CONTENTS

DEFINITION

- Green chemistry is also known as environmentally benign chemistry or sustainable chemistry
- Paul Anastas and John Warner, who defined green chemistry as the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.
- Anastas and Warner formulated the twelve principles of green chemistry in 1998. These serve as guidelines for chemists seeking to lower the ecological footprint of the chemicals they produce and the processes by which such chemicals are made.

INTRODUCTION

- Green chemistry is
  - A reaction that utilizes a green liquid.
  - The design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.
  - Anything, including treatment or recycling, that reduces pollution.
  - Any reaction performed by Kermit the Frog or his relatives.

- It is better to prevent waste rather than to clean it up afterwards
- Indigenous development of pollution free technology
- Minimize the risk of potential accidents
- Non stiochiometric use of catalysts.
- reagents, which are used in excess and work only once.
- **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible.

  generate waste.
- **Maximize atom economy.**
- **Use safer solvents and reaction conditions**
- **Increase energy efficiency.**
- **Design chemicals and products to degrade after use.**

INTRODUCTION

- The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances.
  - 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

HOW TO DEAL WITH GREEN CHEMISTRY

- Need to change our mind set
  - to develop the alternatives for energy generation (photovoltaic's, hydrogen, fuel cells, bio based fuels, etc.)
  - continue the path toward energy efficiency with catalysis and product design at the forefront.
  - Reduce the utilization of non-renewable resources, natural
- resources are being depleted at an unsustainable rate.
- Keeping in view Fossil fuels as central issue.
- Future food production intensity
- Minimum utilization of fertilizers.
- Proper utilization of Agriculture wastage for beneficial & profitable use.

Alternative Reagent

- Assessment of the hazard of reagent
- Evaluation of synthetic transformation associated with use of specific reagents
  - determine product sensitivity
  - reaction efficiency
- Improve reaction efficiency
- Reduce needed quantity
  - eg. Choose catalytic reagent to stoichiometric reagent
- Example
- Use of visible light as reagent
- Practical Application of a Biocatalyst in Pharmaceutical Manufacturing
- Use of Microbes as Environmentally-Benign Synthetic Catalysts
- TAML™ Oxidant Activators: General Activation of Hydrogen Peroxide for Green Oxidation Technologies

Alternative Reaction Conditions

- Reduce or eliminate solvents used in reaction media, separations, formulations
  - use of supercritical fluids as solvents
  - able to tune supercritical fluids by choosing critical region to conduct chemistry
- Use aqueous solvent systems in place of organic solvents in chemical manufacturing
- Use Supercritical CO_2 as a solvent
- Reduce operating temperatures
- Must evaluate impact on case by case basis

Alternative Products

- Identify part of molecule that is providing intended use and part of molecule responsible for toxicity or other hazards
- Reduce toxicity w/o sacrificing efficacy of function
  - eliminate toxic functional groups
  - make molecule less bio available
- Pharmaceutical and pesticide manufacturing
- Change or replace products

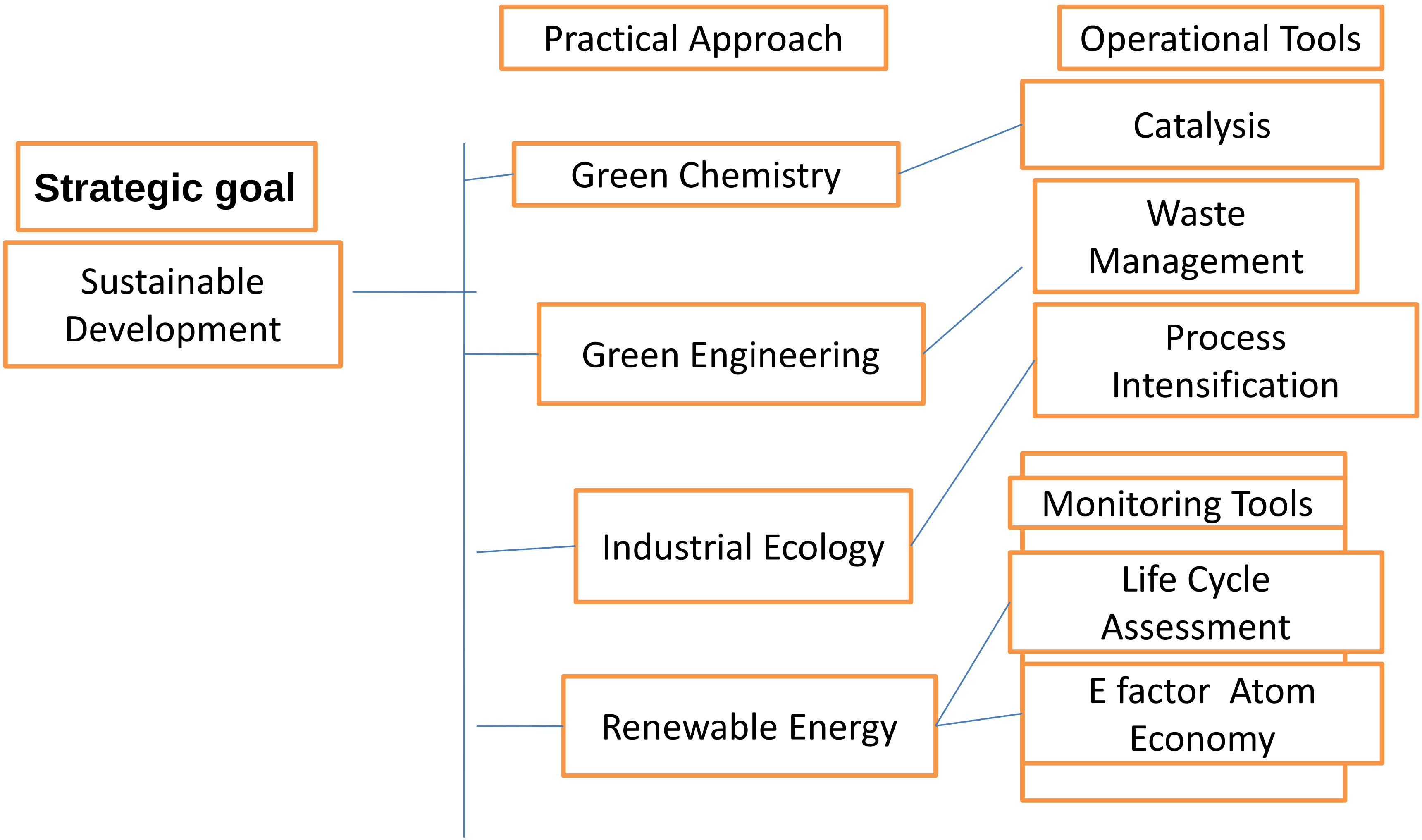
Pollution Prevention Hierarchy

- Prevention & Reduction
- Recycling & Reuse
- Treatment
- Disposal

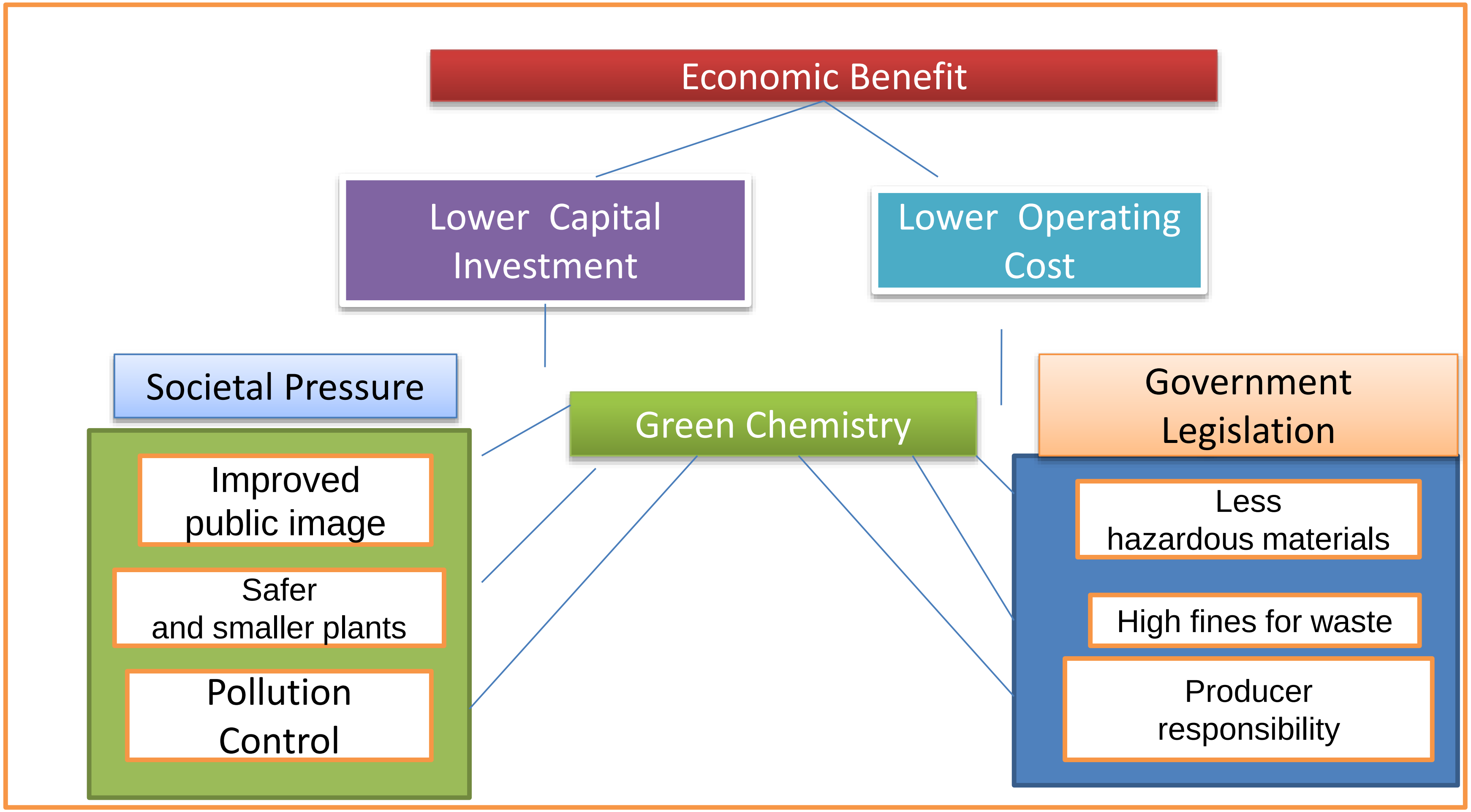
Principles of Green Chemistry

- Paul Anastas of the U.S. Environmental Protection Agency formulated some simple rules of thumb for how sustainability can be achieved in the production of chemicals - the "Green chemical principles":
- Waste prevention instead of remediation
- Atom economy or efficiency
- Use of less hazardous and toxic chemicals
- Safer products by design
- Innocuous solvents and auxiliaries
- Energy efficiency by design
- Preferred use of renewable raw materials
- Shorter syntheses (avoid derivatization)
- Catalytic rather than stoichiometric reagents
- Design products to undergo degradation in the environment
- Analytical methodologies for pollution prevention
- Inherently safer processes

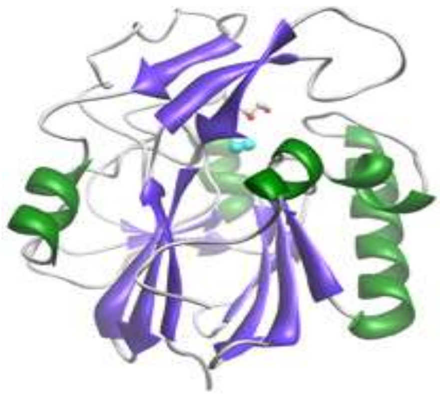
Schematic Diagram of Green Chemistry



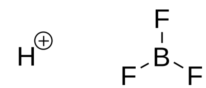
DRIVERS OF GREEN CHEMISTRY



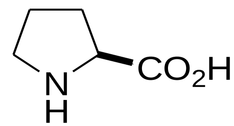
Different Types of Catalysts



Enzyme Bio Catalyst

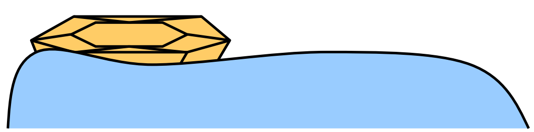


homogeneous acid catalysts

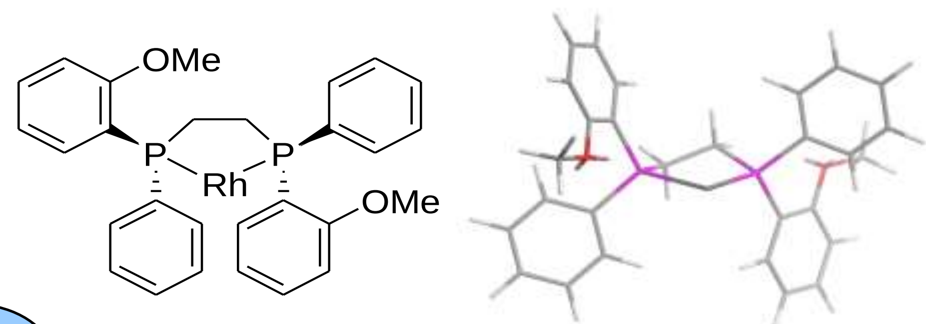


L-proline (organocatalyst)

zeolite (crystalline aluminosilicate)



copper-zinc crystallites on silica



(*R*,*R*)-DiPAMP-Rh (organometallic complex)

APPLICATIONS

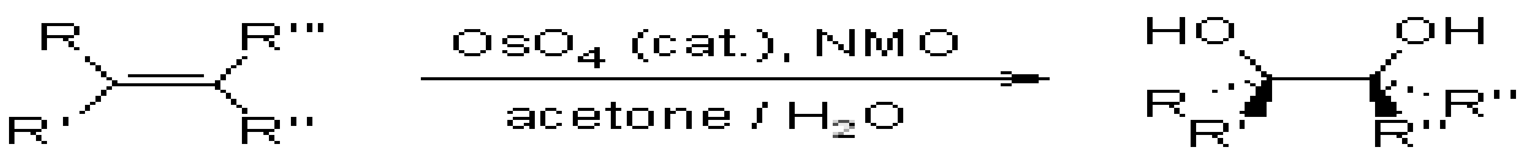
- A typical chemical process generates products and wastes from raw materials such as substrates, solvents and reagents. If most of the reagents and the solvent can be recycled, the mass flow looks quite different:
- the prevention of waste can be achieved if most of the reagents and the solvent are recyclable. For example, catalysts and reagents such as acids and bases that are bound to a solid phase can be filtered off, and can be regenerated (if needed) and reused in a subsequent run. In the production of chemical products on very large scale, heterogeneous catalysts and reagents can be kept stationary while substrates are continuously added and pass through to yield a product that is continuously removed (for example by distillation).
- The mass efficiency of such processes can be judged by the E factor (Environmental factor.
- E factor=Mass of waste/ Mass of product
- Whereas the ideal E factor of 0 is almost achieved in petroleum refining, the production of bulk and fine chemicals gives E factors of between 1 and 50. Typical E factors for the production of pharmaceuticals lie between 25 and 100. Note that water is not considered in this calculation, because this would lead to very high E factors. However, inorganic and organic wastes that are diluted in the aqueous stream must be included. Sometimes it is easier to calculate the E factor from a different viewpoint, since accounting for the losses and exact waste streams is difficult:
- E factor= Mass of Raw material – Mass of Product/ Mass of Product

Experimental atom efficiency = Chemical yield x Theoretical atom efficiency.
Development of green methods is focused on two main aspects:

- Choice of Solvents
- Development of Catalyzed Reactions

Example is Woodward Reaction in development of Steroids

Woodward reaction can be replaced through the use of stoichiometric quantities of OsO_4, but osmium tetroxide is both very toxic and very expensive, making its use on a commercial scale prohibitive. Only in its catalytic variant, which employs *N*-methylmorpholine-*N*-oxide as the stoichiometric oxidant and catalytic quantities of OsO_4, can this be considered a green reaction that can be used on industrial scale.



Upjohn Dihydroxylation

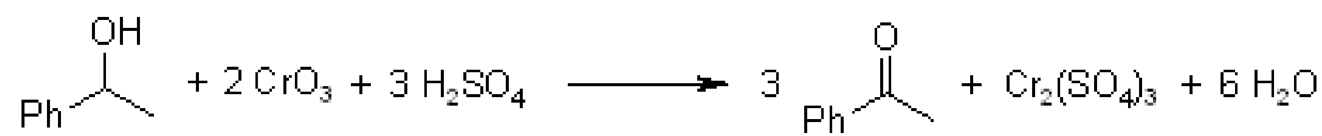
Chemical reactions run under neat conditions (no solvent) and in a supercritical CO_2 medium can also be considered as green choices. Other possible improvements can be considered, such as for example replacement of benzene by toluene (as a less toxic alternative), or use of solvents that can be rapidly degraded by microorganisms.

In any event, the E factor and related factors do not account for any type of toxicity of the wastes. Such a correction factor (an "unfriendliness" quotient, Q) would be 1 if the waste has no impact on the environment, less than 1 if the waste can be recycled or used for another product, and greater than 1 if the wastes are toxic and hazardous. Such discussions are at a very preliminary stage, and E factors can be used directly for comparison purposes as this metric has already been widely adopted in the industry.

Another attempt to calculate the efficiency of chemical reactions that is also widely used is that of atom economy or efficiency. Here the value can be calculated from the chemical equation:

$$\text{atom efficiency} = \frac{\text{molecular weight of desired product}}{\text{molecular weight of all substances formed}} \times 100\%$$

examples:



120 g / mol ▪ 3 392 g / mol 18 g / mol ▪ 6

$$\text{atom efficiency} = \frac{3 \cdot 120}{3 \cdot 120 + 392 + 6 \cdot 18} = 42\%$$

120 g / mol 18 g / mol

$$\text{atom efficiency} = \frac{120}{120 + 18} = 87\%$$

Calculation of Reaction Yield

$$\text{Reaction Yield} = \frac{\text{Quantity of Product isolated}}{\text{Theoretical quantity of product}} \times 100\%$$

The reaction yield is only concerned with the quantity of the desired product that is isolated, relative to the theoretical quantity of the product. Atom economy takes all used reagents and unwanted side products into account along with the desired product. For example, substitutions and eliminations represent the vast majority of uneconomical classical reactions in which inherent wastes are unavoidable

Reaction Mass Efficiency (RME) and Mass Intensity (MI) are additional concepts to evaluate the efficiency of synthetic reactions to take into account the reaction yield

RISK & HAZARDS

- Risk associated with the substance can be calculated by the product of quantifiable hazard and quantifiable exposure to thje hazard.
- Risk = Hazard X Exposure
- By achieving risk reduction through hazard reduction, green chemistry addresses concerns about the cost and potential for failure of exposure controls.
- The term hazard is not restricted to physical hazards such as explosiveness, flammability, and corrosibility, but certainly also includes acute and chronic toxicity, carcinogenicity, and ecological toxicity. It also includes global threats such as global warming, stratospheric ozone depletion, resource depletion and bioaccumulation, and persistent chemicals.

IMPACT OF GREEN CHEMISTRY

- Green Chemistry influences the way of practicing chemistry – be it in teaching children, researching a route to an interesting molecule, carrying out an analytical procedure, manufacturing a chemical or chemical formulation, or designing product

GLOBAL IMPACT

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

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

WHY GREEN CHEMISTRY

- The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances.
  - GREEN CHEMISTRY IS ABOUT
  - Waste Minimisation at Source
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COMPARISON BETWEEN GREEN CHEMISTRY & ENVIRONMENTAL CHEMISTRY

- GREEN CHEMISTRY

- Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substancesEN CHEMISTRY.
- Green chemistry seeks to reduce and prevent pollution at its source.

  Green chemistry applies to organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, physical chemistry and focuses on industrial applications.
- Green Chemistry can be achieved by applying environmentally friendly technologies – some old and some new
- Green chemistry is applicable to all aspects of the product life cycle as well.

- ENVIRONMENTAL CHEMISTRY

- Environmental chemistry is the chemistry of the natural environment, and of pollutant chemicals in nature.
- Environmental chemistry focuses on chemical phenomena in the environment.
- **Environmental chemistry** is the scientific study of the chemical and biochemical phenomena that occur in natural places
- Environmental chemistry is an inter disciplinary science that includes atmospheric, aquatic and soil chemistry heavily relying on analytical chemistry and being related to environmental and other areas of science.

If the chemical reaction of the type

$A + B \longrightarrow P + W$

Find alternate A or B to avoid W

Example 1:

Disinfection of water by chlorination. Chlorine oxidizes the pathogens there by killing them, but at the same time forms harmful chlorinated compounds.

A remedy is to use another oxidant, such as ASCORBIC ACID (Vitamin C) OR Ozone O_3 which boosts aquatic system and is safer , effective neutralization alternative.

O_3 or supercritical water oxidation

Production of allyl alcohol $CH_2{=}CHCH_2OH$

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

$$CH_2{=}\underset{\substack{\uparrow \\ \text{problem}}}{CHCH_2Cl} + H_2O \longrightarrow \underset{\substack{\uparrow \\ \text{product}}}{CH_2{=}CHCH_2OH} + HCl$$

Greener route, to avoid chlorine: Two-step using propylene ($CH_2{=}CHCH_3$), acetic acid (CH_3COOH) and oxygen (O_2)

$$CH_2{=}CHCH_3 + CH_3COOH + 1/_2\ O_2 \longrightarrow CH_2{=}CHCH_2OCOCH_3 + H_2O$$

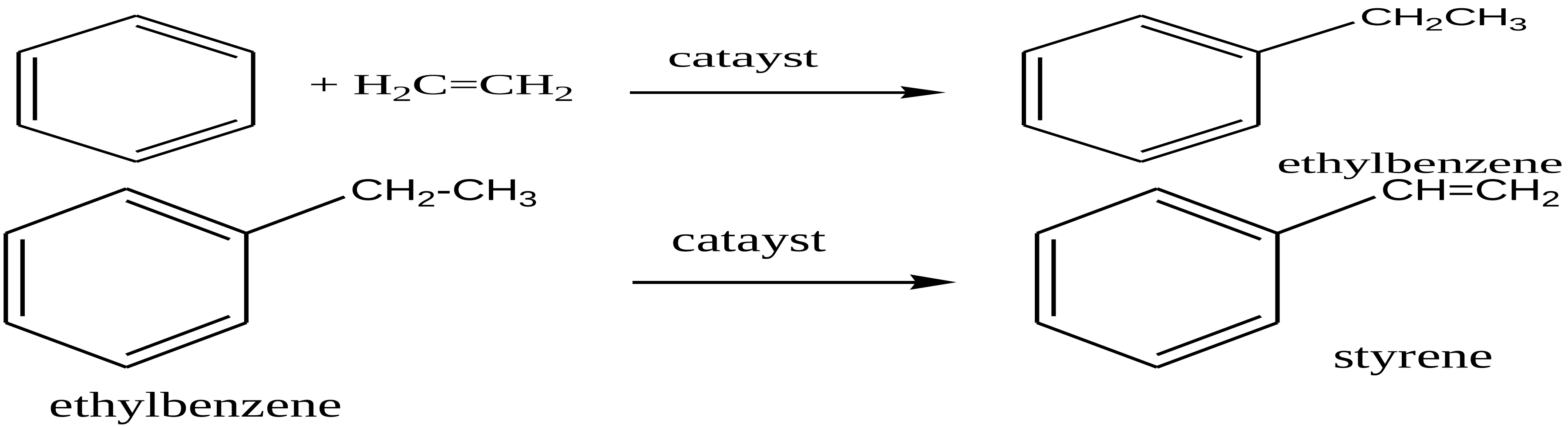
$$CH_2{=}CHCH_2OCOCH_3 + H_2O \longrightarrow CH_2{=}CHCH_2OH + CH_3COOH$$

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

Production of styrene (=benzene ring with $CH=CH_2$ 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 xylene (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).

WHY BIO CATALYST

- Mild conditions: ambient temperature & pressure in water
- Enzymes are derived from renewable source and are biodegradable
- High rates & highly specific : substrate, chemo-, regio-, and enantiospecific
- Higher quality product
- **Green Chemistry (environmental footprint)**

Difference between Catalyst and Enzyme

- Enzymes are biological catalysts, and they are known to be very efficient. They cause rate enhancements, which are in the orders of magnitude greater than that of the best chemical catalysts.
- Catalysts can be either organic or inorganic, and enzymes are organic catalysts.
- Enzymes are specific for substrates. But other catalysts are not so.
- Only a small portion of an enzyme, known as the active site is participating in the catalytic process, which differentiates them from other catalysts.

Difference Between Bio Catalyst & Chemical Catalyst

Bio Catalysts

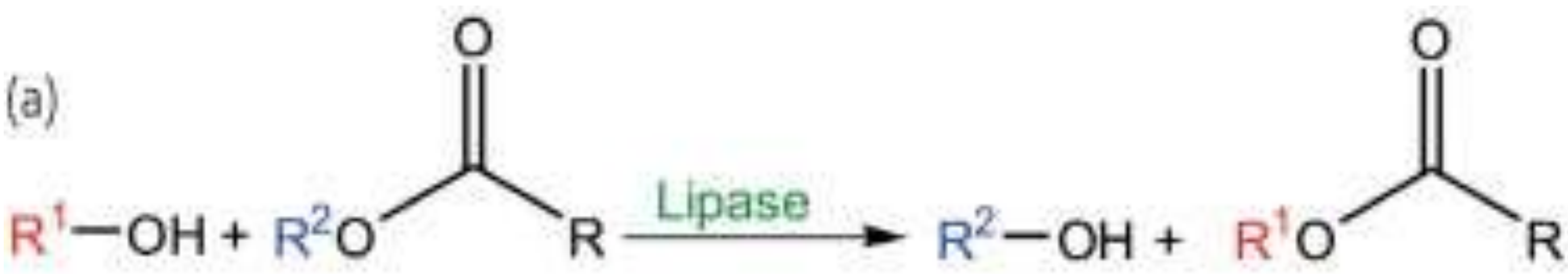
- Biological catalysts or enzymes are high molecular weight globular proteins.
  2.Their composition may change at the end of reaction.
  3.Their catalyzing effect is very high. i.e faster than chemical catalyst.
  4.They are reaction specific. i.e One enzyme or biological catalyst may catalyze only particular type of reaction and not many.
  5.They are intolerant to temperature and pH changes. An enzyme can not function outside its temperature or pH range.
  e.g. amylase ,lipase, pepsin

Chemical Catalysts

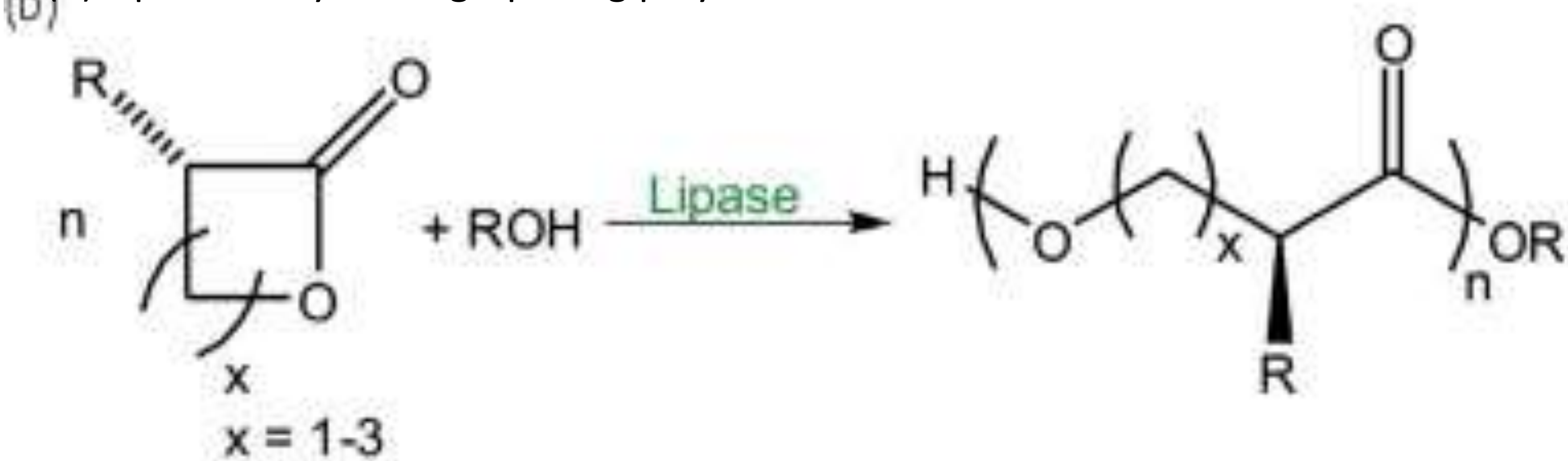
- Chemical catalysts are simple inorganic molecules with low molecular weight.
  2.They remain unchanged at the end of reaction.
  3.They are slower compared to enzymes.
  4.They are not reaction specific.
  5.They function within wide range of temperatures, pH or pressure.
  e.g. vanadium dioxide, platinum

Transesterification..

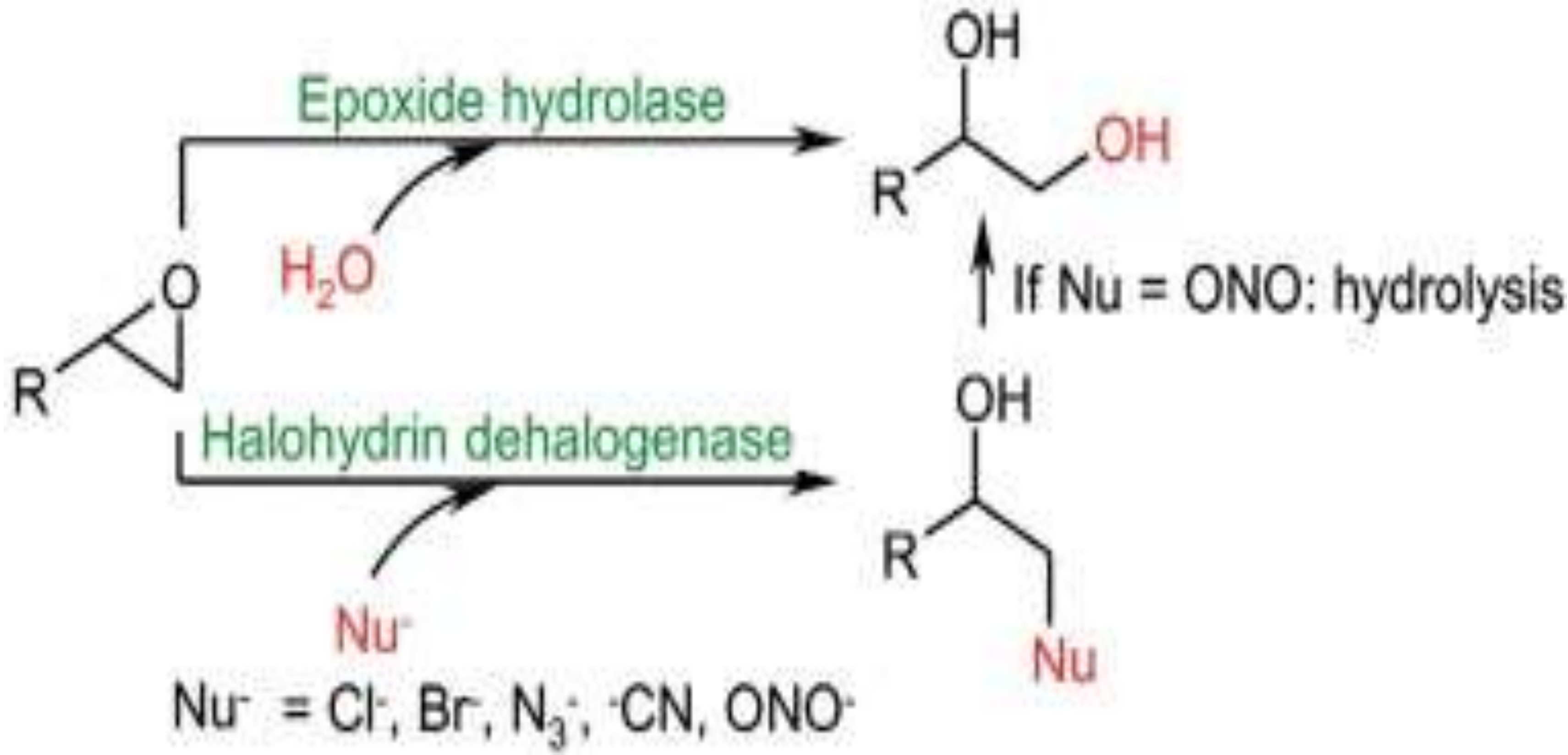
(a) General lipase catalyzed transesterification reaction



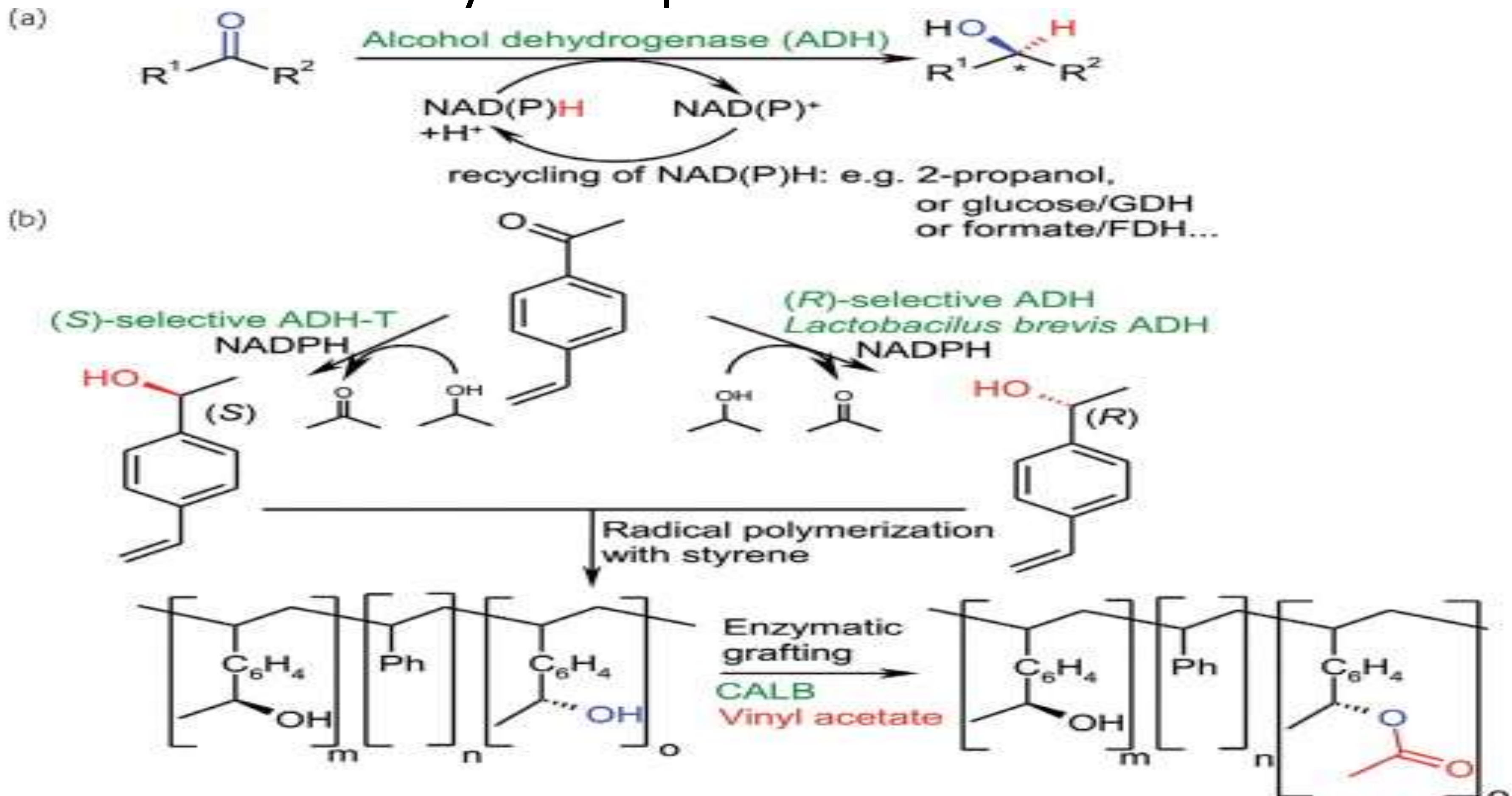
(b) Lipase catalyzed ring-opening polymerization of an α-chiral lactone



Biocatalyzed opening of epoxides by epoxide hydrolases leading to diols and by halohydrin dehalogenases leading to β-substituted alcohol

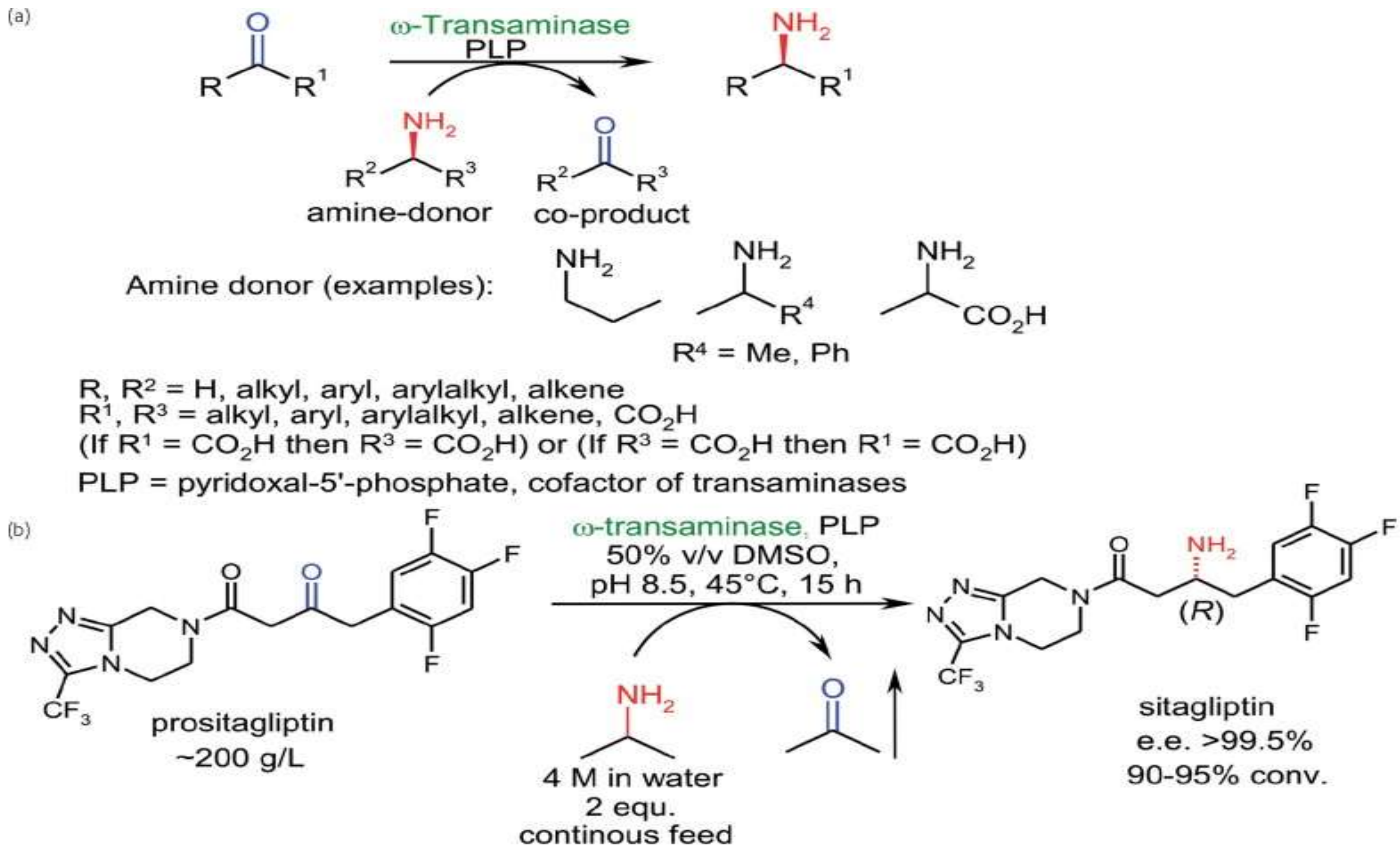


Asymmetric reduction of ketones and application of optically pure monomers for the preparation of an enzyme responsive material.

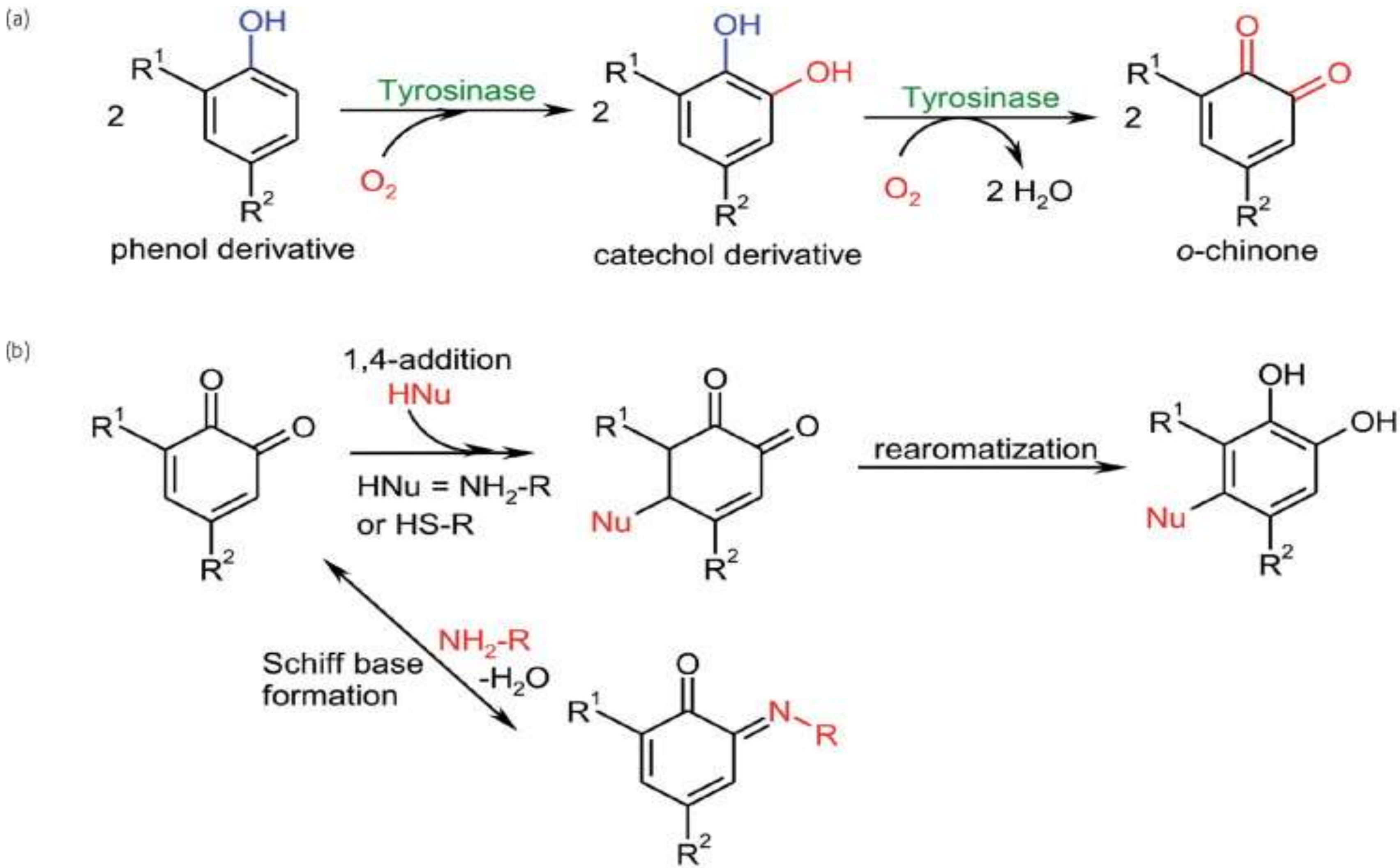


GDH = glucose dehydrogenase
FDH = formate dehydrogenase
CALB = *Candida antarctica* lipase B

(a) Amination of ketones and aldehydes employing ω-transaminases. (b) Employing a modified ω-transaminase the asymmetric amination of a sterically hindered ketone was achieved leading to the preparation of sitagliptin, a drug needed for the treatment of diabetes mellitus type 2.



(a) Oxidation of phenol or catechol derivative to yield o-quinones. (b) Spontaneous follow-up reaction of o-chinones either via a 1,4-Michael addition or Schiff base formation.



APPLICATION OF GREENER CLEANING TECHNOLOGY

- Antibacterial Products
- Laundry
- Water Purification
- Industrial Cleaning

ANTI BACTERIAL PRODUCTS

- Environmentally benign antibacterial agents
  - Alternatives to traditional chlorine or tin containing antibacterial agents
- Applications
  - Bandages, sutures, hospital gowns, acne medication, toothpastes, air filters, antiviral agents
- Magnesiumhydroparaoxyacetate
- HO-O-Mg-OAc
- Magnesium dihydroparoxide
- HO-O-Mg-O-OH

Cleaning Clothes

- TAML catalysts activate hydrogen peroxide
  - Inhibit dye transfer
  - Potential for washing machines that use less water
- Dry cleaning with liquid carbon dioxide
  - current process uses perc (perchloroethylene), a suspected carcinogen and groundwater contaminant
  - new process uses liquid carbon dioxide, a nonflammable, nontoxic, and renewable substance
- Chlorine disinfection
  - Important for preventing disease
  - Toxic to aquatic life
  - Sulfur-based compounds used to neutralize chlorine
- Vitamin C (ascorbic acid)
  - Safer, effective neutralization alternative

CLEANING WATER

- Ultimer^{TM} Polymer Technology
  - manufacture of high molecular weight, water soluble polymers in aqueous salt solution
  - eliminates use of oils and surfactants in manufacture and use
  - uses ammonium sulfate, a waste by-product from the manufacture of caprolactam
  - eliminates need for expensive mixing equipment required for water-in-oil emulsions

Nalco Chemical Company

INDUSTRIAL CLEANING

- Crystal Simple Green®
  - Water based industrial cleaner
  - Non-toxic, biodegradable surfactants
  - Replaces traditional organic solvents
  - Eliminates hazardous waste sludge production and VOC pollution
- Printed circuit boards assembled using Surface Mount Technology (SMT)
  - Lead/tin solder paste stenciled onto substrate
  - Stencils cleaned before reuse
    - CFC solvents
    - Aqueous solvents (high temperature, high pH)
- 440-R SMT Detergent
  - Aqueous-based, contains no VOCs
  - Ultrasonic technology

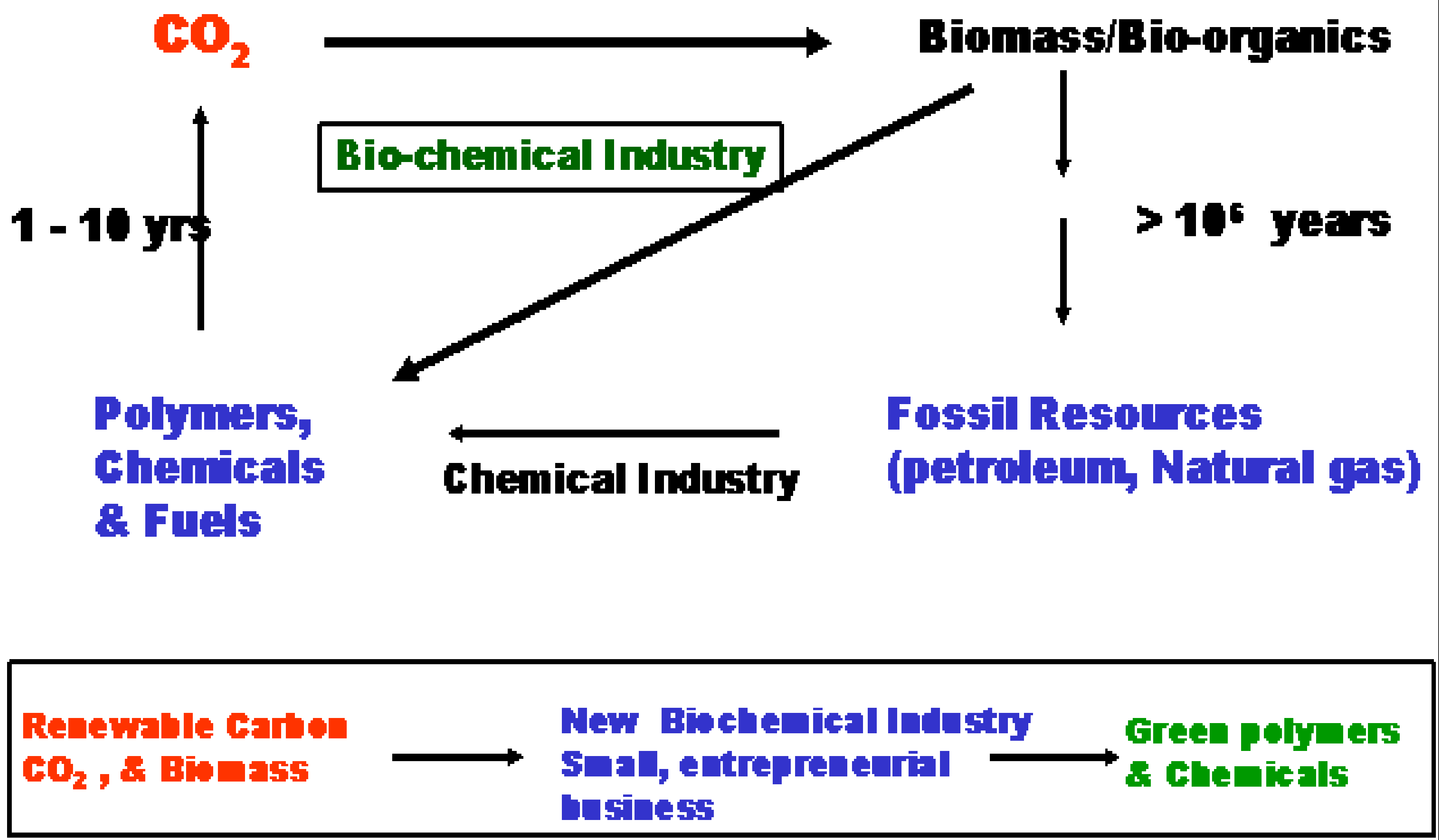
FOOD SUPPLY

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

TOXIC IN 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.

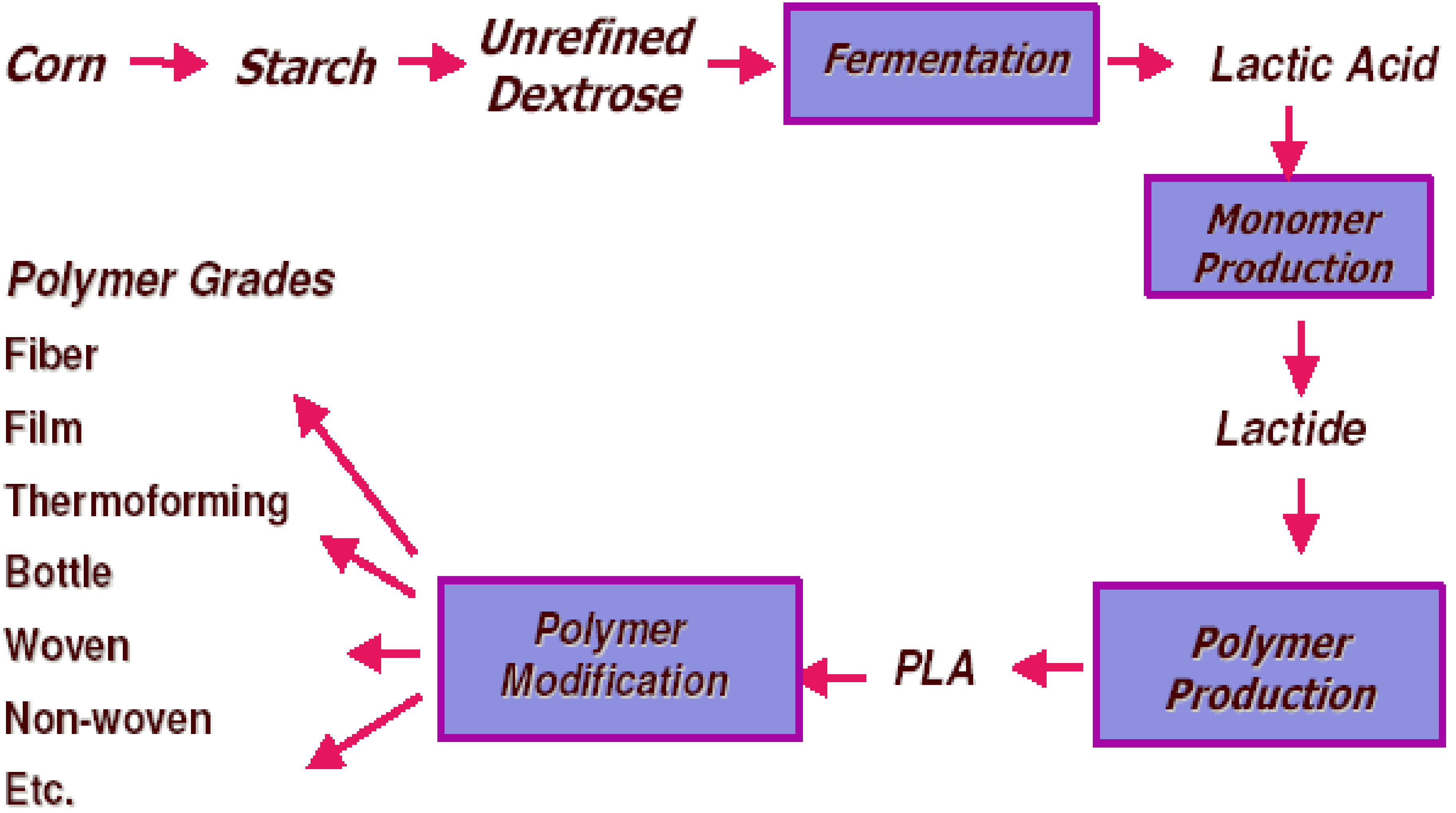
GLOBAL CARBON CYCLING
THE ECO DRIVER



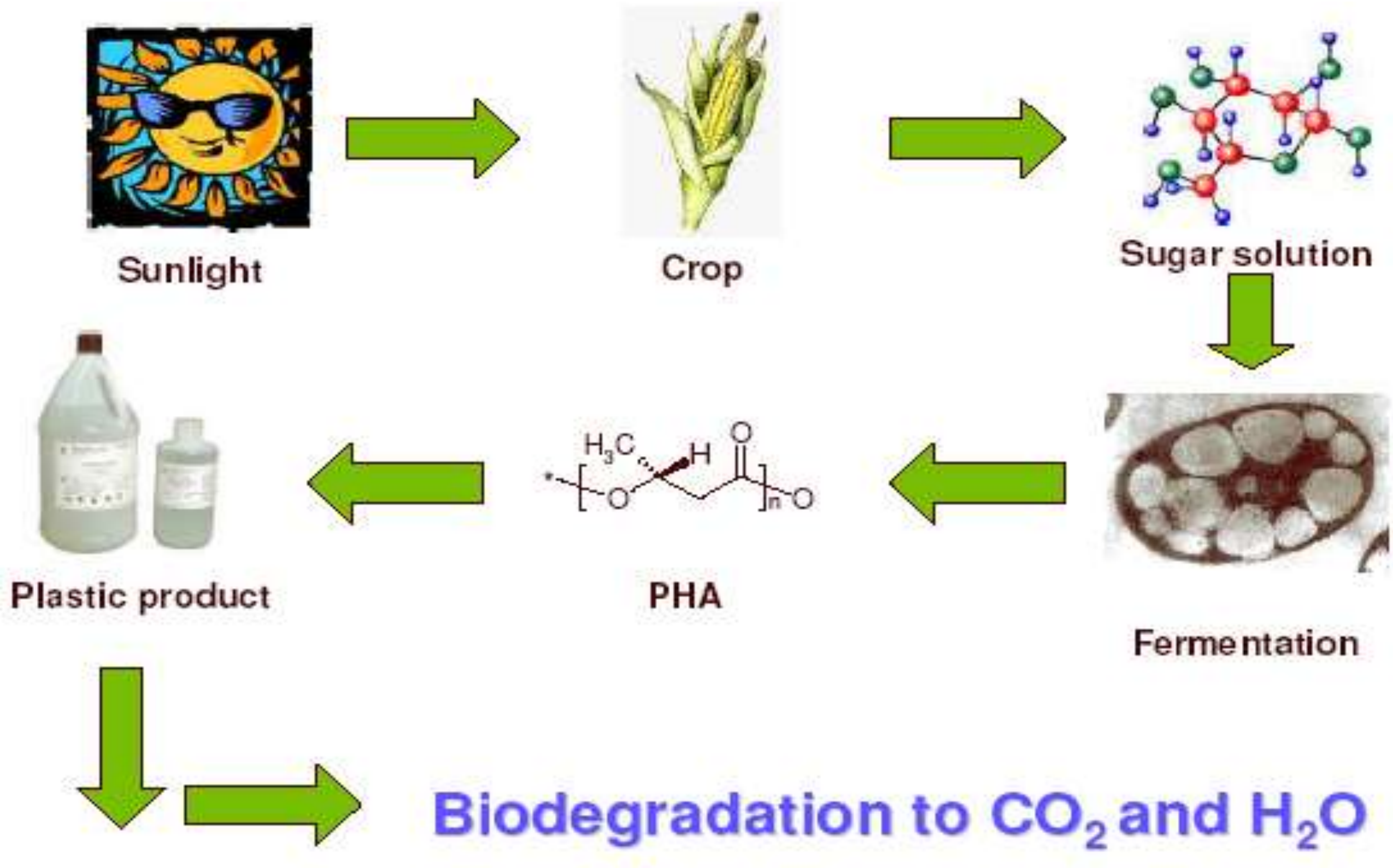
Resource depletion

- Renewable resources can be made increasingly viable technologically and economically through green chemistry.
- Bio Mass Carbon Dioxide
- Nano Science
- Solar Waste Utilization

Poly lactic acid (PLA) for plastics production



Polyhydroxyalkanoates (PHA's



CONCLUSION

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

Thank you