

<http://www.csch.cz/green.htm>



<http://www.dpsc.ca.gov/PollutionPrevention/GreenChemistryResources/index.cfm>

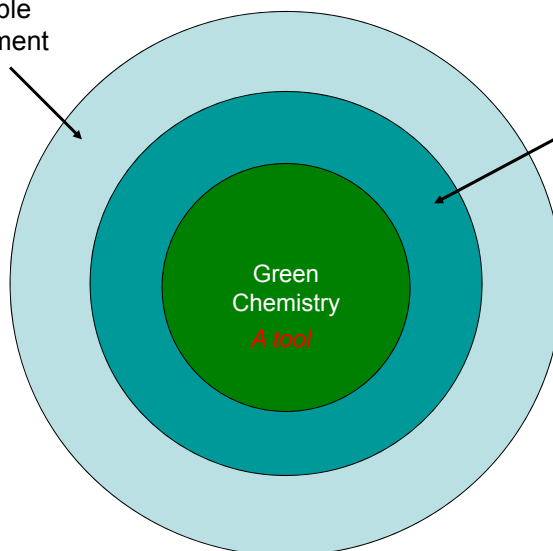
Green Chemistry

Taken in large part from Paul L. Bishop's
Pollution Prevention – Fundamentals & Practice, Chapter 9.

Green chemistry, also called benign chemistry, lies at the heart of Industrial Ecology.

Sustainable
Development

The goal



Industrial
Ecology

The approach

Green
Chemistry

A tool

(Adapted from P. T. Anastas & J. J. Breen, *J. Cleaner Production*, 1997)

The rise of Chemical Engineering

Chemical engineering is a relatively newcomer to the field of engineering. First was civil engineering (in contrast to military engineering), then mechanical engineering. Chemical engineering began in the early 20th century and grew much under the impetus of the oil industry and agriculture.

The history of agriculture is a good example on how chemical engineering followed on the steps of civil and mechanical engineering:

Stage 1:	Field leveling, terracing irrigation ditches	<i>Civil Engineering</i>
Stage 2:	Plows, tractors a tool for every task	<i>Mechanical Engineering</i>
Stage 3:	Fertilizers herbicides, pesticides	<i>Chemical Engineering</i>
Stage 4:	Growth hormones genetic engineering	<i>Biotechnology</i> (<i>Biological Engineering</i>)

As a result of Stage 2 (mechanical engineering), we are witnessing an unprecedented rate of soil erosion (24 billion of topsoil washed away annually in the world, = 7% decrease per decade).

Under Stage 3 (chemical engineering), we have begun to suffer groundwater pollution (due to leaching pesticides and herbicides, like atrazine) and eutrophication of rivers and lakes (caused by excess of nutrients from fertilizer run-off).

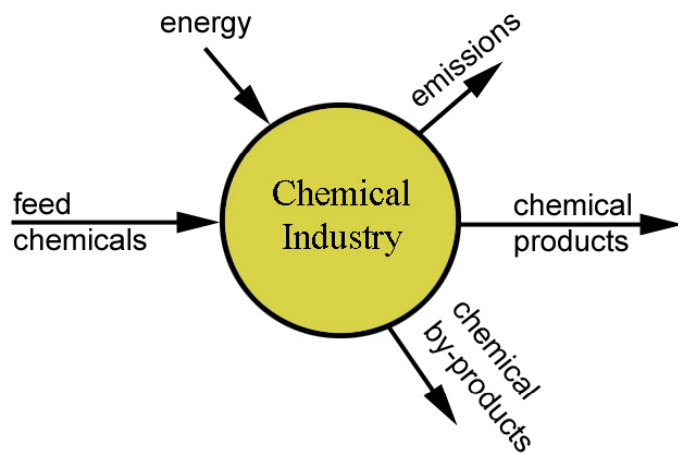
It is hoped that with the advent of Stage 4 (biotechnology) most of these problems will be overcome. Genetic design of crop plants is expected to reduce or eliminate much of the need for tilling the soil and applying chemicals.

But, who knows what the side effects will be? The record of a new technology solving the woes of an earlier one is mixed at best. Will we be improving the situation or taking new risks?

Risks versus risk perception:

<i>Risk level perceived by the public</i>	<i>Corresponding risk level according to US EPA ranking</i>
1. Chemical waste disposal	16. Hazardous waste sites –active 17. Hazardous waste sites - inactive
2. Water pollution	9. Direct point source discharges 10. Indirect point source discharges 11. Non-point source discharges
3. Chemical plant accidents	21. Accidental releases of toxics
4. Outdoor air pollution	1. Criteria air pollutants 2. Hazardous air pollutants
5. Oil tanker spills	22. Accidental release of oil
6. Exposure on the job	31. Worker exposure
7. Pesticide residue in food	25. Pesticide residues in food
8. Pesticides in farming	26. Application of pesticides 27. Other pesticide risks
10. Indoor air pollution	5. Indoor air pollution 30. Consumer product exposure

Conclusion:
People tend to be afraid of chemicals, more than they need to be.



All five arrows generally correspond to environmental impacts, possibly leading to releases of toxic or hazardous substances.

Problems caused by the chemical industry:

Inside the plant:

- Exposure of employees to carcinogenic substances and toxics

Pollution exiting the plant:

- | | |
|-------------------|--|
| - Air emissions | Fugitive emissions from storage tanks
Smokestacks emissions
Evaporating solvents |
| - Water pollution | Accidental releases (ex. Bhopal, India in 1984)
Incompletely treated wastewater
Liquid leaks and groundwater contamination |
| - Solid waste | Sludge from wastewater treatment
Heavy metals |

Impacts of using the chemical product:

- | | |
|------------------------------|---|
| - Fertilizers | Eutrophication or nearby water bodies |
| - Herbicides & pesticides | Residues in food
Groundwater contamination |
| - Chlorofluorocarbons (CFCs) | Stratospheric ozone holes
→ skin cancer |
| - Gasoline | Urban air pollution |
| - MTBE fuel additive | Groundwater pollution |

Impacts after use:

- | | |
|-----------------------------|----------------------|
| - Flame-retardant chemicals | Landfill hazard |
| - Paint pigments | Heavy metals in soil |



Warning: Disney pajamas may damage the health of your children (Greenpeace, UK, 14 Nov. 2003)

According to Greenpeace, many household products like perfumes, shampoos, and plastic goods contain high levels of dangerous chemicals. Disney-branded pajamas available at The Disney Store are amongst the worst offenders.

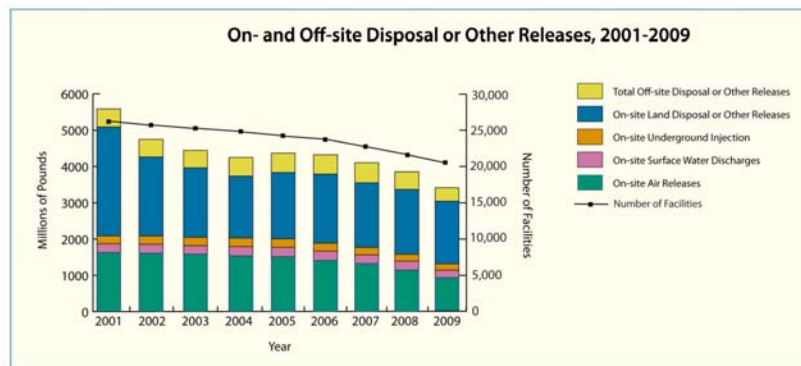
The toxic chemicals are *nonylphenol*, which can interfere with human DNA and effect sperm production in mammals, and *phthalates*, which can cause liver, kidney and testicular damage. These chemicals are probably in the garments as a result of the inks and PVC plastic film used in the design of the front.

Other, milder example: Off-gazing from new carpets and furniture ("new building smell", "new car smell"), due to evaporating formaldehyde used in glue.

The public is begging for improvement at the level of impact **during use** and **after use**.

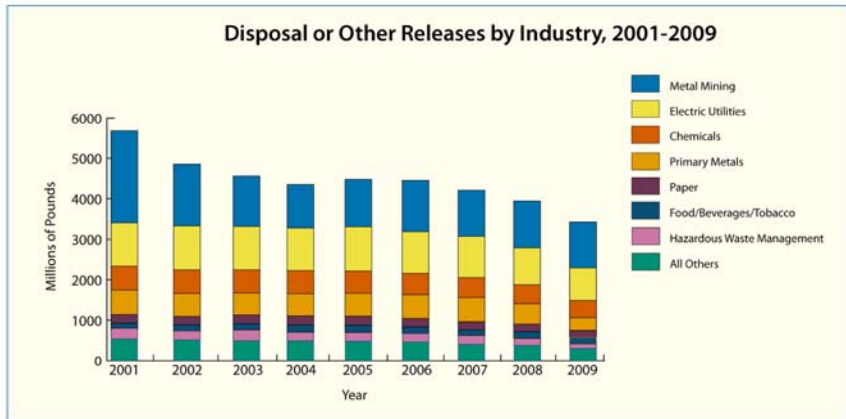
The chemical industry, however, is making the greatest effort in reducing impacts **inside the plant** and in the pollution that comes out of the plant.

There is a mismatch !



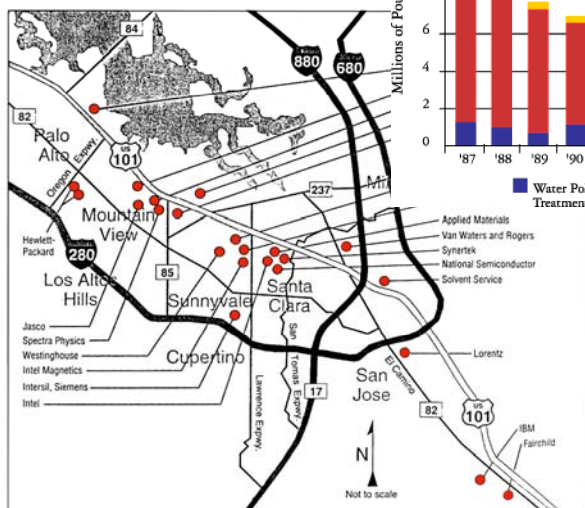
2009 TRI National Analysis

Progress has been made but a limit seems to have been reached.

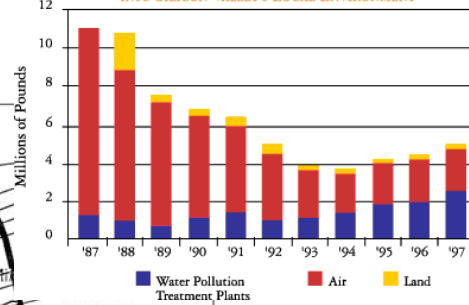


2009 TRI National Analysis

The electronics industry has not been clean and leaves a legacy of heavily polluted spots.



TOXIC RELEASE INVENTORY CHEMICALS RELEASED INTO SILICON VALLEY'S LOCAL ENVIRONMENT



<http://www.maporun.com/svep/hazardous.htm>

[5] California's Silicon Valley has more Federal Superfund sites than any other area of its size in the nation, plus many other toxic sites that are being monitored by state and regional agencies.

Definition, Goals and Methods of Green Chemistry

Green Chemistry, also called **Benign Chemistry** or **Clean Chemistry**, refers to the field of chemistry dealing with:

- synthesis (the path to making chemicals)
- processing (the actual making of chemicals)
- use

of chemicals that reduce risks to humans and impact on the environment.

Shift away from the conventional approach of end-of-pipe treatment to pro-active action by means of

- pollution prevention
- design of clean processes
- design of benign chemicals.

The ultimate *goal* is to develop and institute alternative syntheses for important industrial chemicals in order to prevent environmental pollution.

The *methods* employed are:

- Avoidance of toxics
- Use of benign feedstocks
- Reduction of use of endangered resources
- Production of safe chemicals
- Search for alternative processes to avoid harmful by-products
- Reduction of non-marketable by-products
- Improvement in operational practices

(Taken from Paul L. Bishop, *Pollution Prevention*, 2000, page 357)

Approaches where Green Chemistry plays a role

1. At the most basic level: *Pollution Prevention* (P2)

- Improved operational practices
(lowering energy consumption, improving yields)
- Batch vs. continuous processing?
(batch processes may increase yield but continuous process may save energy)

2. Development of *greener processes* to manufacture unchanged chemical products: (Green Chemistry Level 1)

- *Example:* Avoid chlorine compounds if chlorine is not in the final product

3. Formulation of *alternative chemicals* for the same application: (Green Chemistry Level 2)

- *Example:* CFC substitutes

4. *Avoidance* of chemicals: (Green Chemistry Level 3)

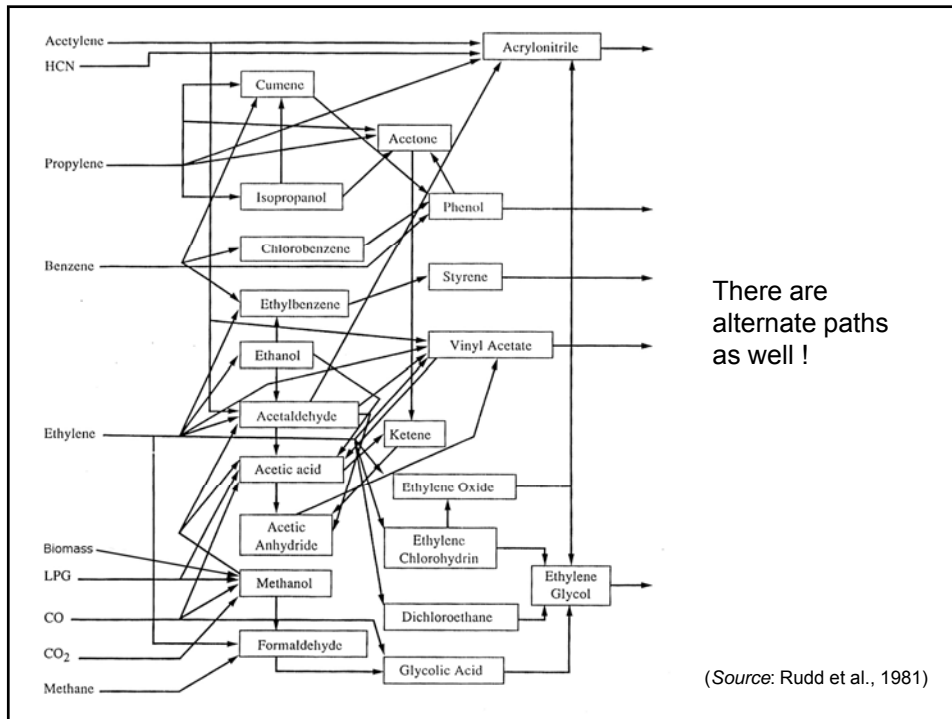
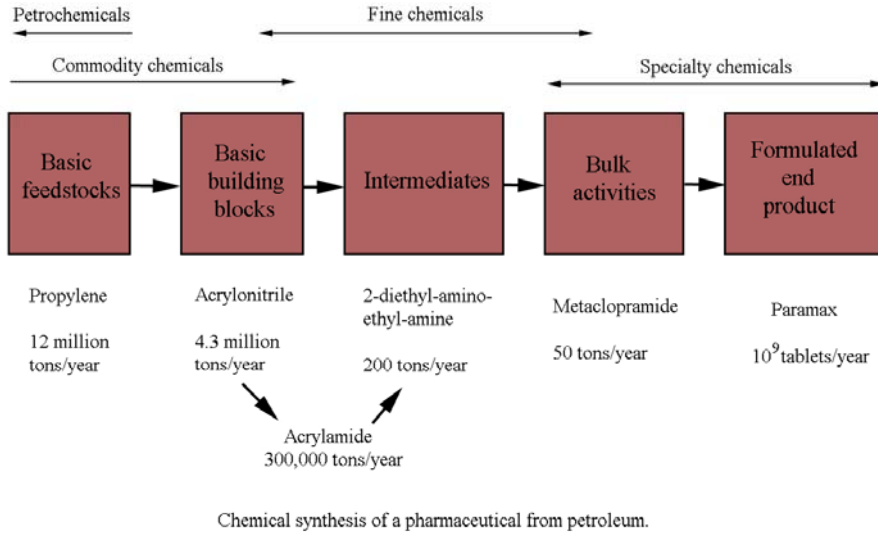
- Switch from herbicides and pesticides to genetic engineering (trade offs?)
- Switch to organic farming (enough land?)
- Switch from traditional to digital photography (other industries, too?)
- Use colored plastics instead of painted metals (or simply avoid color)
- Switch from petroleum fuels to biofuels or hydrogen.

Also:

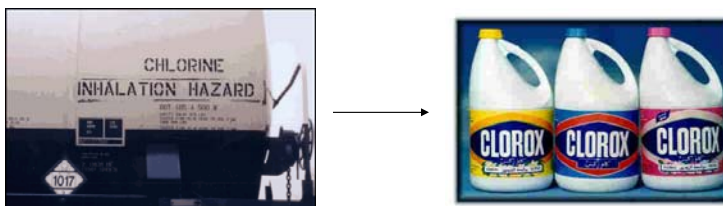
Use of chemistry for improved environmental performance elsewhere:

- Molecular markers in plastics for easier identification during recycling;
- Design of chemical detectors for better monitoring of environmental quality.

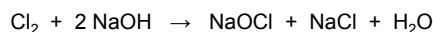
Example of source of waste



Choice in manufacture of sodium hypochlorite (“bleach”)



The conventional way, known as the Berthollet method, is by reacting chlorine gas (Cl_2) with caustic soda (NaOH). The reaction is



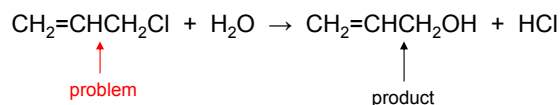
This method is somewhat dangerous because, on an industrial scale, it requires the storage of large quantities of chlorine gas, which is poisonous and has been used as a chemical weapon.

The safer way is to create a concentrated brine solution by dissolving salt (NaCl) in softened water (H_2O) and passing electricity through this solution. Sodium hypochlorite (NaOCl) then forms in the water. A by-product is hydrogen gas (H_2), which is highly flammable and explosive.

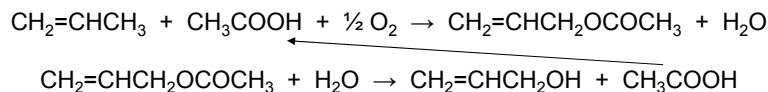
Example 1 of green chemistry

Production of **allyl alcohol** $\text{CH}_2=\text{CHCH}_2\text{OH}$

Traditional route: Alkaline hydrolysis of allyl chloride, which generates the product and hydrochloric acid as a by-product



Greener route, to avoid chlorine: Two-step using propylene ($\text{CH}_2=\text{CHCH}_3$), acetic acid (CH_3COOH) and oxygen (O_2)

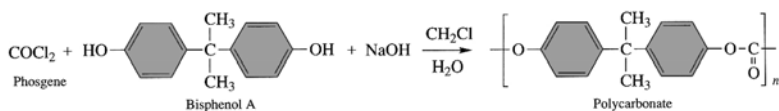
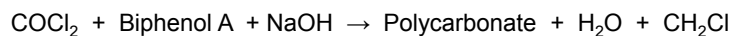


Added benefit: The acetic acid produced in the 2nd reaction can be recovered and used again for the 1st reaction, leaving no unwanted by-product.

Example 2 of green chemistry

Production of **polycarbonate** (polymers)

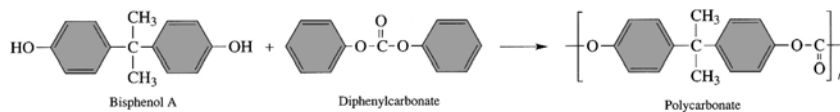
Traditional route: Start with phosgene (COCl_2), which is extremely toxic, and end with methyl chloride (CH_2Cl), as a harmful by-product.



Greener route, to avoid phosgene:



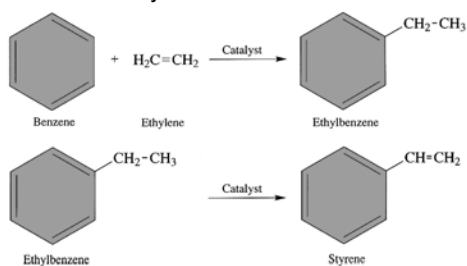
(This process was developed by Ashai Chemicals Co. in Japan.)



Example 3 of green chemistry

Production of **styrene** (= benzene ring with $\text{CH}=\text{CH}_2$ tail)

Traditional route: Two-step method starting with benzene, which is carcinogenic) and ethylene to form ethylbenzene, followed by dehydrogenation to obtain styrene

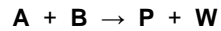


Greener route: To avoid benzene, start with xylenes (cheapest source of aromatics and environmentally safer than benzene).

Another option, still under development, is to start with toluene (benzene ring with CH_3 tail).

Approaches to generic cases:

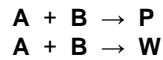
If the reaction is of the type



where **A** and **B** are feeds, **P** is the desired product and **W** a waste by-product

- Find alternate **A** and/or **B** feeds to avoid or decrease the amount of **W**
- Find alternate **A** and/or **B** feeds to create a different **W**, which is a useful by-product
- Find substitute for **P** that does not entail the co-production of **W**.

If the primary reaction is in competition with a secondary reaction, of the type

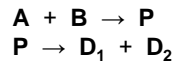


where **A** and **B** are feeds, **P** is the desired product and **W** a competing by-product,

- Find alternate **A** and/or **B** feeds to avoid the competing reaction.

Example: Disinfection of water by chlorination. Chlorine oxidizes the pathogens thereby killing them but simultaneously forms harmful chlorinated compounds. A remedy is to use another oxidant, such as ozone.

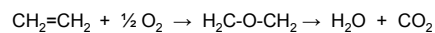
If the primary reaction is followed by an undesirable secondary reaction, of the type



where **A** and **B** are feeds, **P** is the desired product, and **D₁** and **D₂** are decayed parts of **P**,

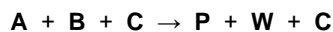
- Adjust temperature and/or pressure to favor the first reaction but impede the second
- Find a benign catalyst that speeds the 1st reaction but not the 2nd, so that **P** can be harvested before much of it has decayed
- Find a more stable substitute for **P**.

Example: Production of ethylene oxide, a precursor in the production of ethylene glycol (antifreeze)



Inhibitors, such as halogenated organics (somewhat problematic, however) may be added to slow down the decay of ethylene oxide.

If the reaction requires a harmful catalyst

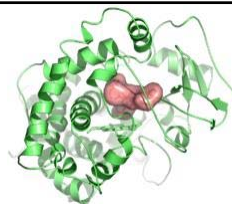


where **A** and **B** are feeds, **C** a harmful catalyst, **P** the desired product, and **W** a wasteful by-product,

- Find a substitute catalyst
- Find an alternate path to make **P**.

Example: Production of the analgesic ibuprofen by Friedel-Craft alkylation catalyzed by aluminum trichloride (AlCl_3). Aluminum trichloride is far from a perfect catalyst and decays significantly during the process (4 kg of catalyst are required to produce 5kg of product), generating gaseous emissions of chloric acid (HCl). The remedy is to use hydrogen fluoride (HF) as a substitute catalyst. This catalyst does not decay and can be easily separated from the product mix and recycled back into the process.

Biocatalysis (= use cells as miniature chemical plants)



In biocatalysis, enzymes and antibodies are used to mediate reactions.

Biocatalysis may involve the use of whole living micro-organisms or only of enzymes that are separated from the cell and immobilized in a support medium. In other words, entire cells or cell components are used as micro-engines.

Reactions that use biocatalysis often proceed with exceptionally high selectivity.

In some cases, they have also been shown to increase reaction rates between 9 and 15 orders of magnitude in comparison with uncatalyzed reactions.

Therefore, biotechnology offers much hope for progress in green chemistry.

US EPA's "Presidential Green Chemistry Challenge"


U.S. Environmental Protection Agency

Green Chemistry

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Presidential Green Chemistry Challenge



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The Presidential Green Chemistry Challenge

The Presidential Green Chemistry Challenge promotes pollution prevention through an EPA Design for the Environment partnership with the chemistry community. Through high level recognition and support, the Challenge promotes innovative developments in and uses of green chemistry for pollution prevention. EPA's [Office of Pollution Prevention and Toxics \(OPPT\)](#) is leading this voluntary partnership program with other EPA offices, other federal agencies, members of the chemical industry, trade associations, scientific organizations, and academia.

2005 Award Recipients of the EPA's Presidential Green Chemistry Challenge

Alternative Synthetic Pathways Award

[Archer Daniels Midland Company](#) [Novozymes](#)

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

Alternative Synthetic Pathways Award

[Merck & Co., Inc.](#)

A Redesigned, Efficient Synthesis of Aprepitant, the Active Ingredient in Emend®: A New Therapy for Chemotherapy-Induced Emesis

Alternative Solvents/Reaction Conditions Award

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Designing Safer Chemical Award

[Archer Daniels Midland Company](#)

Archer RC™: A Nonvolatile, Reactive Coalescent for the Reduction of VOCs in Latex Paints

Small Business Award

[Metabolix, Inc.](#)

Producing Nature's Plastics Using Biotechnology



Academic Award

[Professor Robin D. Rogers](#) [The University of Alabama](#)

A Platform Strategy Using Ionic Liquids to Dissolve and Process Cellulose for Advanced New Materials