RV College of Engineering®

Section : SPARK

Course: CHEMISTRY OF SMART MATERIALS AND DEVICES

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Syllabus

UNIT-I	Sustainable chemistry and E-waste management:	08 Hrs

Biomaterials: Introduction, bio-degradable and bio-compatible polymeric materials: synthesis and applications (Polymers and hydrogels in drug delivery).

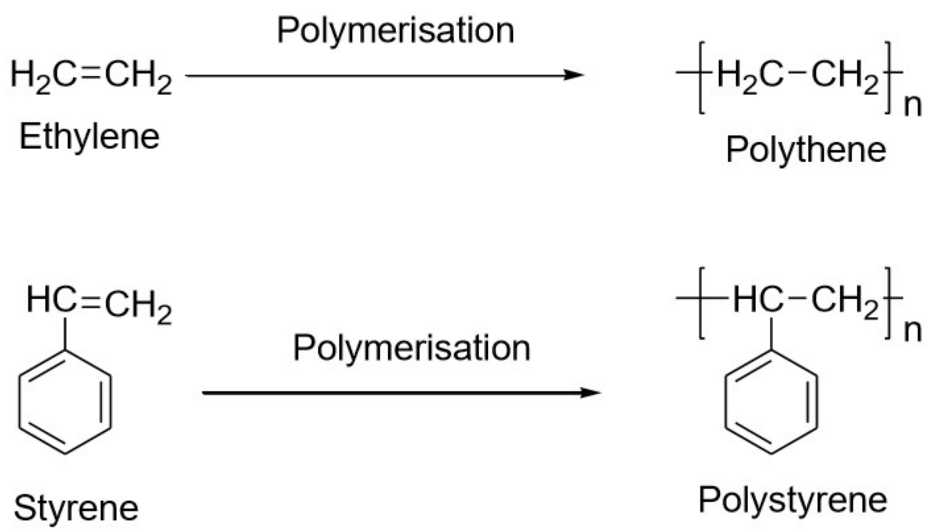
Green Chemistry: Introduction, 12 principles with real life examples, validation of greenness.

E-waste: Hazards and toxicity, segregation and recycling (Hydrometallurgy, pyrometallurgy and direct recycling). Extraction of valuable metals from E-waste. Battery waste management and recycling, circular economy- case studies.

Polymers

- A polymer is a macromolecule having high molecular mass more than 10,000.
- Formation of such molecule requires combination of large number of small molecules. Such small molecules are called **monomers** and they should possess at least two functional groups or unsaturated bonds that can combine with similar or different type of simple molecules.
- The process involved in combining of monomers to get a polymer is called **polymerisation.**
- The number of times the monomer units repeat in a polymer is called **degree of polymerisation.**

Polymerization



Where **n** is called degree of polymerisation.

Classification of Polymers

Polymers are classified in following ways.

Based on method of polymerisation: Addition polymers and Condensation polymers.

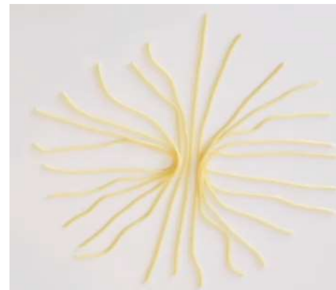
Based on effect of heat: Thermoplastic and thermosetting polymers

Based on the way of repeating units linked: Linear, branched and cross linked polymers.

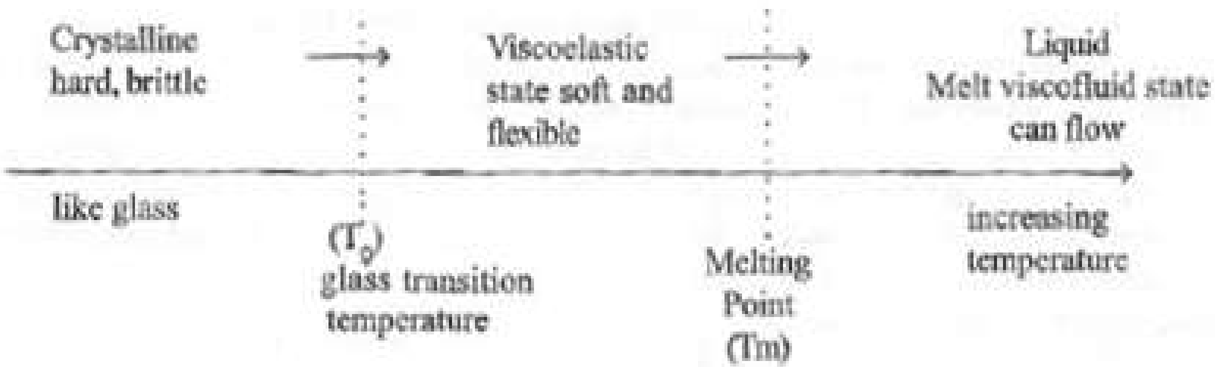
Based on origin: Natural and Synthetic polymers.

Based on arrangement of molecules: Crystalline and amorphous polymers.

Glass Transition Temperature (T_g)



Hard | Rubber ball | fluid



Segmental motion molecular motion

The temperature at which a polymer transforms from **stiff, hard**, **glossy** state to **rubbery state** is called glass transition temperature

- Plastic bucket kept in sunlight and rain for long time loses its lustre and strength.
- This deterioration in properties is due to a phenomenon called 'polymer degradation', which is characterised by an uncontrolled change in the molecular weight or constitution of the polymer.
- The degradation is a reduction in the molecular weight of the polymer.
- "Thus the biodegradable polymers are the polymers which will degrade by the action of naturally occurring microorganisms like bacteria, fungi or sunlight".

Requirements of Biodegradable polymers:

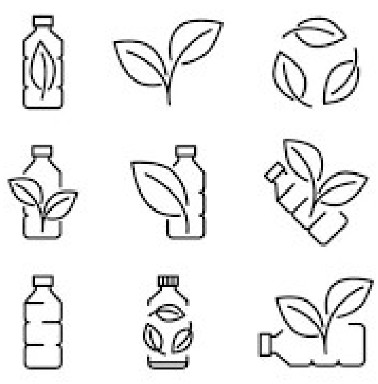
1. Biodegradable polymers should have hydrolysable linkages like esters, amides or ether.
2. They should be hygroscopic in nature.
3. The product formed after degradation should act as compost.

Biodegradable polymers

These are the polymers which gets decomposed by the process of biodegradation.

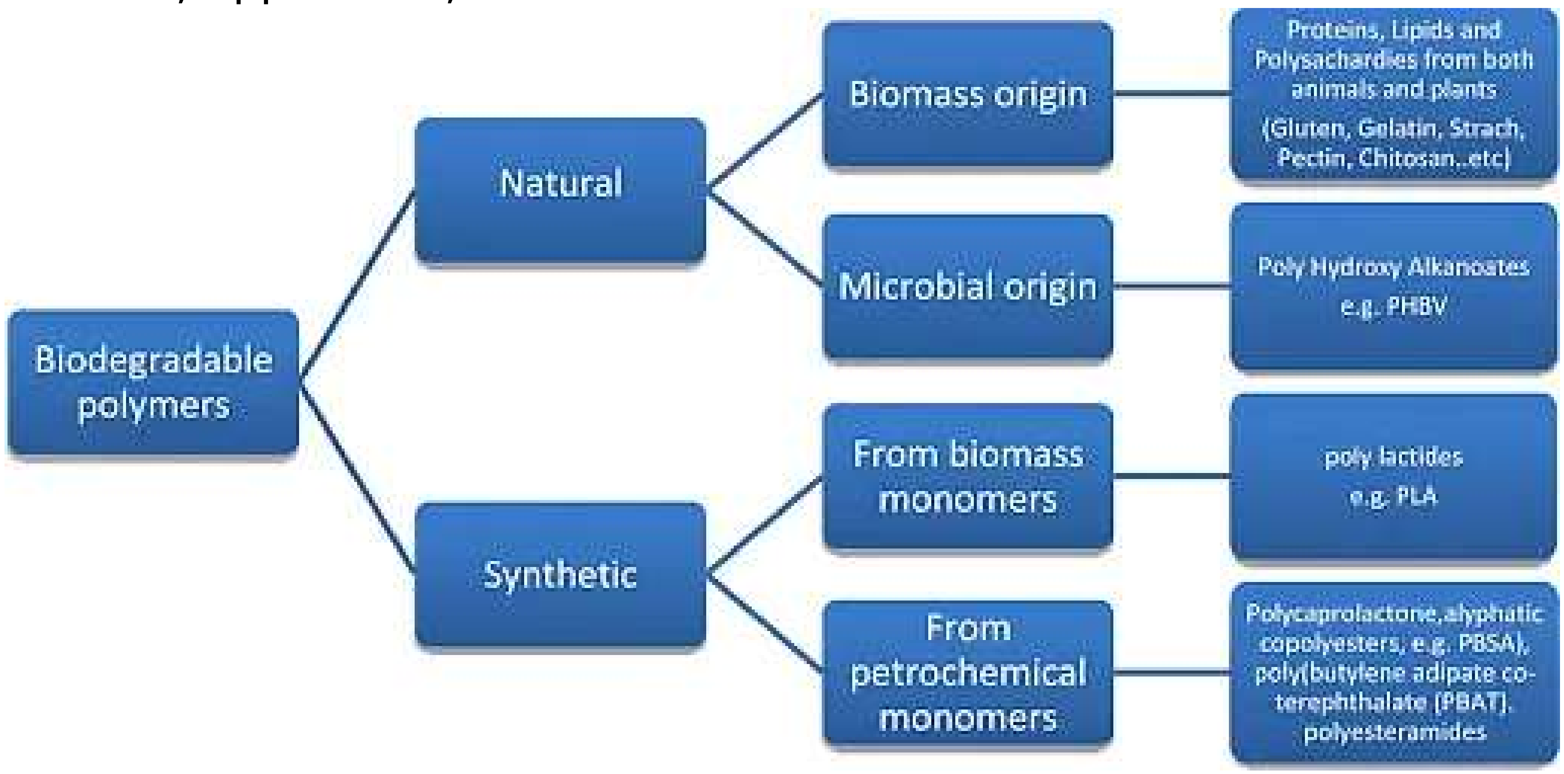
Biodegradation is defined as a process carried out by biological systems usually fungi or bacteria wherein a poly chain is cleaved via enzymatic activity.

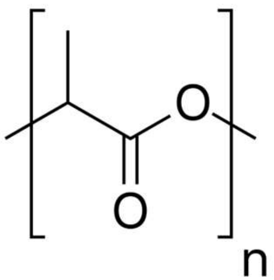
They are broken down into biologically acceptable molecules that are metabolized and removed from the body via normal metabolic pathways. They slowly disappear from the site of administration in response to a chemical reaction such as hydrolysis.

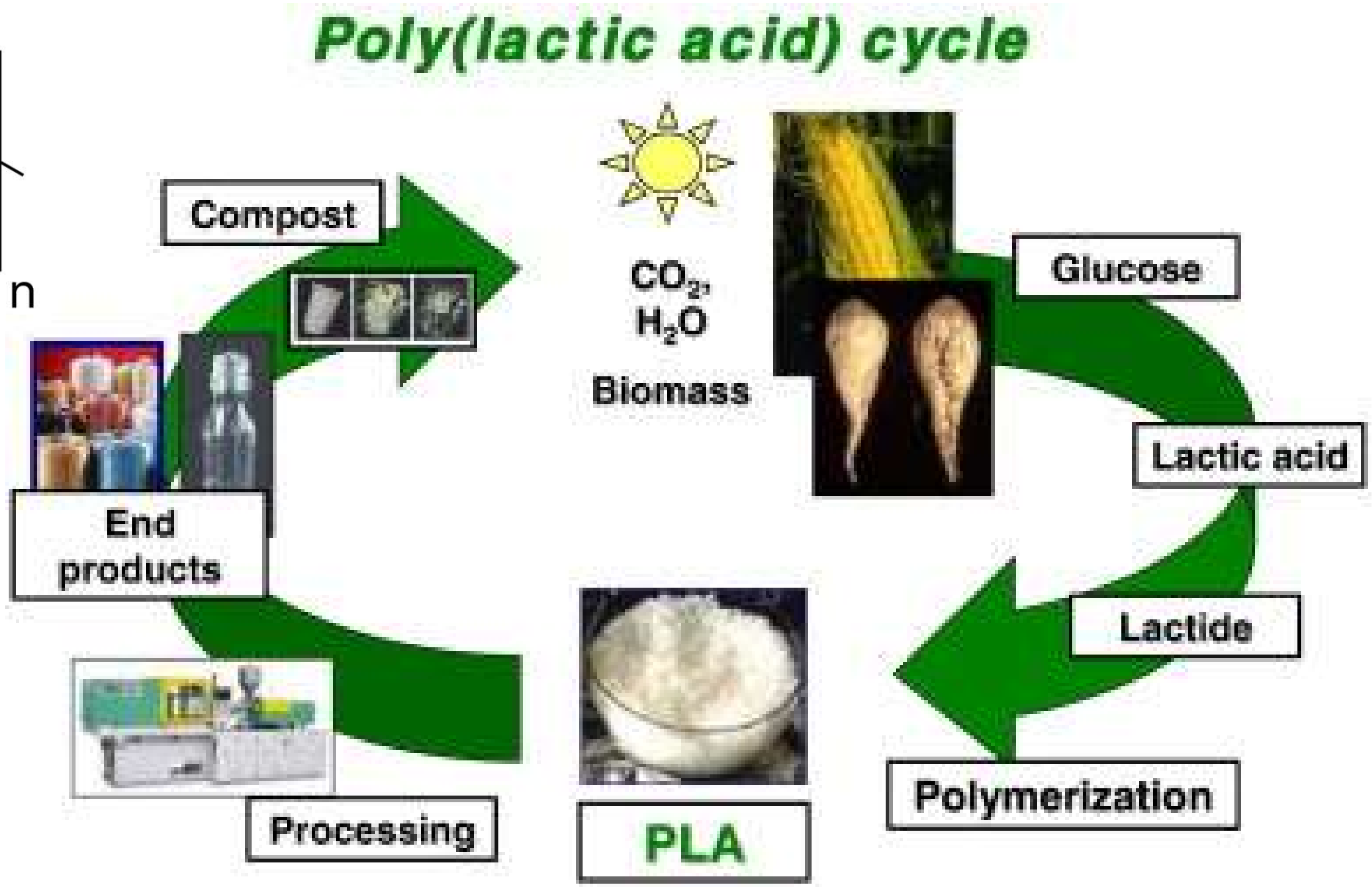


Classification of biodegradable polymers:

- The biodegradable polymers can be classified according to their chemical composition, origin and synthesis method, processing method, economic importance, application, etc.






Poly(lactic acid) cycle
Compost
CO2, H2O
Biomass
Glucose
Lactic acid
Lactide
Polymerization
PLA
Processing
End products

Poly Lactic acid (PLA)

Properties:

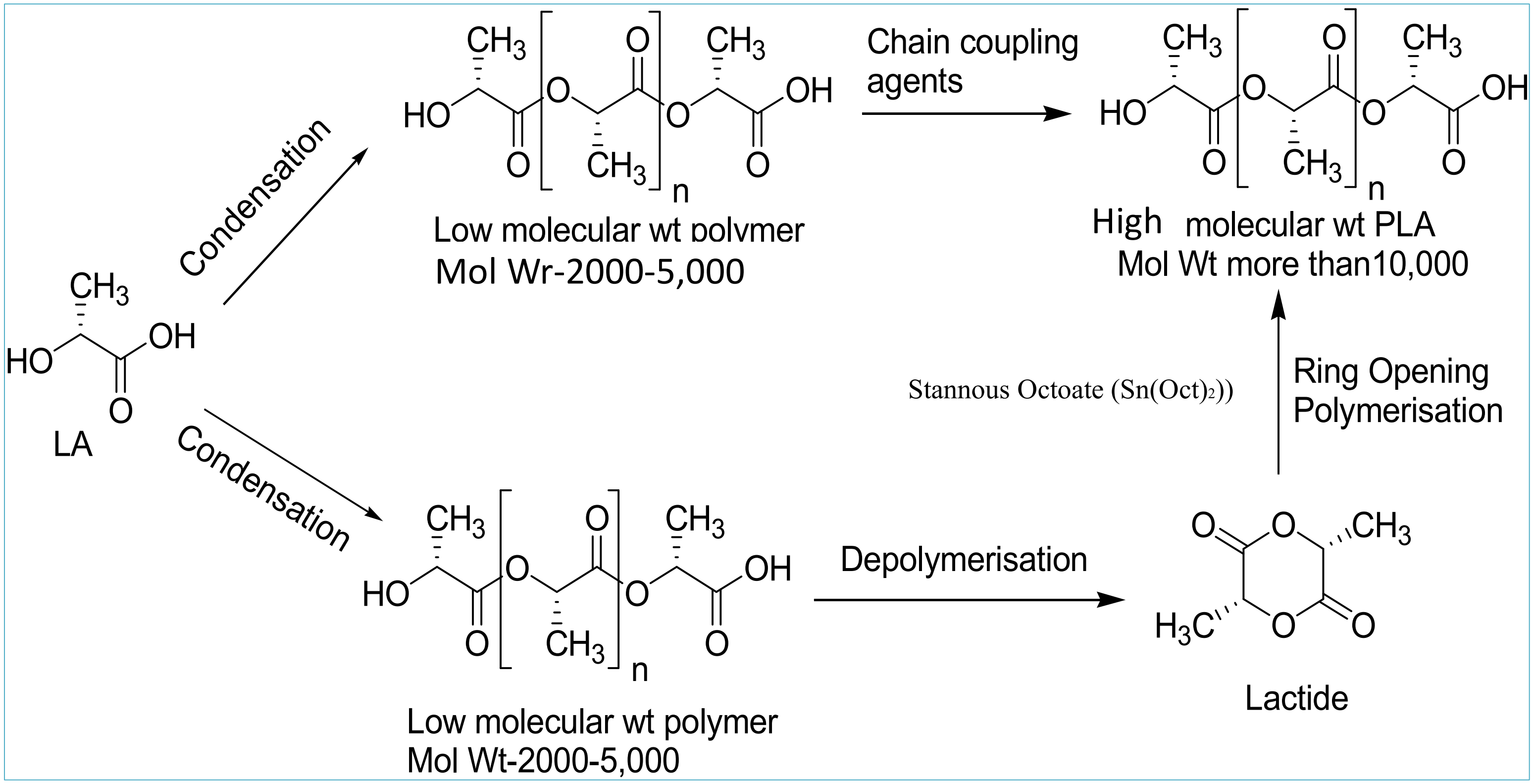
- The PLA is a semi-crystalline polymer with glass transition temperature around 55 to 59 °C and melting point 174-184 °C.
- It shows a good mechanical strength, high Young's modulus, thermal plasticity and has good processability.
- It is unstable in wet conditions, which can undergo chain disruption in the human body and degrades into nontoxic by- products, lactic acid, carbon dioxide and water which are subsequently eliminated through the Krebs cycle and in the urine.

Synthesis of Poly Lactic Acid:

There are two important methods for PLA synthesis:

(i) Direct polycondensation of lactic acid and
(ii) Ring opening polymerization of lactic acid cyclic dimer, known as lactide.

Synthesis of Poly Lactic acid



Note

- In direct condensation, solvent is used and higher reaction times are required.
- Ring-opening polymerization (ROP) of the lactide needs catalyst (Stannous octoate ($Sn(Oct)_2$)) but results in PLA with controlled molecular weight.


Transportation
Electronics industry
Agriculture
Application of Polylactic acid (PLA)
Textile
Packaging
Biomedical industry

Applications of biodegradable polymers

- Polycaprolactum can be used as micropsheres for drug delivery systems.
- Polycaprolactum can be used as medical implants.
- Ultrahigh-strength PLA are used to make bone nails and screws

PLA are used in Fracture fixation and Ligament augmentation

Medical Applications

Wound management
Sutures
Staples
Clips
Adhesives
Surgical meshes

Orthopedic devices
Pins
Rods
Screws
Tacks
Ligaments

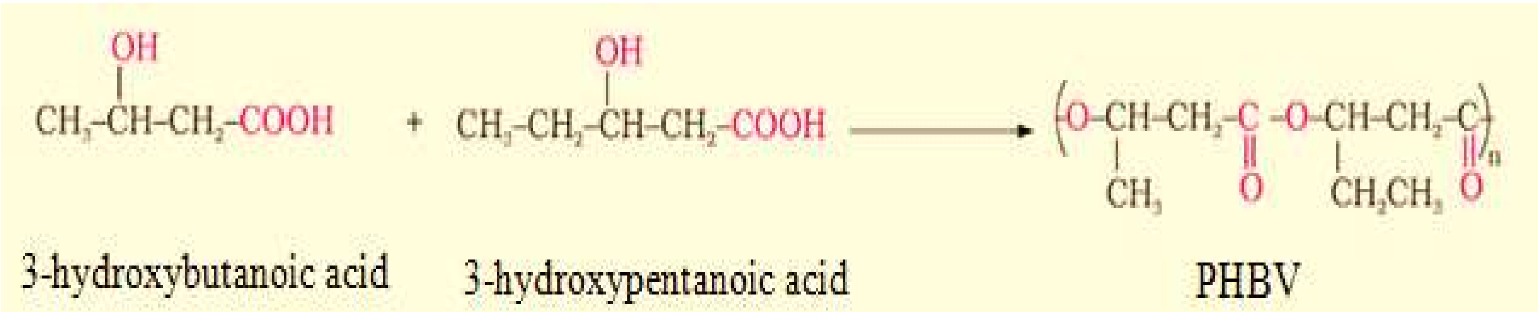
Limitations

- Biodegradable polymers are very expensive.
- They are not easily available.
- In order to store potentially hazardous materials, landfills are built to be free of moisture and air tight. These anaerobic conditions which serve to guard against the release of hazardous chemicals from landfills also retard biodegradation.
- Biodegradable polymers are not suitable candidates in the recycling of commingled plastics.

Bio-compatible polymeric materials:

- Biocompatible polymers are both synthetic (man-made) and natural
- Helps in living system or work with living cells.
- These are used to gauge, treat, boost, or substitute any tissue, organ or function of the body.

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) OR PHBV



It is a thermoplastic linear aliphatic polyester. It is obtained by the copolymerization of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.

PHBV

Properties: It may be biodegradable, nontoxic

- biocompatible plastic produced naturally/synthetic by bacteria and a good alternative for many non-biodegradable synthetic polymers.
- PHBV undergoes bacterial degradation in the environment.

Degradation

When disposed, PHBV undergo bacterial degradation to give carbon dioxide and water.

Applications:

(1) It is used in controlled release of drugs, medical implants and repairs, specialty packaging, orthopaedic devices and manufacturing bottles for consumer goods.

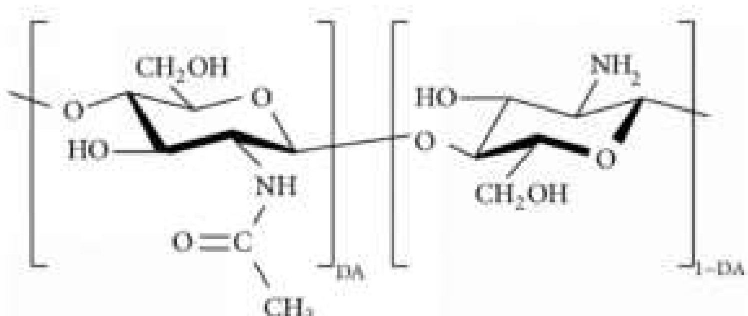
(2) It is also biodegradable which can be used as an alternative to non-biodegradable plastics

Hydrogels

Hydrogels are **crosslinked hydrophilic polymer structures that can imbibe large amounts of water or biological fluids**.

Source – Natural, Synthetic

Natural polymers : includes macromolecule extracted from animal collagen, plants, and seaweed. These natural macromolecules are typically polysaccharides and proteins comprised of glycosidic and amino acid repeating units, respectively. Example cellulose, chitosan etc

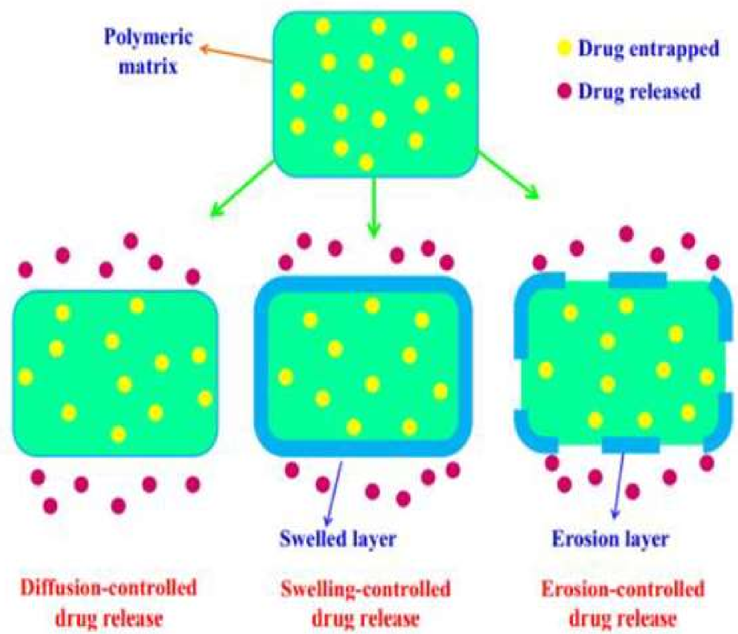


Chitosan it is a polysaccharide synthetically obtained by N-Deacetylation of Chitin

Synthetic Hydrogels : synthetic and biodegradable polymers, aliphatic polyesters such as poly (glycolic acid), poly (lactic acid), poly (caprolactone) and polydioxanone, are most commonly used and applied to drug delivery systems**.** Poly ethylene (PEG), Polyvinyl alcohol (PVA)

Properties of Hydrogels

- mechanical strength
- biocompatibility
- biodegradability
- swell ability
- stimuli sensitivity



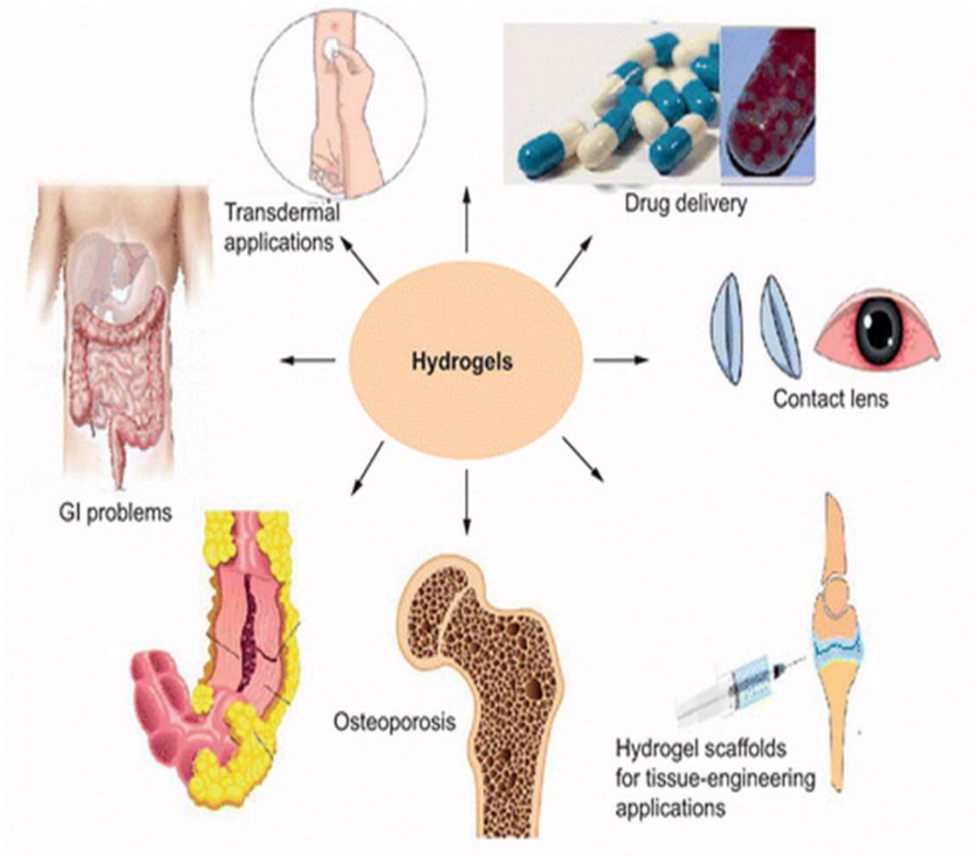
Mechanism of drug release from a polymeric matrix including diffusion, swelling, and erosion controlled methods

Mechanism

The swelling-controlled drug release from hydrogels uses drugs dispersed within a glassy polymer which when in contact with a bio-fluid begins swelling. The expansion during swelling occurs beyond its boundary facilitating the drug diffusion along with the polymer chain relaxation

Applications of Hydrogels

producing contact lenses, hygiene products, wound dressings, drug delivery, tissue engineering



Green Chemistry

GREEN CHEMISTRY

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 defined as environmentally benign chemical synthesis to minimize pollution
- Usage of non toxic starting materials and prevention of hazardous by-products
- Scientists trying for benign green synthesis for new and existing chemicals

Need for Green Chemistry

Minimata Disease * 1950 village in Japan: Disease caused by mercury poisoning (in fish) occurred in Minimata bay of Japan

Itai-Itai Disease *1912 in Japan: Disease caused due cadmium poisoning (in rice). Due to acute pain people cried “Itai-Itai”

Bhopal Gas tragedy *1984 : Union carbide in Bhopal: Methyl isocyanate (MIC) (used manufacturing of insecticide “seven”)

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**

12 principles of Green Chemistry

1. Prevention.

2. Atom Economy

3. Less Hazardous Chemical Synthesis

4. Designing Safer Chemicals

5. Safer Solvents and Auxiliaries

6. Design for Energy Efficiency

7. Use of Renewable Feedstocks

8. Reduce Derivatives

9. Catalysis

10 Design for Degradation

11 Real-time Analysis for Pollution Prevention

12 Inherently Safer Chemistry for Accident Prevention

Prevention

It is better to prevent waste than to treat or clean up waste after it has been created

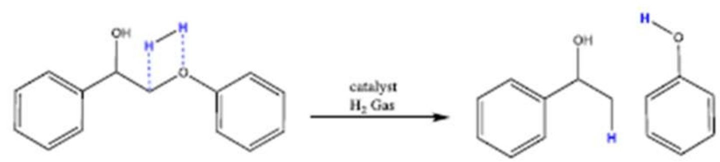
Prevention is better than cure

“It is better to prevent waste than to treat or clean up waste after it is formed”

Chemical Process

No waste

Case Study : Phenols are used widely as intermediates for industrial synthesis and in household products. Conventional method used to obtain phenol is from Petroleum products/derivatives. The alternative way is to obtain from Bio mass waste.



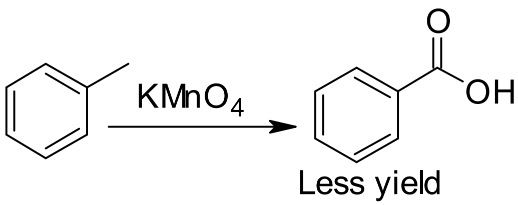
Biomass Phenols

Atom Economy

Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product

$$\% \, yield = \frac{Actual\ yield\ of\ the\ product}{Theoretical\ yield\ of\ the\ product} \text{ X } 100$$

If one mole of starting material produces one mole of the product, the yield is 100%. However , such a synthesis may generate significant amount of waste or by products not visible in the yield calculation



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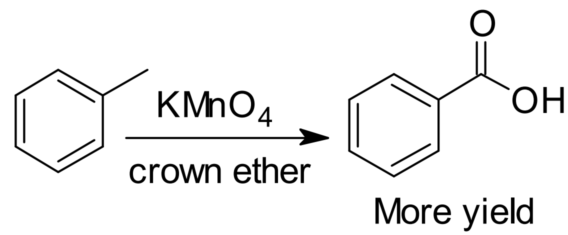


A reaction is considered to be green if there is maximum incorporation of the starting materials or reagents in the final product. One should consider % of atom economy

$$\% \, atom\ economy = \frac{Formula\ weight\ of\ atoms\ utilized}{Formula\ weight\ of\ the\ reactants\ used\ in\ reaction} \text{ X } 100$$

$$H_3C-CH_2-CH_2-CH_2-OH + Na-Br + H_2SO_4 \longrightarrow H_3C-CH_2-CH_2-CH_2-Br + NaHSO_4 + H_2O$$

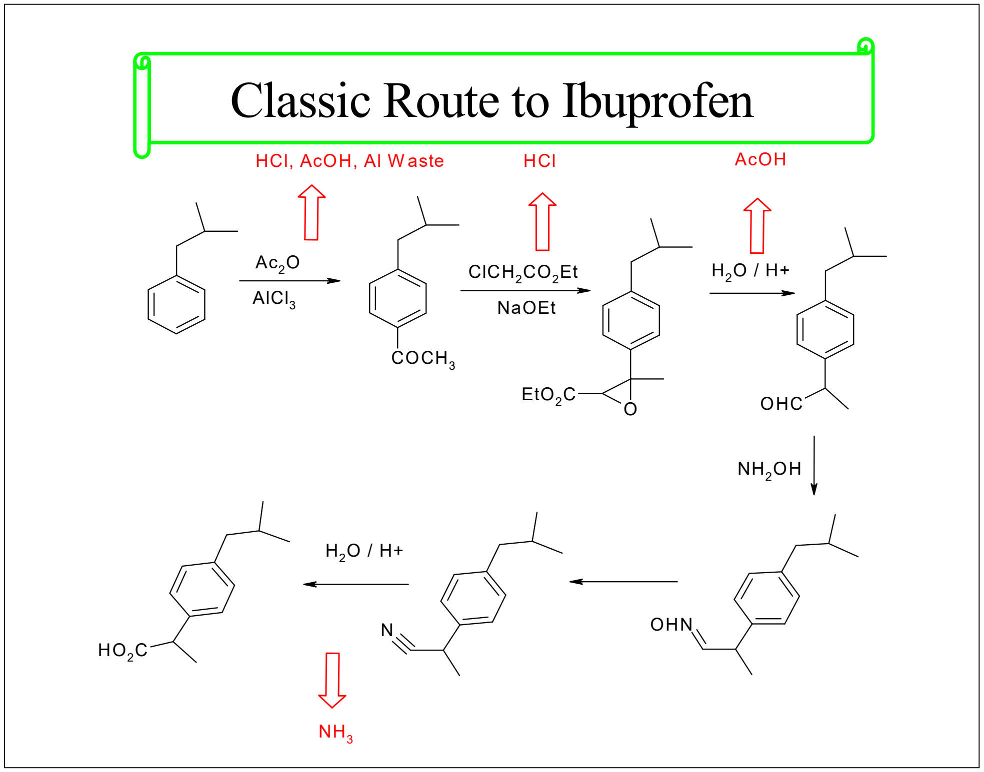
1 2 3 4 5 6

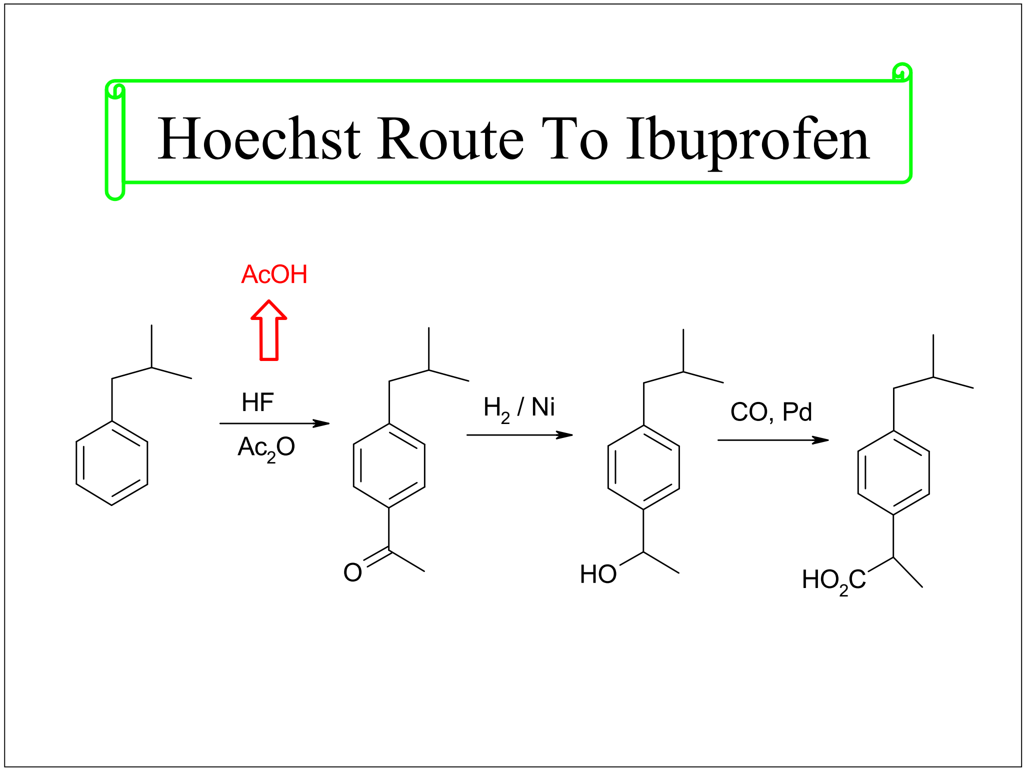
It seen that of all the atoms of the reactants (4C, 12H, 5O, 1Br, 1Na and 1S) only 4C, 9H, and 1Br are utilized in the desired product and the bulk (3H, 5O, 1Na, 1S) are wasted as components of unwanted products. This is an example of poor atom economy!

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
1 C_4H_9OH	74	4C,9H	57	HO	17
2 NaBr	103	Br	80	Na	23
3 H_2SO_4	98	-----	0	2H,4O,S	98
Total 4C,12H,5O,BrNaS	275	4C,9H,Br	137	3H,5O,Na,S	138

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100

= (137/275) X 100 = 50%





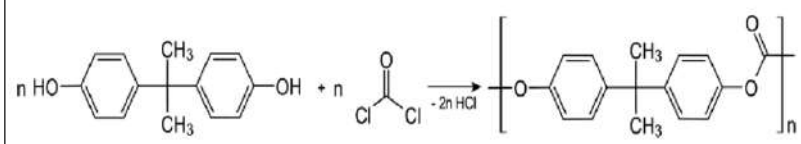
AcOH – Acetic acid

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.

One of the most important principle of green chemistry is to prevent or at least minimize the formation of hazardous products which may be toxic and or environmentally harmful. In case hazardous products are formed their effects on the workers must be minimized by the use of protective clothing, respirator etc. It will add more cost, sometimes control fails causing more risk. Green chemistry offers a scientific option to deal with such situations.

Case study: Synthesis of Polycarbonate: Phosgene process



Monomers: Bisphenol-A and Phosgene

Disadvantages:

(i) Phosgene is highly toxic and corrosive

(ii) It requires large amount of CH_2Cl_2 (Phosgene)

(iii) Polycarbonate is contaminated with Cl impurities

Alternative method (Greenery approach) for above synthesis of Polycarbonate suggested using Bisphenol-A & Diphenyl carbonate.

Its advantages are (i) eliminates the use of phosgene (ii) It produces higher-quality Polycarbonates.

Designing Safer Chemicals

Chemical products should be designed to effect their desired function while minimising their toxicity.

It is extremely important that the chemicals synthesized (dye, paints, cosmetics etc) should be safe to use. A typical example of an unsafe drug is thalidomide (introduced in 1961) for reducing the effects of nausea and vomiting during pregnancy (morning sickness).The children born to those women taking thalidomide suffered birth defects. Later use of thalidomide was banned. It was found thalidomide exists in racemic forms. One enantiomer caused birth defect and another enantiomer was curing morning sickness. With the advancement of technology it is possible to manipulate molecular structure to produce safer chemicals.

Before synthesizing any chemicals we can make use of

(i) Related literature report if already available.

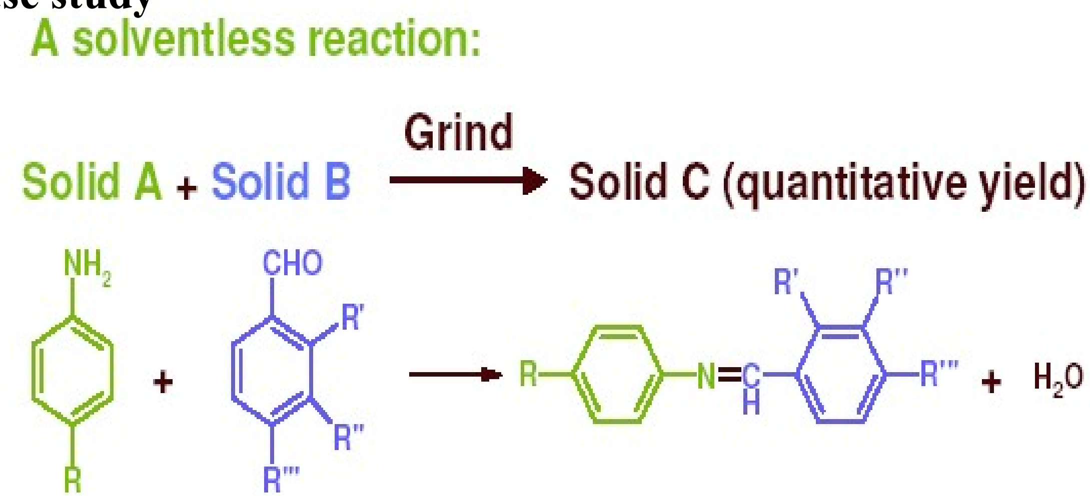
(ii) **Toxicology study** -that involves the study of the adverse effects of chemical substances on living organisms.

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.

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

Case study



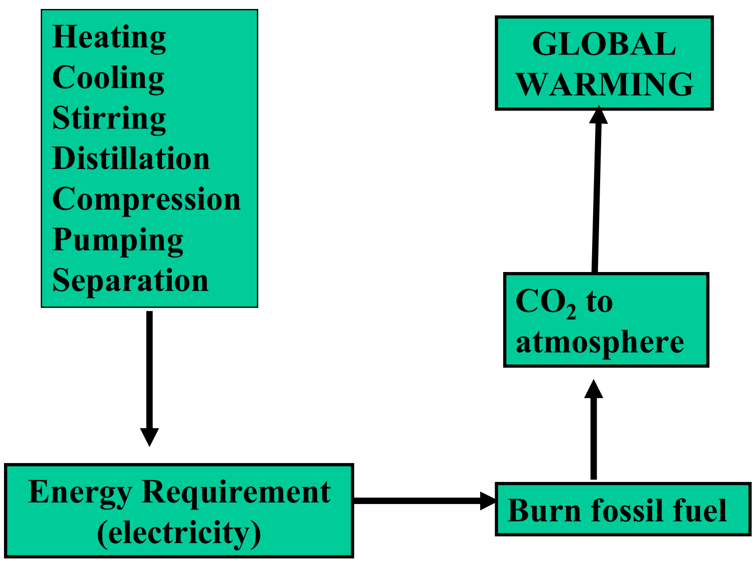
**Mechanochemistry (above reaction as it involves grinding).If done with alcohol it takes 12 hours

Chicken feathers are used in computer chips. Chicken feathers because they have shafts that are hollow but strong and made mostly of air , a good conductor of electricity.

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.

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



Alternatives

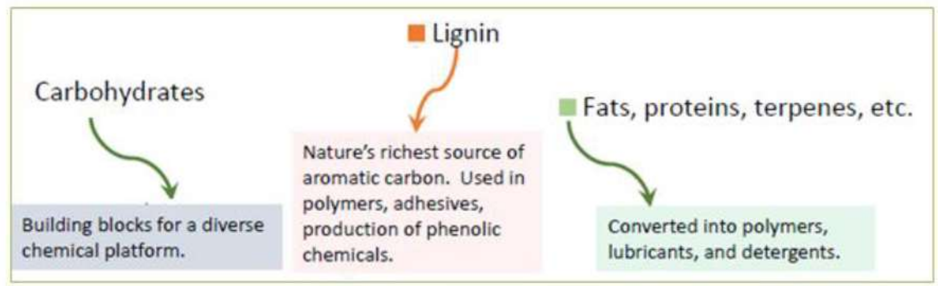
Sonochemistry (ultrasound),
mechanochemistry (grinding) ,
microwave chemistry (high frequency electromagnetic wave),
catalysis, photo assisted synthesis,
green synthesis (Natural products)

Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

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

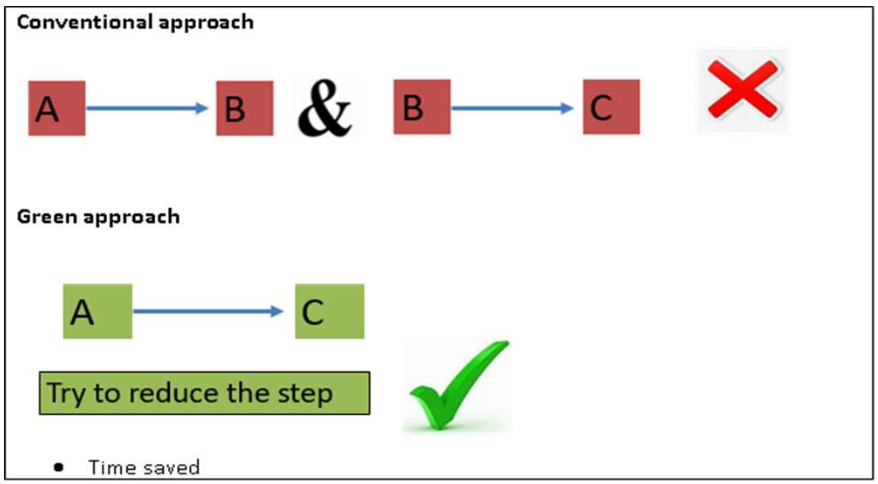
Biomass produced in nature nearly 180 billion metric tons/year. But only 4% utilized by human (food, ethanol, sweetener)



Case study: Producing polymers from renewable resources Polyhydroxyalkanoates (PHAs) are a broadly useful family of natural, environmentally friendly, and high performing, bio based plastics. The development of microorganisms that produce Polyhydroxyalkanoates (PHAs) are from renewable feedstocks such as cornstarch and cellulose hydrolysate.

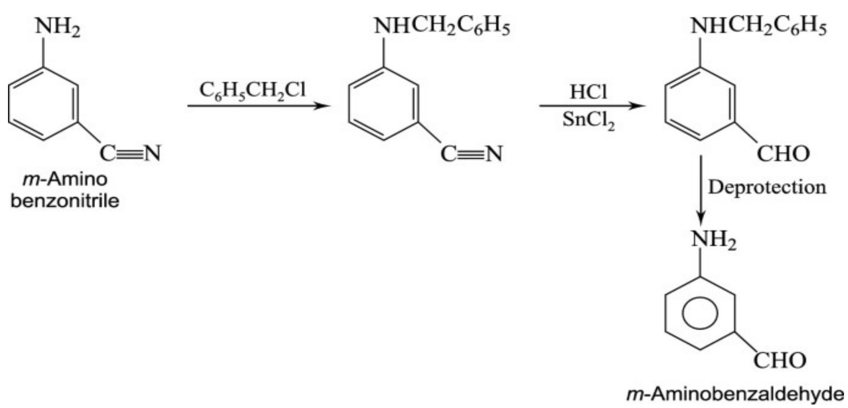
Reduce Derivatives

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.



Case study: Synthesis of **Ibuprofen** developed by the Boots Company of England has 6 step process, with **atom economy 40%** and lot of waste (by-products).

Greenery approach: Contains only 3 steps for the synthesis of Ibuprofen with **atom economy 77 %** with less number by-products.



A commonly used technique in organic synthesis is the use of protecting or blocking group. These groups are used to protect a sensitive moiety from the conditions of the reaction, which may make the reaction to go in an unwanted way if it is left unprotected. A typical example is protection of amine by making benzyl ether in order to carry out a transformation of another group present in the molecule. After the reaction is complete, the NH2 group can be regenerated through cleavage of the benzyl ether

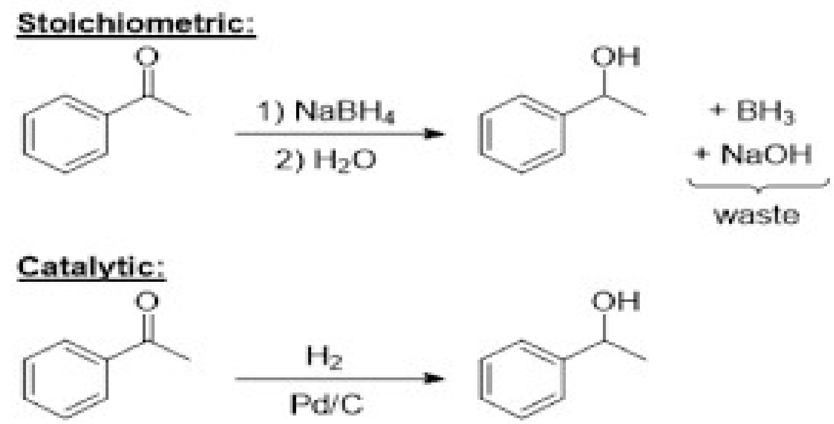
Catalysis

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

Even if the yield is 100% some unreacted starting material will be left over as waste. In some cases if reagents A and B do not give 100 % of the product both excess of unreacted reagents will form part of waste. Catalyst wherever available offer distinct advantages over typical stochiometric reagents. The catalyst facilitates the transformations without being consumed or without being incorporated into the final product.

Hydrogenation of olefins (propene to propane) in presence of nickel catalyst gives much better yields.

$$H_3C\text{-}CH{=}CH_2 + H_2 \xrightarrow{Ni} H_3C\text{-}CH_2\text{-}CH_3$$

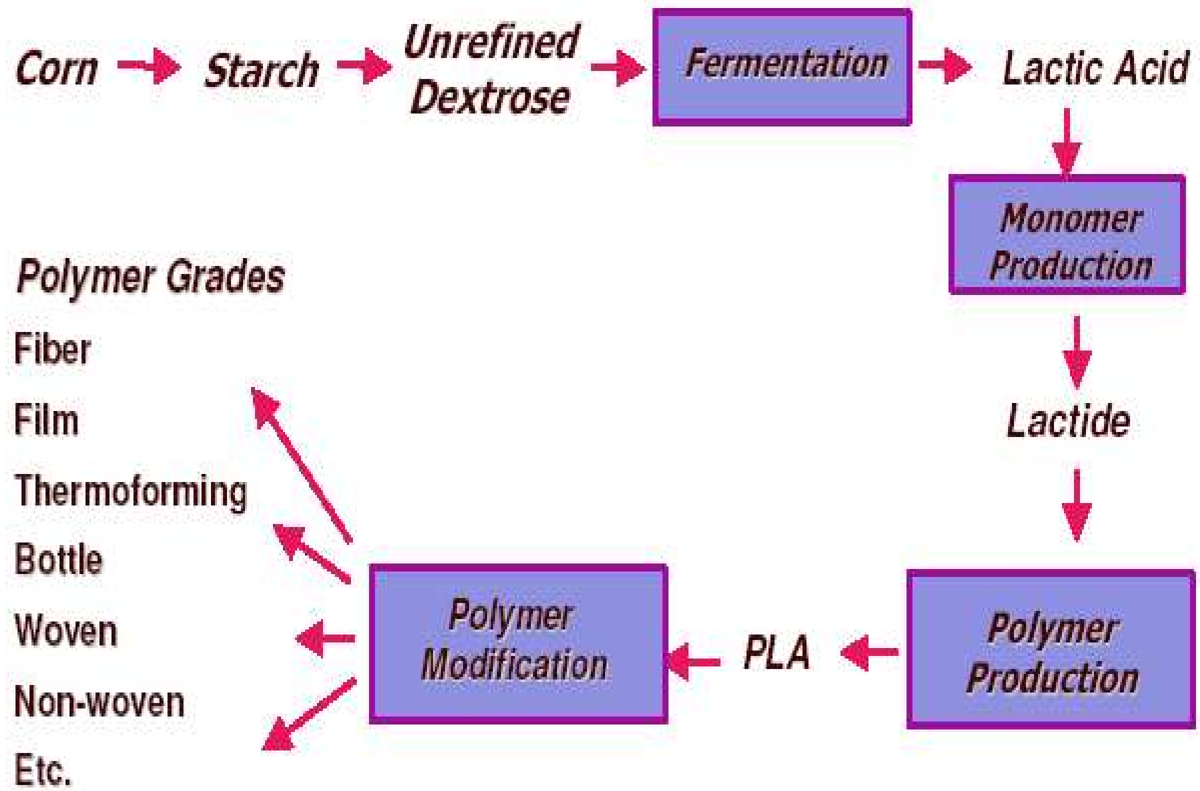


As Pd/C is used highly unsafe

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.

Poly lactic acid (PLA) for plastics production



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.

- Need for accurate and reliable sensors, monitors and analytical techniques to assess the hazards that are present in the process
- Analytical methodologies and technology can prevent accidents which may occur in chemical plants

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.

- The occurrence of accidents in chemical industry must be avoided. The accidents in Bhopal and many others have resulted in the loss of thousands of life
- Possibility in increasing no of accidents, while attempting to minimize waste generation or attempt to recycle solvents
- A process must balance the accident prevention with a desire for preventing pollution
- A possible solution not to use volatile substance, instead solids or low vapour pressure substance can be used

In the end we can say that Green chemistry is not a solution to all environmental problems but the most fundamental approach to prevent/minimize pollution.