Green Chemistry

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GREEN CHEMISTRY

Green chemistry (sometimes called "sustainable chemistry") is a design strategy. It aims to prevent problems rather than clean them up later.

DEFINITION

Green Chemistry is the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products .

GREEN CHEMISTRY IS ABOUT

- **Waste Minimisation at Source**
- **Use of Catalysts in place of Reagents**
- **Using Non-Toxic Reagents**
- **Use of Renewable Resources**
- **Improved Atom Efficiency**
- **Use of Solvent Free or Recyclable Environmentally Benign Solvent systems**

Green Chemistry Is About...

Reducing

- **Waste**
- **Materials**
- **Hazard**
- **Risk**
- **Energy**
- **Cost**

Why do we need Green Chemistry ?

- Chemistry is undeniably a very prominent part of our daily lives.
- Chemical developments also bring new environmental problems and harmful unexpected side effects, which result in the need for ‘greener’ chemical products.
- A famous example is the pesticide DDT.

- **Green chemistry** looks at pollution prevention on the molecular scale and is an extremely important area of Chemistry due to the importance of Chemistry in our world today and the implications it can show on our environment.
- The **Green Chemistry** program supports the invention of more environmentally friendly chemical processes which reduce or even eliminate the generation of hazardous substances.
- This program works very closely with the twelve principles of **Green Chemistry.**

The 12 Principles of Green Chemistry (1-6)

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 maximise the incorporation of all materials used in the process into the final product.

3. **Less Hazardous Chemical Synthesis**
   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.

4. **Designing Safer Chemicals**
   Chemical products should be designed to effect their desired function while minimising their toxicity.

5. **Safer Solvents and Auxiliaries**
   The use of auxiliary substances (e.g., solvents or separation agents) should be made unnecessary whenever possible and innocuous when used.

6. **Design for Energy Efficiency**
   Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimised. If possible, synthetic methods should be conducted at ambient temperature and pressure.

The 12 Principles of Green Chemistry (7-12)

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/de-protection, and temporary modification of physical/chemical processes) should be minimised 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.

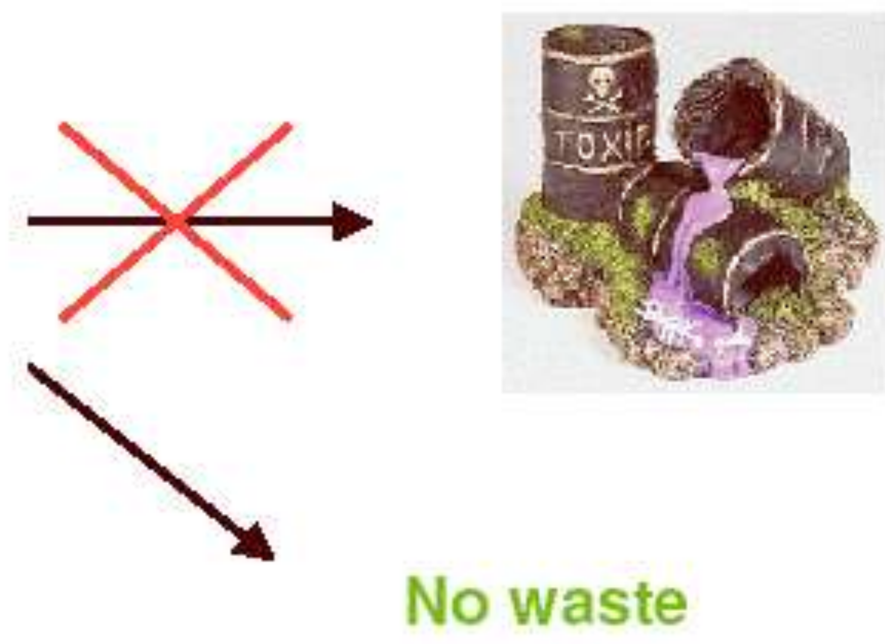
12 Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions, and fires.

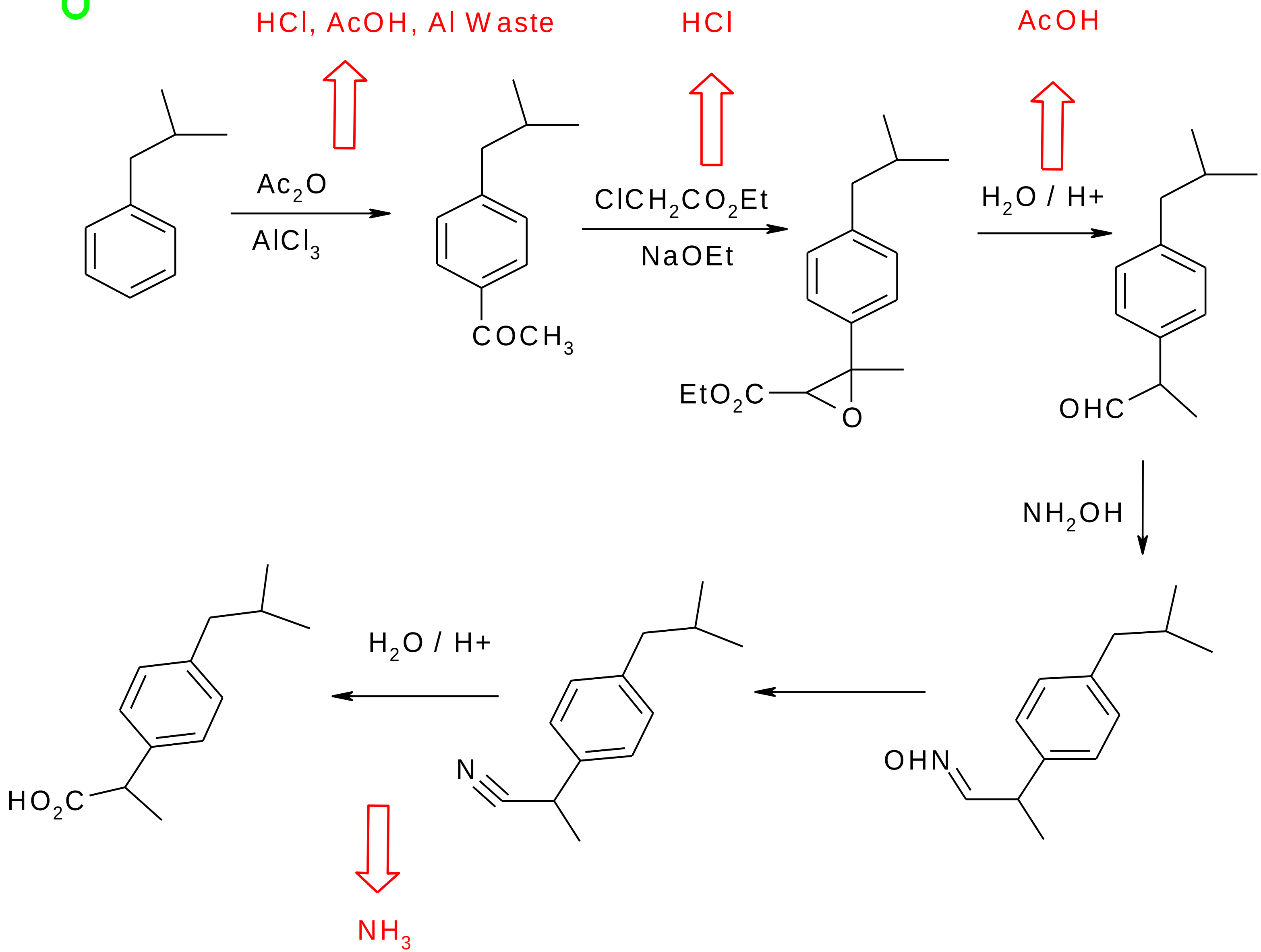
Some examples of Green synthesis as per the principles

Prevention (1): **It is better to prevent waste than to treat or clean up waste after it is formed.**

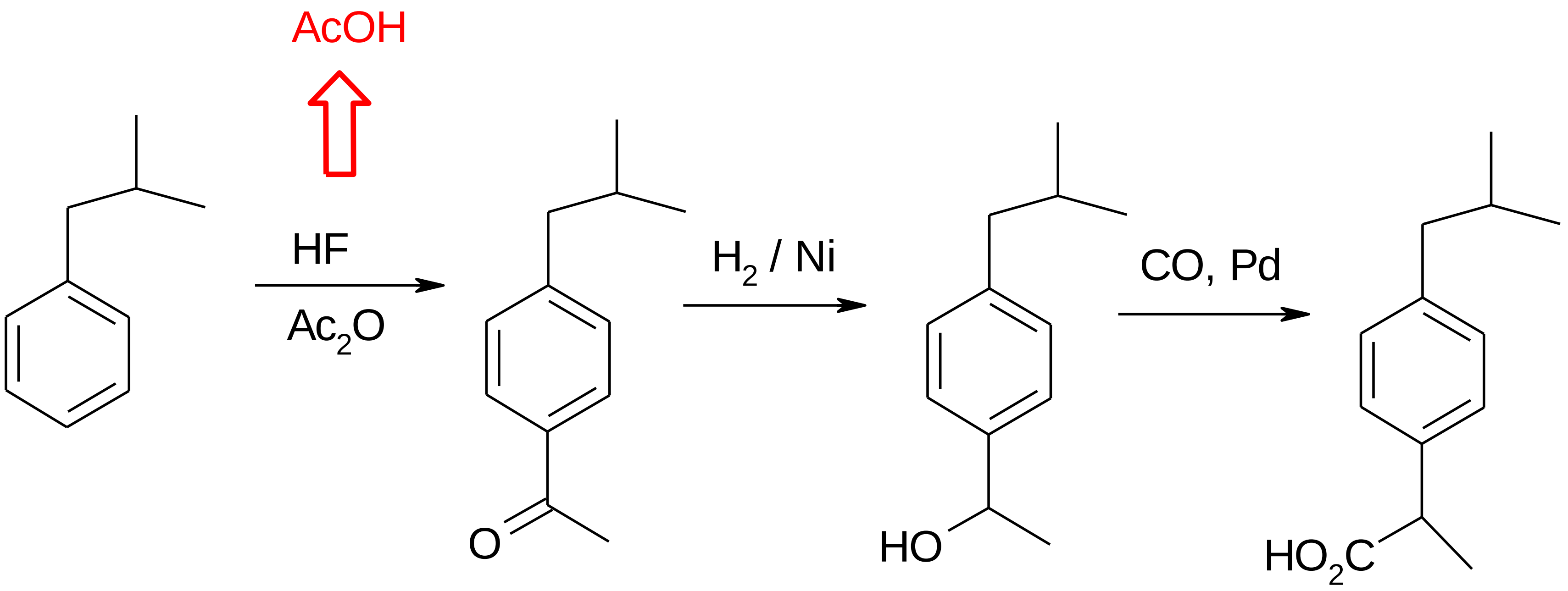
Chemical Process



Classic Route to Ibuprofen



Hoechst Route To Ibuprofen



Atom Economy (2): Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

The atom economy (a measure of atom utilization or efficiency) is a measure of the amount of starting materials that end up as useful products. It is important for sustainable development and for good economic reasons to use reactions with high atom economy.

$$\text{ATOM ECONOMY} = 100 \times \frac{\text{MASS of desired USEFUL PRODUCT}}{\text{TOTAL MASS of all REACTANTS}}$$

Ex: Hydrogen can be manufactured by reacting methane with steam:

$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$

Calculate the atom economy for the reaction.

(A_r of H = 1, A_r of C = 12, A_r of O = 16)

M_r of CH_4 = 12 + (4 × 1) = 16

M_r of H_2O = (2 × 1) + 16 = 18

total M_r of reactants = 16 + 18 = 34

A_r of H_2 = (2 × 1) = 2

total M_r of desired product = 3 × 2 = 6 (there are three H_2 in the balanced equation)

atom economy = $\frac{\text{total } M_r \text{ of the desired product}}{\text{total } M_r \text{ of all reactants}} \times 100$

atom economy = $\frac{6}{34} \times 100$

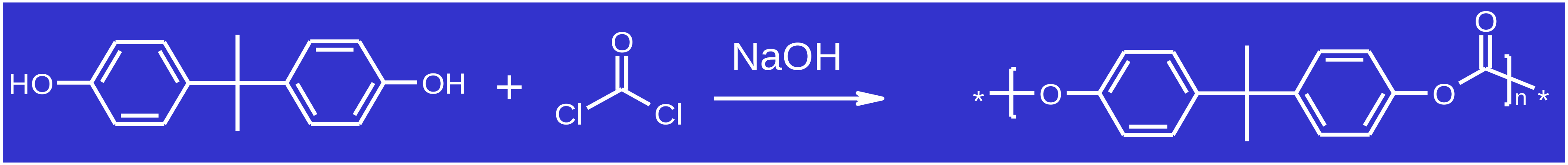
atom economy = 17.6% (to 3 significant figures)

Less Hazardous Chemical Synthesis (3):

Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Less Hazardous Chemical Synthesis

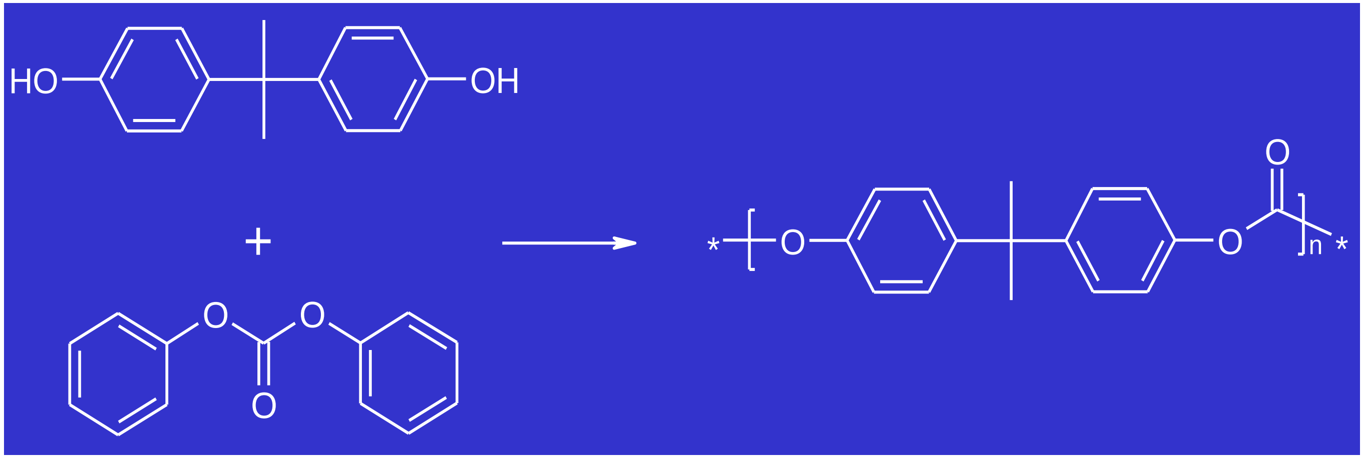
Polycarbonate Synthesis: Phosgene Process



- Disadvantages
  - phosgene is highly toxic, corrosive
  - requires large amount of CH_2Cl_2
  - polycarbonate contaminated with Cl impurities

Less Hazardous Chemical Synthesis

Polycarbonate Synthesis: Solid-State Process

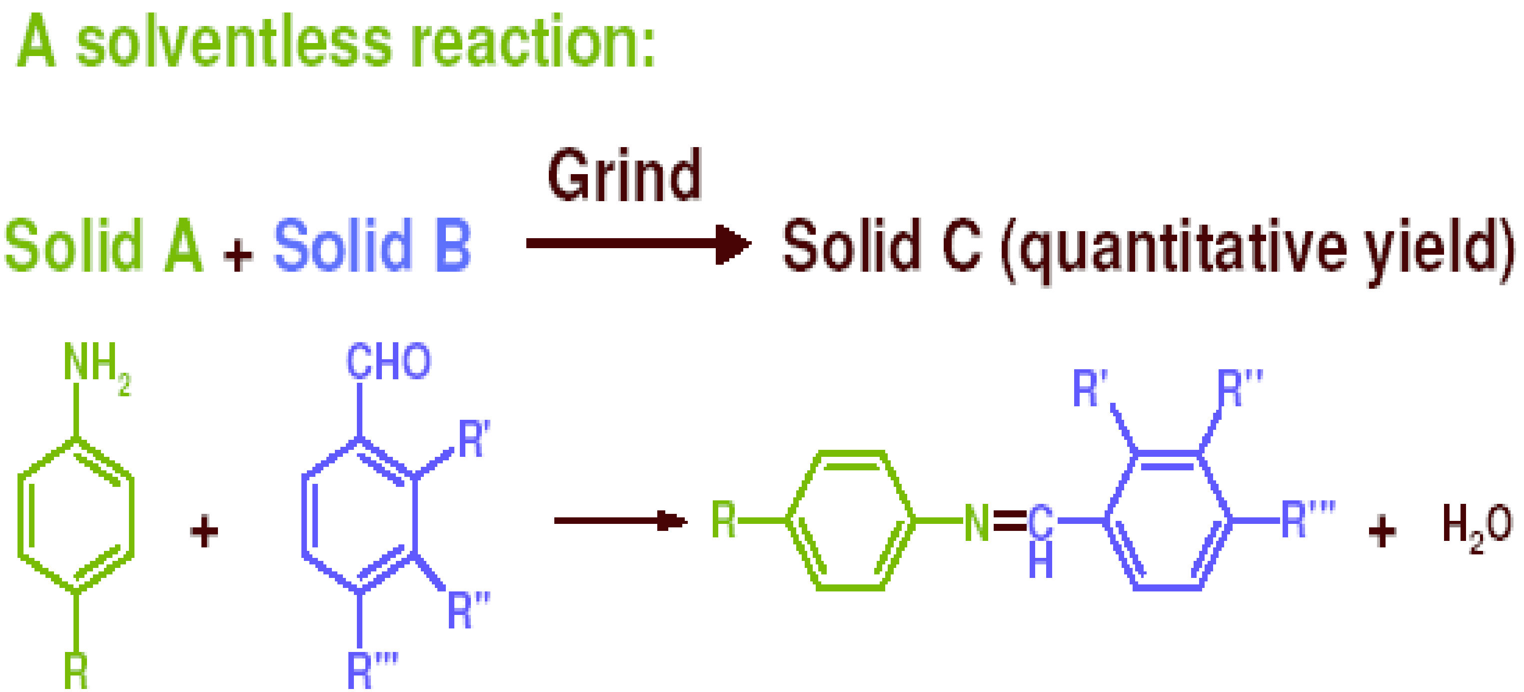


- Advantages
  - diphenylcarbonate synthesized without phosgene
  - eliminates use of CH_2Cl_2
  - higher-quality polycarbonates

Komiya *et al.*, Asahi Chemical Industry Co.

Safer Solvents and Auxiliaries (5):

The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible, and innocuous when used.



Safer Solvents

- Solvent Substitution
- Water as a solvent
- New solvents
  - Ionic liquids
  - Supercritical fluids

Solvent Selection

Preferred	Useable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Heptane	Hexane(s)
Ethanol	Toluene	Di-isopropyl ether
2-Propanol	Methylcyclohexane	Diethyl ether
1-Propanol	Methyl t-butyl ether	Dichloromethane
Ethyl acetate	Isooctane	Dichloroethane
Isopropyl acetate	Acetonitrile	Chloroform
Methanol	2-MethylTHF	Dimethyl formamide
Methyl ethyl ketone	Tetrahydrofuran	N-Methylpyrrolidinone
1-Butanol	Xylenes	Pyridine
t-Butanol	Dimethyl sulfoxide	Dimethyl acetate
	Acetic acid	Dioxane
	Ethylene glycol	Dimethoxyethane
		Benzene
		Carbon tetrachloride

"Green chemistry tools to influence a medicinal chemistry and research chemistry based organization" Dunn and Perry, et. al., Green Chem., 2008, 10, 31-36

Red Solvent	Flash point (° C)	Reason
Pentane	-49	Very low flash point, good alternative available.
Hexane(s)	-23	More toxic than the alternative heptane, classified as a HAP in the US.
Di-isopropyl ether	-12	Very powerful peroxide former, good alternative ethers available.
Diethyl ether	-40	Very low flash point, good alternative ethers available.
Dichloromethane	n/a	High volume use, regulated by EU solvent directive, classified as HAP in US.
Dichloroethane	15	Carcinogen, classified as a HAP in the US.
Chloroform	n/a	Carcinogen, classified as a HAP in the US.
Dimethyl formamide	57	Toxicity, strongly regulated by EU Solvent Directive, classified as HAP in the US.
N-Methylpyrrolidinone	86	Toxicity, strongly regulated by EU Solvent Directive.
Pyridine	20	Carcinogenic/mutagenic/reprotoxic (CMR) category 3 carcinogen, toxicity, very low threshold limit value (TLV) for worker exposures.
Dimethyl acetate	70	Toxicity, strongly regulated by EU Solvent Directive.
Dioxane	12	CMR category 3 carcinogen, classified as HAP in US.
Dimethoxyethane	0	CMR category 2 carcinogen, toxicity.
Benzene	-11	Avoid use: CMR category 1 carcinogen, toxic to humans and environment, very low TLV (0.5 ppm), strongly regulated in EU and the US (HAP).
Carbon tetrachloride	n/a	Avoid use: CMR category 3 carcinogen, toxic, ozone depletor, banned under the Montreal protocol, not available for large-scale use, strongly regulated in the EU and the US (HAP).

"Green chemistry tools to influence a medicinal chemistry and research chemistry based organization"
Dunn and Perry, et. al., Green Chem., 2008, 10, 31-36

Solvent replacement table

Undesirable Solvent	**Alternative**
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or diethyl ether	2-MeTHF or *tert*-butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or *tert*-butyl methyl ether
Chloroform, dichloroethane or carbon tetrachloride	Dichloromethane
Dimethyl formamide, dimethyl acetamide or N-methylpyrrolidinone	Acetonitrile
Pyridine	Et_3N (if pyridine is used as a base)
Dichloromethane (extractions)	EtOAc, MTBE, toluene, 2-MeTHF
Dichloromethane (chromatography)	EtOAc/heptane
Benzene	Toluene

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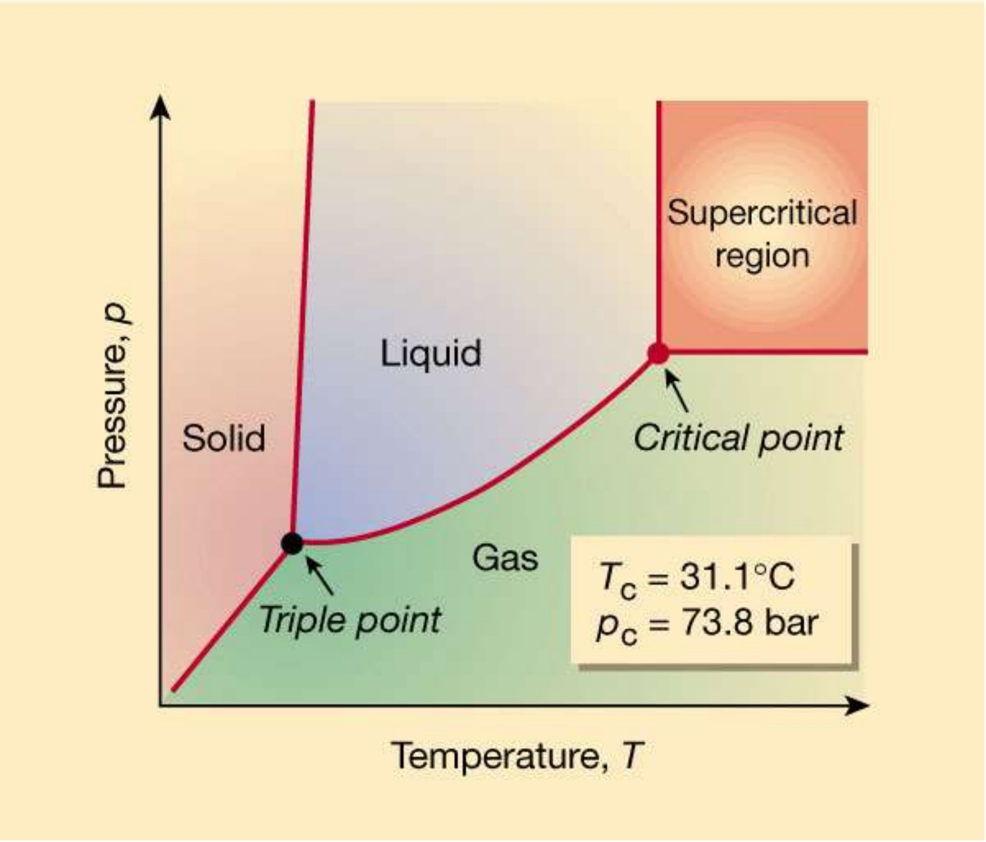
Safer solvents: Supercritical fluids



A SCF is defined as a substance above its critical temperature (T_C) and critical pressure (P_C). The critical point represents the highest temperature and pressure at which the substance can exist as a vapor and liquid in equilibrium.

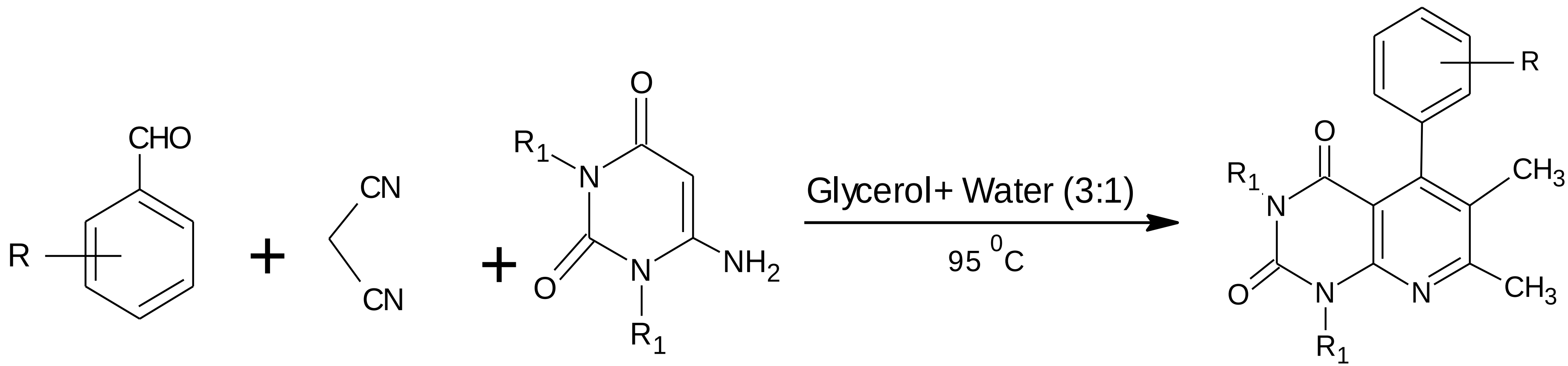
http://www.chem.leeds.ac.uk/People/CMR/whatarescf.html

- Regarding the green chemistry principles, the biomass-derived glycerol is a "green solvent" and also considered as "organic water" owing to its promising properties like non-toxicity, biodegradability, non-volatility, non-corrosiveness, non-flammability and inexpensiveness.

- It is a polar protic solvent which has capability to form strong hydrogen bonds and many organic compounds are easily dissolved in glycerol that are not or less soluble in water.

- As a consequence of these encouraging properties, in recent years many synthetic strategies have been effectively carried out by using glycerol as a promising reaction medium .

Example: Catalyst-free synthesis of pyrido[2,3-d]pyrimidine frameworks by one-pot reaction of aromatic aldehyde, malononitrile and 6-amino uracil or 6-amino-1,3- dimethyl uracil in glycerol-water medium (3:1) at 95 °C.



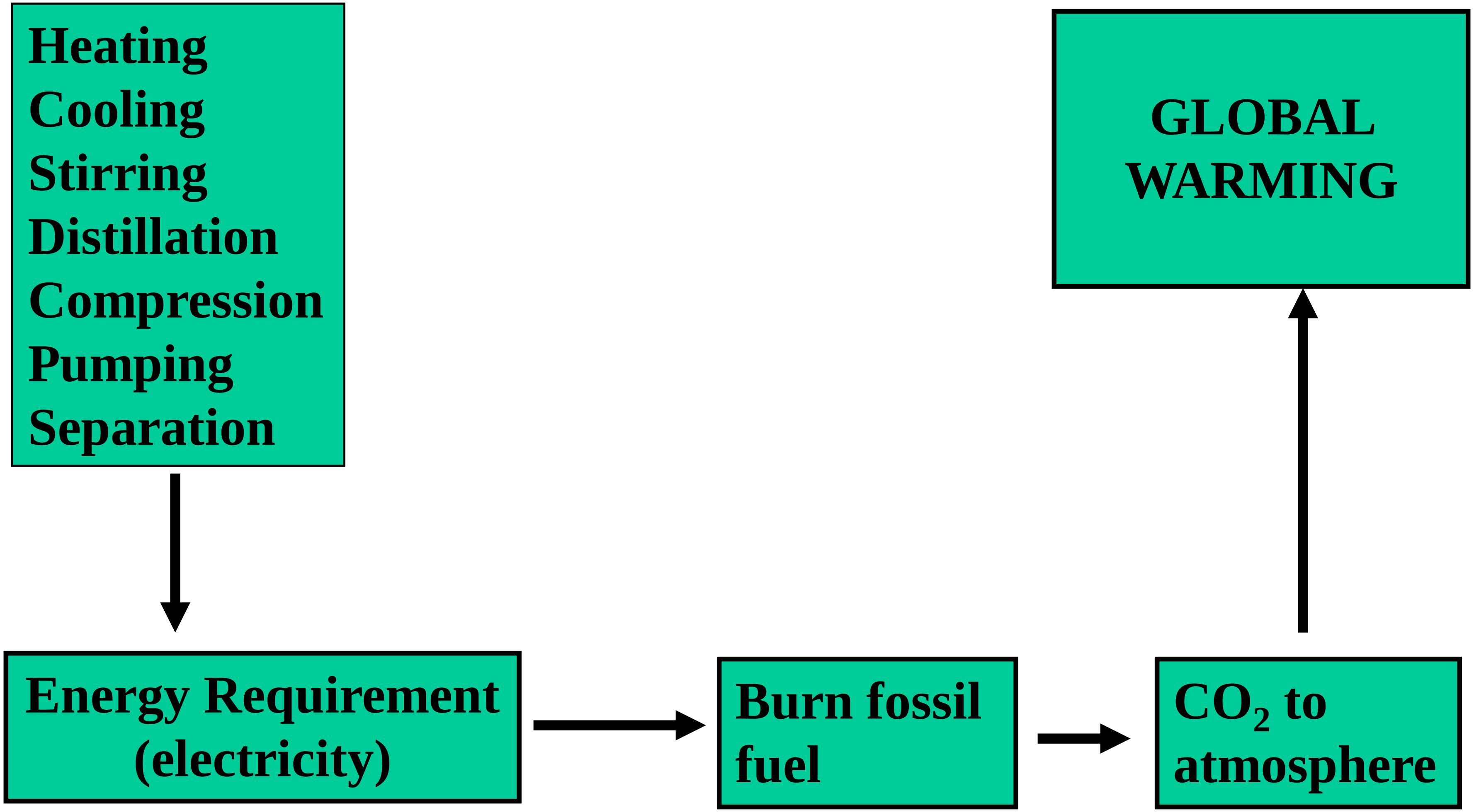
1 2 3 4

Scheme: Synthesis of pyrido[2,3-d] pyrimidine derivatives

Design for Energy Efficiency(6):

Energy requirements should be recognized for their environmental impacts and should be minimized. Synthetic methods should be conducted at ambient pressure and temperature.

Energy in a chemical process



Source of energy:

Power plant – coal, oil, natural gas

Energy usage

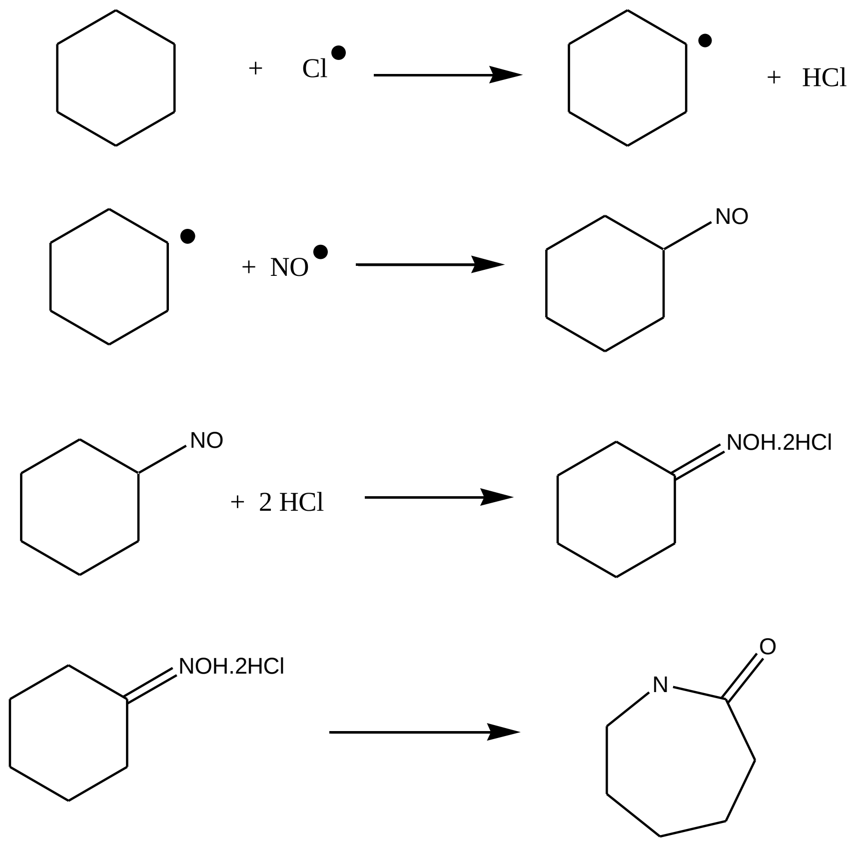
Chemicals and petroleum industries account for 50% of industrial energy usage.

~1/4 of the energy used is consumed in distillation and drying processes.

Alternative energy sources:
Photochemical Reactions

1. Caprolactam process

$$NOCl \rightarrow NO^{\bullet} + Cl^{\bullet}\ \textbf{(535nm)}$$



Alternative energy sources:
Microwave chemistry

- Wavelengths between 1 mm and 1 m
  - Frequency fixed at 2.45 GHz
- More directed source of energy
- Heating rate of 10 ^{0}C per second is achievable
- Possibility of overheating (explosions)
- Solvent-free conditions are possible
- Interaction with matter characterized by penetration depth

Use of Renewable Feedstocks (7):

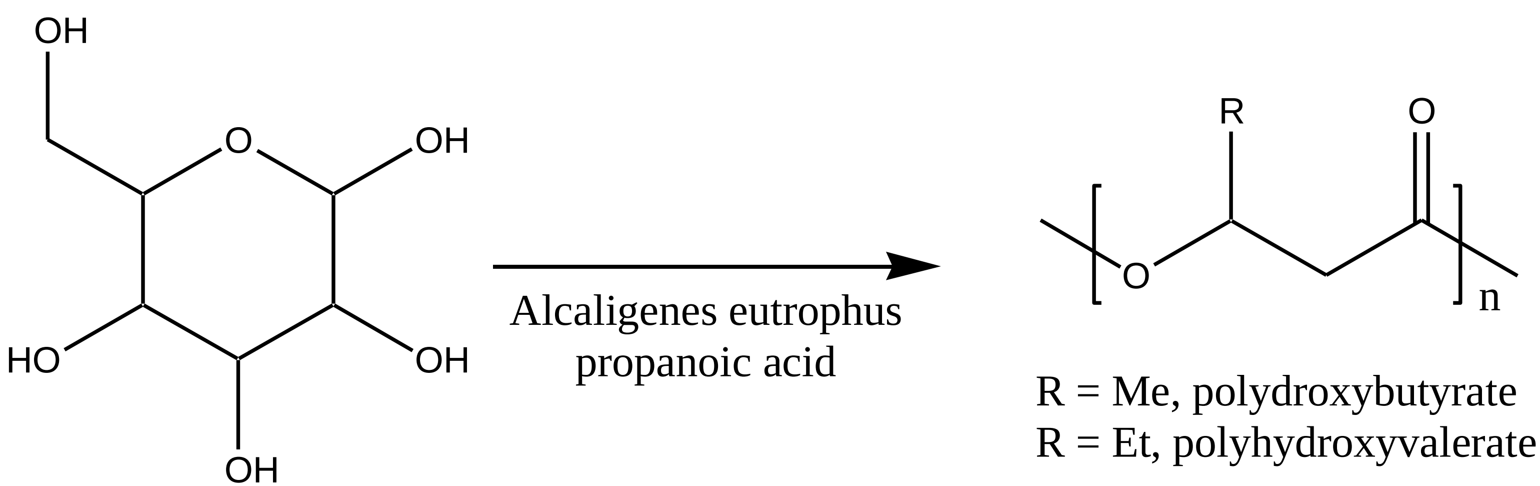
A raw material of feedstock should be renewable rather than depleting wherever technically and economically practical.

Non-renewable

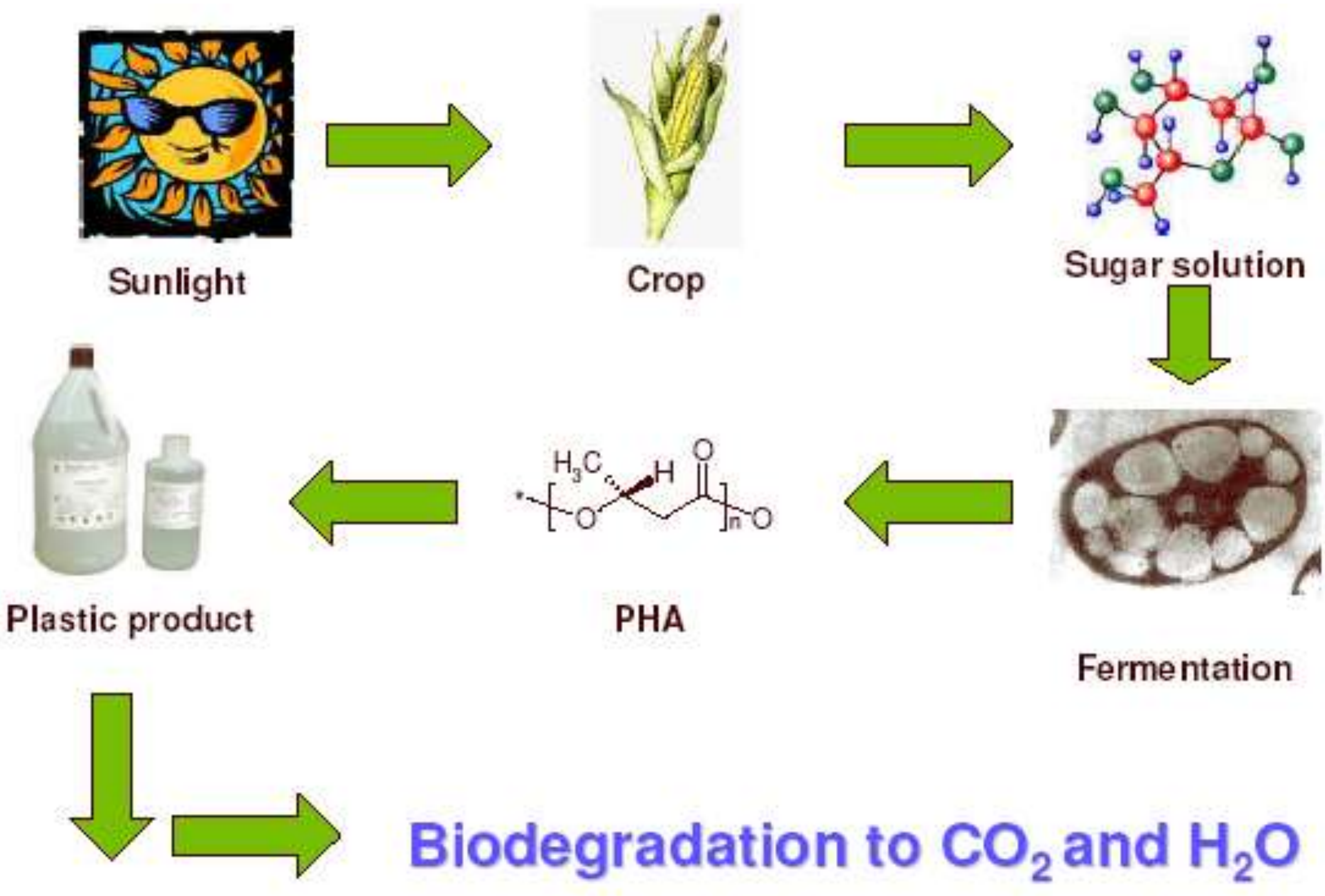
Renewable

Polymers from Renewable Resources: Polyhydroxyalkanoates (PHAs)

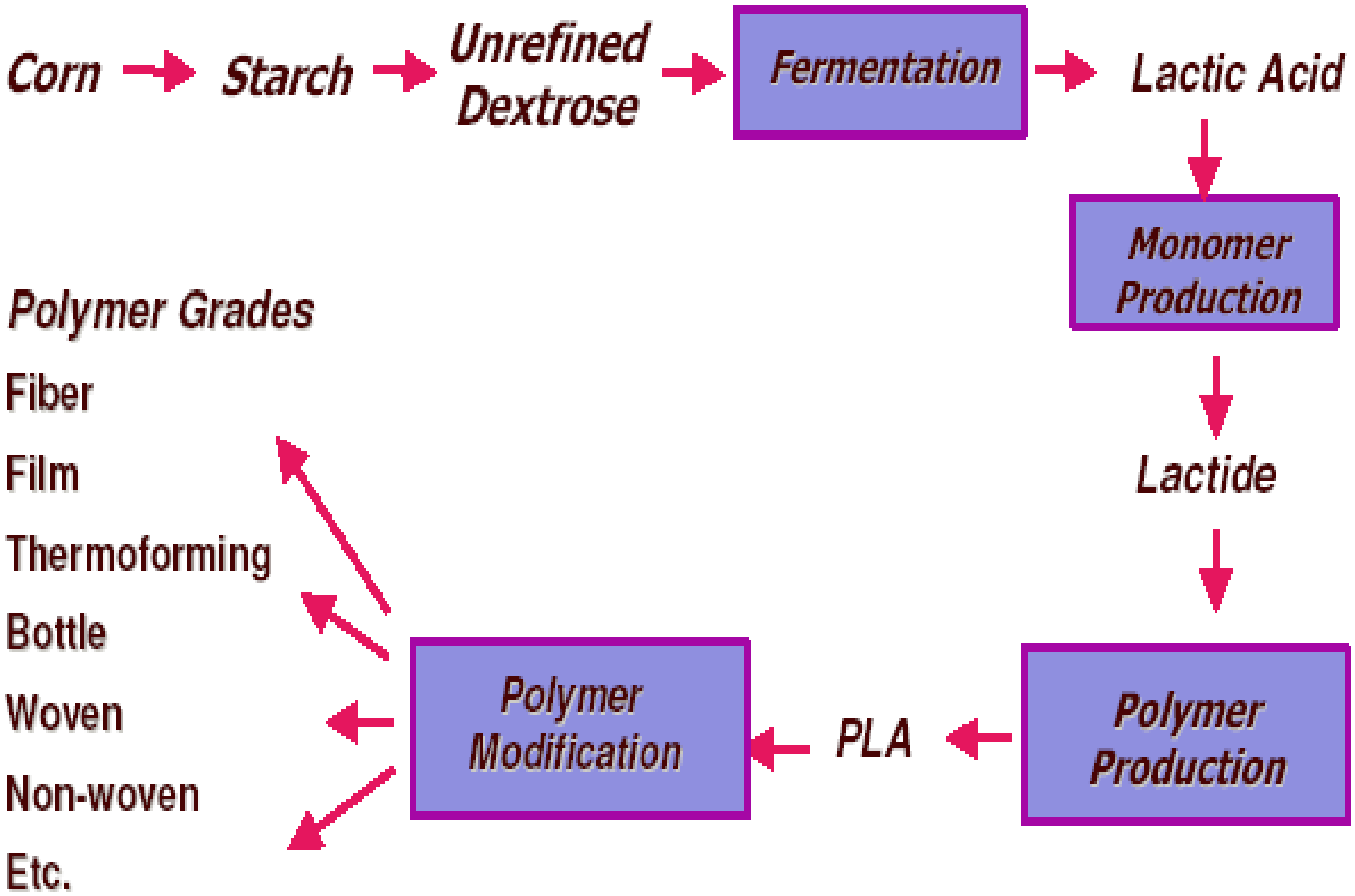
- Fermentation of glucose in the presence of bacteria and propanoic acid (product contains 5-20% polyhydroxyvalerate)
- Similar to polypropene and polyethene
- Biodegradable (credit card)



Polyhydroxyalkanoates (PHAs)



Poly lactic acid (PLA) for plastics production



Polymers from Renewable Resources: Poly(lactic acid)

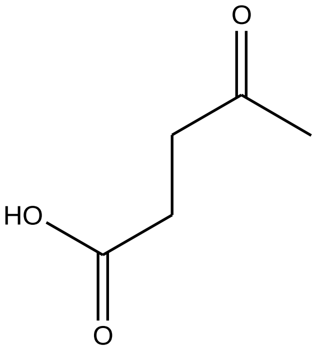
Cutesy: http://www.natureworksllc.com/corporate/nw_pack_home.asp

Raw Materials from Renewable Resources: The BioFine Process

Paper mill sludge

Agricultural residues, Waste wood

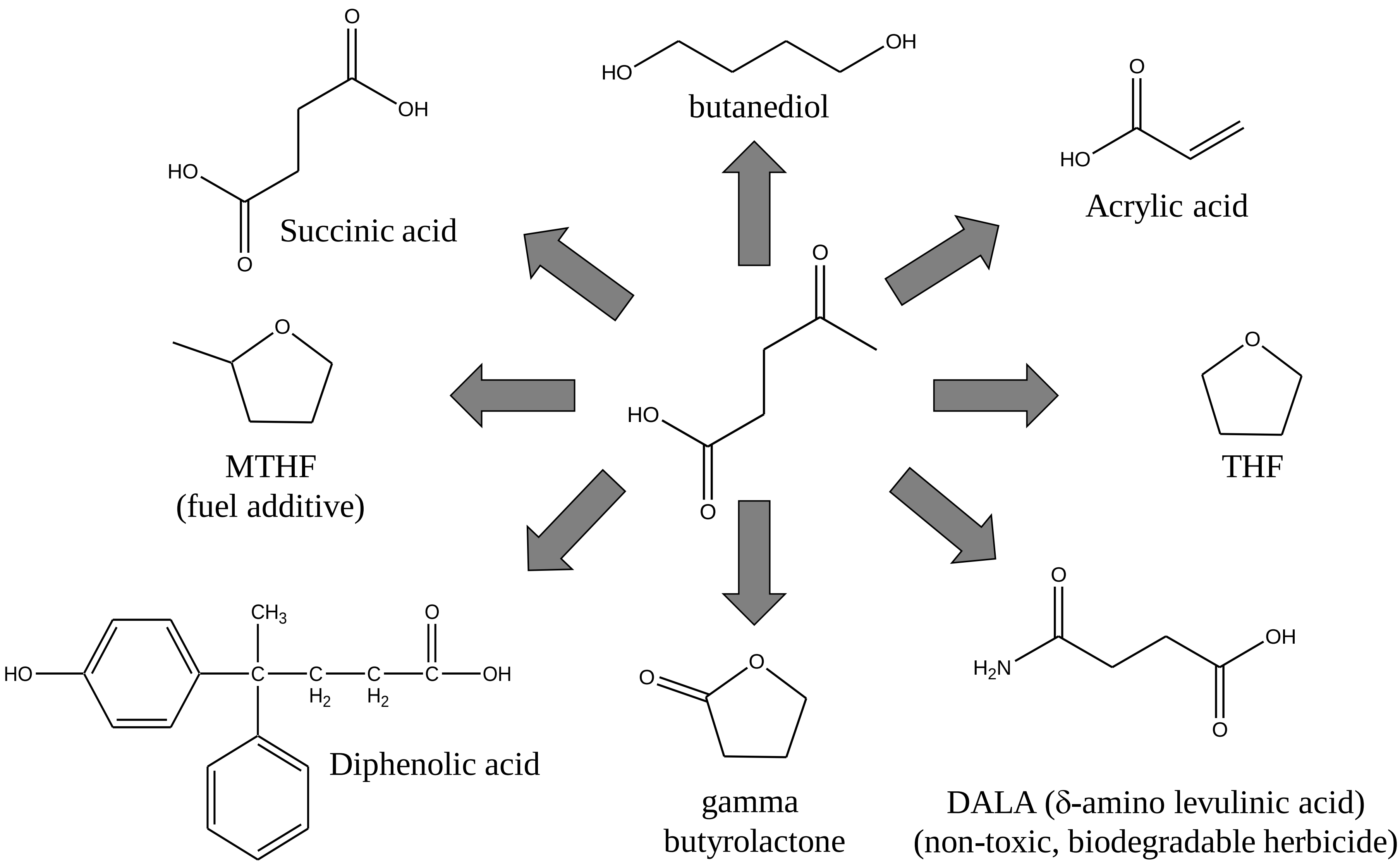
Municipal solid waste and waste paper



Levulinic acid

Green Chemistry Challenge Award
1999 Small Business Award

Levulinic acid as a platform chemical



The major uses of GREEN CHEMISTRY

- **Energy**
- **Global Change**
- **Resource Depletion**
- **Food Supply**
- **Toxics in the Environment**

Energy

- The vast majority of the energy generated in the world today is from non-renewable sources that damage the environment.
  - Carbon dioxide
  - Depletion of Ozone layer
  - Effects of mining, drilling, etc
  - Toxics

Energy

- Green Chemistry will be essential in
  - developing the alternatives for energy generation (photovoltaics, hydrogen, fuel cells, biobased fuels, etc.) as well as
  - continue the path toward energy efficiency with catalysis and product design at the forefront.

Global Change

- Global Change concerns for climate change, oceanic temperature, stratospheric chemistry and global distillation can be addressed through the development and implementation of green chemistry technologies.

Resource Depletion

- Due to the over utilization of non-renewable resources, natural resources are being depleted at an unsustainable rate.
- Fossil fuels are a central issue.

Resource Depletion

- Renewable resources can be made increasingly viable technologically and economically through green chemistry.
  - Biomass
  - Nanoscience & technology
  - Solar
  - Carbon dioxide
  - Chitin
  - Waste utilization

Food Supply

- While current food levels are sufficient, distribution is inadequate
- Agricultural methods are unsustainable
- Future food production intensity is needed.
- Green chemistry can address many food supply issues

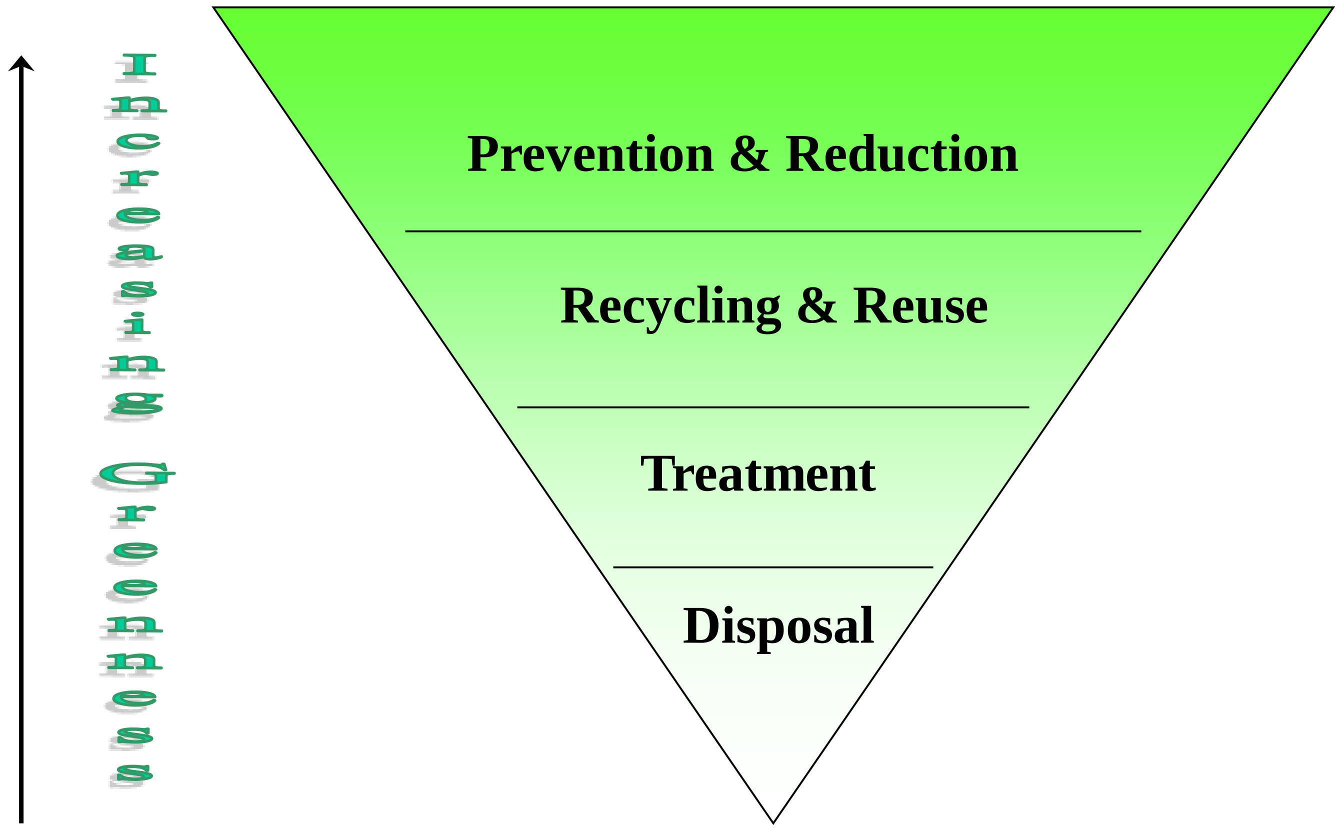
Food Supply

- Green chemistry is developing:
  - Pesticides which only affect target organisms and degrade to innocuous by-products.
  - Fertilizers and fertilizer adjuvants that are designed to minimize usage while maximizing effectiveness.
  - Methods of using agricultural wastes for beneficial and profitable uses.

Toxics in the Environment

- Substances that are toxic to humans, the biosphere and all that sustains it, are currently still being released at a cost of life, health and sustainability.
- One of green chemistry’s greatest strengths is the ability to design for reduced hazard.

Pollution Prevention Hierarchy



Conclusion

Green chemistry **Not** a solution to all environmental problems **But** the most fundamental approach to preventing pollution.

Thank you