Green Chemistry

James E. Girard. “Principles of Environmental Chemistry”

Chemistry

Pros

- Pharmaceuticals that have improved health and extended life
- Fertilizers that have greatly increased food productivity
- Semiconductors that have made possible computers and other modern electronic devices

Cons

- Pollutants
- Toxic substances
- Nonbiodegradable plastic containers

These have resulted in harm to the environment

The Pollution Prevention Act (PPA) states:

1. Pollution should be prevented or reduced at the source whenever feasible

2. Pollution that cannot be prevented or reduced should be recycled

3. Pollution that cannot be prevented or reduced or recycled should be treated, and

4. Disposal or other releases into the environment should be employed only as a last resort.

- **Green chemistry** looks at pollution prevention on the molecular scale

  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.**

GREEN CHEMISTRY

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 system**

Green Chemistry Is About...

Reducing

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

12 Principles of Green Chemistry

1. **Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
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 Synthesis.** Whenever practicable, synthetic methodologies 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 preserve efficacy of the function while reducing toxicity.
5. **Safer Solvents and Auxiliaries.** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
6. **Design for Energy Efficiency.** Energy requirements should be recognized for their environmental and economic impacts and should be minimized. 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 practical.

8. **Reduce Derivatives.** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible .

9. **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

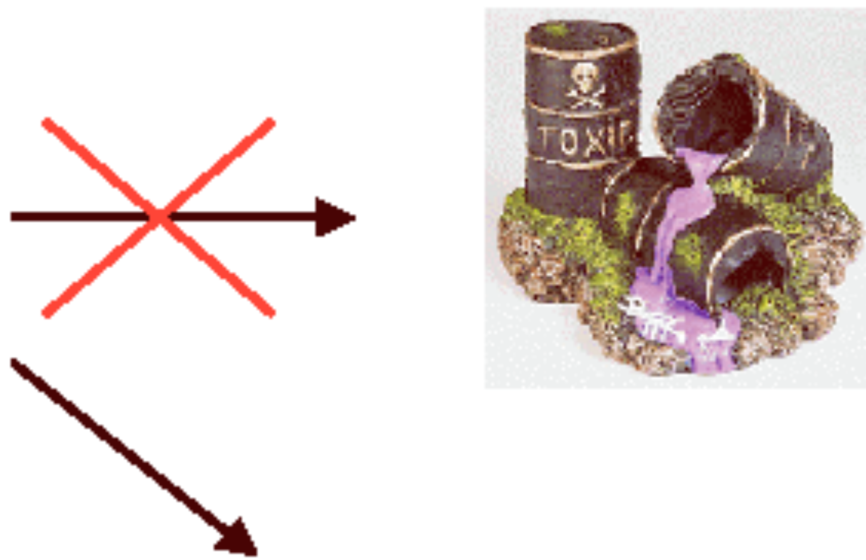
10. **Design for Degradation.** Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

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.** Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

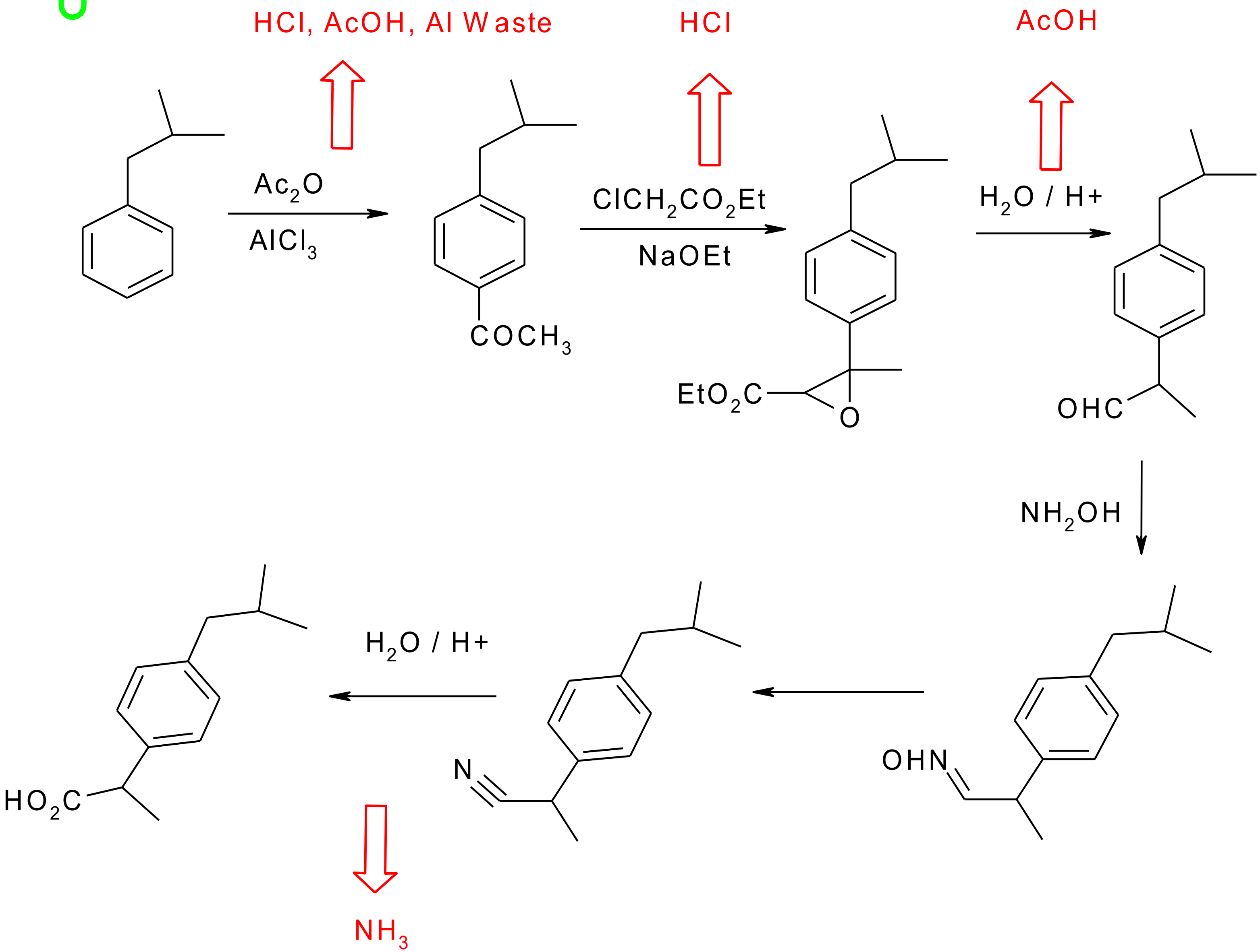
Prevention. It is better to prevent waste than to treat or clean up waste after it is formed.

Chemical Process

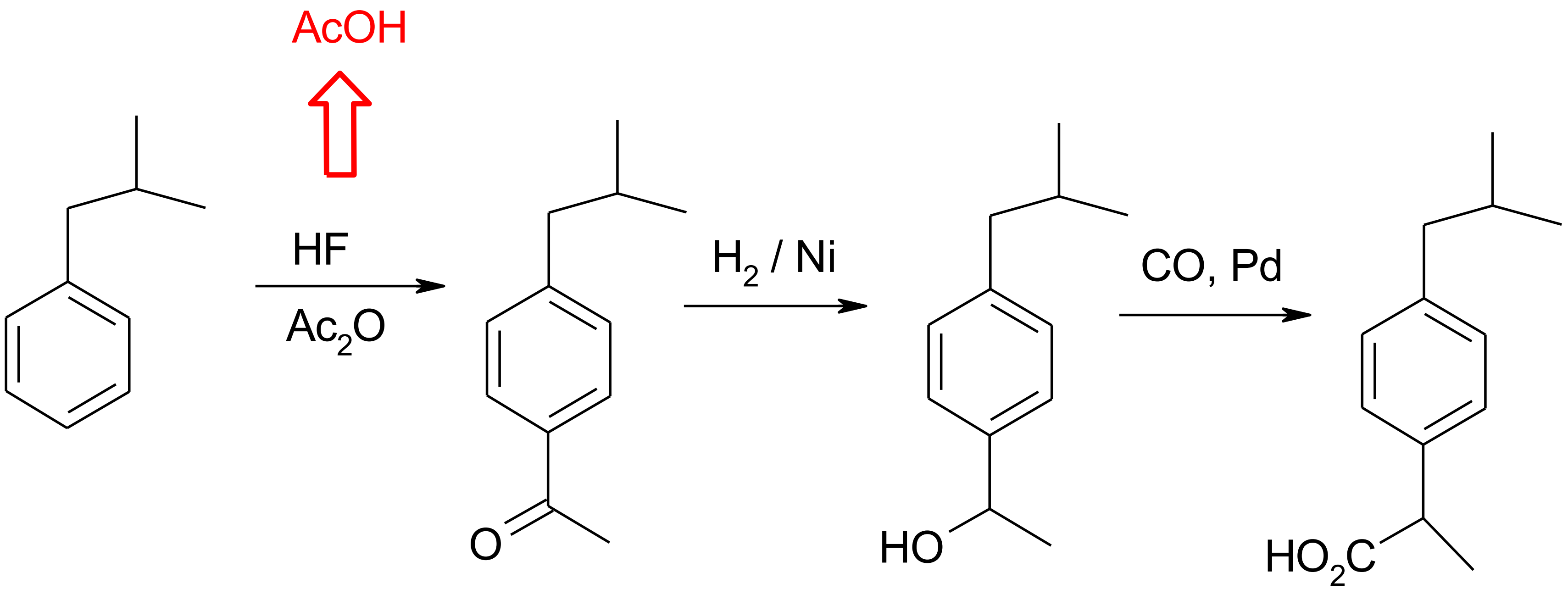


No waste

Classic Route to Ibuprofen



Hoechst Route To Ibuprofen

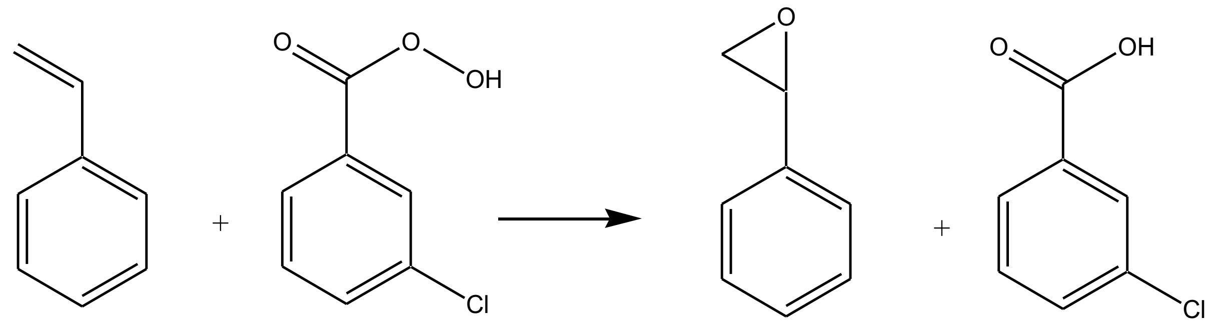


BHC company synthesis of Ibuprofen

"an industry model of atom efficiency in chemical processing technology"

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

Epoxidation of an alkene using a peroxyacid



What is missing?

100% yield

What co-products are made?

How much waste is generated?

Is the waste benign waste?

Are the co-products benign and/or useable?

How much energy is required?

Are purification steps needed?

What solvents are used? (are they benign and/or reusable?

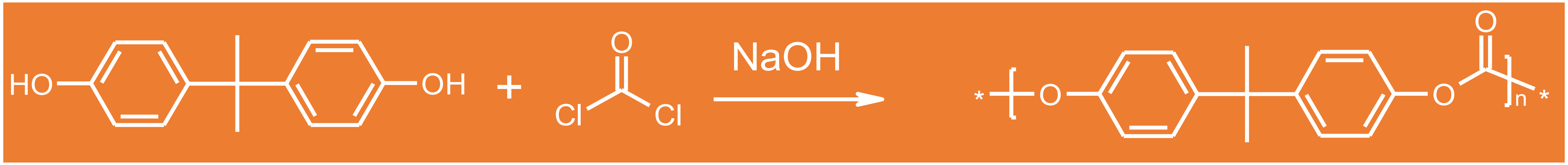
Is the “catalyst” truly a catalyst? (stoichiometric vs. catalytic?)

A.E. of this reaction is 23%.

77% of the products are waste.

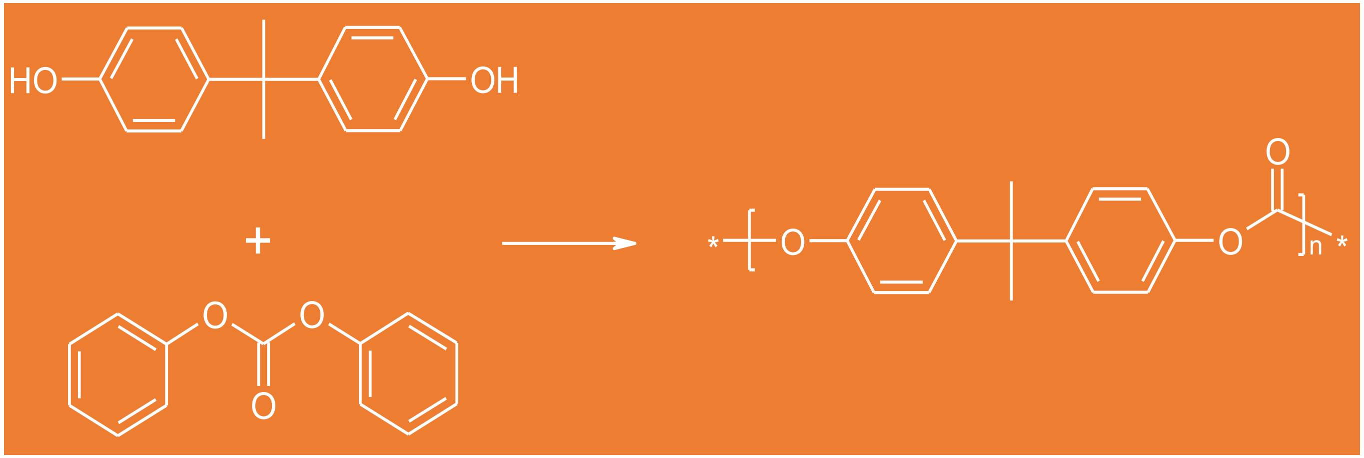
Less Hazardous Chemical Synthesis. Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Polycarbonate Synthesis: Phosgene Process



bisphenol A

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



diphenylcarbonate

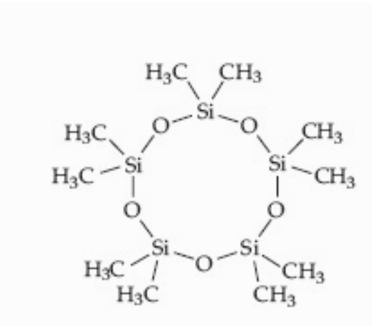
Safer Solvents and Auxiliaries. The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.

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	

“CO2, when compressed into a liquid state, has long been recognized as an ideal solvent.

CO2 solutions are nontoxic, nonflammable, energy-efficient, cost-effective, waste minimizing, and reusable.

Through green chemistry initiatives, CO2 has replaced many polluting solvents.”

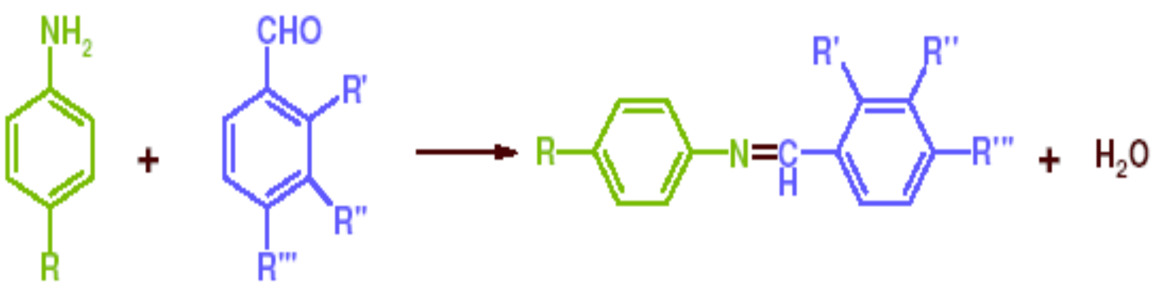


“Dry Cleaning of Clothes: perchloroethylene versus Liq. CO2

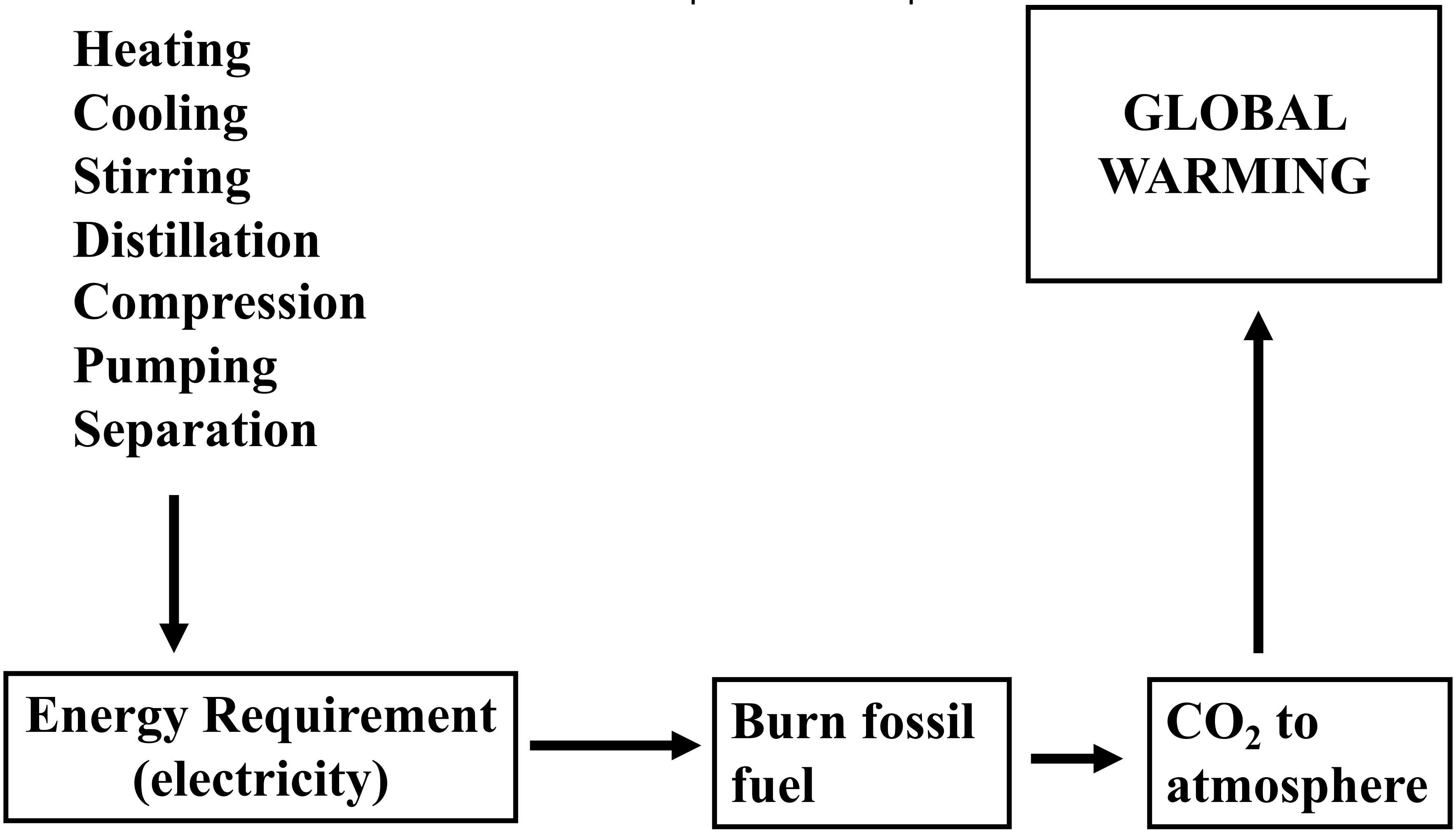
Undesirable Solvent	Alternative
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or diethyl ether	2-MeTHF or *tert*-butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or *tert*-butyl methyl ether
Chloroform, dichloroethane or carbon tetrachloride	Dichloromethane
Dimethyl formamide, dimethyl acetamide 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

A solventless reaction:

Solid A + Solid B $\xrightarrow{\text{Grind}}$ Solid C (quantitative yield)



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



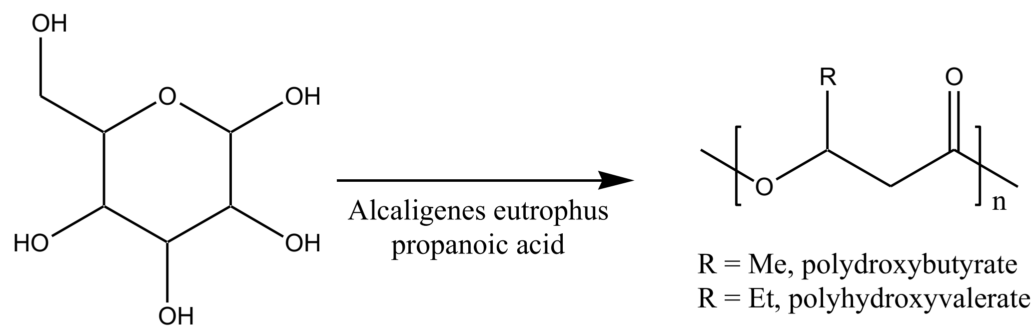
Use of Renewable Feedstocks. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

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

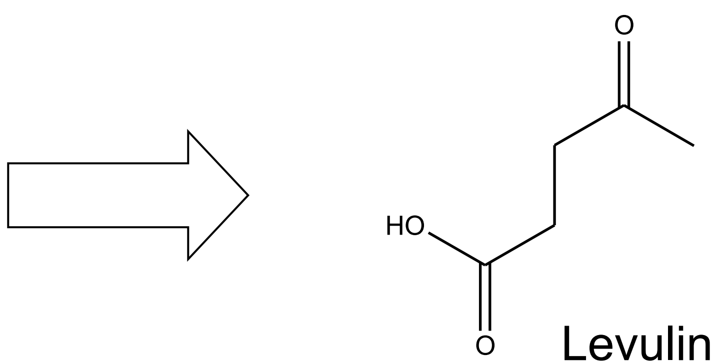


Raw Materials from Renewable Resources: The BioFine Process

Paper mill sludge

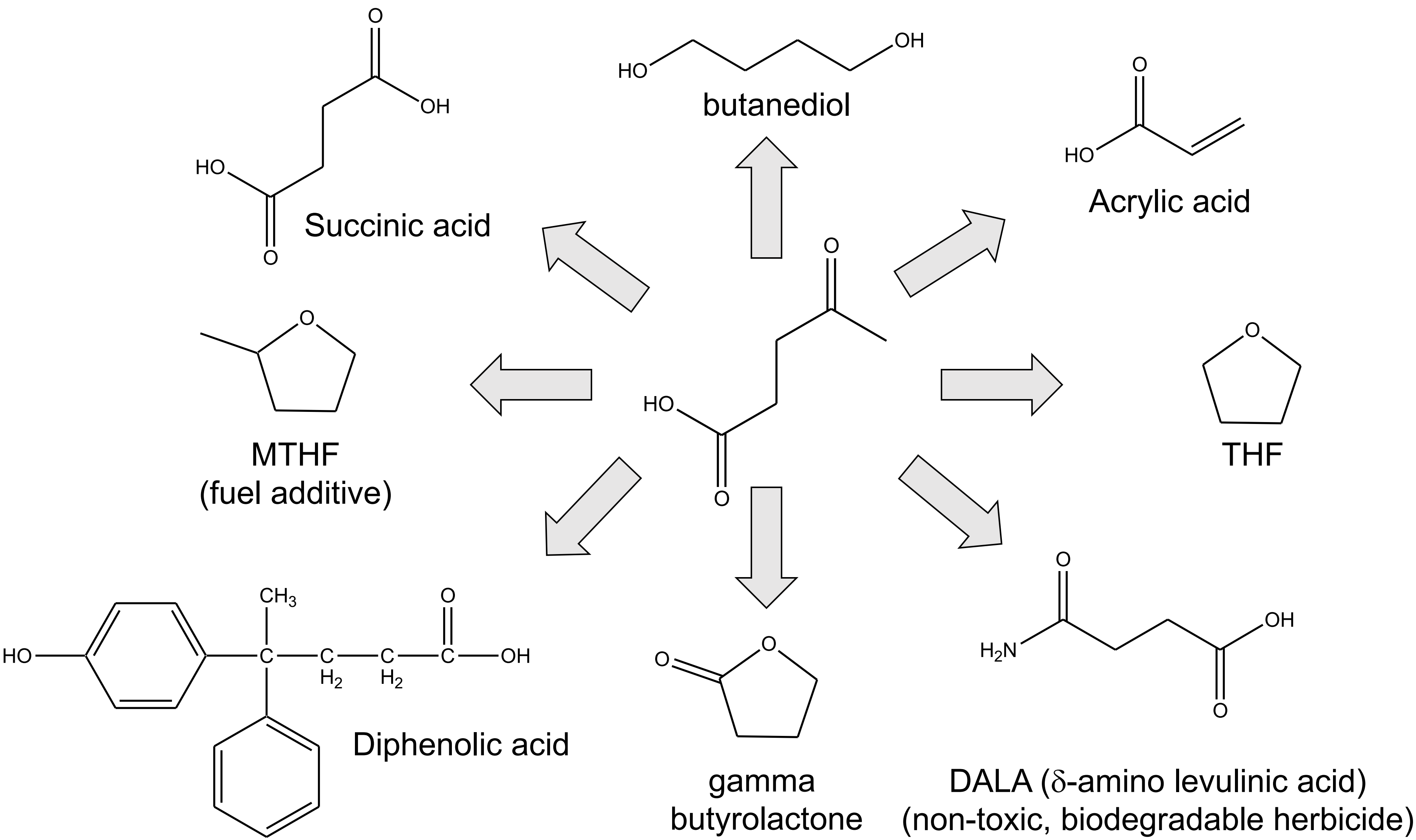
Agricultural residues,
Waste wood

Municipal solid waste
and waste paper

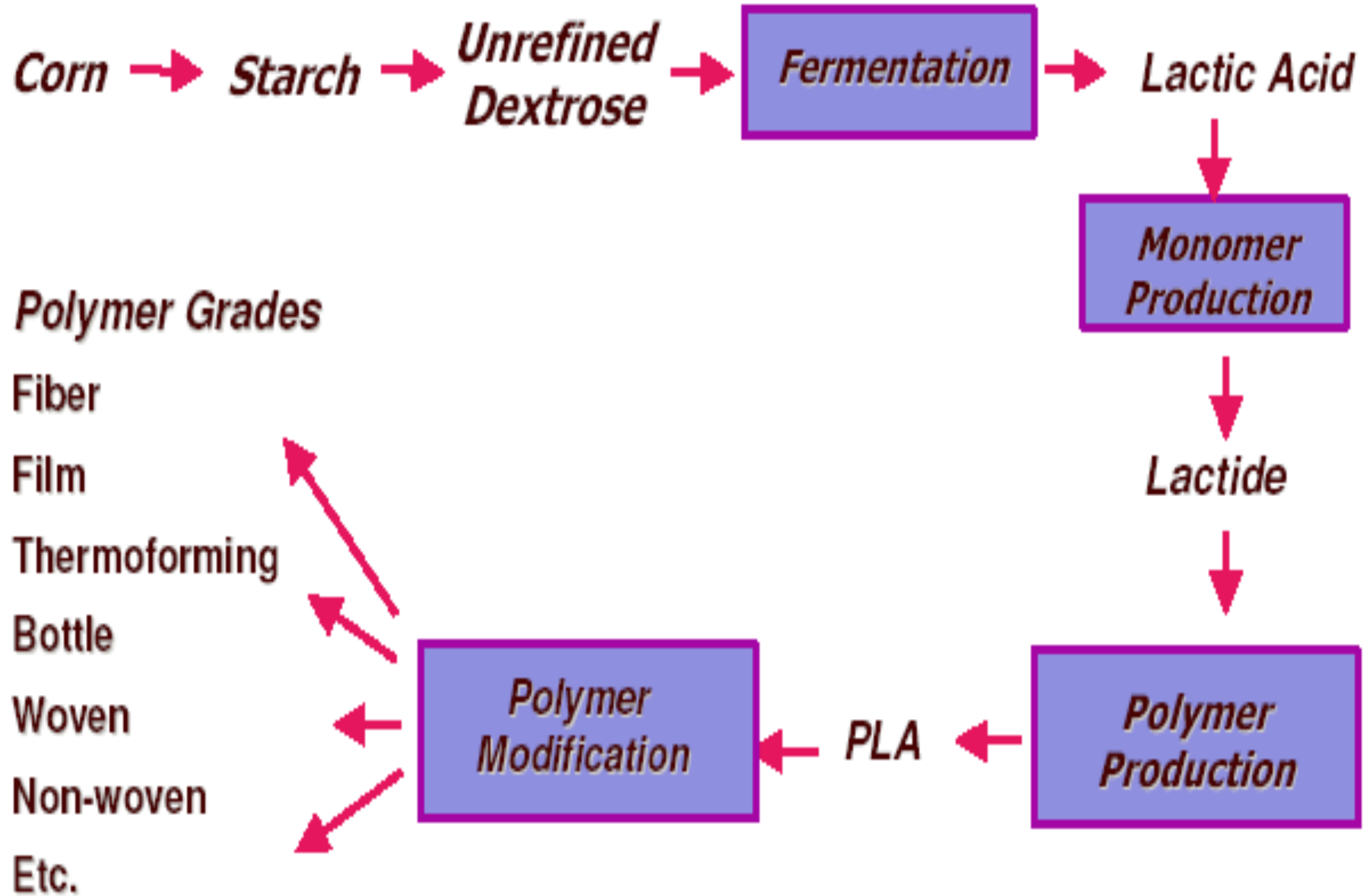


Levulinic acid

Levulinic acid as a platform chemical

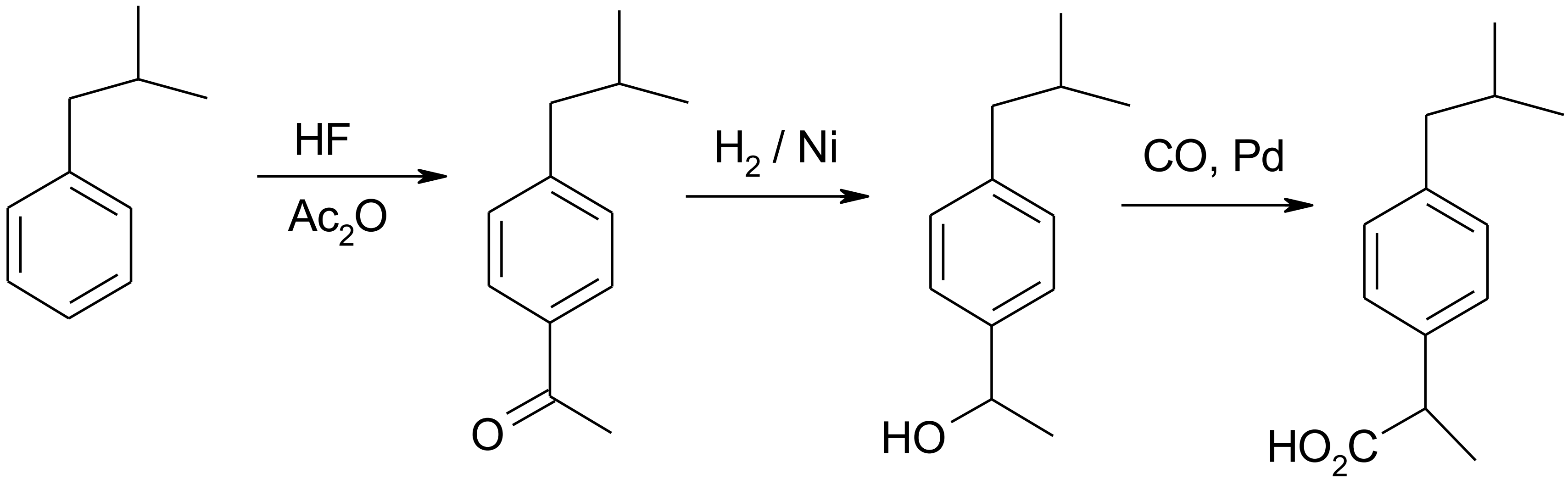


Poly lactic acid (PLA) for plastics production



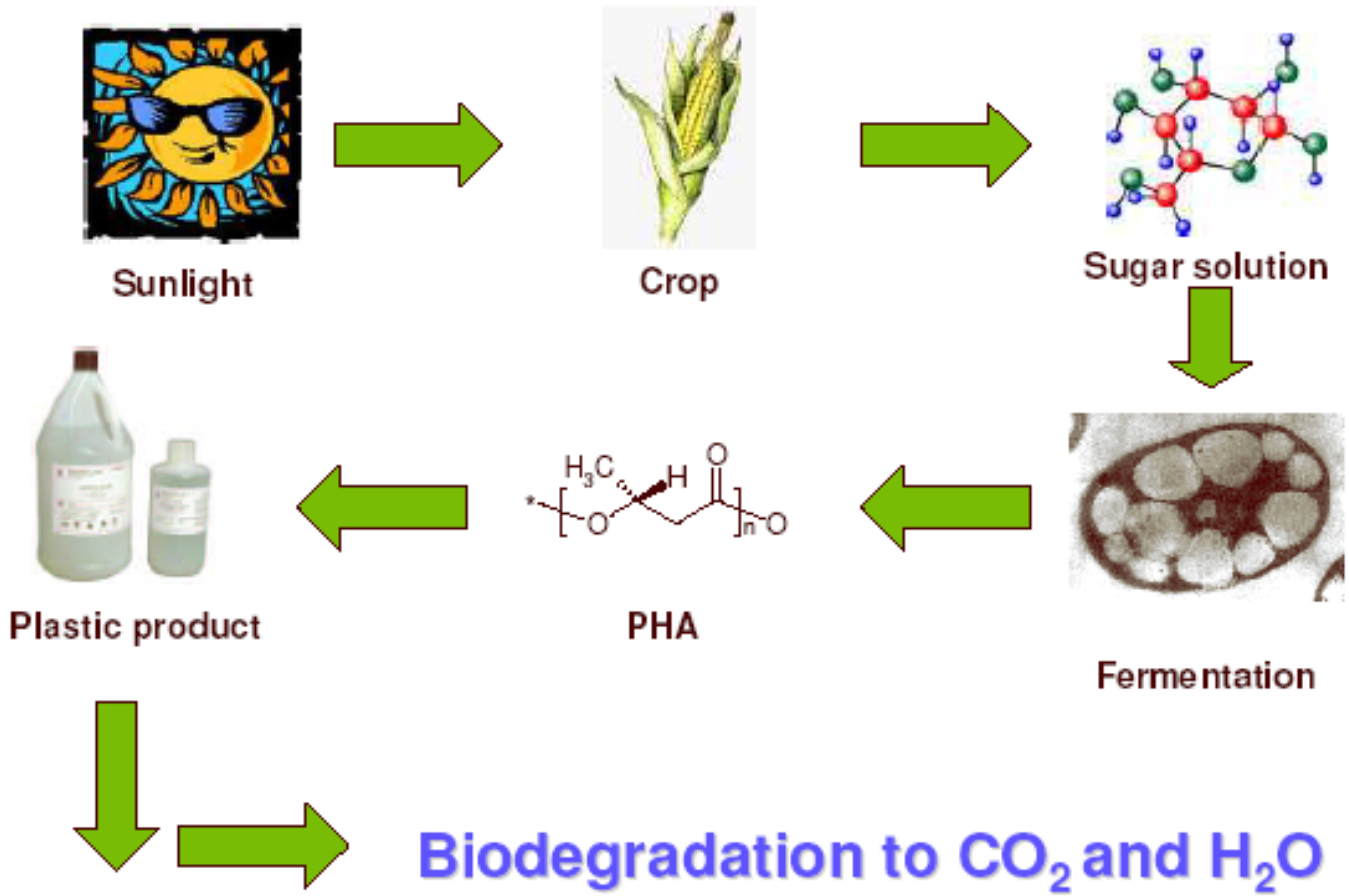
"In 2002, Nature Works, a Cargill company, won a green chemistry award for producing a biodegradable plastic, polylactic acid (PLA), from corn"

Catalysis. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents



Design for Degradation. Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products

Polyhydroxyalkanoates (PHA's)



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.

Inherently Safer Chemistry for Accident Prevention. Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

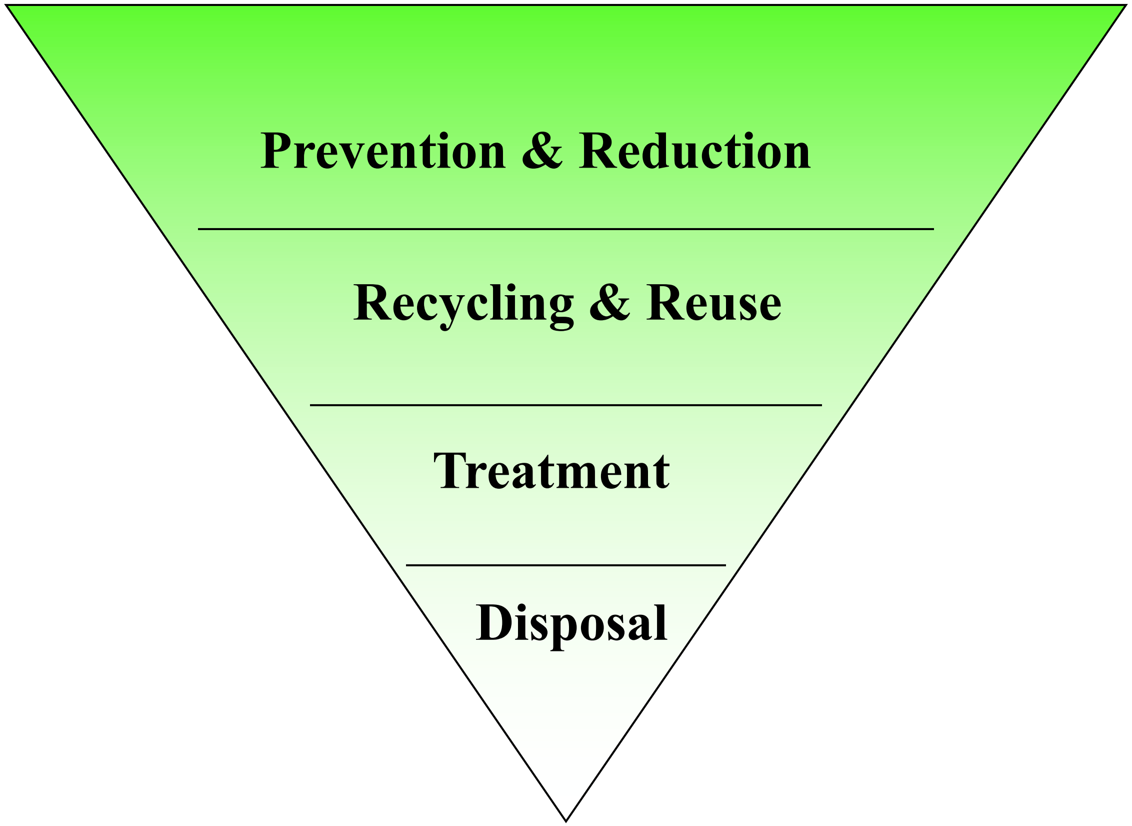
Tragedy in Bhopal, India - 1984

In arguably the worst industrial accident in history, 40 tons of methyl isocyanate were accidentally released when a holding tank overheated at a Union Carbide pesticide plant, located in the heart of the city of Bhopal. 15,000 people died and hundreds of thousands more were injured.

The major uses of GREEN CHEMISTRY

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

Pollution Prevention Hierarchy



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