litre	333% less
Wing Coating	700gm/litre	<150gm/litre	366% less
Touch up Coating	750gm/litre	<150gm/litre	400% less
Erosion Resistant	800gm/litre	<150gm/litre	433% less
Missiles or Single Use Target Craft	840gm/litre	<150gm/litre	460% less
Primer Compatible with Rain	850gm/litre	<150gm/litre	467% less
Erosion Resistant Coating Fire Resistant - Military	970gm/litre	<150gm/litre	546% less
Electrostatic Discharge Protection	1000gm/litre	<150gm/litre	566% less

1-1-02 = Solvent Borne D45 AMS= Waterborne

http://dodconf.swri.org/2003Papers/Oxenford.pdf

The early stigma that waterborne formulations were inferior to solvent borne formulations have largely been eliminated in industry but more importantly in the laboratory and in actual use and practice. Waterborne formulations have been developed that outperform solvent based materials and greatly reduce emissions and operational costs for manufacturers. The Department of Defense has been significantly responsible for demonstrating the practical and environmental benefits of this shift in technology.

Demonstration/Validation of a Zero-VOC Waterborne Polyurethane Topcoat

http://www.estcp.org/documents/techdocs/199802.pdf

Department of Defense facilities have made significant contributions to demonstrating the cost savings and environmental benefits of waterborne coatings.

The number of waterborne formulations for a variety of materials, including adhesives, provide ample opportunities for many manufacturers to greatly reduce the environmental impacts of products and processes.

Many consumer products have also taken advantage of waterborne re-formulation.

Alternative Synthesis Pathways

Ibuprofen Case Study- BHC Company Synthesis for the Production of Ibuprofen

http://www.acs.org/portal/resources/ACS/ACSContent/education/greenchem/case.pdf#search=%22BASF%20Celanese%20Ibuprofen%22

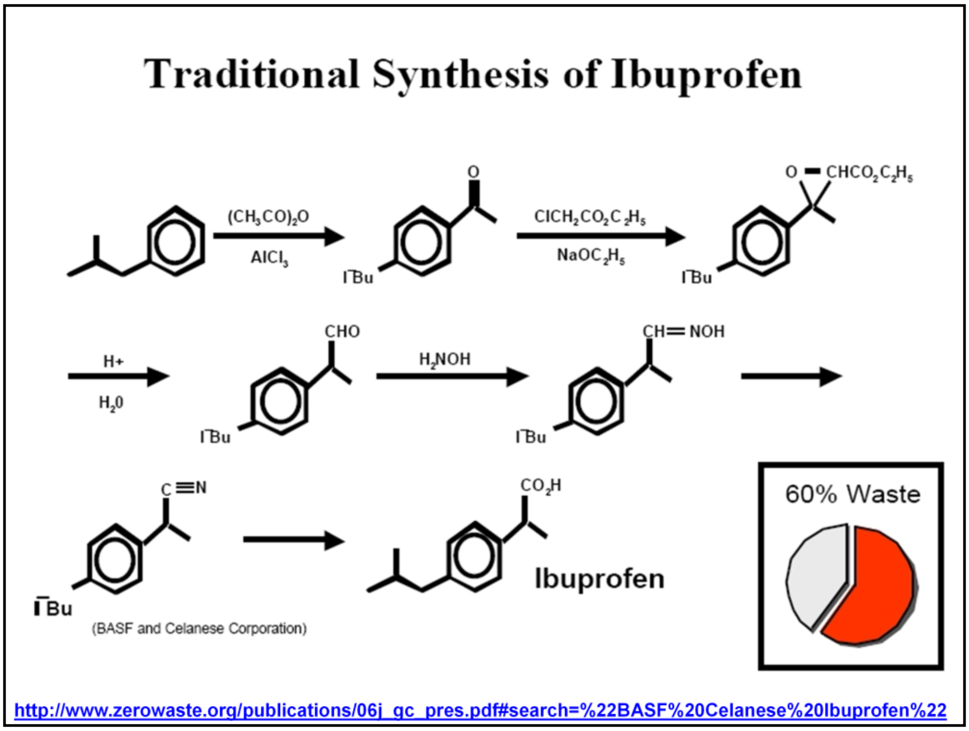
Polycarbonate Case Study- Elimination of Phosgene in the Production of Polycarbonate

http://www.gscn.net/awardsE/images/GSC-AW2002E.PDF

Adipic Acid Case Study- Renewable Feedstock Alternative for the Production of Adipic Acid

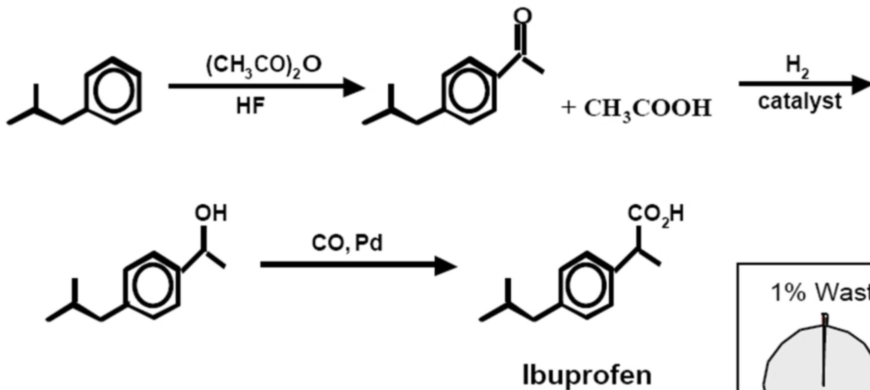
http://www.epa.gov/greenchemistry/pubs/pgcc/winners/aa98b.html

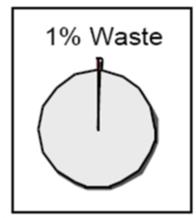
Another important aspect of green chemistry is the discovery of alternative synthesis pathways. A classic example of this is the traditional synthesis of Ibuprofen which previously produced large quantities of hazardous waste and had a relatively low yield of product.



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

Green Chemistry Alternative Synthesis of Ibuprofen



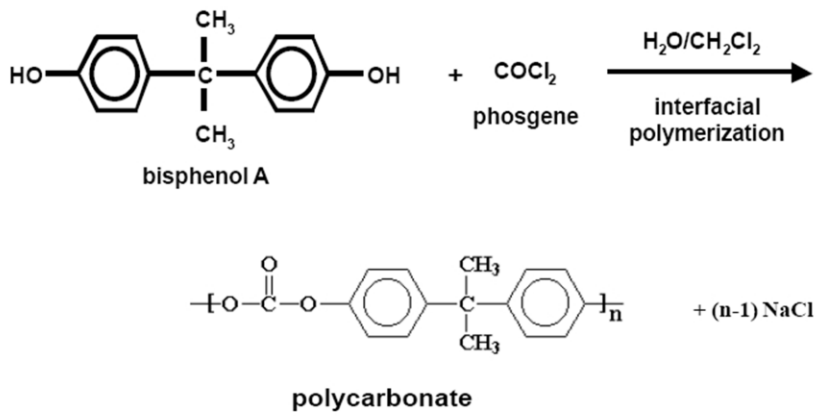


(BASF and Celanese Corporation)

http://www.zerowaste.org/publications/06j_gc_pres.pdf#search=%22BASF%20Celanese%20Ibuprofen%22

The BHC Company has developed and implemented a new greener industrial synthesis of ibuprofen that is only three steps (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). This results in only small amounts of unwanted byproducts (very good atom economy/atom utilization)4–10 thus lessening the need for disposal and mediation of waste products.

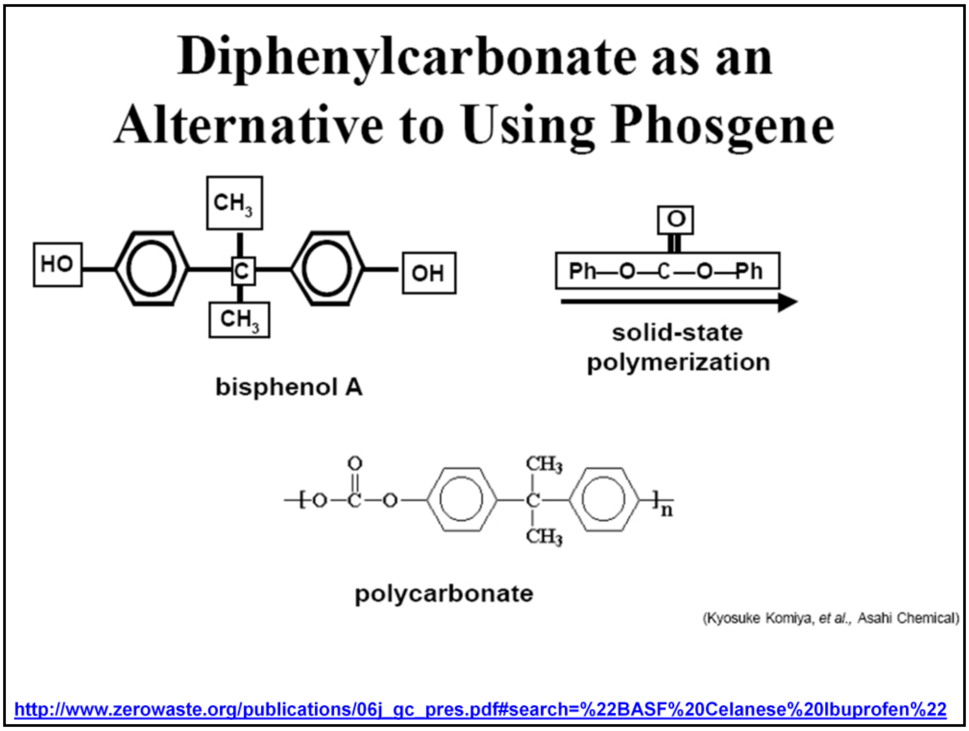
The Use of Phosgene in the Synthesis of Polycarbonates



(Kyosuke Komiya, *et al.*, Asahi Chemical)

http://www.zerowaste.org/publications/06j_gc_pres.pdf#search=%22BASF%20Celanese%20Ibuprofen%22

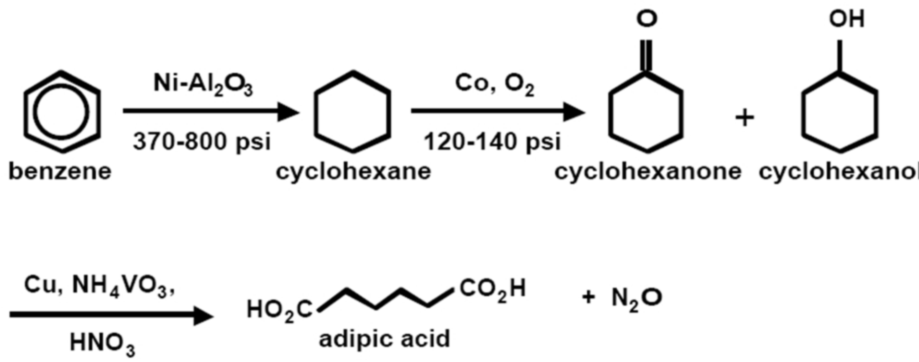
The vast majority of polycarbonate is made in a process where CO and chlorine are combined to form phosgene, a toxic gas, as an intermediate material. The phosgene process entails a number of drawbacks in environmental terms including the toxicity of phosgene, the use of the low-boiling-point solvent methylene chloride to which exposure must be restricted, and the large quantity of waste water containing methylene chloride which must be treated.



This technology uses ethylene oxide, its by-product CO2, and bisphenol-A as starting materials to produce high-quality polycarbonate and high-purity ethylene glycol at high yield. Because CO2 has low chemical reactivity, it was considered to be difficult to incorporate it into the polycarbonate main chain. However, this technology

successfully integrates all of the CO2 used into the products through deft utilization of chemical reactions. The CO2 used as starting material is a by-product generated in the production of ethylene oxide (generally used to make ethylene glycol for PET bottles and polyester fiber), and is usually released to the atmosphere.

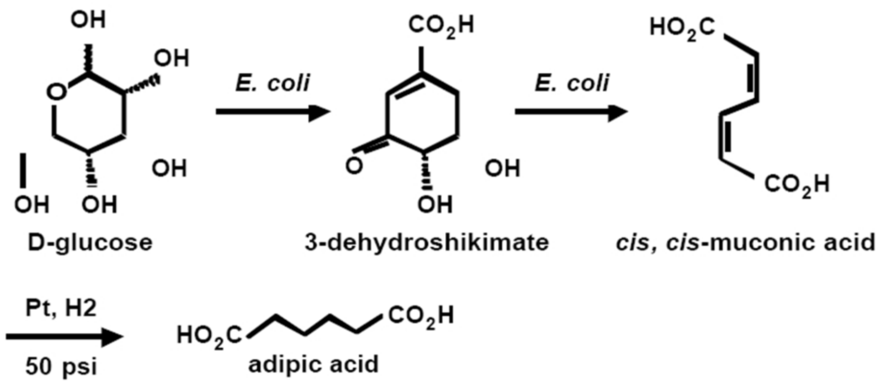
Traditional Feedstock in the Synthesis of Adipic Acid



http://www.zerowaste.org/publications/06j_gc_pres.pdf#search=%22BASF%20Celanese%20Ibuprofen%22

In excess of 4.2 billion pounds of adipic acid are produced annually and used in the manufacture of nylon 6,6. Most commercial syntheses of adipic acid use benzene, derived from the benzene–toluene–xylene (BTX) fraction of petroleum refining, as the starting material. In addition, the last step in the current manufacture of adipic acid employs a nitric acid oxidation resulting in the formation of nitrous oxide as a byproduct. Due to the massive scale on which it is industrially synthesized, adipic acid manufacture has been estimated to account for some 10 percent of the annual increase in atmospheric nitrous oxide levels.

Alternative Feedstock in the Synthesis of Adipic Acid



(John W. Frost, *et al.*, Michigan State)

http://www.zerowaste.org/publications/06j_gc_pres.pdf#search=%22BASF%20Celanese%20Ibuprofen%22

In this reaction nontoxic glucose is employed as a starting material, which, in turn, is derived from renewable carbohydrate feedstocks, such as starch, hemicellulose, and cellulose. In addition, water is as the primary reaction solvent, and the generation of toxic intermediates and environment-damaging byproducts is avoided.

Alternative Synthetic Pathways Category

Archer Daniels Midland Company
Novozymes

NovaLipid™: Low *Trans* Fats and Oils Produced by Enzymatic Interesterification of Vegetable Oils Using Lipozyme®

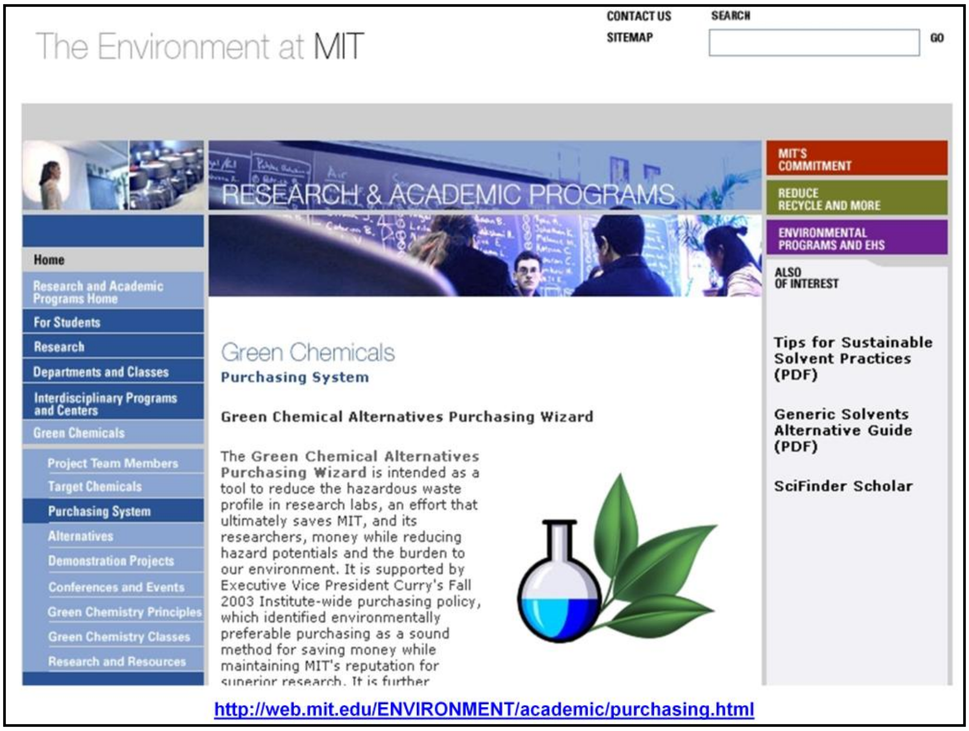
The ADM/Novozymes process has the potential to save 400 million pounds of soy bean oil, eliminate 20 million pounds of sodium methoxide, 116 million pounds of soaps, 50 million pounds of bleaching clay, and 60 million gallons of water each year.

http://www.epa.gov/greenchemistry/pubs/docs/award_recipients_2005.pdf

An exciting area of research and product development is the replacement of many material intensive chemical processes with natural processes using biological action to create renewable and non toxic production scenarios.

Biomimicry BioSynthesis

By studying processes in nature, many products may be possible that are superior in performance to many existing industrial materials.



A major factor in the push to improve the efficiency and safety of chemical formulations is demand. As more companies work at efforts to “green” their input chemicals and their supply chain, green chemistry creates market advantage for companies who reformulate or create new chemicals which are more effective.

Green chemistry Information for Further Study

Next Generation Environmental Technologies
http://www.rand.org/pubs/monograph_reports/MR1682/

25 Green Chemistry Case Studies
http://www.rand.org/pubs/monograph_reports/MR1682/MR1682.appa.pdf

Index of Green Chemistry Challenge Winners by Technology
http://www.epa.gov/greenchemistry/pubs/pgcc/topics.html

Five Chemicals- Alternatives Assessment Study
(Lead, Formaldehyde, Perchloroethylene, Hexavalent Chromium & DEHP)
http://www.turi.org/content/content/download/3194/29300/file/Master5Chem-final-2.pdf

For organizations or individuals interested in exploring this topic in more depth, the above references are provided to guide you to specific applications where green chemistry principles are being employed. Numerous other publications are also referenced in the earlier slides of this presentation which have extensive literature on technologies and approaches to green chemistry.

Other Related Programs

Sustainable Futures- USEPA TSCA Chemical Development

http://www.epa.gov/oppt/newchems/pubs/sustainablefutures.htm

Toxics Use Reduction Institute

http://www.turi.org/

Product Stewardship Institute

http://www.productstewardship.us/

MBDC Cradle to Cradle Certification

http://www.mbdc.com/certified.html

There are numerous formal programs and approaches to implementing green chemistry and green design options into products and processes. Represented here are a few with extensive resources for assisting with greening a product or process.