



Semester: I/II

CHEMISTRY OF SMART MATERIALS AND DEVICES

(Category: Professional Core Course) Stream: CS (Theory and Practice)

Course Code	:	22CHY12A	CIE	:	100+50 Marks
Credits: L:T:P	:	3:0:1	SEE	:	100 Marks
Total Hours	:	42L+ 30P	SEE Duration	:	3 Hours

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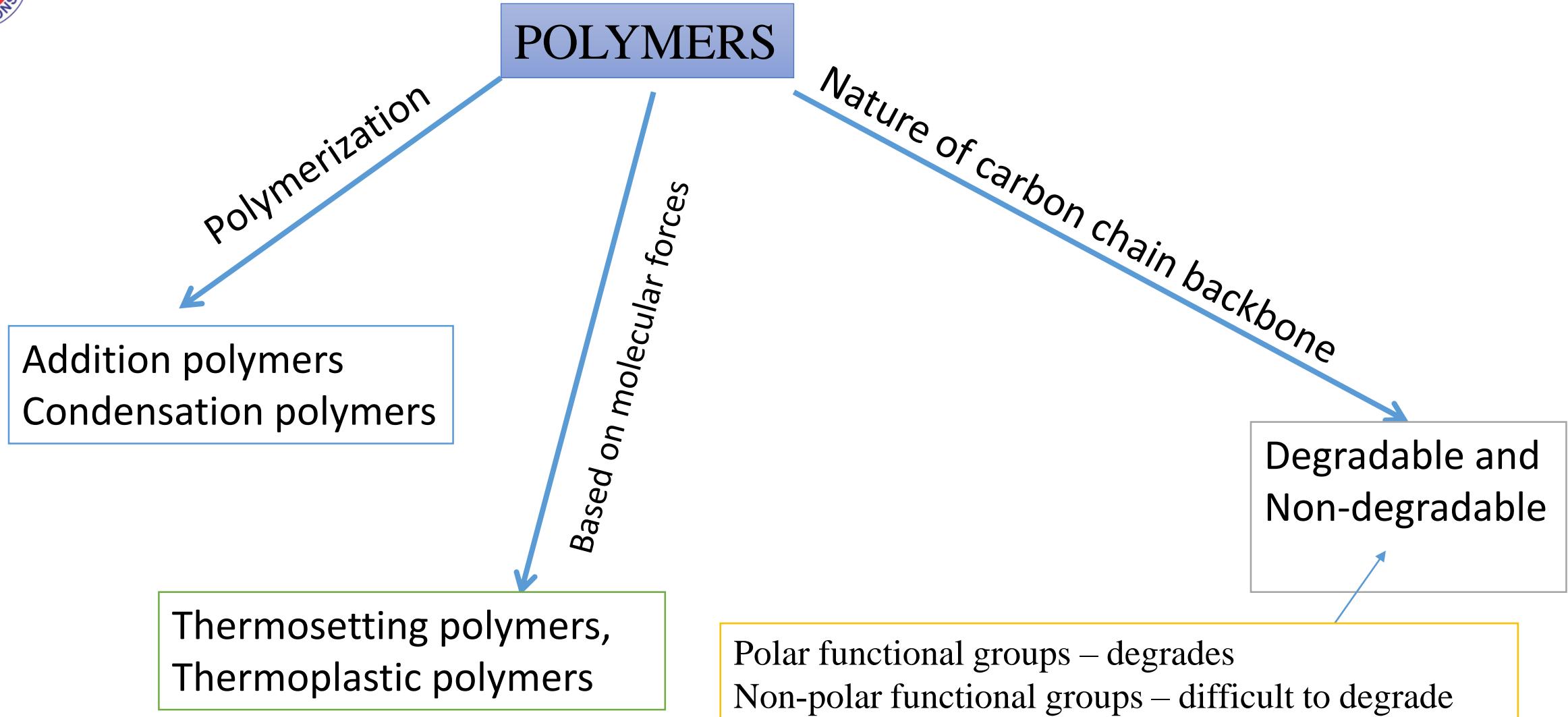
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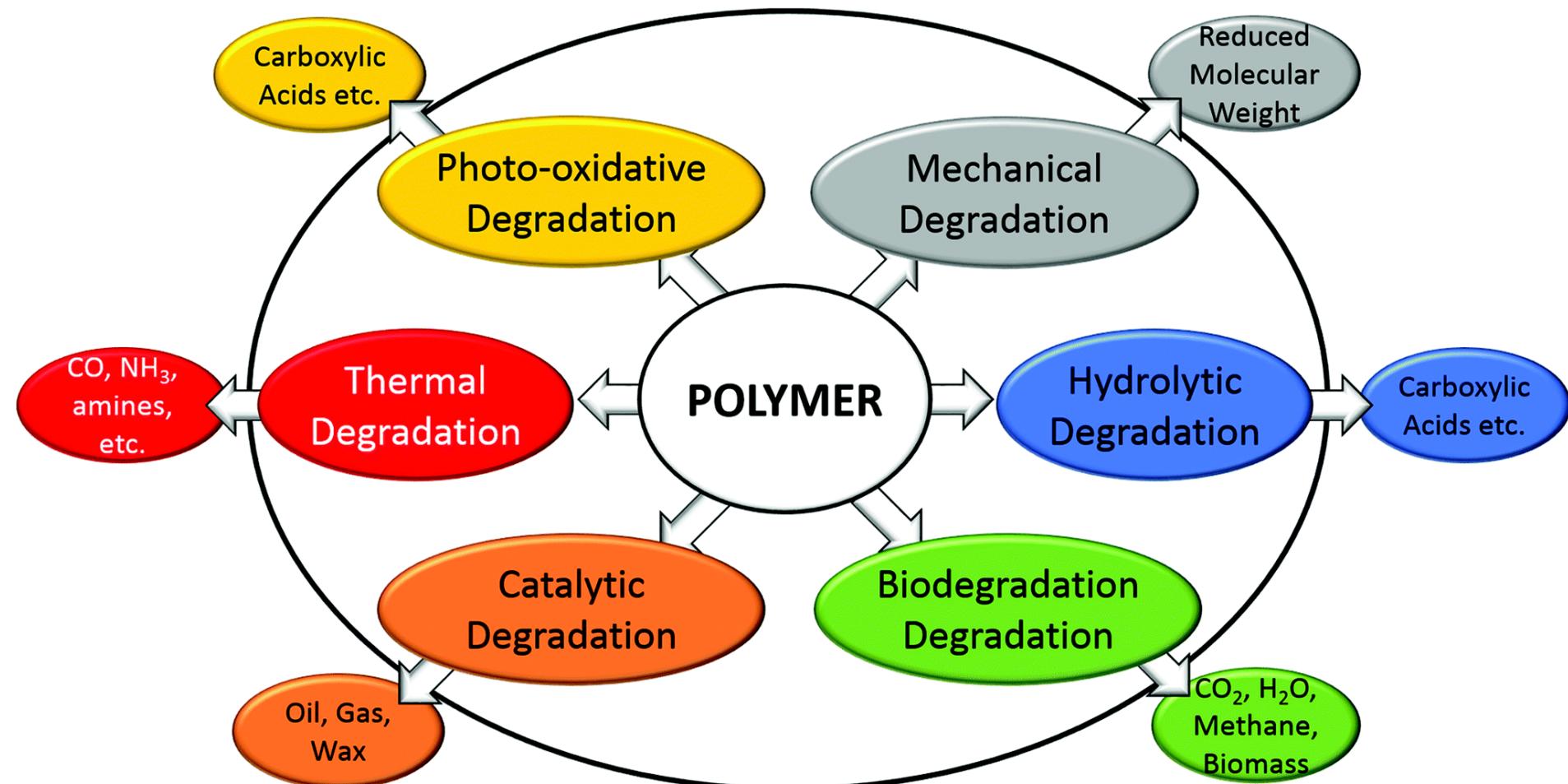


UNIT-I: Sustainable chemistry and E-waste management:

- **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.

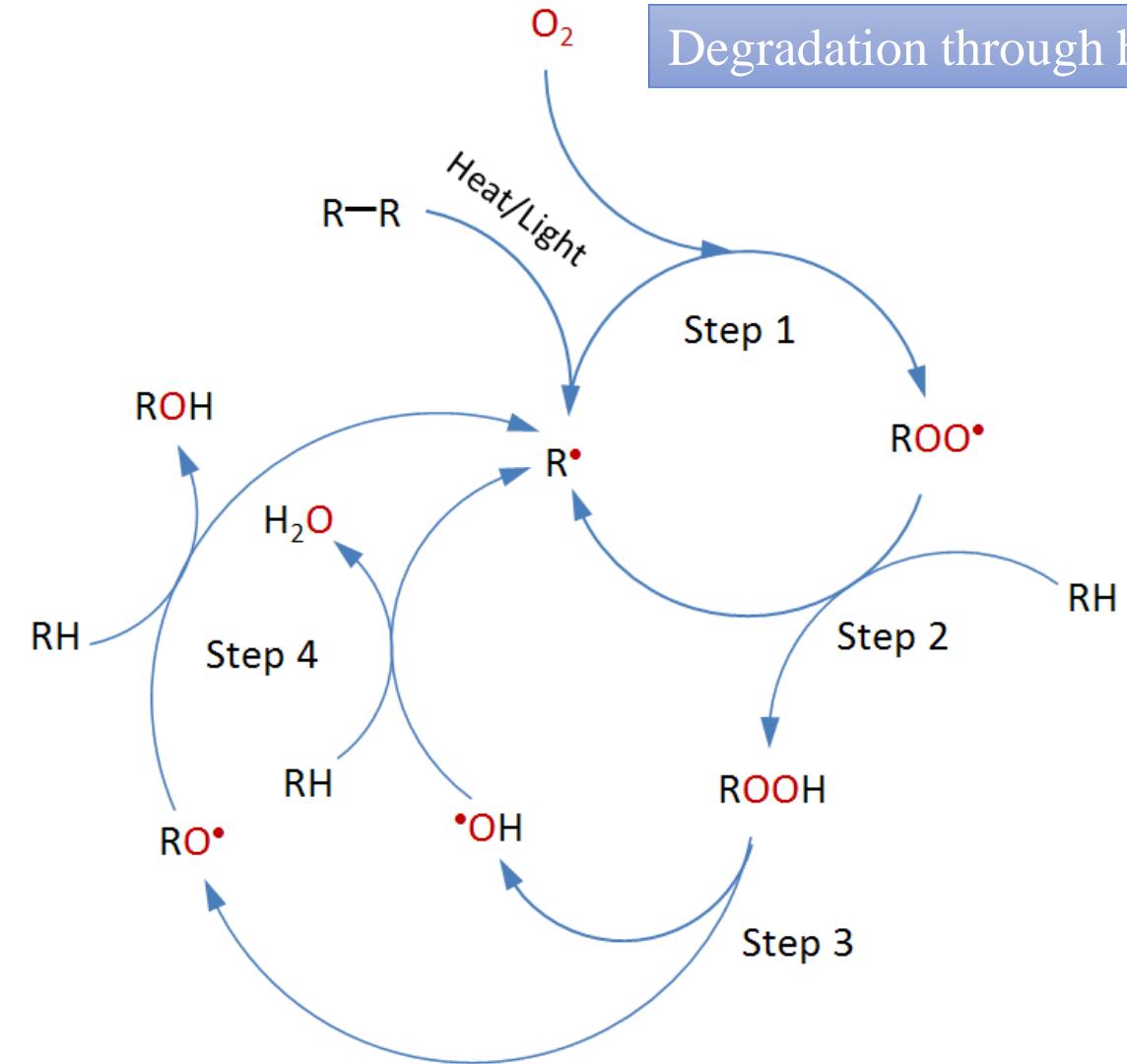
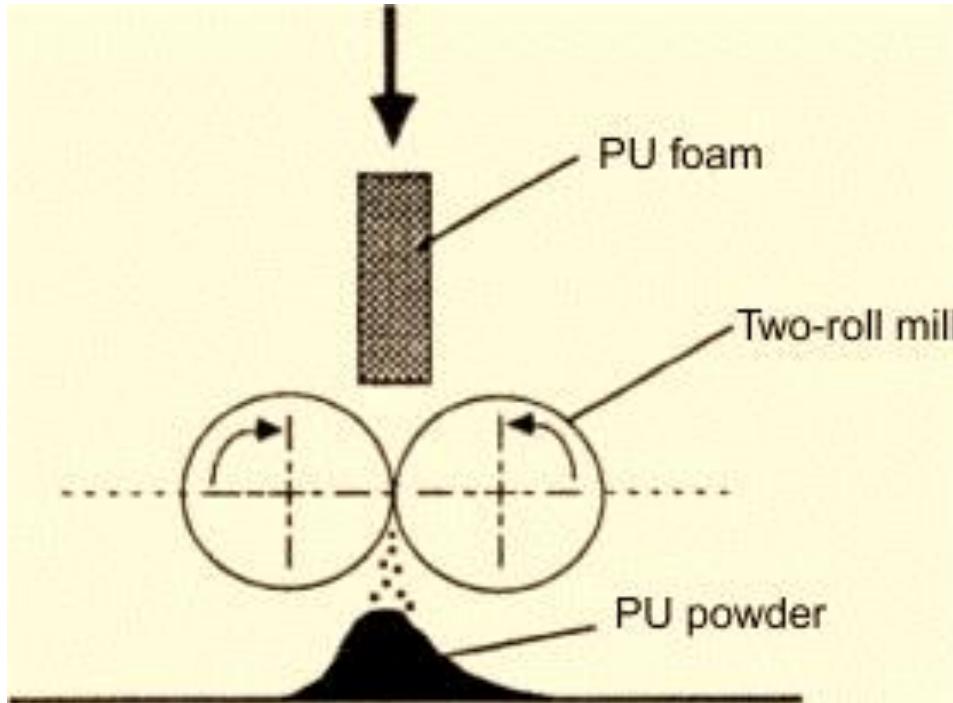


Degradation



Degradation through heat/light

Mechanical Degradation



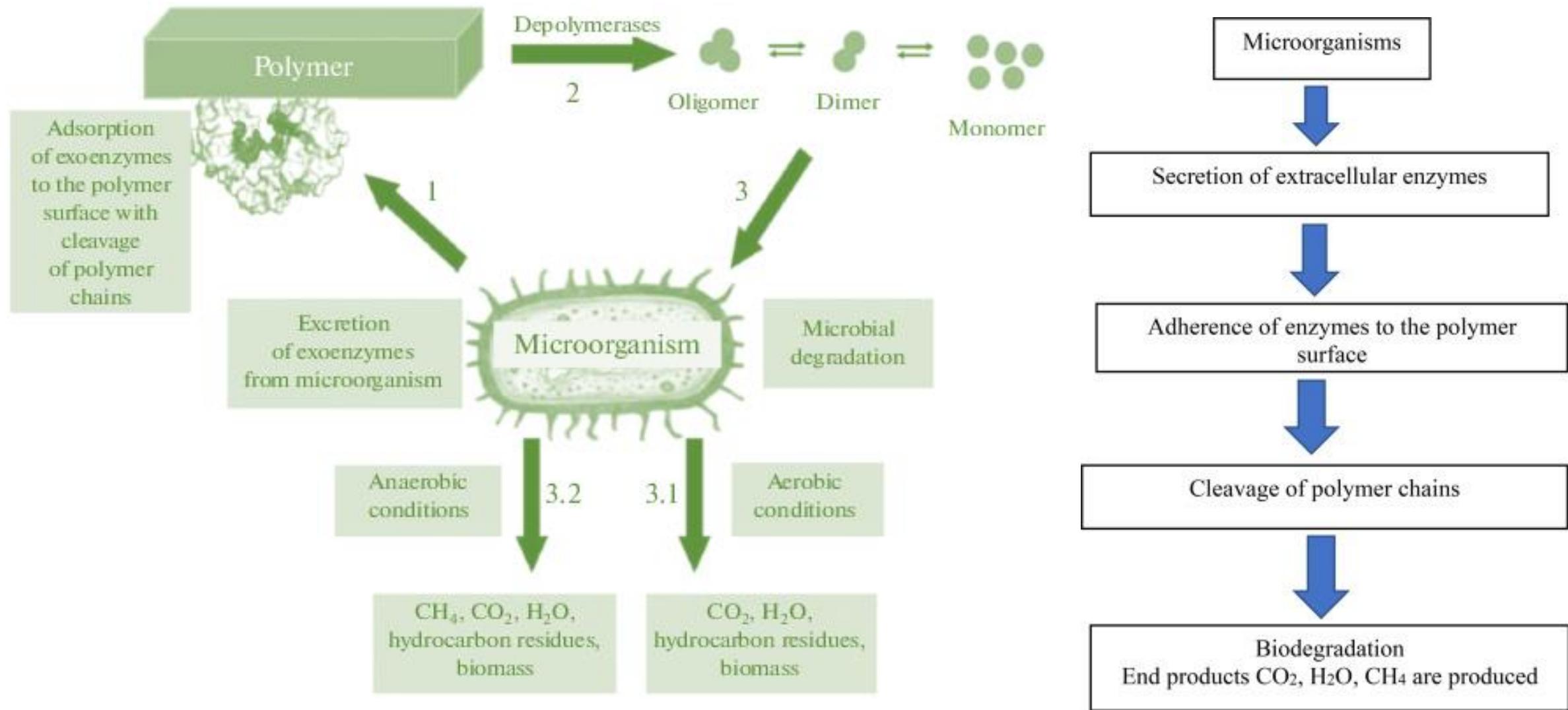
<https://www.sciencedirect.com/topics/engineering/mechanical-degradation>

<https://polymerdatabase.com/polymer%20chemistry/Thermal%20Degradation.html>

Biodegradation

- Initiated by enzymes – hydrolase (phosphatases, esterases, protease)
- Polymers breaks down to monomers, dimers and oligomers
- Initiated by acids/peroxides
- Enzymes are specific to attack various bonding sites
 - -C-C- bonds : Oxaloacetase
 - -C-O- bonds : Esterase
 - -C-N- bonds: Asparaginase
 - -P-N- bonds: Phosphoamidase

Mechanism of degradation:



Requirements for degradation

- Rate of degradation should be always greater than rate of accumulation
- Intermediate products should be less toxic
- End products – mineral acids, CO₂ and biomass
- Duration – Must be short (week or months) and not years from the prospect of cost-effectiveness.

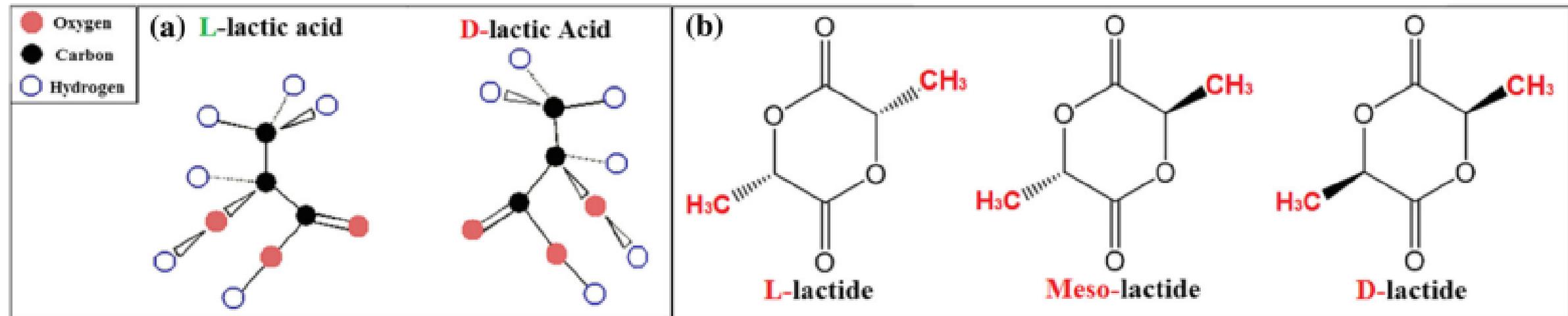
Factors influencing the degradation

- * Environmental factors: Humidity, Temperature, pH, ionic strength
- * Polymers: Molar masses, crystallinity, porosity, extent of cross-linking

- **Biodegradable polymers:** Polymers which degrade quickly in aqueous medium in the presence of microorganisms, and their byproducts are eco-friendly (biocompatible) such as CO₂, water, methane, and inorganic compounds or biomass that is easily scavenged by microorganisms.
- These polymers are degraded by simple hydrolysis of the ester bonds, which does not require the presence of enzymes and in turn prevents inflammatory reactions.
- The hydrolytic products from such degradation process are then transformed into non toxic subproducts that are eliminated through normal cellular activity and urine.

- **Poly-lactic acid (PLA)** is one of the most promising biopolymers produced from non toxic renewable and naturally occurring organic acid- **lactic acid**.
- It is thermoplastic with good mechanical property profile, high biocompatibility and biodegradability properties.
- Lactic acid can be produced by fermentation of sugars obtained from renewable resources such as sugarcane.
- Therefore, PLA can be produced and used in an environmentally friendly cycle.

Poly lactic acid, prepared by different polymerization process from lactic acid including: polycondensation, ring opening polymerization and by direct methods like azeotropic dehydration and enzymatic polymerization.



(a) The stereoisomers of LA. (b) Chemical structures of dimeric D-lactide, L-lactide, and meso-lactide

DOI 10.1007/s10965-017-1227-2

CORN TO LACTIC ACID PREPARATION



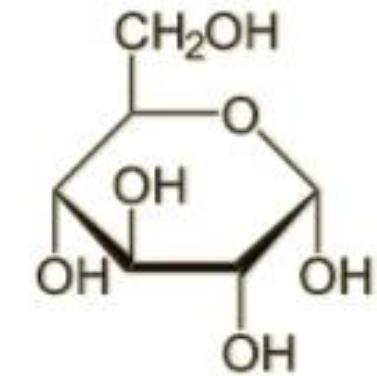
Shelled Corn

Wet Milling
→

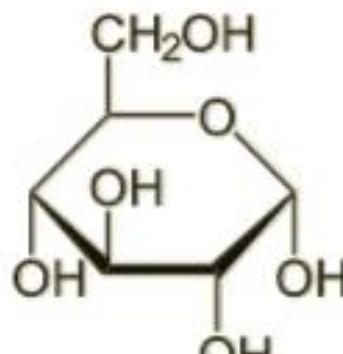


Corn Starch

Enzymes
→
A-Amylase

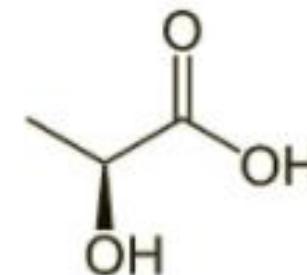


Dextrose



Dextrose

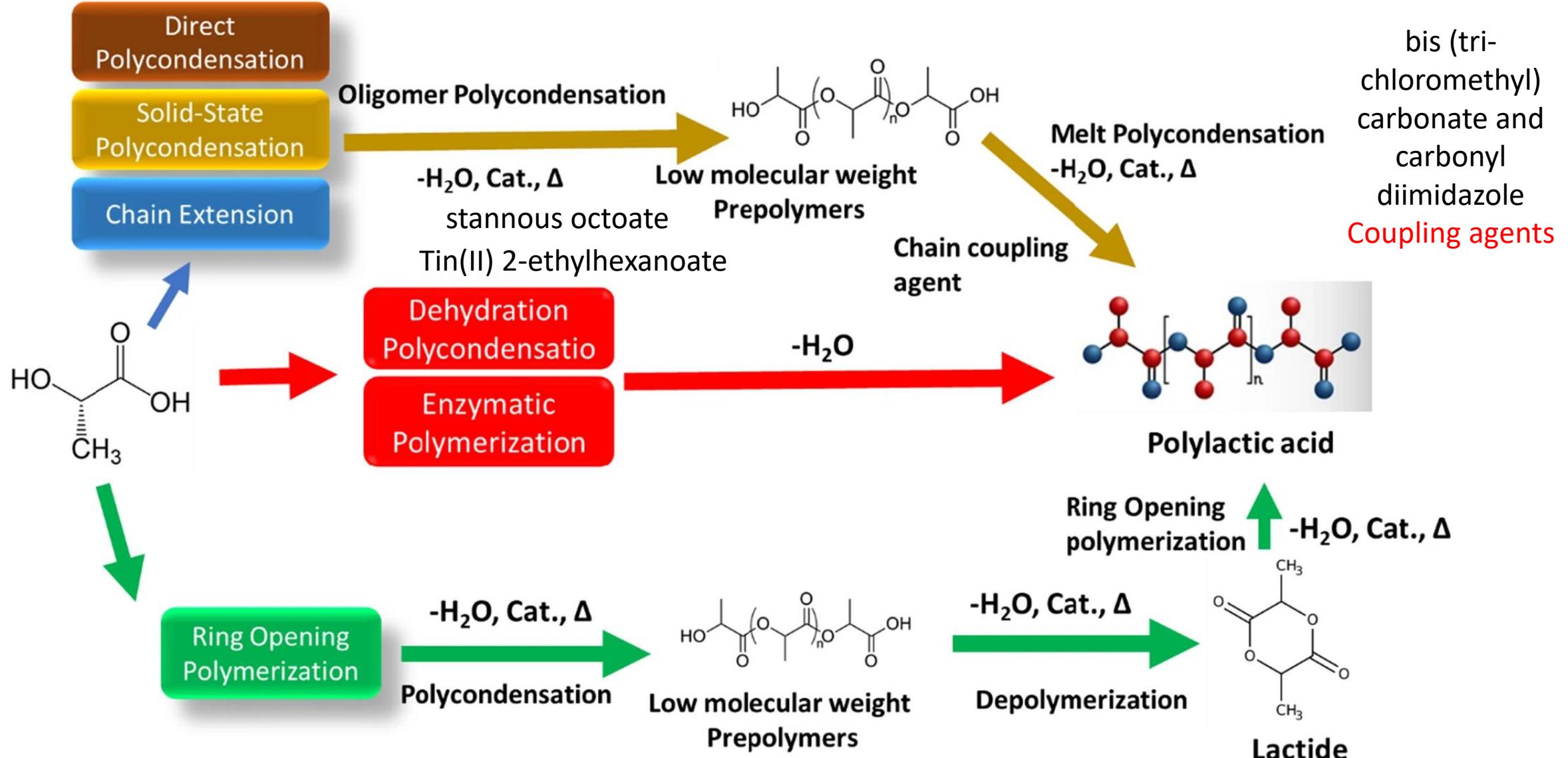
Fermentation
→
Lactase



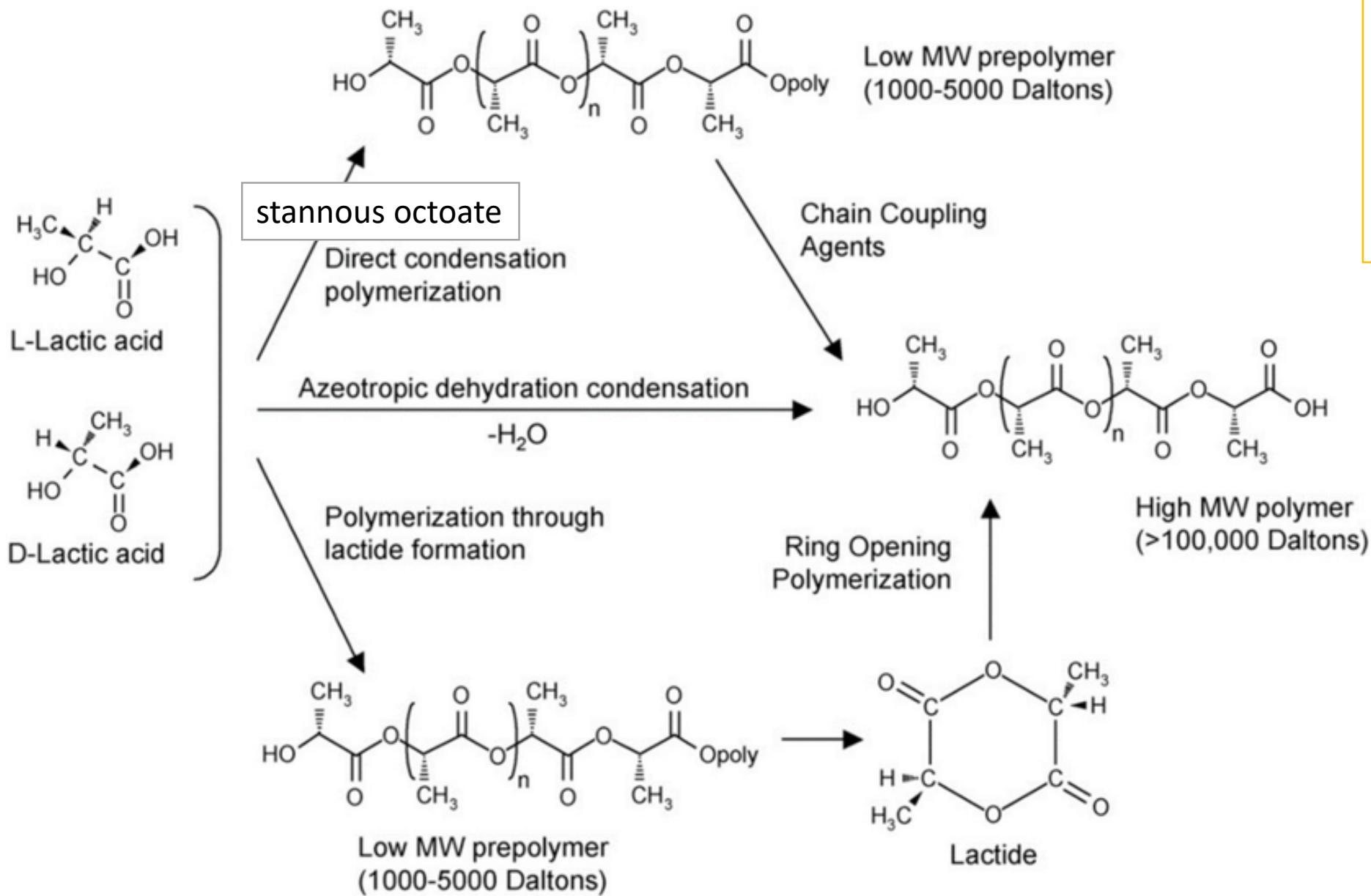
Lactic Acid



LACTIC ACID TO POLYLACTIC ACID (PLA) PREPARATION



LACTIC ACID TO POLYLACTIC ACID (PLA) PREPARATION

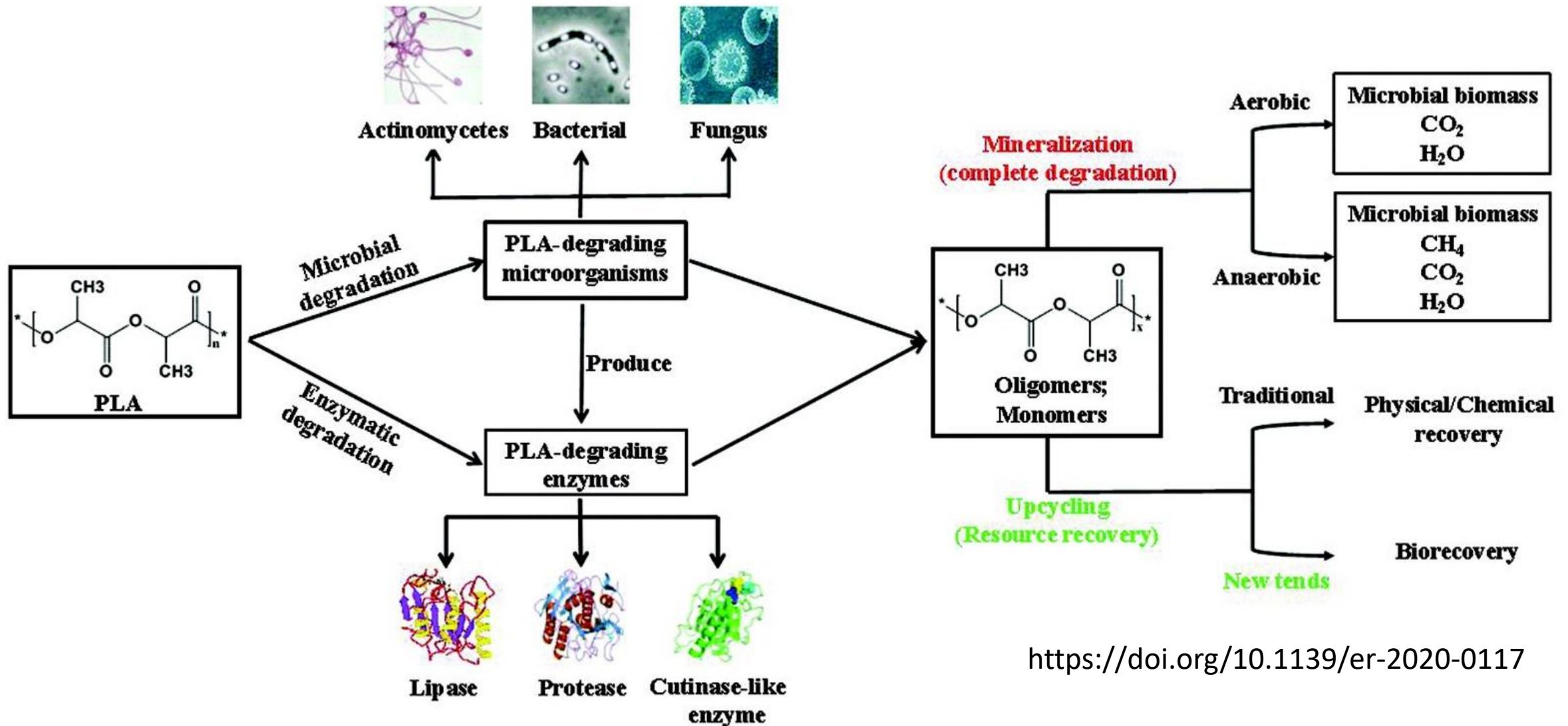


bis (tri-chloromethyl) carbonate and carbonyl diimidazole **Coupling agents**

Characteristics	Description
Physical state	Pallets
Colour	Translucent white
Odour	No odour
Density	1.25 g/mol
Melting point	150–170 °C
Glass transition temperature	55–60 °C
Molecular weight	74,000 g/mol



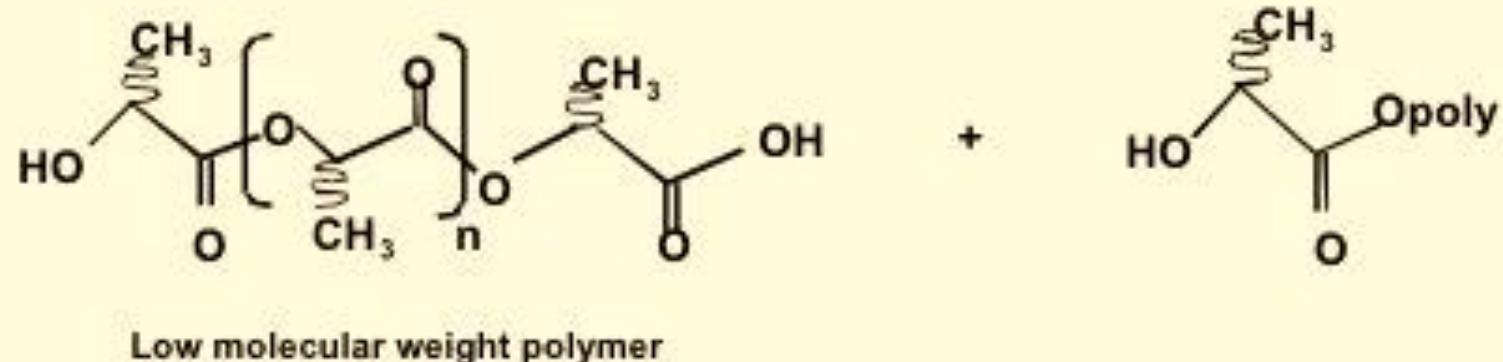
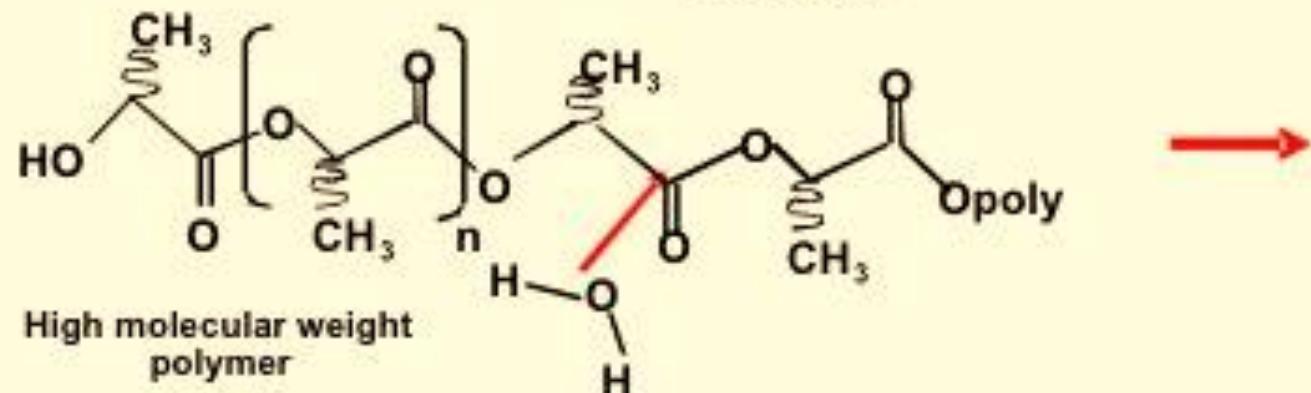
Mechanism of degradation/recovery:



<https://doi.org/10.1139/er-2020-0117>

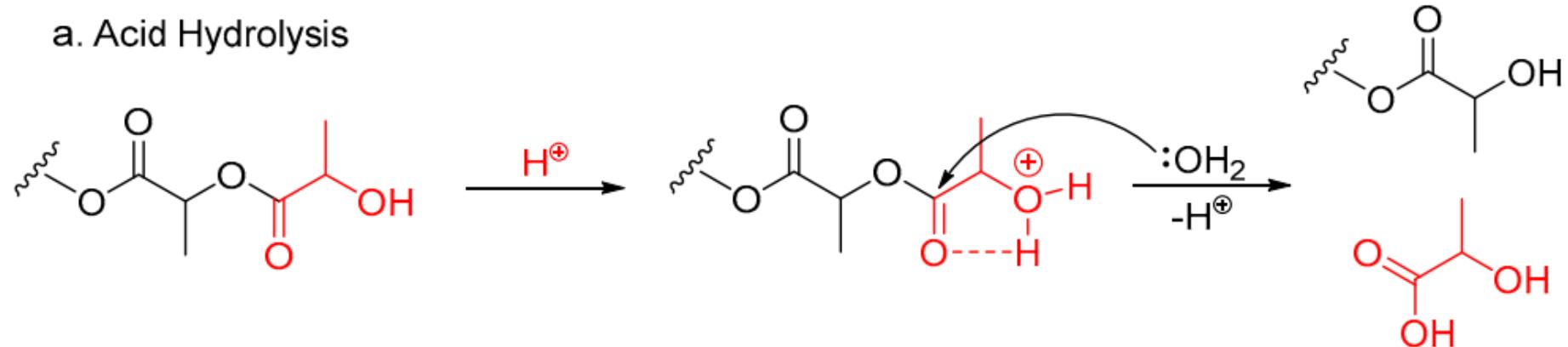
Mechanism of degradation:

Hydrolysis and cleavage of the ester linkage

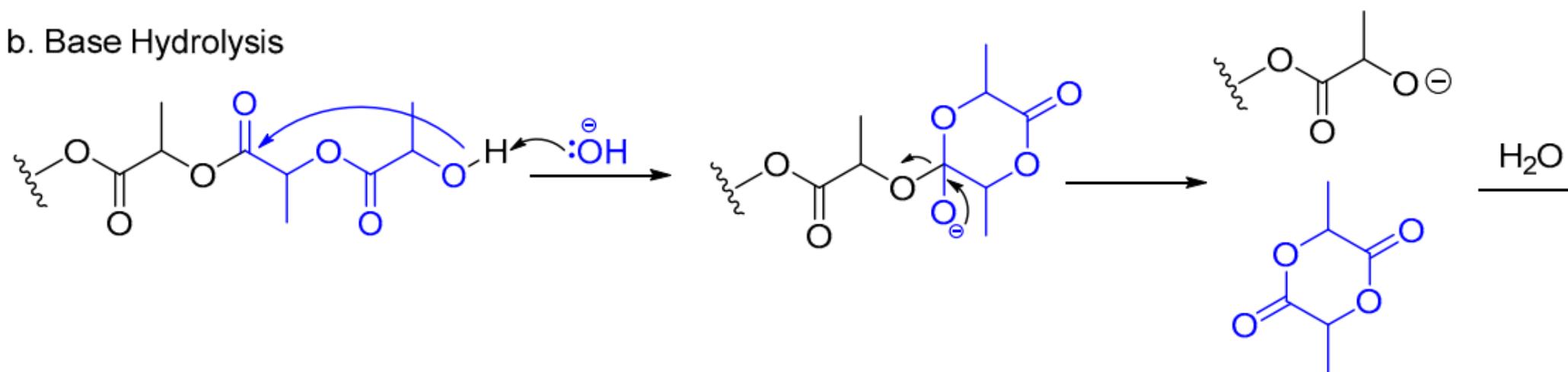


Mechanisms for PLA hydrolysis via (a) acid catalysis and (b) base catalysis

a. Acid Hydrolysis



b. Base Hydrolysis



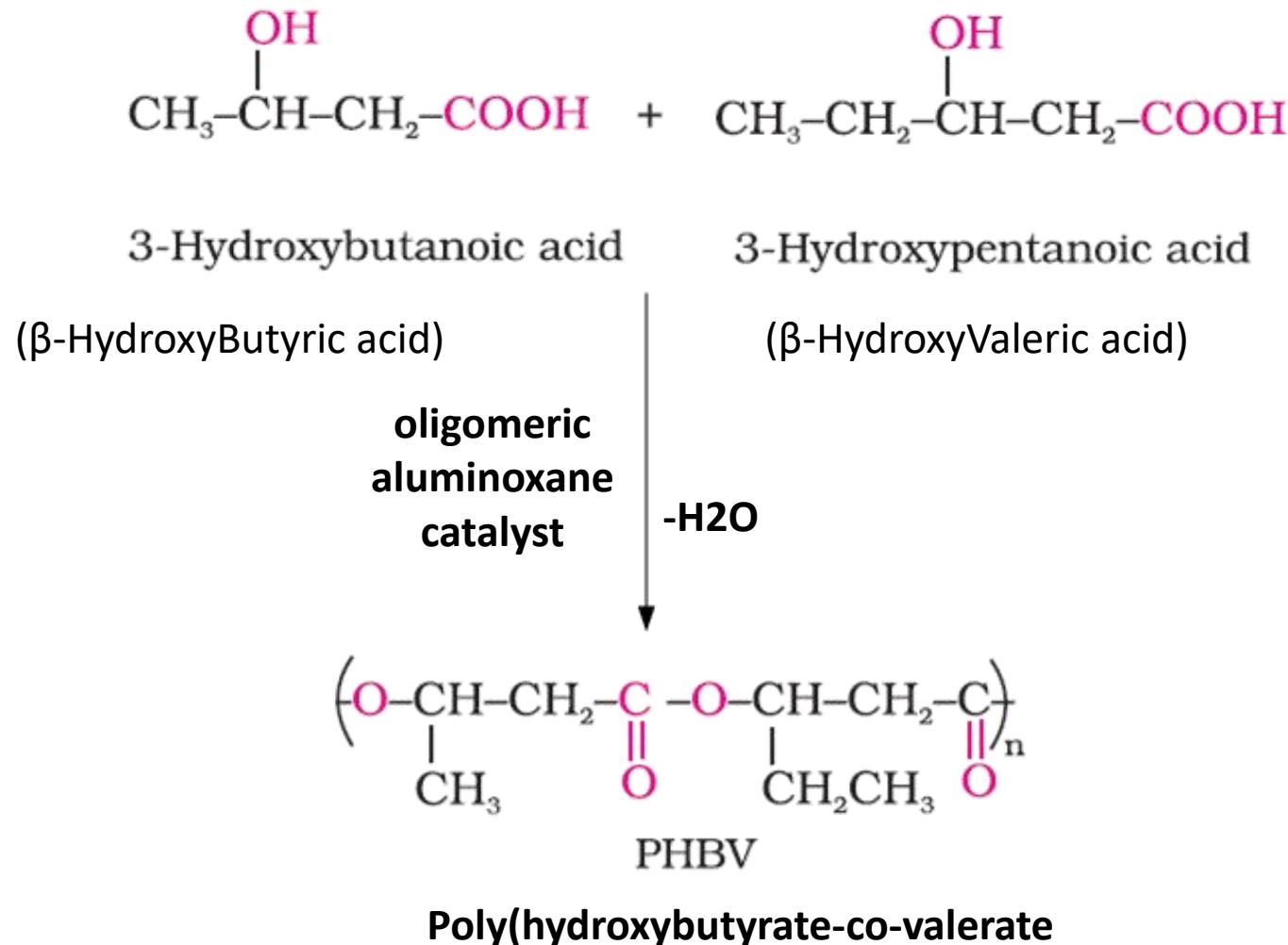
De Jong, S.J.; Arias, E.R.; Rijkers, D.T.S.; Nostrum, C.F.. Polymer 2001, 42, 2795–2802.



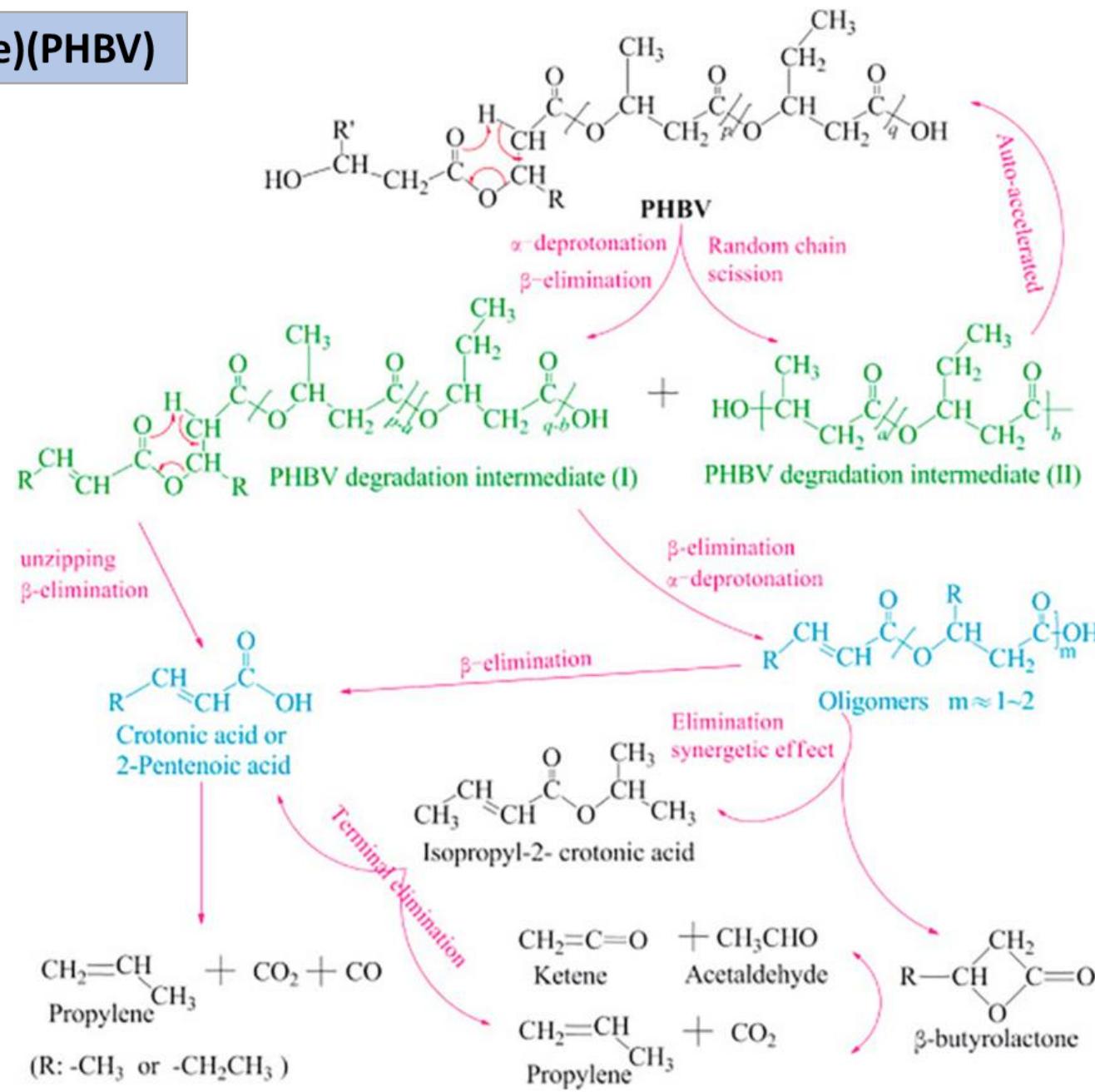
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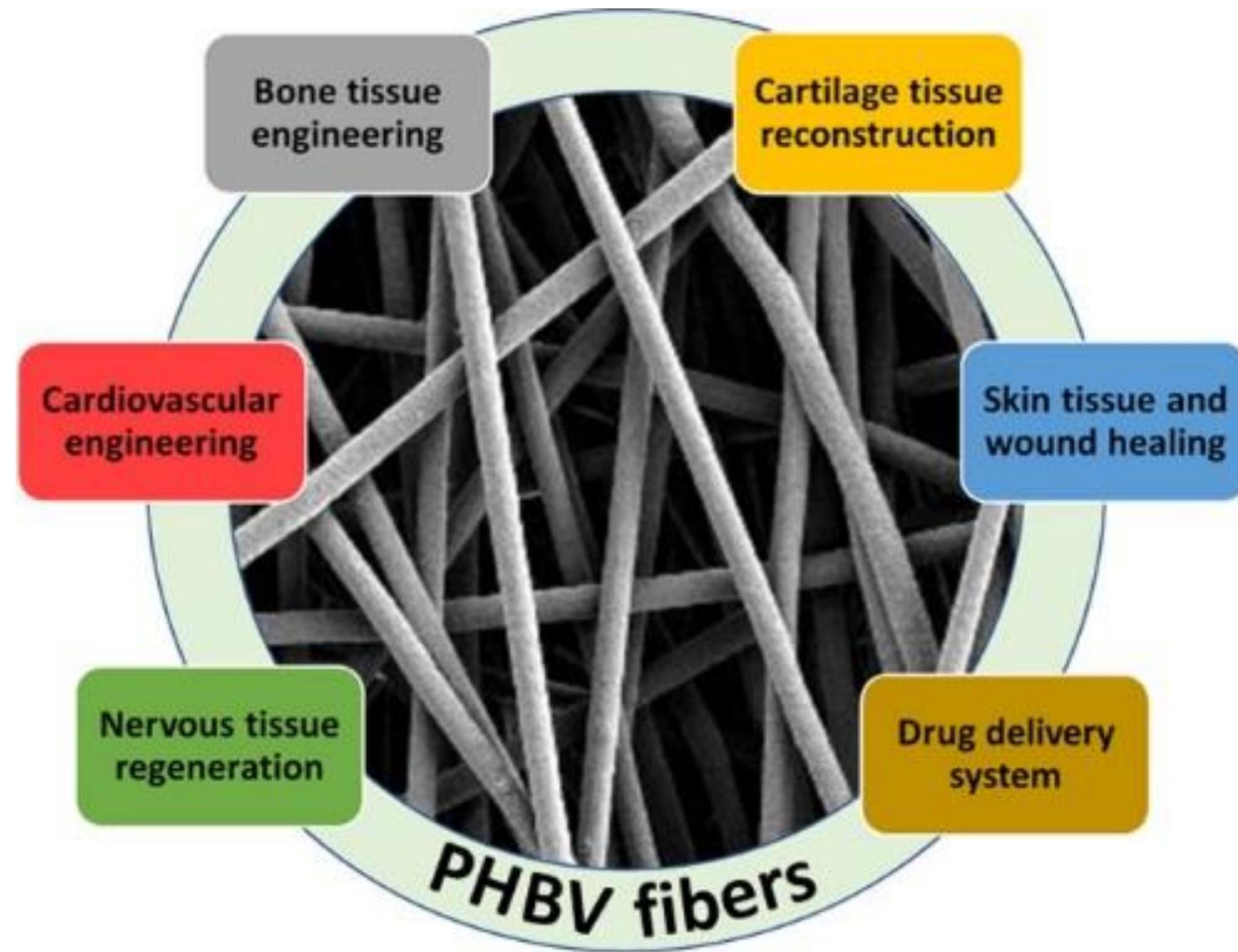
Poly(hydroxybutyrate-co-valerate)(PHBV)

is a completely biodegradable thermoplastic polyester produced by microbial fermentation, which has an excellent biocompatible and biodegradable properties



Poly(hydroxybutyrate-co-valerate)(PHBV)





Biocompatible polymeric materials:

Biocompatible – materials (polymers, metals, ceramics) that functions with the living cells and do not produce any deleterious effects when administered into the human body.

They are intended to interface with biological systems to treat or replace any tissues/organs of the body.

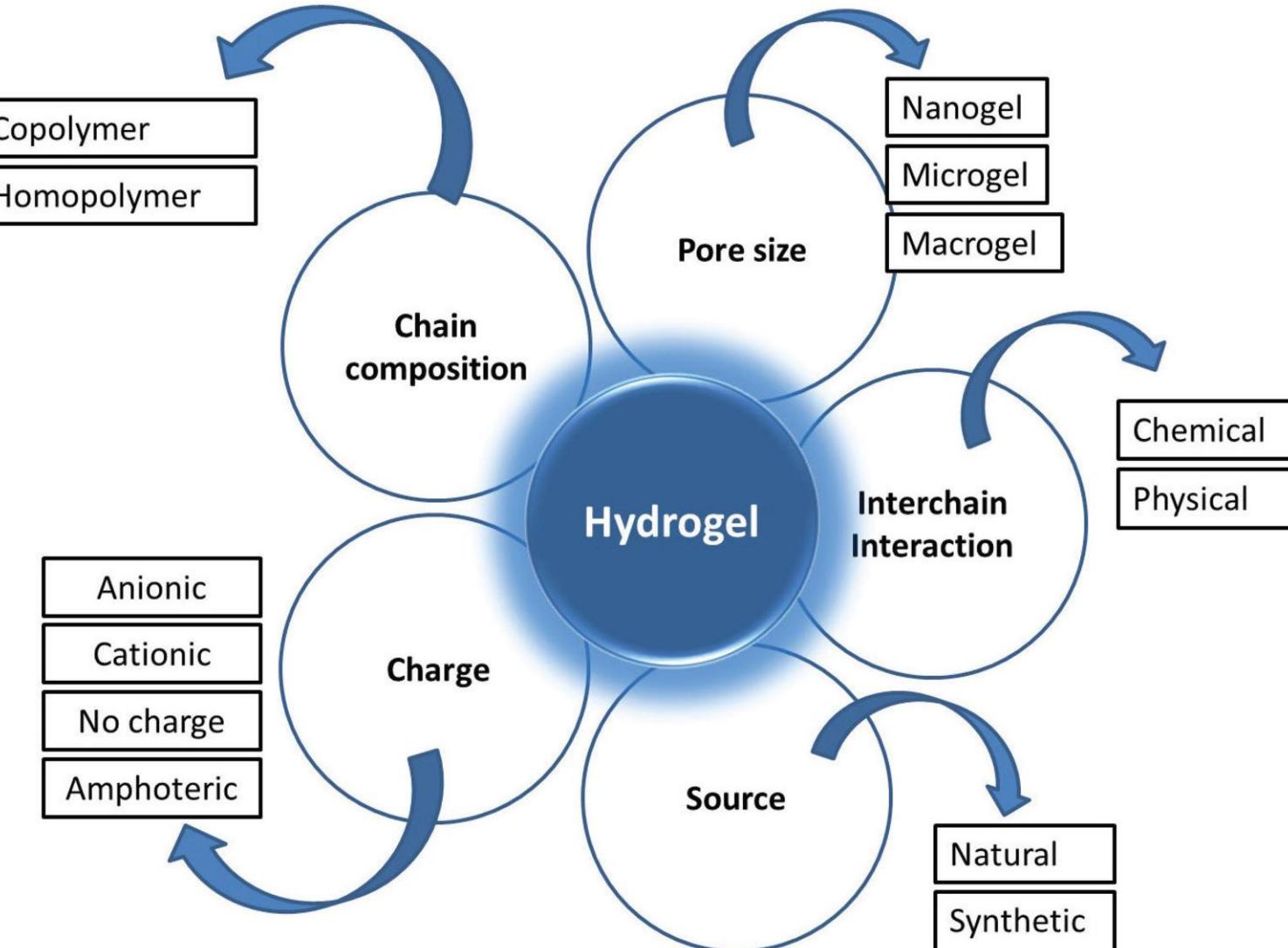
Applications: Vaccinate the wild animals – bio bullets

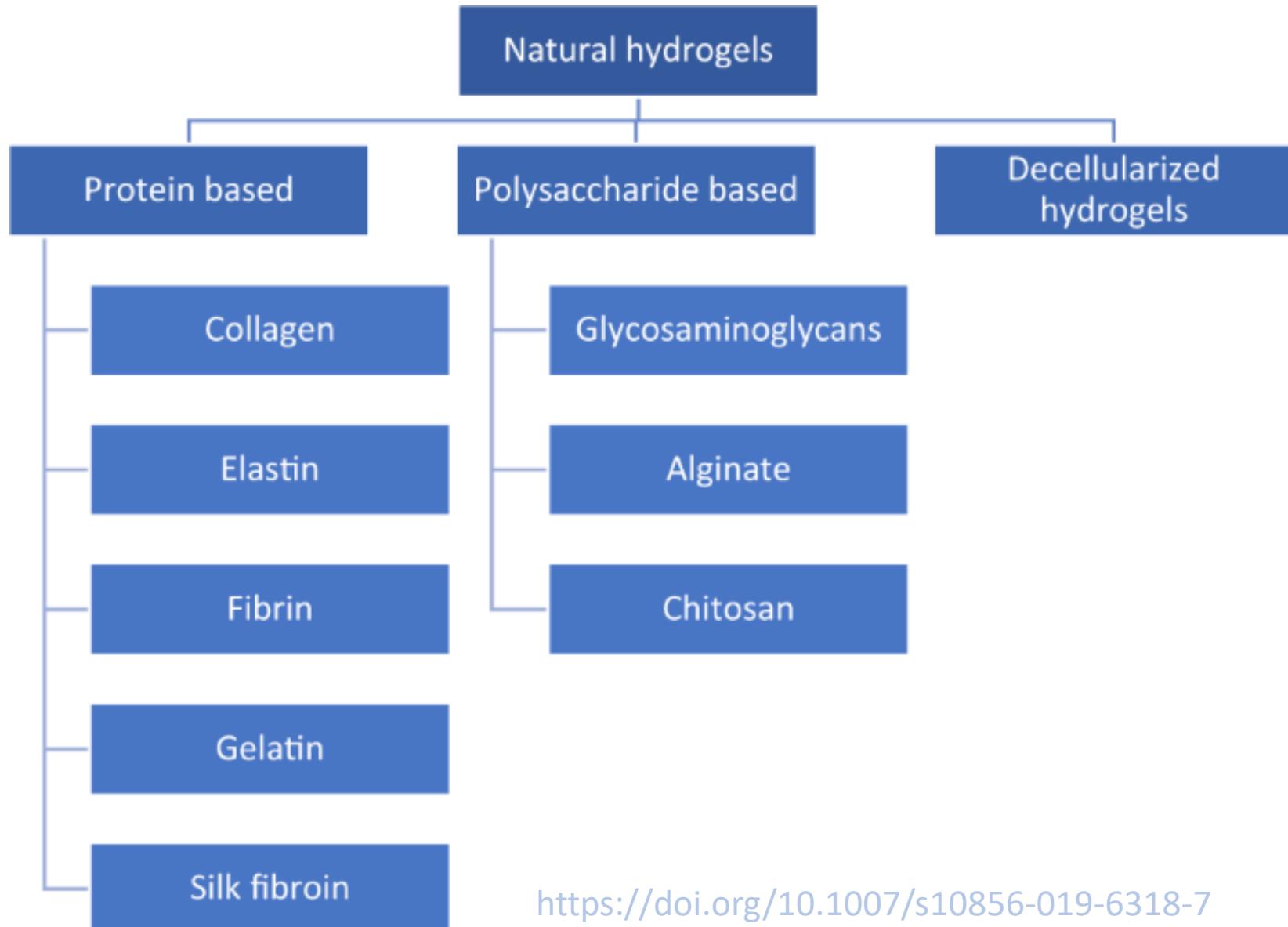
Hydrogels: It is a three-dimensional (3D) network of hydrophilic polymers that are capable of holding the large amount of water in their 3D network. These 3D network can retain the original structure through chemical or physical cross-linking of individual polymer chains.

The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains.

The hydrophilicity of the network is due to the presence of hydrophilic groups such as $-\text{NH}_2$, $-\text{COOH}$, $-\text{OH}$, $-\text{CONH}_2$, $-\text{CONH}-$, and $-\text{SO}_3\text{H}$.







Due to their superior biocompatibility and low toxicity, hydrogels play a significant role in the biomedical fields

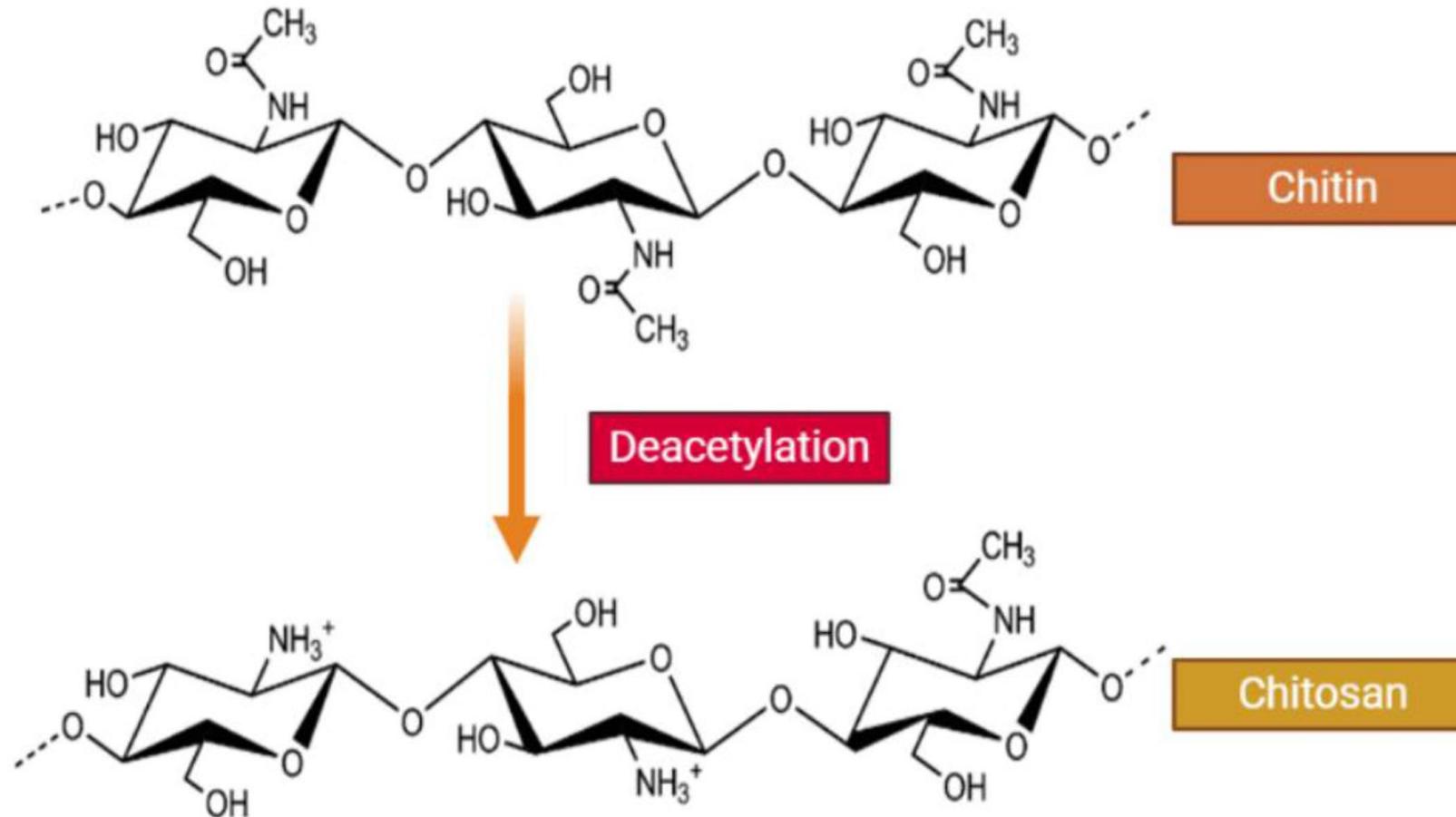
Examples:

Chitosan, a Natural Polymer : N, O-carboxymethyl chitosan incorporated fayalite (Fe_2SiO_4), which could release bioactive ions with mild heating function to in wound area to enhance angiogenesis and chronic wound healing.

PVA, a synthetic hydrophilic polyhydroxyl polymer, PVA has been largely employed in tissues such as the bone, heart, nerve, and vascular network

Structure of chitin and chitosan

Chitosan (CH) is a modified biopolymer obtained *via* partial de-acetylation of the naturally occurring polysaccharide called chitin, which contains randomly distributed (1→4)-linked N-acetyl glucosamine and glucosamine units

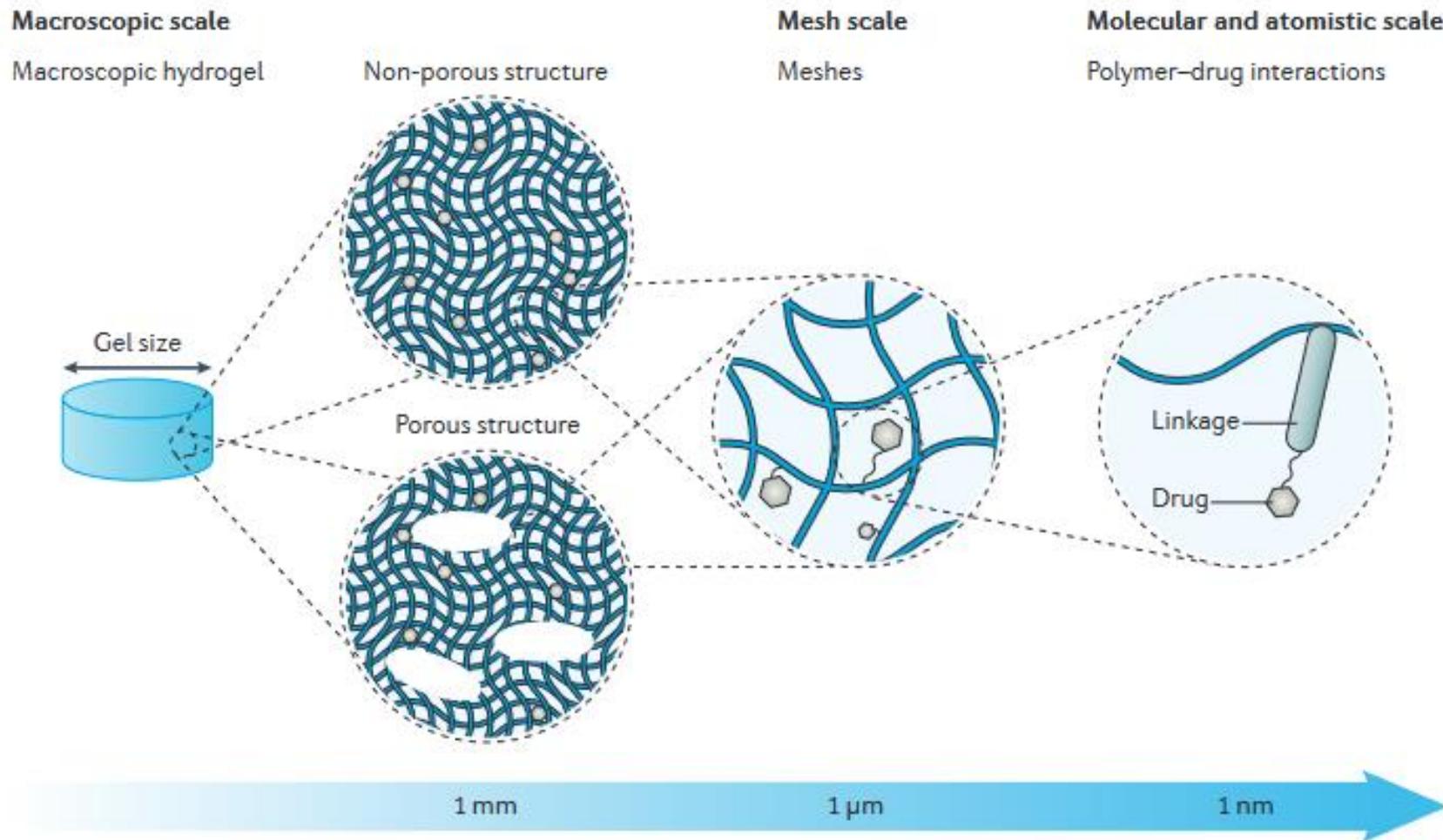


CH has advantages such as

- biodegradability
- hydrophilicity
- biocompatibility
- Bioactivity
- obtained from renewable and natural sources.

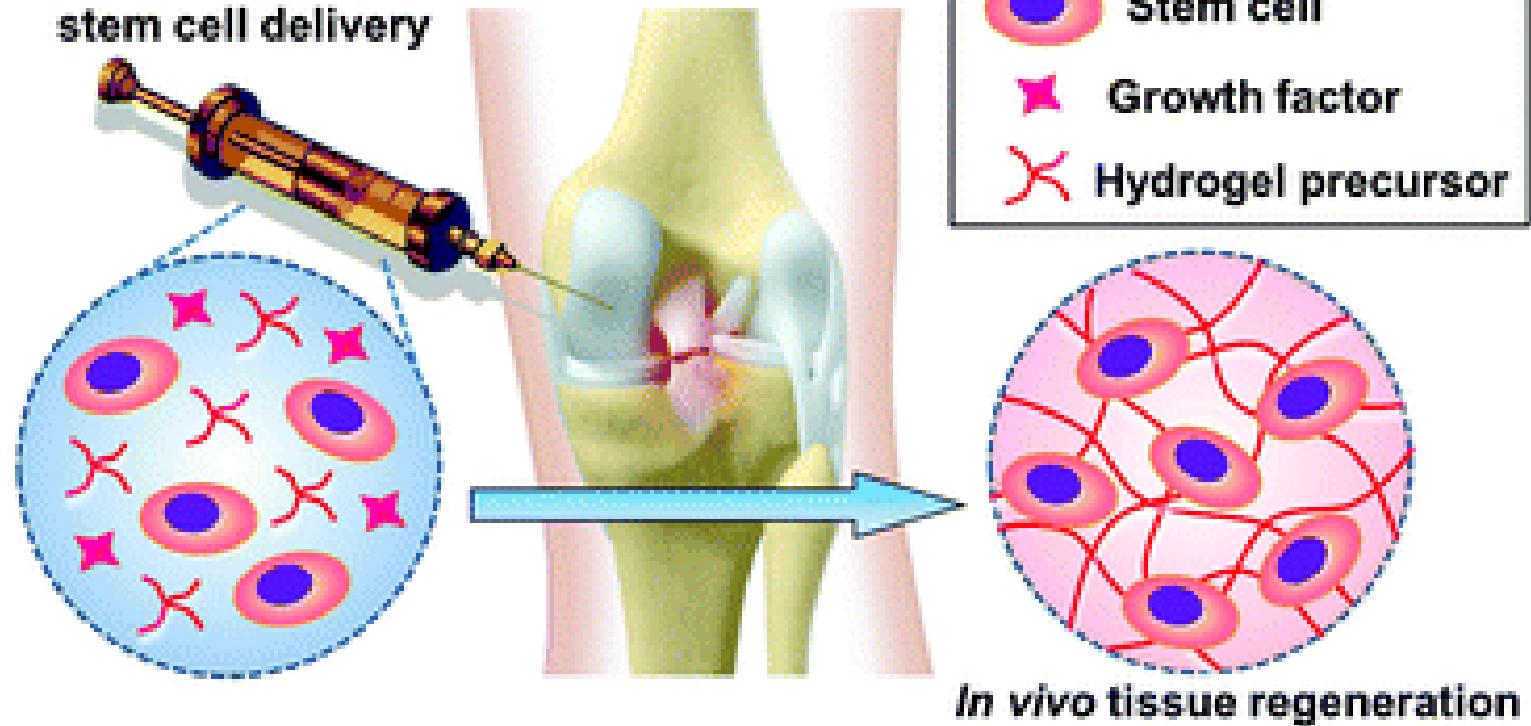
It can be processed into distinct forms

- ❖ solutions
- ❖ blends
- ❖ sponges
- ❖ membrane
- ❖ gels
- ❖ paste
- ❖ tablets

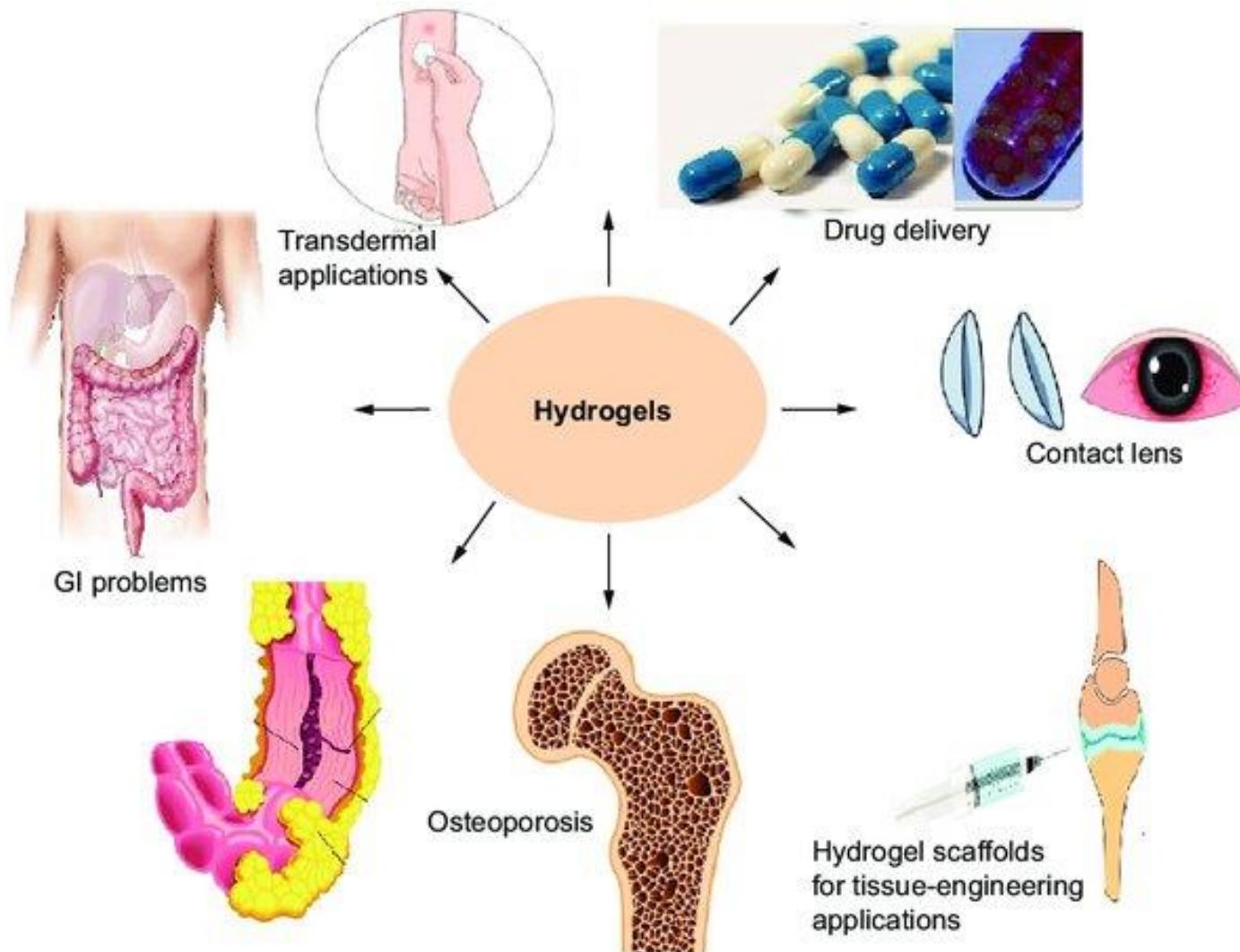


Biomedical Applications of Hydrogel

Injectable hydrogel for stem cell delivery



Biomedical Applications of Hydrogel



Gastrointestinal Diseases

Osteoporosis **causes bones to become weak and brittle**

<http://dx.doi.org/10.4155/tde-2020-0114>

Biomedical Applications of Hydrogel

Table 1. Overview of hydrogels and their applications

Hydrogel	Application
Temperature responsive hydrogels	Skin tissue engineering, wound covering, cell carriers
Light responsive hydrogels	Drug delivery, microfluidic devices
Electro responsive hydrogels	Membrane and implant-based drug delivery
Magnetic responsive hydrogels	Drug delivery, tissue repair, targeted MRI for disease diagnosis
pH-responsive hydrogels	Drug and protein delivery, 3D cell culture
Glucose responsive hydrogels	Immunoisolation devices
Biochemical responsive hydrogels	Smart sensors and actuators
Collagen-based hydrogels	Corneal, tendon tissue engineering
Injectable hydrogels	Bone, cartilage and meniscus tissue engineering, drug delivery, Osteo-arthritis therapy



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Green Chemistry

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.



Prevention



Atom Economy



Less Hazardous Chemical Syntheses



Designing Safer Chemicals



Safer Solvents and Auxiliaries



Design for Energy Efficiency



Use of Renewable Feedstocks



Reduce Derivatives



Catalysis



Design for Degradation



Real-Time Analysis for Pollution Prevention



Inherently Safer Chemistry for Accident Prevention

Green Chemistry: Introduction-Basic principles.

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

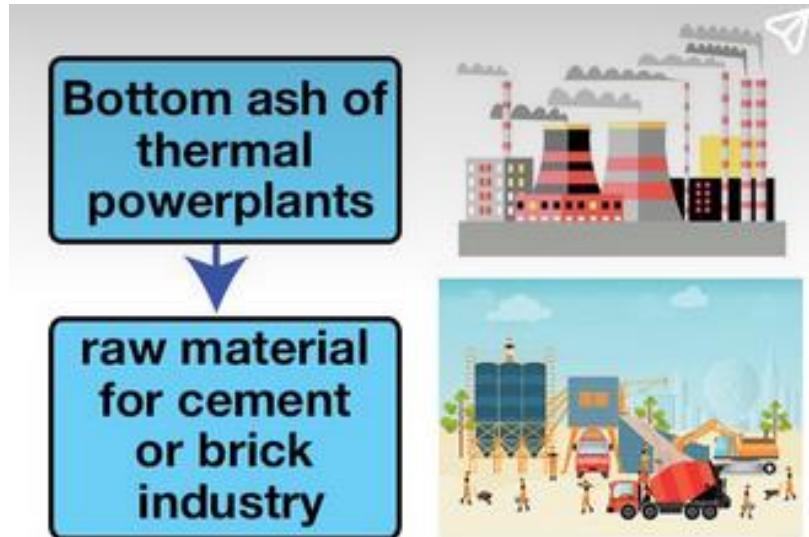
The twelve principles of green chemistry are:

- 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 maximize incorporation of all materials used in the process into the final product.
- 3. Less hazardous chemical syntheses:** Wherever practicable, synthetic methods 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 function while reducing toxicity.
- 5. Safer solvents, and auxiliaries:** The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.
- 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

- 6. Use of renewable feedstock:** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- 7. Reduce derivatives:** Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- 8. Catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- 9. Design for degradation:** Chemical products should be designed so that at the end of their function they break down into harmless degradation products and do not persist in the environment.
- 10. 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.
- 11. Inherently safer chemistry for accident prevention:** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

GC1. PREVENTION

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



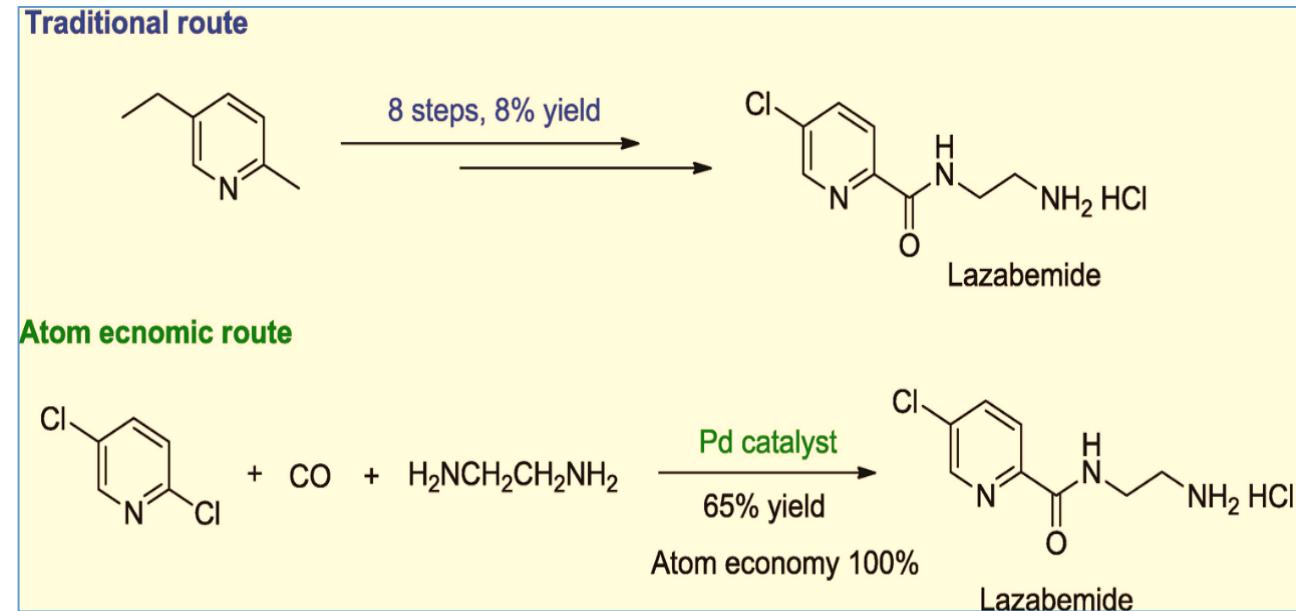
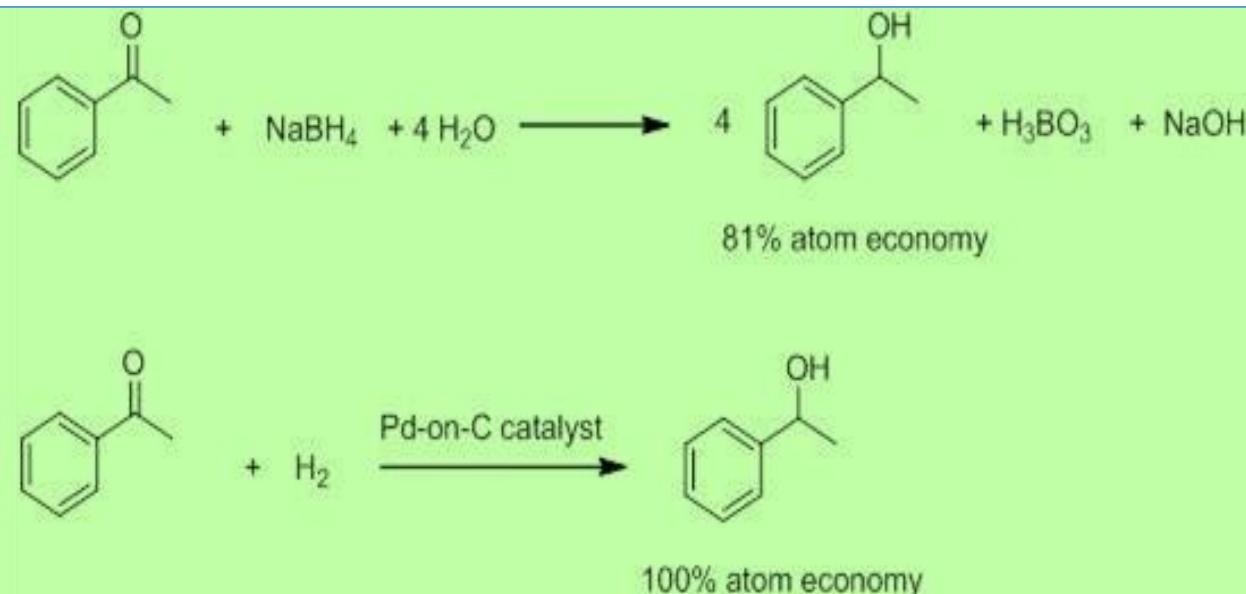
For example, bottom ash of thermal powerplants can be used as a raw material for cement or brick industry.



GC2. ATOM ECONOMY

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

$$\text{Atom Economy} = \frac{\text{Mol. weight of Desired product}}{\text{Mol. weight of all reactants}} \times 100$$

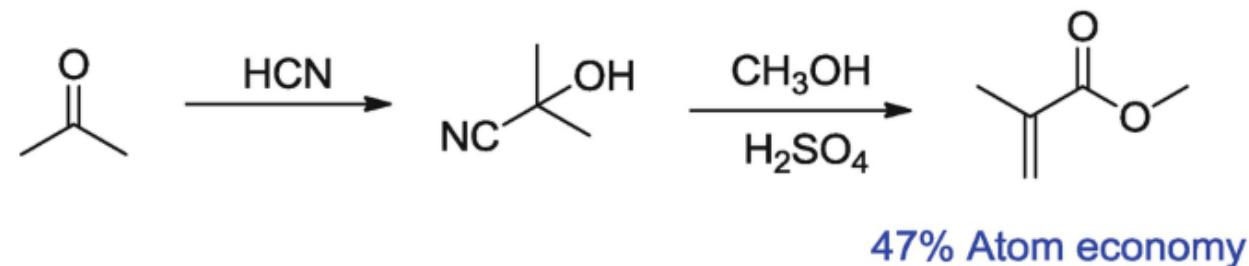


GC2. ATOM ECONOMY

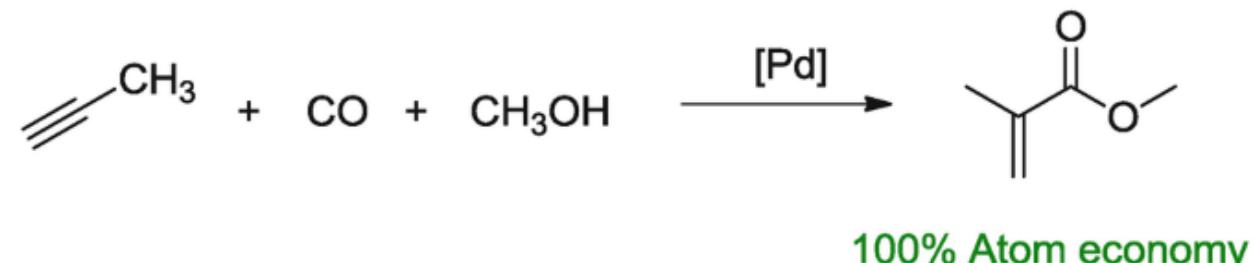
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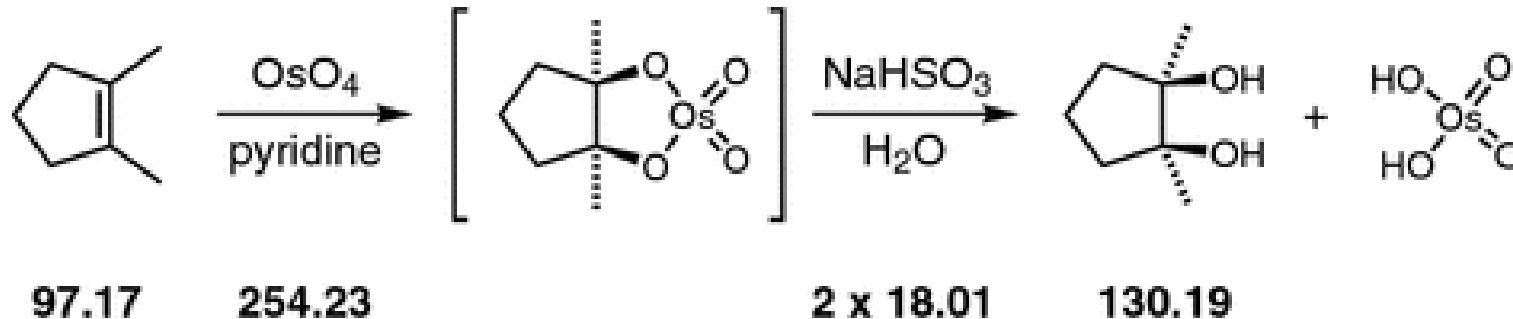
Traditional technology



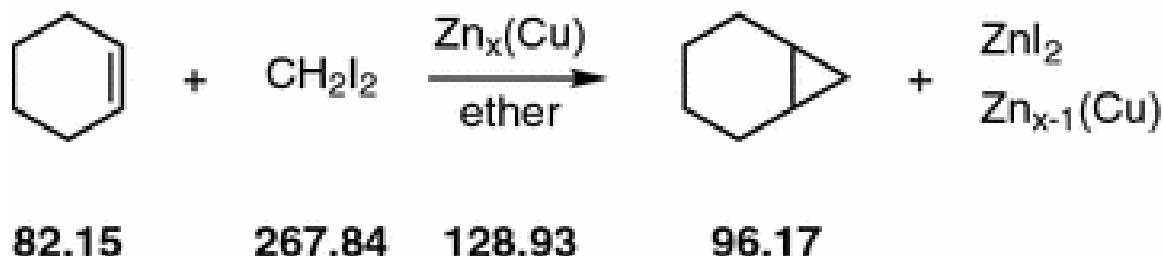
New technology



GC2. ATOM ECONOMY



$$\% \text{ Atom Economy} = \frac{130.19}{97.17 + 254.23 + 2 \times 18.01} \times 100\% = 34\%$$



$$\% \text{ Atom Economy} = \frac{96.17}{82.15 + 267.84 + 128.93} \times 100\% = 20\%$$

GC2. ATOM ECONOMY

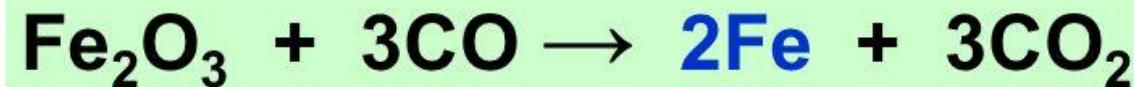
ATOM ECONOMY is the mass of product you want as a % of the mass of all the products you make



RFM: 48	32	80
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RAM
Mg 24
Fe 56
C 12
O 16

$$\text{Atom Economy} = 80 / 80 \times 100\% = \underline{\underline{100 \%}} \text{ (obviously)}$$

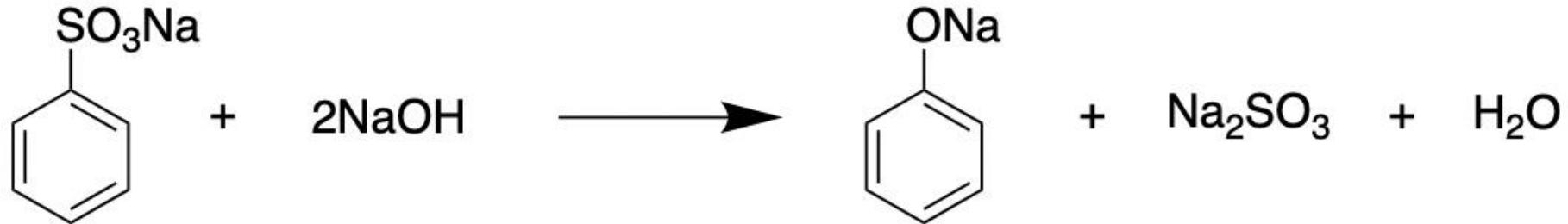


160	84	112	132
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$$\text{Atom Economy} = 112 / 244 \times 100\% = \underline{\underline{45.9 \%}}$$

GC2. ATOM ECONOMY



MW's;	180	2×40	116	126	18
MW Product: 116			MW waste: 144		

GC3. LESS HAZARDOUS CHEMICAL SYNTHESIS

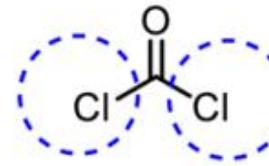
Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Ex: Phosgene is hazardous, therefore we should replace it with a safer one.

Bis(trichloromethyl)carbonate (BTC, triphosgene) is a versatile compound that enables highly efficient syntheses. In addition, because of its solid state, it is a very convenient compound for small-scale phosgenations.

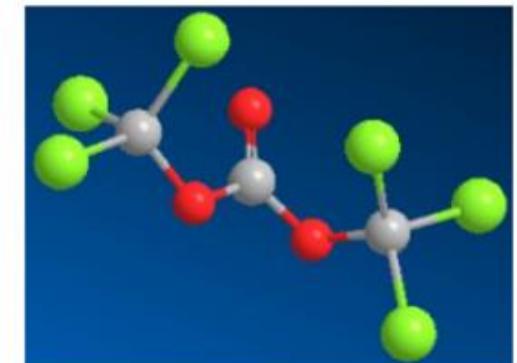
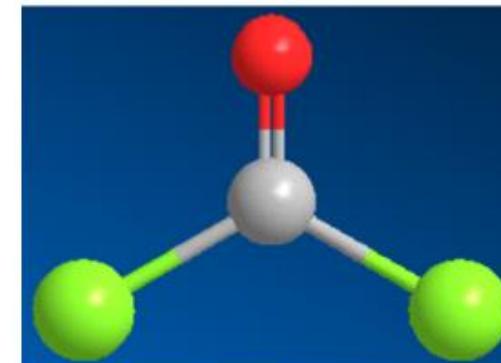
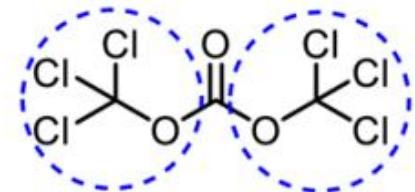
A

Phosgene



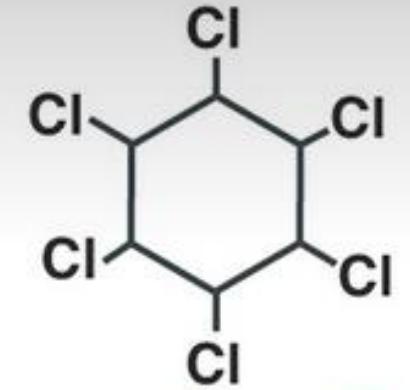
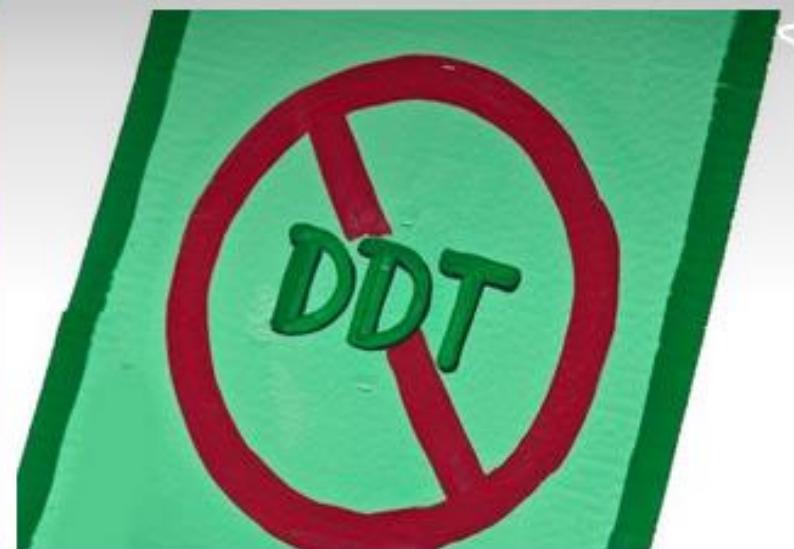
B

Bis(trichloromethyl) Carbonate (BTC)



GC4. DESIGNING SAFER CHEMICALS

Chemical products should be designed to preserve efficacy of function while reducing toxicity.



Benzene Hexachloride

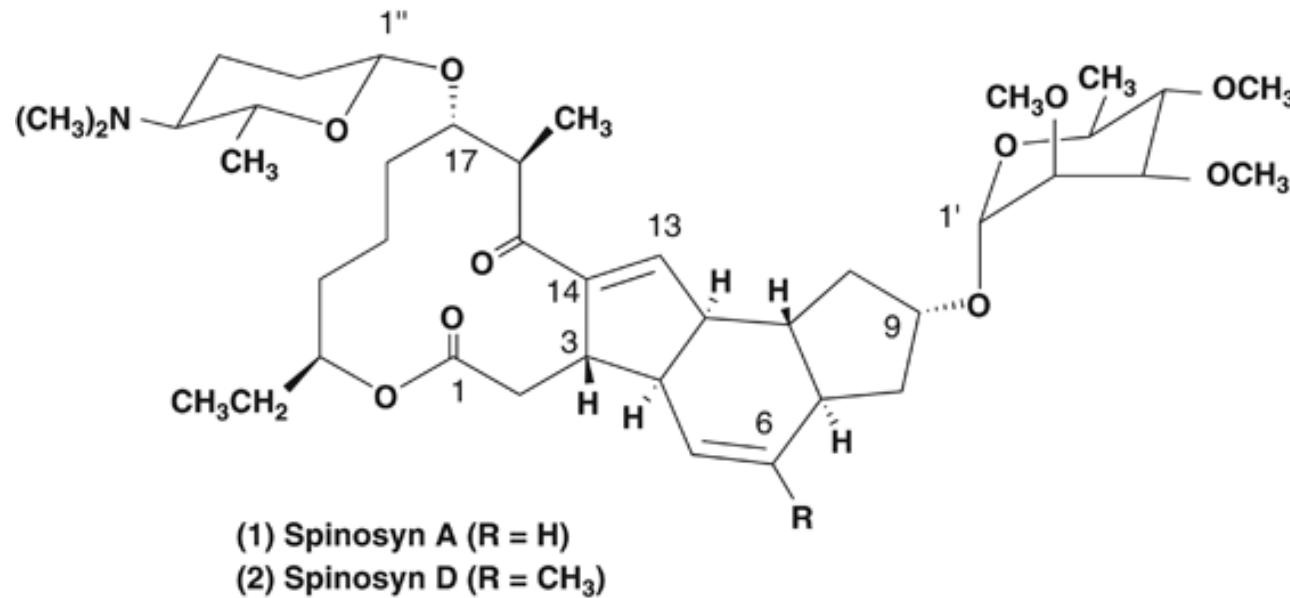
Earlier DDT(Dichloro diphenyl trichloroethane) was used as an insecticide to control diseases like typhoid and malaria

Later, it was realized that DDT is harmful to living beings.

Nowadays, benzene hexachloride is used as an insecticides because it is less toxic than DDT.

GC4. DESIGNING SAFER CHEMICALS

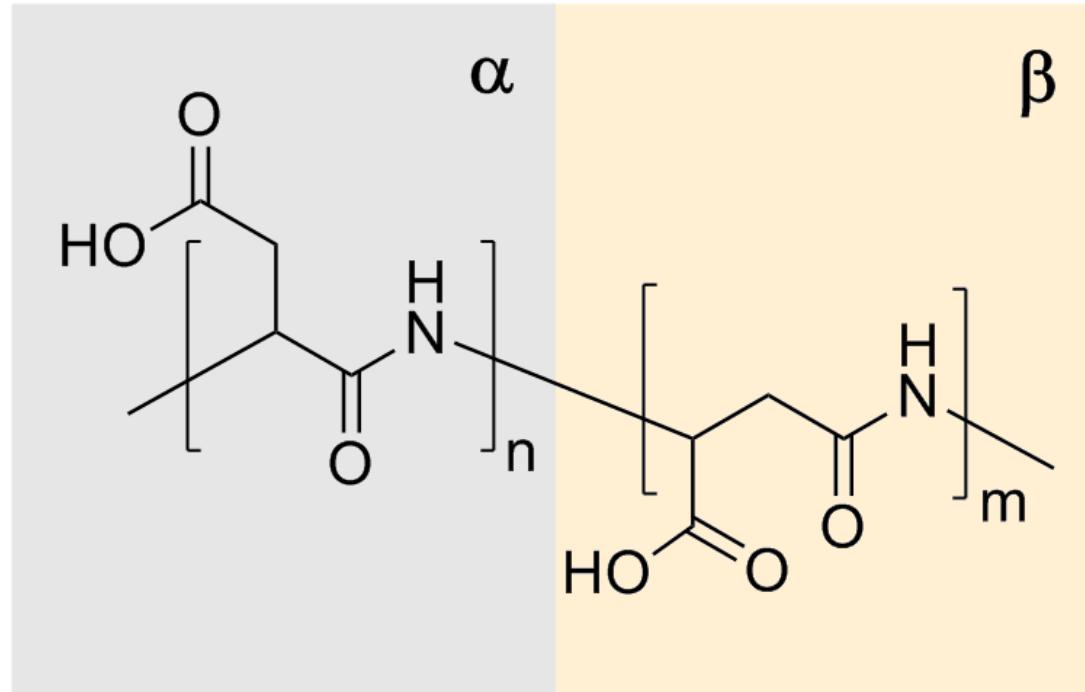
SPINOSAD: biological mosquito larvicide whose active ingredient, spinosad, is biologically derived from the fermentation of *Saccharopolyspora spinosa*, a naturally occurring soil organism. A natural product for insect control. It is isolated from Caribbean soil sample. It demonstrates high selectivity and low toxicity.



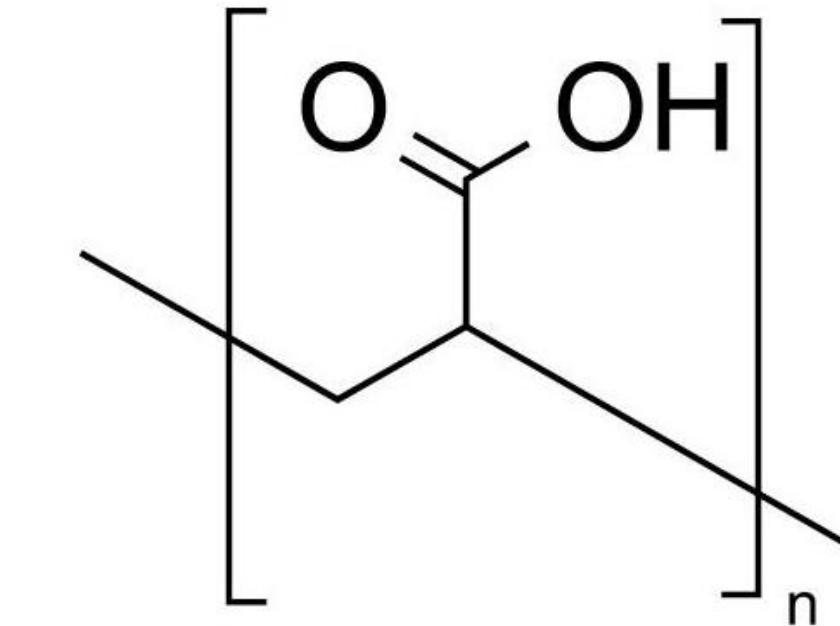
Spinosad is broken down rapidly by sunlight. In the presence of sunlight, half-lives on leaves are 2 to 16 days and less than one day in water. In the absence of sunlight, spinosad breaks down very slowly in water. Spinosad also sticks to soil and has a very low potential to move through soil towards ground water. In field studies, no break down products of spinosad were found below a soil depth of two feet. In the top layers of soil, spinosad is rapidly broken down by microbes.

GC4. DESIGNING SAFER CHEMICALS

Thermal Polyaspartic acid (TPA): It is a substitute for non-biodegradable polyacrylic acid (PAC).



Polyaspartic acid (TPA)



polyacrylic acid (PAC).

GC5. SAFER SOLVENTS, AND AUXILIARIES

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

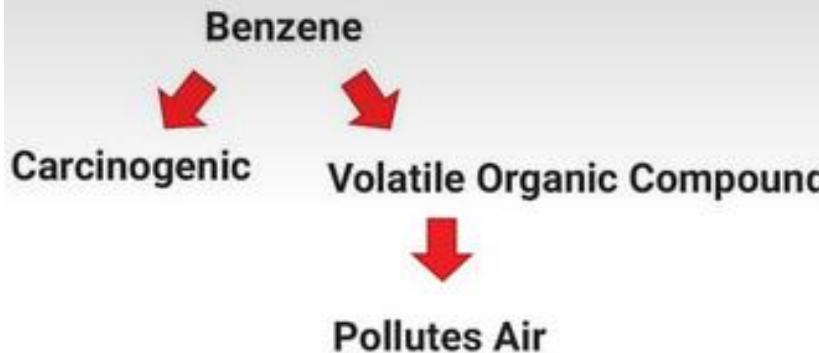


Chemical reactions should be designed to use safer solvents.

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

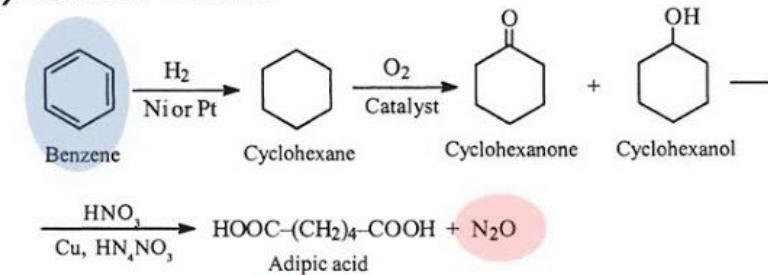
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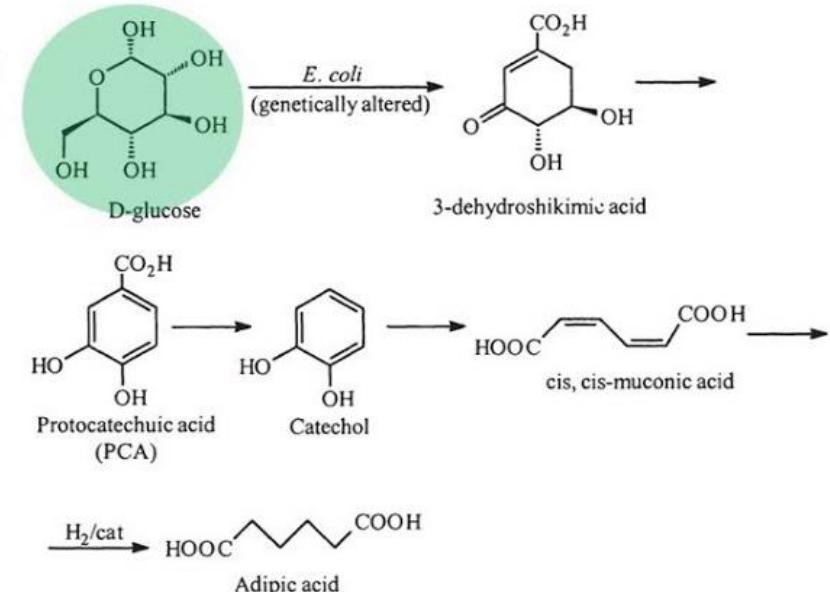


Benzene, however, is carcinogenic and it pollutes the air.

Adipic acid:
Conventional Synthesis Route

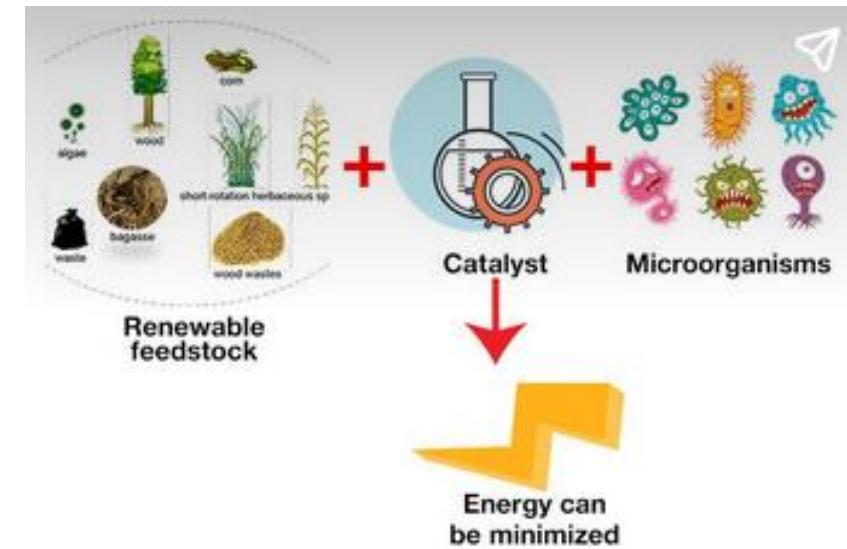


Green Synthesis Route



GC6. 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

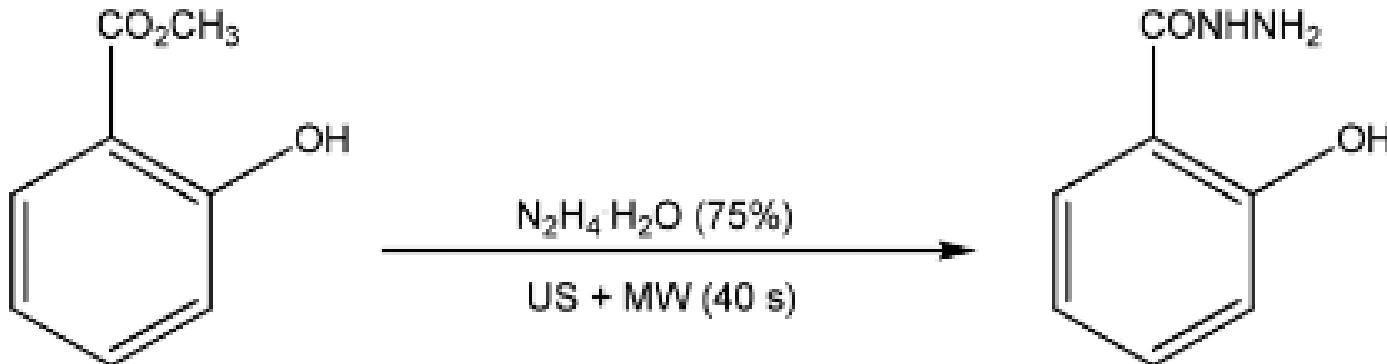


Chemical synthesis should be designed to minimize the use of energy.

This can be achieved by use of bio catalyst, microorganisms for organic synthesis, using renewable materials, etc.

GC6. DESIGN FOR ENERGY EFFICIENCY

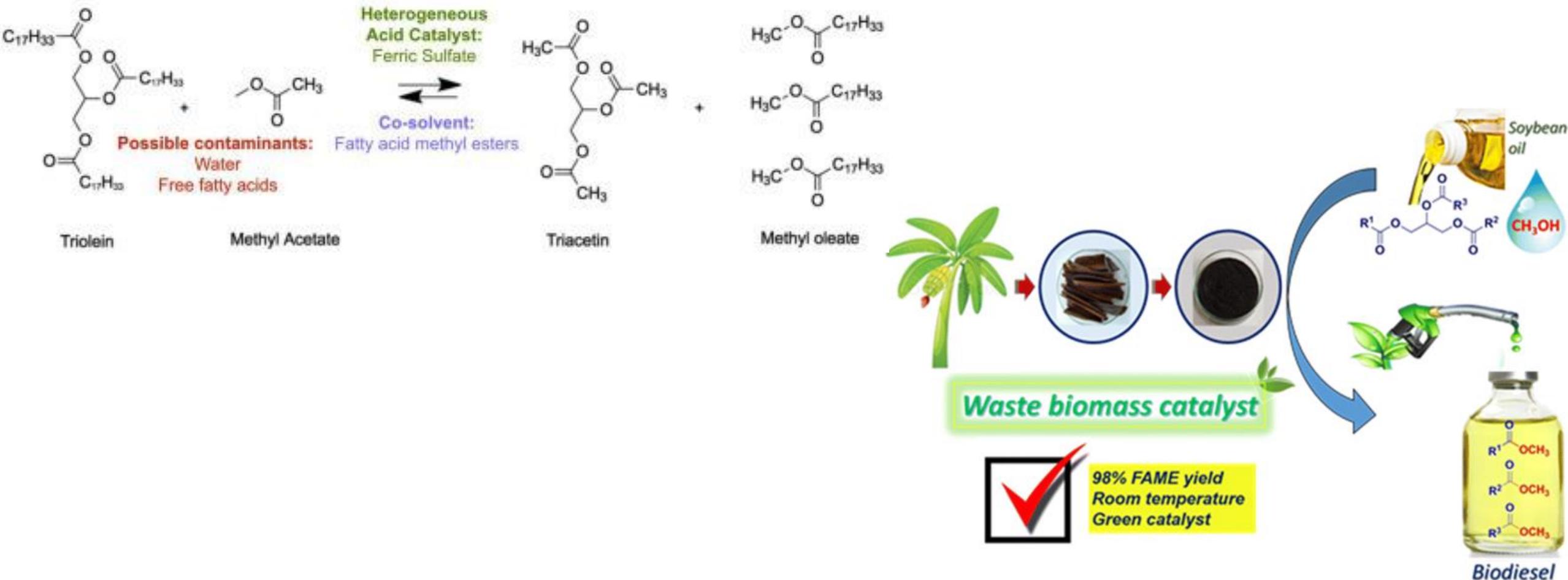
Hydrazinolysis of methyl salicylate using different method



Entry	Method	Reaction time	Isolated yield (%)
1	Conventional reflux	9 h	73
2	Ultrasound (20 kHz, 50 W) + reflux	1.5 h	79
3	Microwave (2.45 GHz, 200 W)	18 min	80
4	Simultaneous MW (200 W) and US (50 W)	40 s	84

GC7. USE OF RENEWABLE FEEDSTOCK

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



GC7. USE OF RENEWABLE FEEDSTOCK:



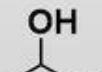
Petrochemical resources

Acetaldehyde

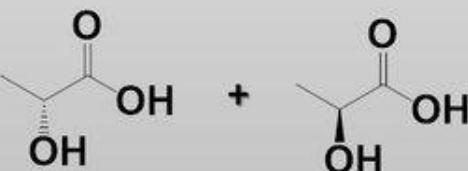


Addition of HCN and catalyst

Lactonitrile



Hydrolysis by H_2SO_4



Racemic DL-Lactic acid



Renewable resources

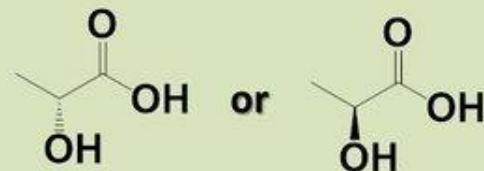
SSF*

Fermentable carbohydrates

Microbial fermentation

Fermented broth

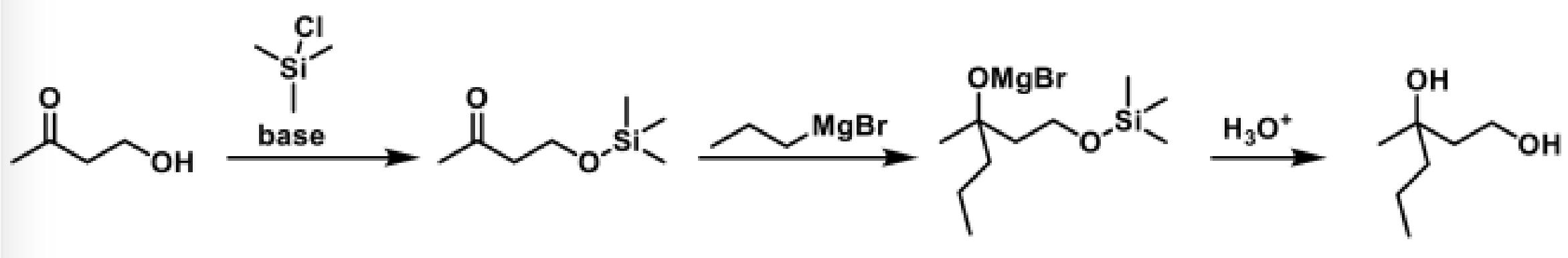
Recovery and purification



Optically pure D(-)- or L(+) -lactic acid

*SSF: Simultaneous Saccharification and Fermentation

Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste

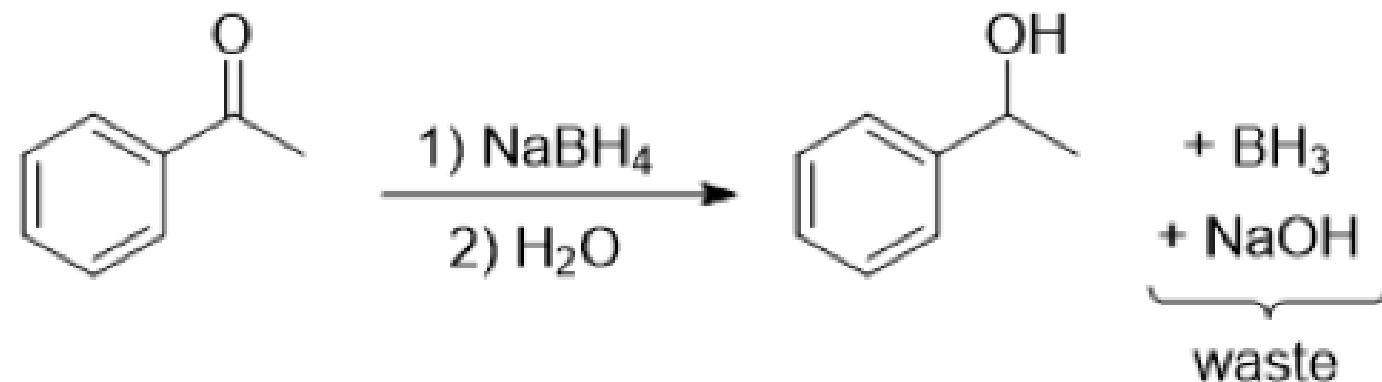


This example of a selective reaction uses a protecting group, but this requires 3 steps to only make 1 change. Instead, we can eliminate the need for protecting groups by designing new and more selective reactions that are much more efficient.

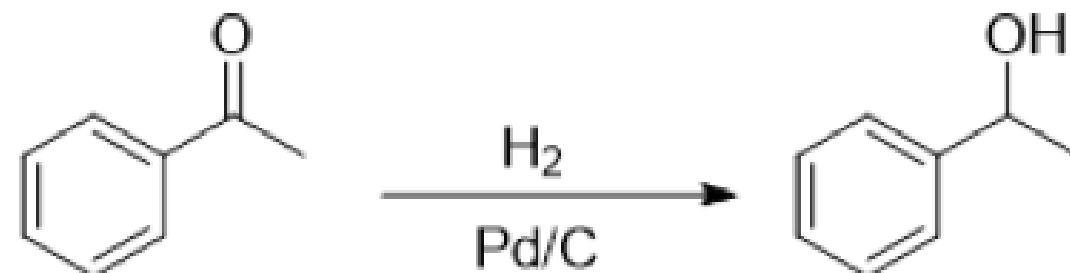
GC9. CATALYSIS

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

Stoichiometric:



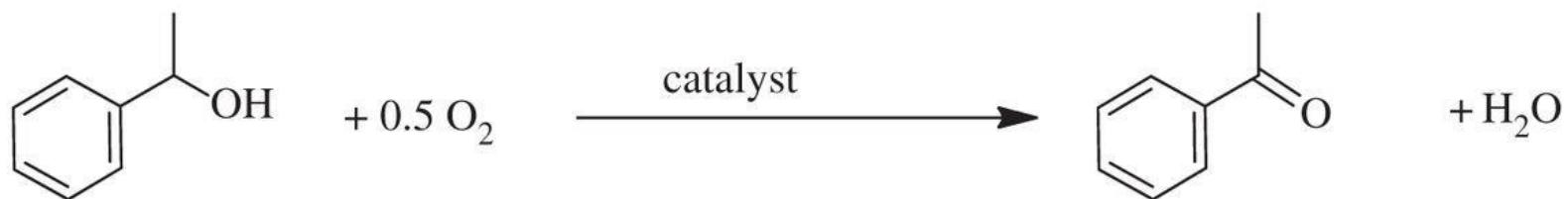
Catalytic:



GC9. CATALYSIS



atom economy = 44 %
E factor > 3
Cr-containing waste



atom economy = 91%
E factor ≤ 0.1
water as waste

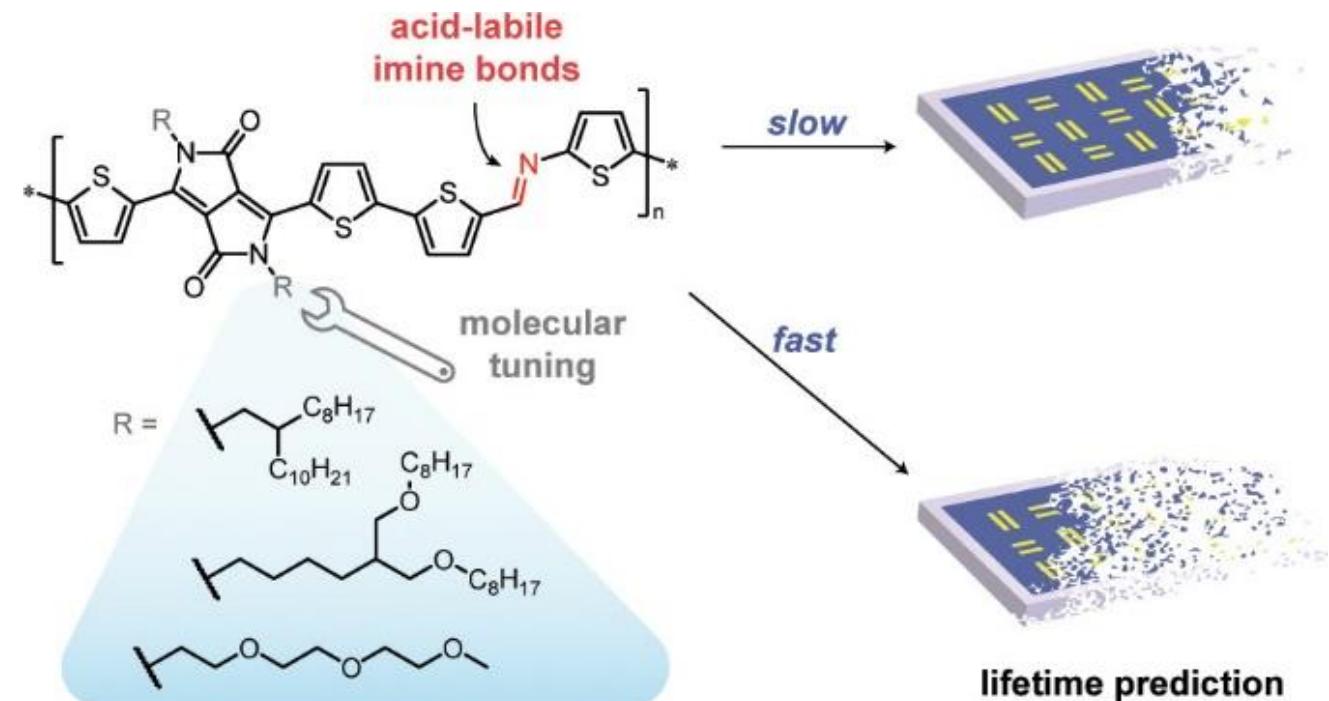
- catalyst: water soluble Pd (II) complex
- air as oxidant
- aqueous biphasic system
- no organic solvent
- catalyst recycled via phase separation

GC10. DESIGN FOR DEGRADATION

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

Polymer semiconductors

Systematically designed and characterized a series of **fully degradable diketopyrrolopyrrole-based polymers** with engineered sidechains to investigate the impact of several molecular design parameters on the degradation lifetimes of these polymers.

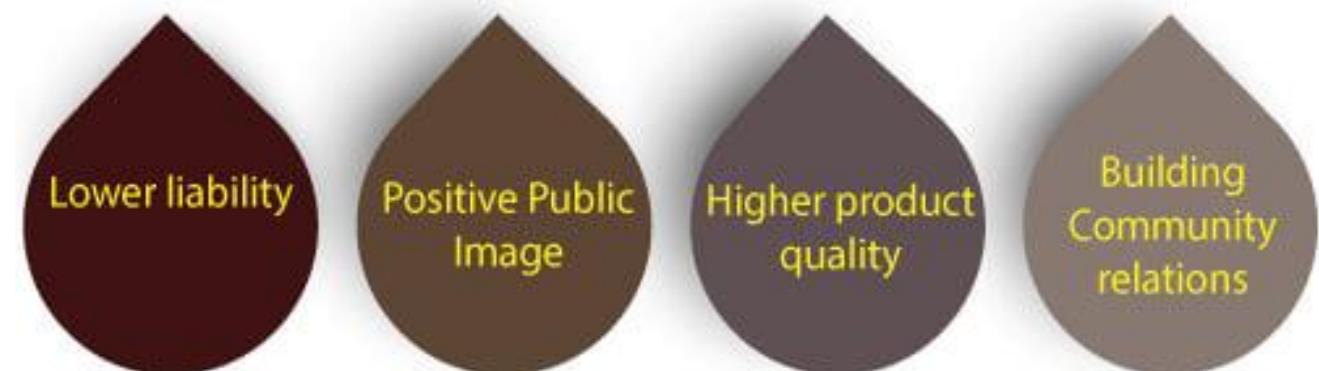


GC11. REAL-TIME ANALYSIS FOR POLLUTION PREVENTION

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances



Benefits of Industrial Pollution Prevention



GC12. INHERENTLY SAFER CHEMISTRY FOR ACCIDENT PREVENTION

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



Inherently Safer Chemistry
for Accident Prevention



E-WASTE RECYCLING



“E-waste”, “electronic waste”, “e-scrap” Are used electronics that are nearing the end of their useful life, and are discarded.

Waste printed circuit boards (PCBs)

- PCBs comprise metals (Cu, Sn, Pb, Ag, Au, Pd, Fe, Ni, and Cr), nonmetals (glass fibers, electronic component insulators, capacitors, resistors, and so on), and organic compounds (epoxy resin, paints...).
- Copper is the primary component of PCB, which is employed as an electric current conductor.
- These discarded metals without treatment threaten the economy, the environment, and human health.

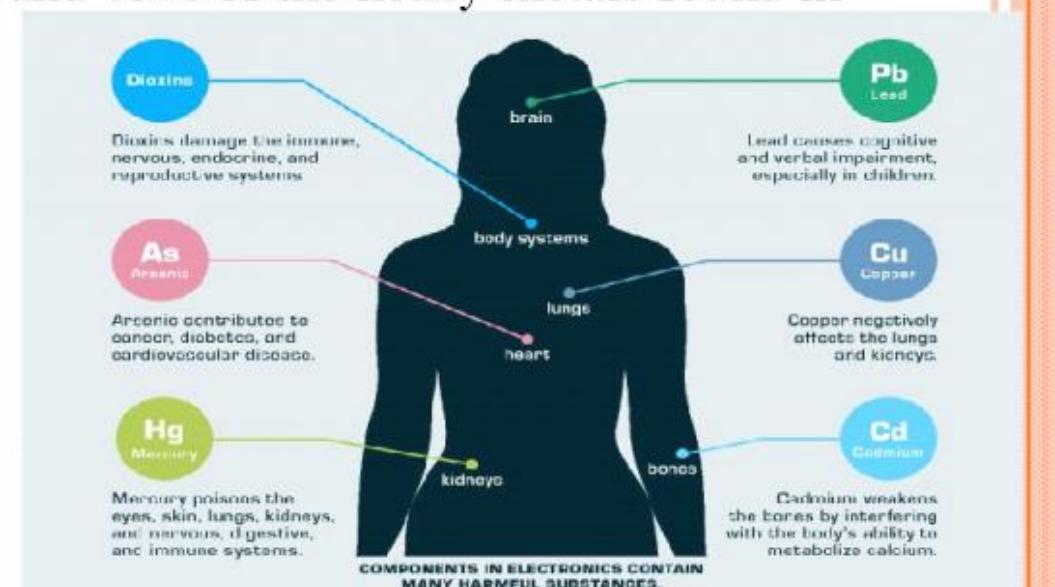
EFFECTS OF HAZARDOUS E-WASTE

On Environment

- ❑ Pollution of ground water
- ❑ Acidification of soil
- ❑ Air pollution
- ❑ E waste accounts for 40% of lead and 75% of the heavy metals found in landfills

On Human Health

- ❑ DNA damage
- ❑ Lung cancer
- ❑ Damage to heart,liver, and spleen
- ❑ Chronic damage to the brain
- ❑ Asthmatic bronchitis





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E-Waste Component	Process Used	Potential Environmental Hazard
Cathode ray tubes (used in TVs, computer monitors, ATM, video cameras, and more)	Breaking and removal of yoke, then dumping	Lead, barium and other heavy metals leaching into the ground water and release of toxic phosphor
Printed circuit board (image behind table – a thin plate on which chips and other electronic components are placed)	De-soldering and removal of computer chips; open burning and acid baths to remove metals after chips are removed.	Air emissions and discharge into rivers of glass dust, tin, lead, brominated dioxin, beryllium cadmium, and mercury
Chips and other gold plated components	Chemical stripping using nitric and hydrochloric acid and burning of chips	PAHs, heavy metals, brominated flame retardants discharged directly into rivers acidifying fish and flora. Tin and lead contamination of surface and groundwater. Air emissions of brominated dioxins, heavy metals, and PAHs
Plastics from printers, keyboards, monitors, etc.	Shredding and low temp melting to be reused	Emissions of brominated dioxins, heavy metals and hydrocarbons
Computer wires	Open burning and stripping to remove copper	PAHs released into air, water and soil.

Environment and health hazards

Lead: Exerts toxic effects on various systems in the body such as the **central and peripheral nervous systems**, the hemopoietic system (anaemia), the genitourinary system (capable of causing damage to all parts of nephron) and the **reproductive systems** (male and female).

Mercury: causes damage to the genitourinary system (tubular dysfunction), **the central and peripheral nervous systems** as well as the foetus. When inorganic mercury spreads out in the water, it is transformed into **methylated mercury**, which bio-accumulates in living organisms and concentrates through the food chain, particularly by fish.

Cadmium: is a potentially long-term cumulative poison. Toxic cadmium compounds accumulate in the human body, especially in the **kidneys**.

Polycyclic aromatic hydrocarbons (PAH): Affects **lung, skin and bladder**. Epidemiological studies in the past on occupational exposure to PAH provide sufficient evidence of the role of PAH in the induction of **skin and lung cancers**.

Table 1. Chemical composition of mechanically treated WPCBs.

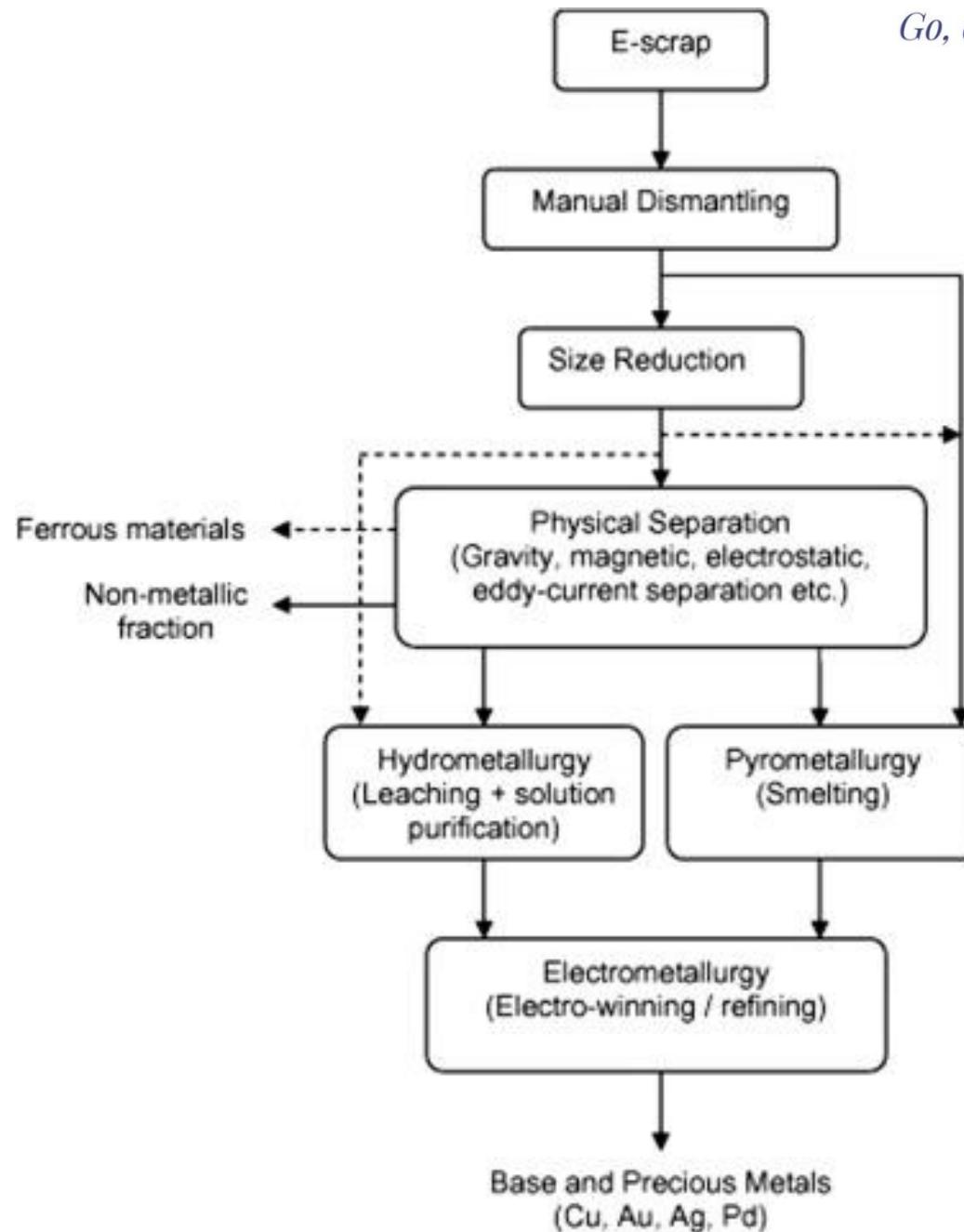
Material	Share	Unit
Metals		
Cu	25.51	wt. %
Sn	3.57	wt. %
Pb	2.47	wt. %
Zn	2.18	wt. %
Fe	0.85	wt. %
Ni	0.18	wt. %
Al	<0.1	wt. %
Sb	960	ppm
Co	620	ppm
Ag	6800	ppm
Au	203	ppm
Glass/Ceramic		
SiO ₂	21.94	wt. %
Al ₂ O ₃	6.16	wt. %
TiO ₂	0.88	wt. %
Na ₂ O	0.14	wt. %
Polymer	~35	wt. %

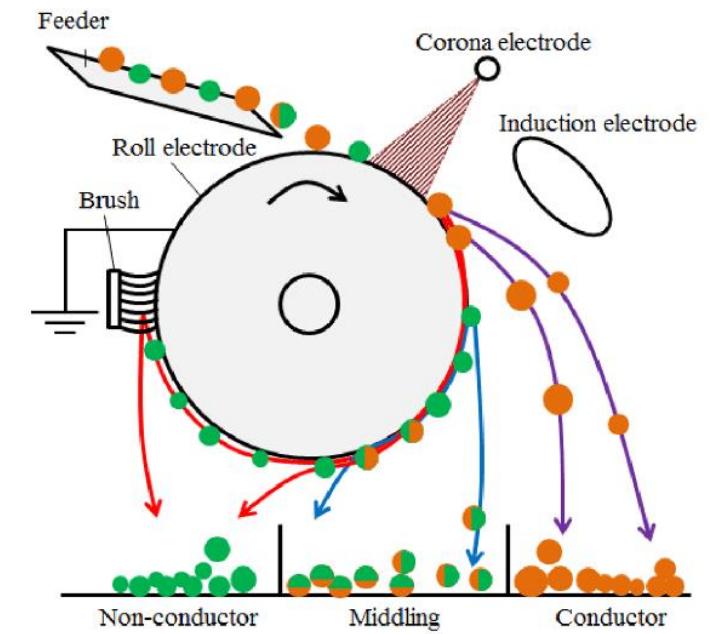
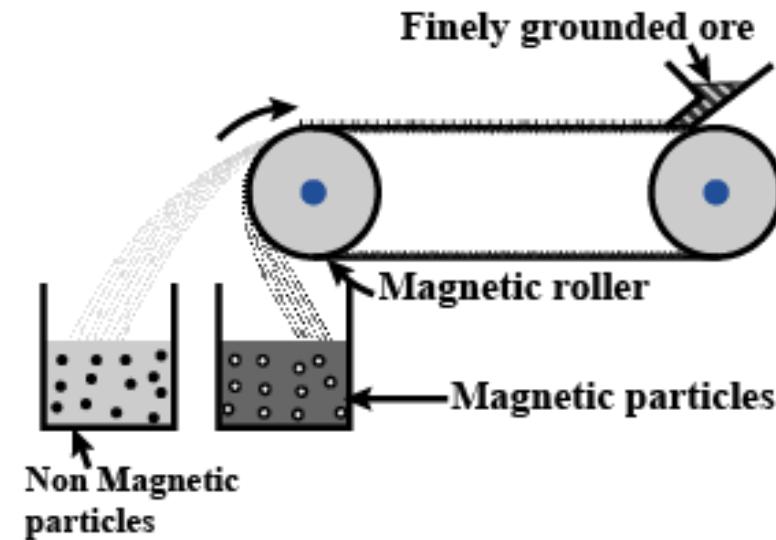
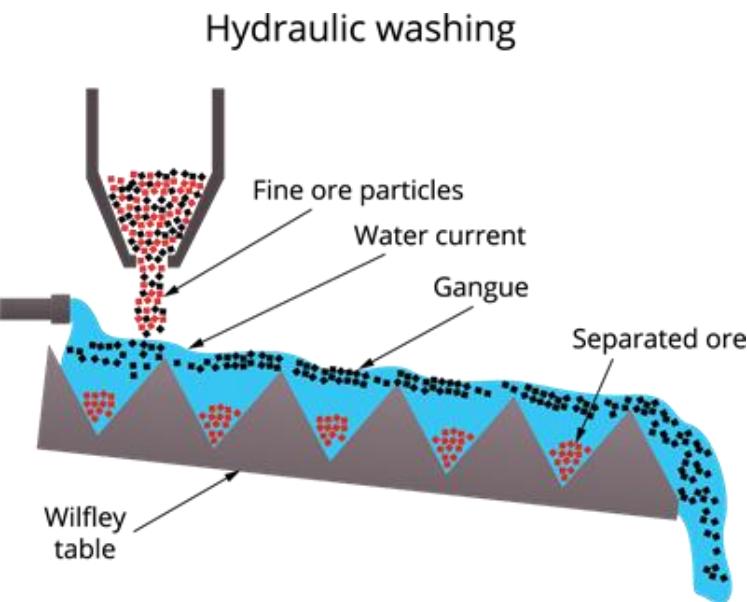
A typical PCB comprises 40% metals, 30% plastics and 30% ceramics, with the metal fraction comprising 10–27% Cu, 2–8% Al, 1–4% Pb, 1–8% Fe, 1–6% Sn, 0.2–3.6% Ni, 0.1–1.5% Zn and <0.1% precious metals

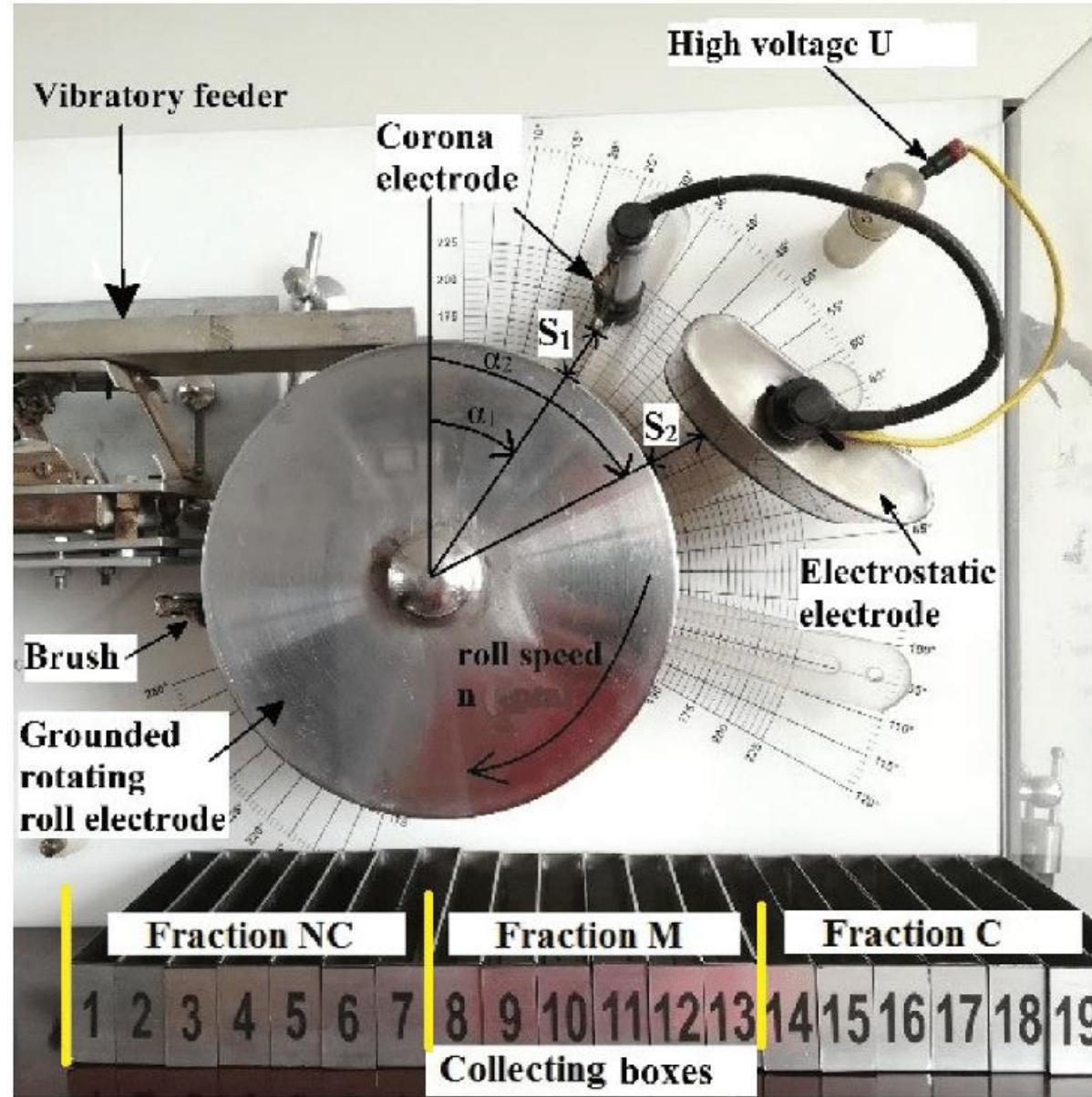
Commonly used examples of ferrous metals include steel, stainless steel, carbon steel, cast iron and wrought iron:

- Steel. A combination of iron and carbon, steel is renowned for its strength and machinability. ...
- Stainless Steel. ...
- Carbon Steel. ...
- Cast Iron. ...
- Wrought Iron.

Non-ferrous metals include **aluminium, copper, lead, nickel, tin, titanium and zinc**, as well as **copper alloys like brass and bronze**.

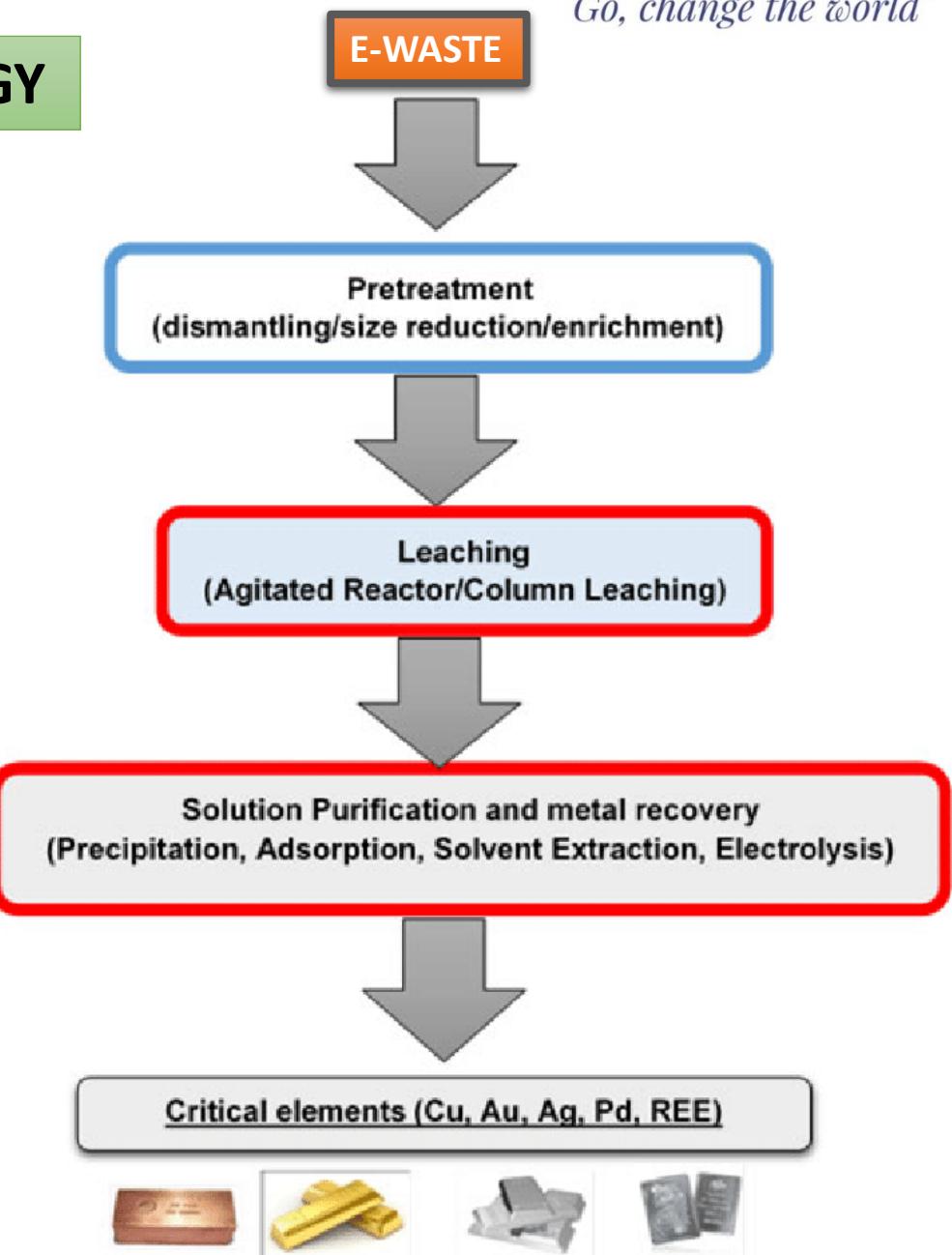






HYDROMETALLURGY

- It involves the use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual materials.
- It is generally used to extract the metals having relatively less electro positive such as gold, copper, silver, platinum, palladium etc.
- The steps involved in this method are (1) Leaching, (2) Solution concentration and purification, and (3) Metal recovery.
- **Leaching:** After mechanical segregation and powdering of the e-waste, The e-waste powder is dissolved in concentrated aqueous solutions of acids ($\text{HNO}_3/\text{HCl}/\text{HClO}_4/\text{H}_2\text{SO}_4$) and alkali to selectively dissolve and precipitate the metals. By carefully optimizing the oxidation potential, temperature, and pH of the solutions, the metals are dissolved selectively.



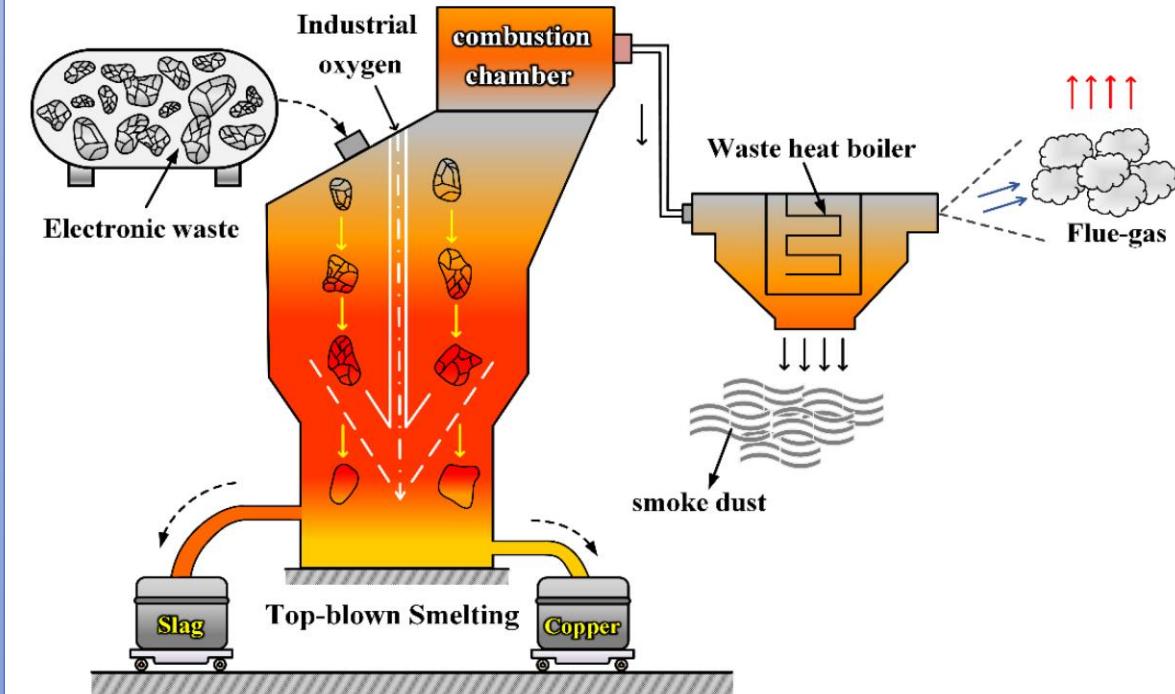
- **Solution Concentration and Purification :** After leaching, the solution is concentrated by removing the unwanted other metals (retaining the metal to be recovered in solution). By using precipitating agents, adsorbents like charcoal, activated carbon, by solvent extraction, or by electrolysis methods, the interfering metals, non metals are removed from the solution.
- **Metal Recovery:** It is the final step in a hydrometallurgical process which involves the electrolysis, gaseous reduction, and precipitation of precious metals. Metals suitable for sale as raw materials are often directly produced in the metal recovery step.



Pyrometallurgy is the predominantly used technology for industrial e-waste treatment. It involves **smelting in furnaces at high temperatures/ incineration/ combustion, and pyrolysis**. It is a conventional process to recover nonferrous and precious *metals from electronic waste*.

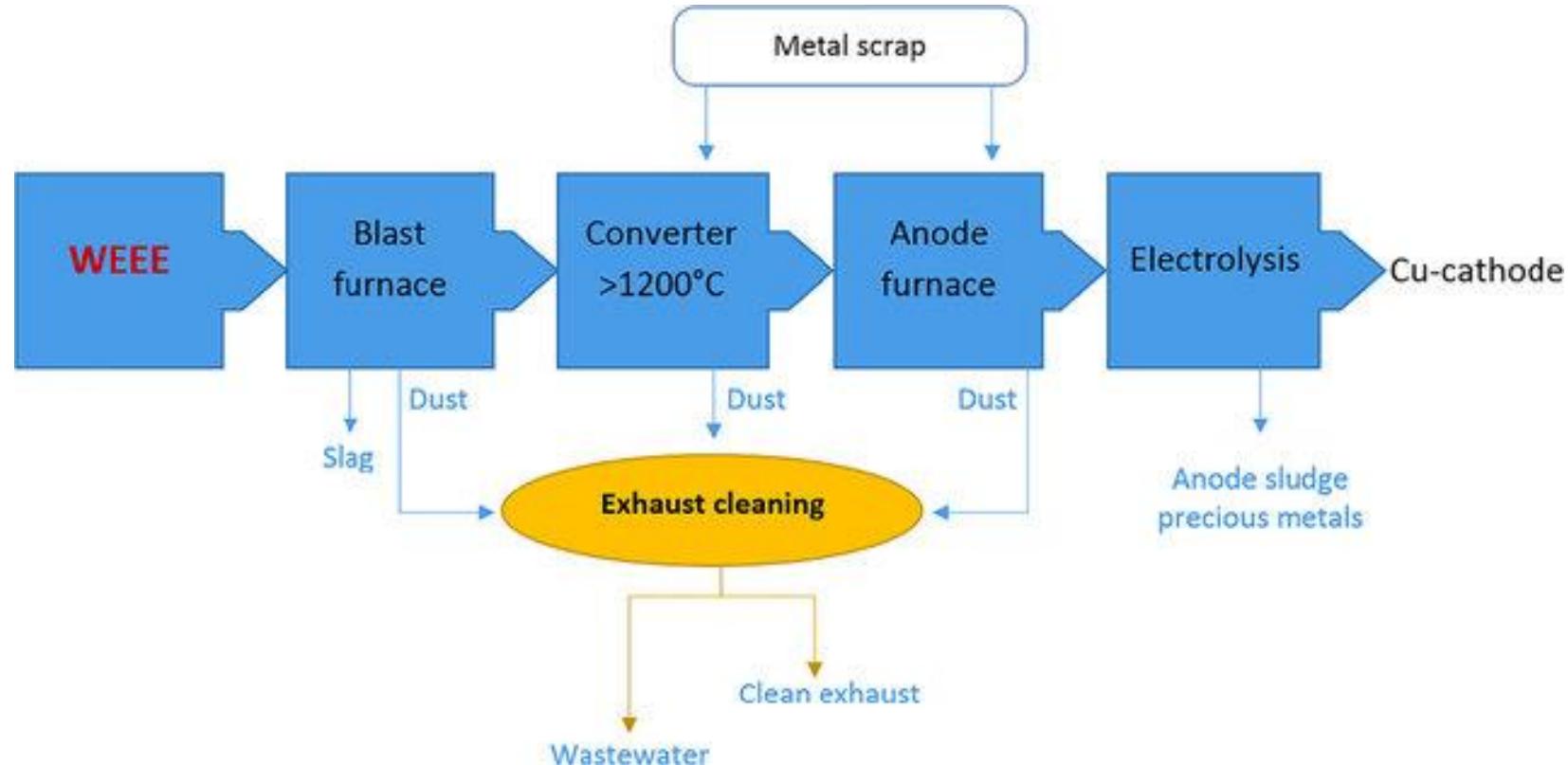
In the pyrometallurgy process, the crushed scraps are liquefied in a furnace or in a molten bath to remove plastics

1. firstly, the crushed electronic waste, slagging flux, and additives are put into the high-temperature furnace together with air.
2. The refractory oxides such as plastics and glass fibers are burned and removed from the molten pool in the form of high-temperature flue gas.
3. Then the impurity metal is oxidized to form the slag phase with slagging flux, at the same time, the copper and precious metals such as gold, silver, platinum, and palladium form a molten metal phase.
4. Finally, the metal phase and the slag phase are stratified due to the difference in immiscibility and density.



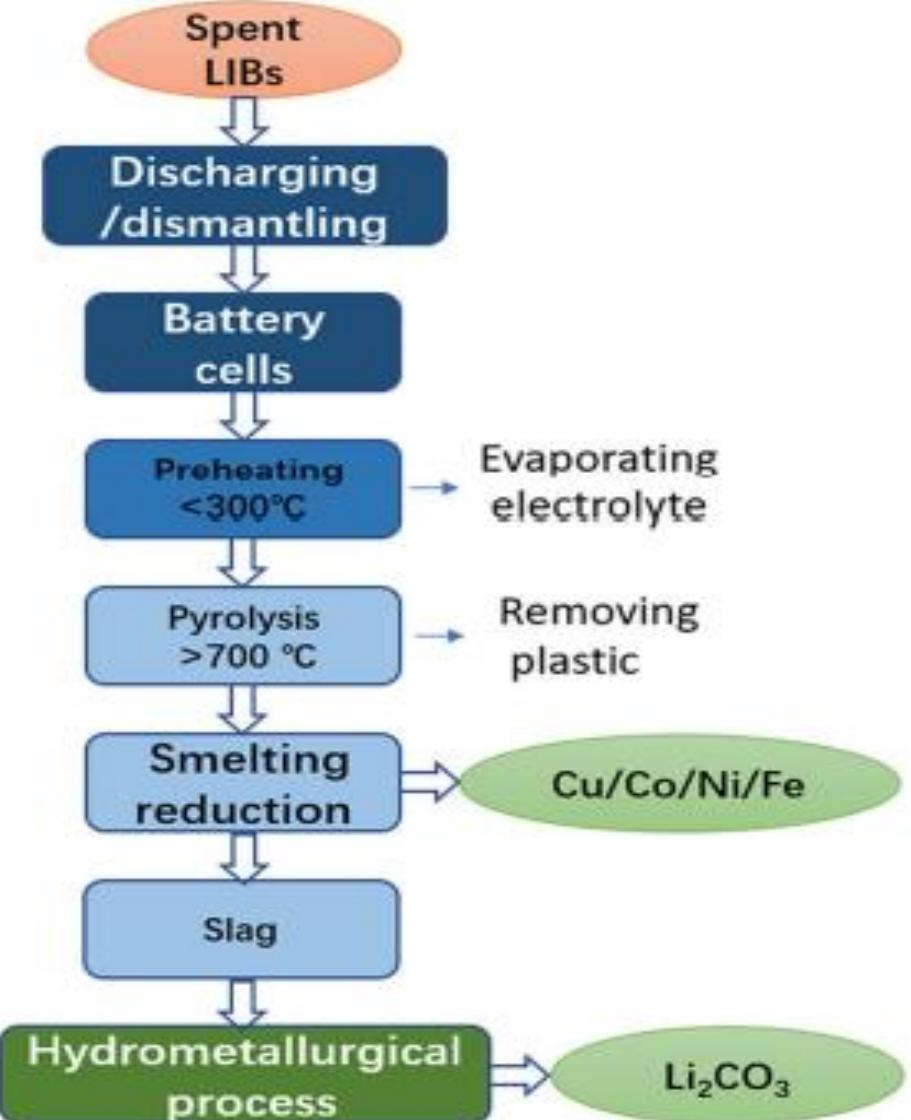
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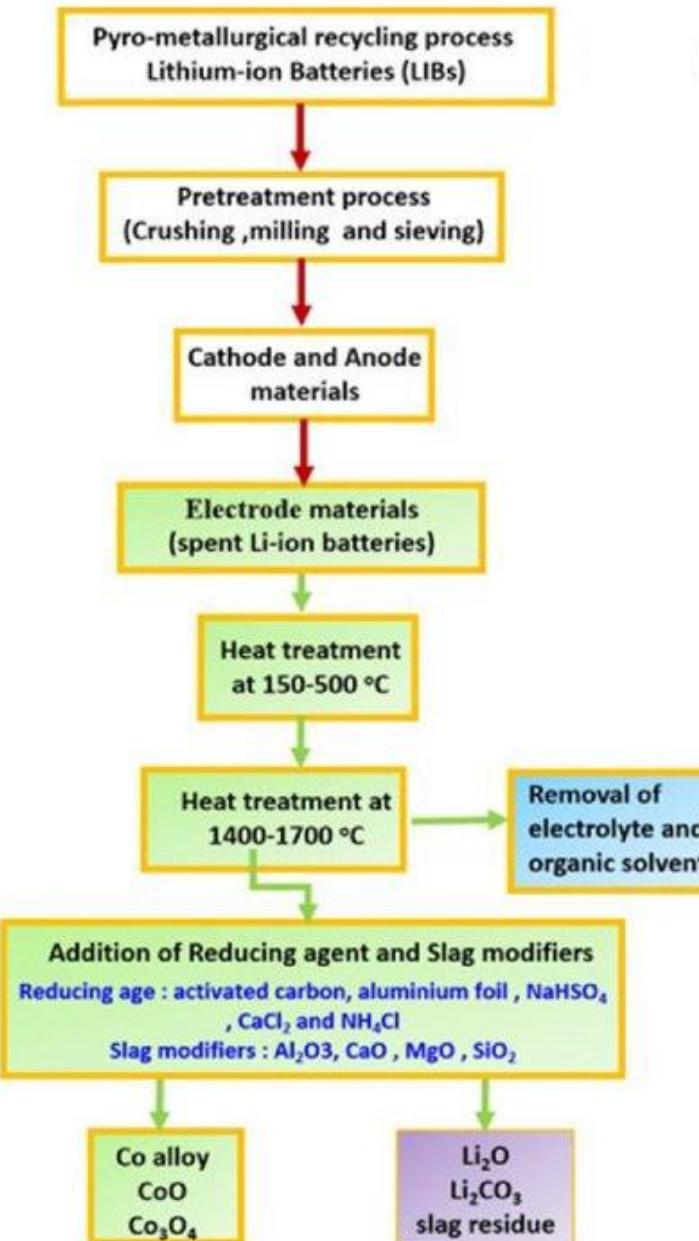
Pyrometallurgy process includes smelting in a plasma arc furnace, blast furnace or copper smelter, incineration, and high heat roasting in the presence of selective gases to recover mainly nonferrous metals



Pyrometallurgical processing scheme based on industrial copper/WEEE smelting process

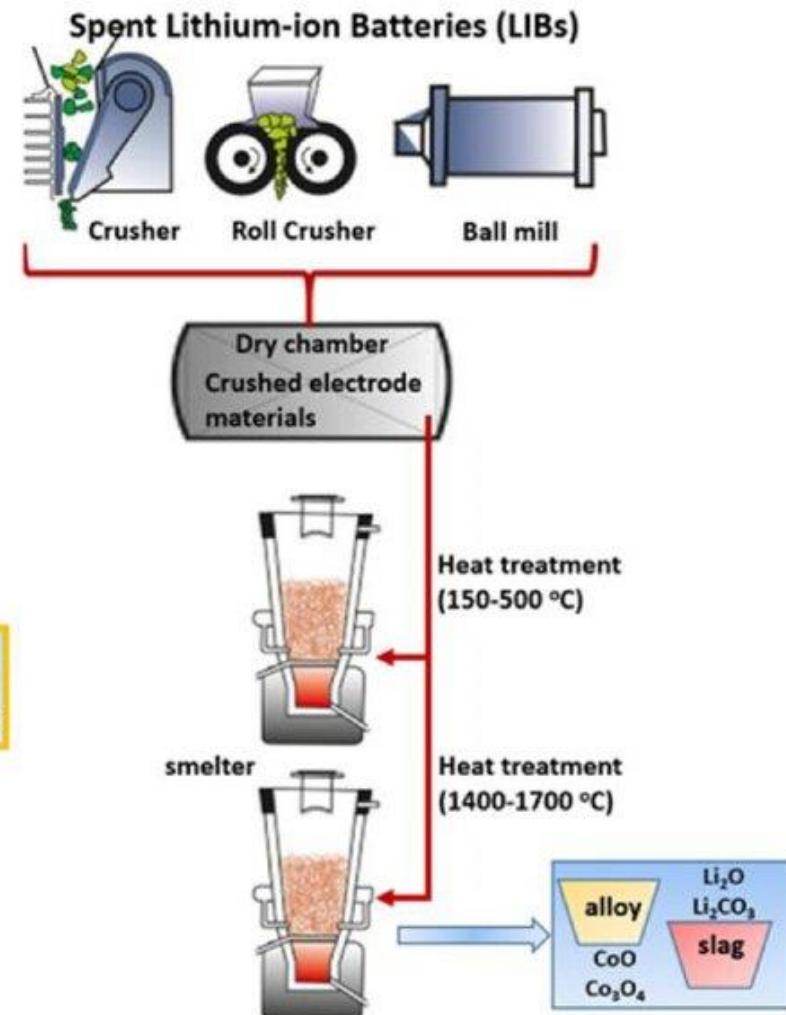
<https://doi.org/10.1007/s11356-020-09630-2>





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PYRO-METALLURGICAL PROCESSES



Batteries are subjected to preheating, pyrolysis and smelting,

1. Firstly, the waste battery (Li or Co battery) are disassembled into separate cells and then fed into a heating furnace.
2. Then the electrode materials are transferred to preheating zone of the furnace, having temperature below 300 °C to ensure complete evaporation of the electrolyte without explosion.
3. After evaporating electrolyte, the furnace temperature is increased above 700 °C to remove the plastic of the battery.
4. In the smelting reduction zone, the material is smelted into alloys of Cu, Co, Ni, and Fe, along with Li, Al, Si, Ca, and some Fe slag. This method is usually only used to recover Cu, Co, Ni, and small amounts of Fe. Since Co plays an irreplaceable role in commercial LIBs, and thermal metallurgy has a high efficiency in recovering Co rather than Li.
5. Then to recover Li from the spent LIBs, the selective pyrolysis method of an arc furnace can be used to convert some electrode materials into Co alloys and Li concentrate Li_2CO_3 , which can be separated based on difference in gravity, solubility and density. Or by hydrometallurgy.

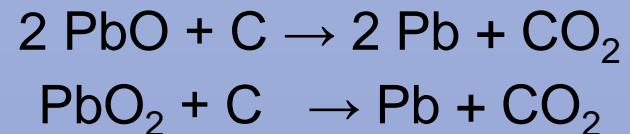
Metallurgical aspects of lead recycling from battery scrap

Lead acid batteries are recycled pyrometallurgically with initial physical separation and subsequent hydrometallurgical steps

1. Spent batteries are broken/crushed into small pieces.
2. After breaking, the material is passed to a sink/float operation. This hydrodynamic process separates the metal from separators and casing material.
3. The casing material is usually polypropylene (PP), although acrylonitrile butadiene styrene is becoming more widespread because of its higher strength. Separation is accomplished by virtue of the density difference between materials using a fluid of intermediate density between the solid phases. Since the density of PP is less than that of water, while the density of lead metal/compound is much higher, sink/float operation is extremely effective, achieving almost complete quantitative segregation.
4. Plastics are subsequently cleaned and sent for recycling into new battery cases or for other uses. Lead, grid straps, posts and battery paste (a combination of the PbO_2 , PbO and $PbSO_4$) are removed from the bottom of the sink/float operation and sent to storage for water removal prior to smelting.

Lead recovery: Either the components of an accumulators like lead, plastics, acids, etc. are at first separated and then processed individually

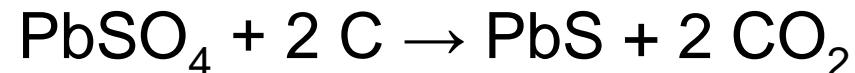
The first type of chemical reaction converts PbO (PbO_2) into Pb through a reduction process:



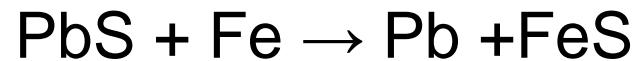
Sulphur removal: The second type converts PbSO_4 into PbS , again through a reduction process:



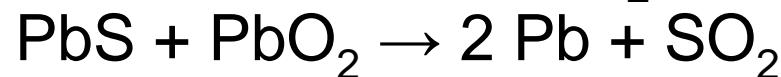
Sulphur removal: The second type converts PbSO_4 into PbS , again through a reduction process:



Finally PbS is converted into Pb through the following reactions:



or



Removal of Sulphuric acid can be done by neutralizing with soda ash or caustic soda





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