

GREEN CHEMISTRY

1. PROBLEMS CAUSED BY THE CHEMICAL INDUSTRY

1. *Inside the plant:*

- Exposure of employees to carcinogenic fumes and toxics

2. *Pollution exiting the plant:*

- Air emissions Fugitive emissions from storage tanks
Evaporating solvents
Accidental releases (Bhopal, India in 1984)
- Water pollution Wastewater incompletely treated
Groundwater contamination
- Solid waste Sludge from wastewater treatment

3. *Impacts of using the chemical product:*

- Fertilizers Eutrophication, soil erosion
- Herbicides & Pesticides Residues in food
Groundwater contamination
- Chlorofluorocarbons (CFCs) Ozone holes (skin cancer)
- Gazoline Urban pollution
- MTBE fuel additive Underground water pollution

4. *Impacts after use:*

- Flame-retardant materials Landfill hazard
- Paint pigments Heavy metals in soils

Where public is begging for greatest improvement: Level 3
Where chemical industry is making the greatest effort: Level 2
Quite a mismatch...



**Warning:
Disney pyjamas may damage the health of your children**

(Greenpeace, UK, 14-11-2003)

We have carried out tests on a range of household products to find out if they are harbouring harmful chemicals. The results are disturbing. Many products like perfumes, shampoos, and plastic goods were found to contain high levels of dangerous chemicals. Shockingly, Disney-branded pyjamas available at The Disney Store and other big retailers were amongst the worst offenders. We were astounded to learn that a brand aimed at children could sell products which could damage their health.

The toxic chemicals found were *nonylphenol* that can interfere with human DNA and effect sperm production in mammals, and *phthalates* which can cause liver, kidney and testicular damage. Phthalates are banned from teething toys under emergency legislation.

These harmful chemicals are probably in the garments as a result of the inks and PVC plastic film used in the design on the front.

2. WORST POLLUTERS IN USA

Numbers are the total environmental releases reported in the company's required Toxic-Release Inventory (TRI)

- [PHELPS DODGE BAGDAD INC.](#), Bagdad, AZ: [114,385,617](#) pounds
- [PHELPS DODGE MIAMI INC.](#), Claypool, AZ: [98,172,204](#) pounds
- [PHELPS DODGE TYRONE INC.](#), Tyrone, NM: [48,495,735](#) pounds
- [US ECOLOGY IDAHO INC.](#), Grand View, ID: [33,350,894](#) pounds
- [SOLUTIA INC.](#), Cantonment, FL: [24,079,894](#) pounds
- [CP&L ROXBORO STEAM ELECTRIC PLANT](#), Semora, NC: [21,018,040](#) pounds
- [CHEMICAL WASTE MANAGEMENT INC.](#), Kettleman City, CA: [20,188,244](#) pounds
- [PEORIA DISPOSAL CO. 1](#), Peoria, IL: [19,605,013](#) pounds
- [RELIANT ENERGIES INC. KEYSTONE POWER PLANT](#), Shelocta, PA: [18,202,113](#) pounds
- [BASF CORP.](#), Freeport, TX: [17,704,256](#) pounds
- [CHEMICAL WASTE MANAGEMENT OF THE NORTHWEST INC.](#), Arlington, OR: [17,683,287](#) pounds
- [SOLUTIA CHOCOLATE BAYOU](#), Alvin, TX: [17,585,235](#) pounds
- [VICKERY ENVIRONMENTAL INC.](#), Vickery, OH: [16,266,255](#) pounds
- [BP CHEMICALS INC.](#), Lima, OH: [15,942,753](#) pounds
- [BP CHEMICALS GREEN LAKE FACILITY](#), Port Lavaca, TX: [14,586,843](#) pounds
- [BRANDON SHORES & WAGNER COMPLEX](#), Baltimore, MD: [13,969,214](#) pounds
- [DU PONT DELISLE PLANT](#), Pass Christian, MS: [13,863,356](#) pounds

(excluding mines and metal smelters, which tend to be among the worse polluters)

3. DEFINITION, GOAL AND METHODS OF GREEN CHEMISTRY

(From Paul L. Bishop, 2000, p. 357)

Green chemistry, also called *benign chemistry* or *clean chemistry*, refers to the field of chemistry dealing with:

- synthesis,
- processing, and
- use

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

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

The *methods* are:

- Avoid toxics
- Use benign feedstocks only
- Reduce use of endangered resources
- Produce only safe chemicals (find substitutes to harmful chemicals)
- Find alternate processes to avoid harmful by-products
- Reduce generation of non marketable by-products
- Improve operational practices.

4. SYSTEMATIC APPROACHES IN *GREEN CHEMISTRY*

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

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

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

- Use intermediates that come from better primary feedstocks
(Ex. Production of ethylene glycol)
- Avoid chlorine compounds if chlorine is not in the final product
(Ex. Production of allyl alcohol)

3. *Formulation of alternative products for same use:* (Green Chemistry – Level 2)

- CFC substitutes

4. *Avoidance of chemicals:*

- Switch from herbicides and pesticides to genetic engineering (trade-offs?)
(Ex. Monsanto's "NewLeaf Plus" potatoes genetically improved to resist the Colorado beetle and leaf roll virus)
- Switch to organic farming
- Switch from traditional to digital photography
- Use colored plastics instead of painted metals
- Switch from petroleum fuels to biofuels or hydrogen

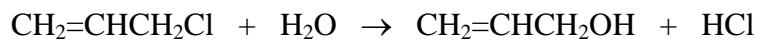
ALSO: *Use of chemistry for improved environmental performance elsewhere:*

- Molecular markers in plastics for easier identification during recycling
- Design of chemical detectors to monitor environmental quality

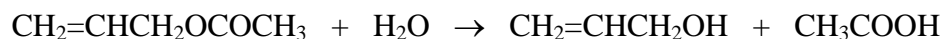
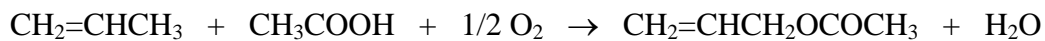
Example 1 of green chemistry:

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, acetic acid and oxygen

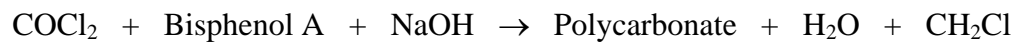


Added benefit: The acetic acid (CH_3COOH) produced in the second reaction can be recovered and used again for the first reaction, leaving no unwanted by-product.

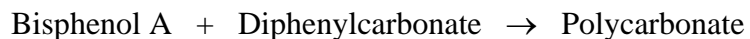
Example 2 of green chemistry:

Production of **polycarbonate** (polymers)

Traditional route: Start with phosgene (COCl_2), which is extremely toxic, and end with methyl chloride (CH_2Cl), which is harmful, too.



Greener route, to avoid phosgene:

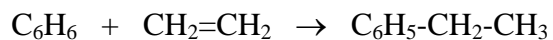


This was developed by Ashai Chemicals Co. in Japan.

Example 3 of green chemistry:

Production of **styrene** (benzene ring with CH=CH₂ tail)

Traditional route: Two-step method starting with benzene and ethylene to form ethylbenzene



and followed by dehydrogenation to obtain styrene:



Both steps give high yields with low production of by-products, but benzene is a known human liver carcinogen (at the rate of 13 billion pounds a year!).

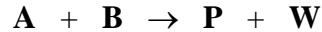
Greener route, to avoid benzene: Start with mixed xylenes (cheapest source of aromatics and environmentally safer than benzene).

Another option, still under development, is to start with toluene.

5. APPROACHES TO GENERIC CASES

1)

If reaction is of the type



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

- Procure **A** and **B** made from renewable sources and clean processes
- Find alternate **A** and/or **B** feeds to avoid or decrease 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**.

2)

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



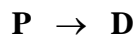
where **A** and **B** are feeds, **P** is the desired product and **C** a competing waste by-product:

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

Example: Chlorination of water by disinfection. Chlorine oxidizes the pathogens to the point of killing them but simultaneously forms harmful chlorinated organic compounds. Remedy is to use another oxidant besides chlorine (Cl₂), such as ozone (O₃)

3)

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 **D** a decay product from **P**:

- Adjust temperature and/or pressure to favor the first reaction but impede the second.
- Find catalyst that would speed the first reaction, so that product **P** can be harvested before much of it has decayed.
- Find a more stable substitute for **P**.

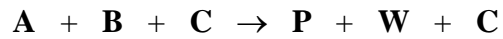
Example: Production of ethylene oxide, a precursor in the production of ethylene glycol (antifreeze)



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

4)

If the reaction requires a harmful catalyst



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

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

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

6. GREEN CHEMISTRY AND ECONOMICS

Example: Production of *carbaryl*

1) The way Union Carbide used to make carbaryl (in India):

Methyl isocyanate + alpha-naphtol → carbaryl

Economics:

Methyl-isocyanate (57 grams/mole) purchased at \$2.50/kg and

Alpha-naphtol (144 grams/mole) purchased at \$3.99/kg

Carbaryl (201 grams/mole) sold at \$5.81/kg

$$\begin{aligned}\text{Profit per kg of carbaryl} &= \$5.81 - \$2.50 \times 0.057 \times 4.98 - \$3.99 \times 0.144 \times 4.98 \\ &= \$5.81 - \$0.71 - \$2.86 \\ &= \$2.24\end{aligned}$$

2) The optimum solution from an environmental perspective:

Methyl formamide + alpha-naphtol → carbaryl + hydrogen

Economics:

Methyl formamide (59 grams/mole) purchased at 1.54/kg

Alpha-naphtol (144 grams/mole) purchased at \$3.99/kg

Hydrogen (2 grams/mole) sold at \$0.10/kg

Carbaryl (201 grams/mole) sold at \$5.81/kg

$$\begin{aligned}\text{Profit per kg of carbaryl} &= \$5.81 + \$0.10 \times 0.002 \times 4.98 \\ &\quad - \$1.54 \times 0.059 \times 4.98 - \$3.99 \times 0.144 \times 4.98 \\ &= \$5.81 + \$0.001 - \$0.45 - \$2.86 \\ &= \$2.50\end{aligned}$$

7. BIOCATALYSIS

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

Biocatalysis may involve the use of whole living micro-organisms or 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.