Topic 6 - Mitigation techniques and methodologies
Bioplastics

Ulisses

UNIVERSITY OF LISBON
INTERDISCIPLINARY STUDIES
ON SUSTAINABLE ENVIRONMENT AND SEAS

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United Nations Sustainable Development Knowledge Platform the 2030 Agenda for Sustainable Development. Available online: https://sdgs.un.org/2030agenda (accessed on 15 April 2021).

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PLASTICS

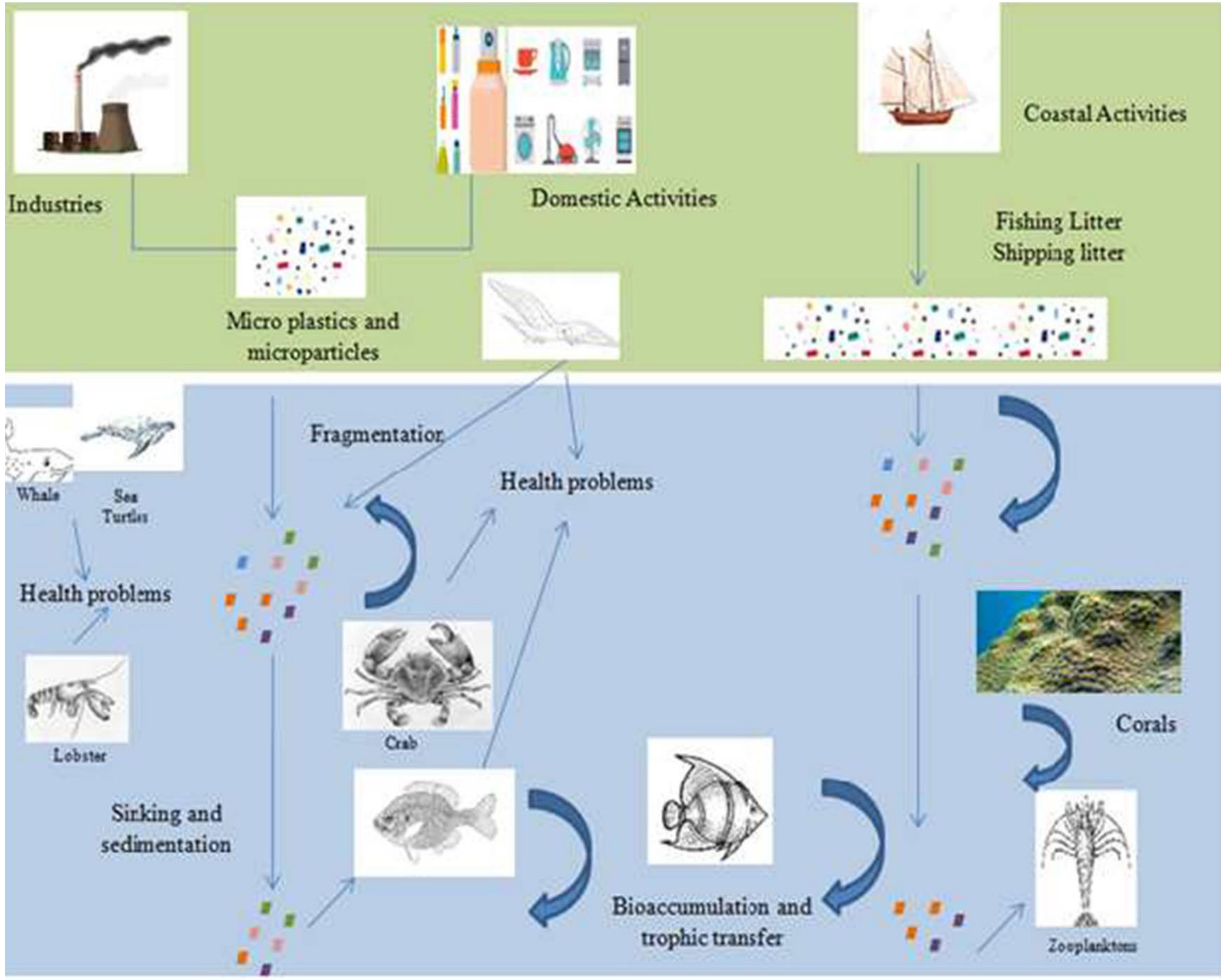
Scavengers collect plastic materials at a garbage dump in Banda Aceh, Indonesia. *Chaideer Mahyuddin/AFP/Getty Images*

The European Union is working towards the 2050 net-zero emissions goal and tackling the ever-growing environmental and sustainability crisis by implementing the *European Green Deal*.

The European Green Deal [1] is the action plan outlined by the European Commission (EC) to tackle the ever-growing environment and climate-related challenges our society faces. The plan aims at transforming "the EU into a fair and prosperous society, with a modern, resource-efficient and competitive economy where there are no net emissions of greenhouse gases in 2050 and where economic growth is decoupled from resource use" [1] (p. 2). As also stated in its communication "A new Circular Economy Action Plan for a Cleaner and More Competitive Europe"

1. European Commission. The European Green Deal COM(2019) 640 Final; European Commission: Brussels, Belgium, 2019.
2. European Commission. A New Circular Economy Action Plan For a Cleaner and More Competitive Europe COM(2020) 98 Final; European Commission: Brussels, Belgium, 2020.

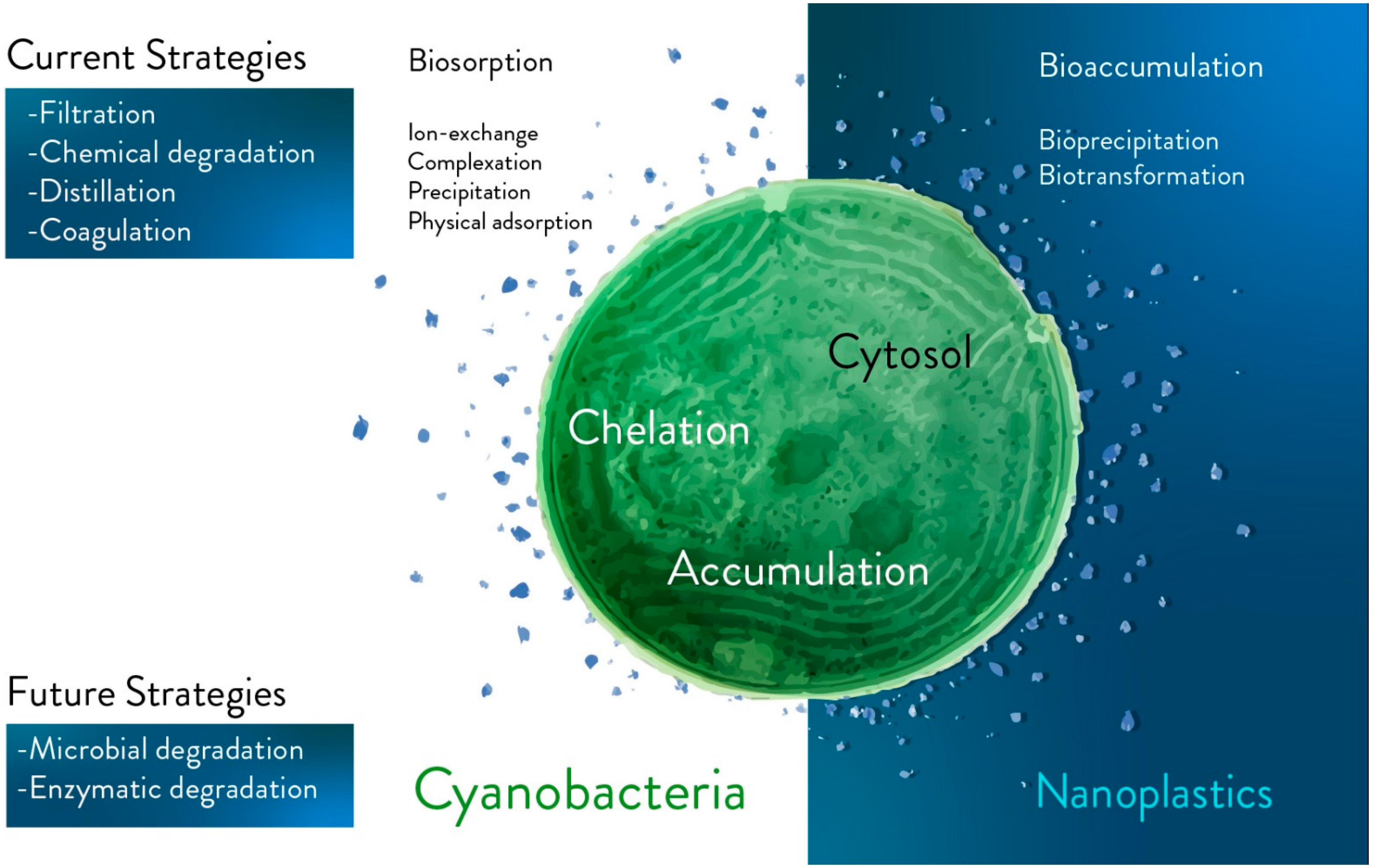
PLASTICS



https://www.google.com/search?q=microplastics+and+ocean

Plastics Mitigation Strategies

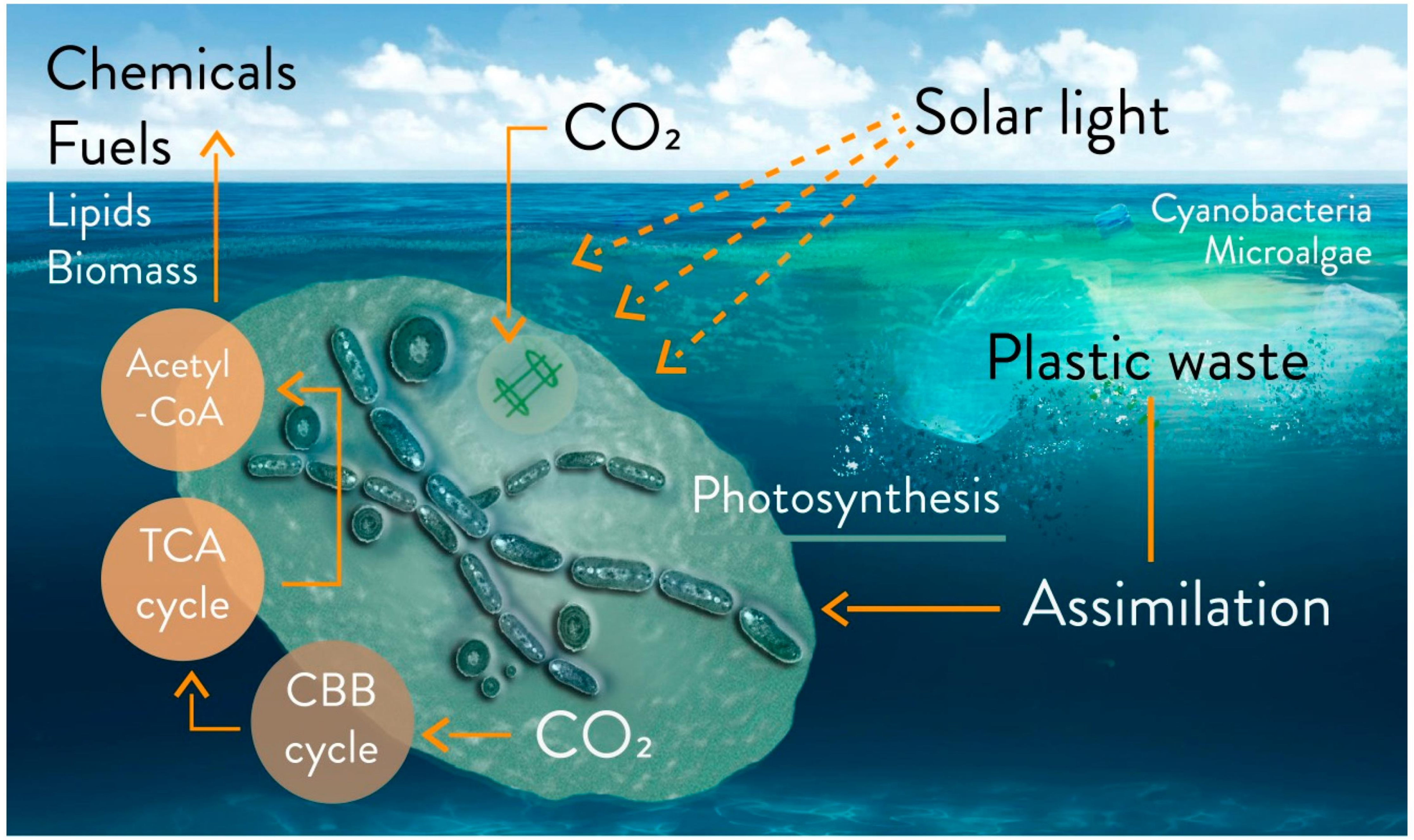
Main current (e.g., filtration, chemical degradation, distillation, and coagulation) and future (e.g., in vivo degradation via microorganisms, and enzyme-based degradation) strategies



https://www.mdpi.com/2071-1050/12/24/10449/htm

Future strategies are based on biological tools and potentially on in vivo approaches.
Biosorption (e.g., ion-exchange, complexation, precipitation, and physical absorption),
intracellular bioaccumulation (e.g., bioprecipitation and biotransformation)
and extracellular mechanisms are approaches to be further investigated with the aim of capturing fragments of plastic comparable in size to photosynthetic microorganisms (e.g., the dimensions of nanoplastics and cyanobacteria).

Microbial Degradation: Cyanobacteria and Microalgae



CBB cycle: Calvin–Benson–Bassham cycle; TCA cycle: tricarboxylic acid cycle; acetyl-CoA: acetyl coenzyme A.

https://www.mdpi.com/2071-1050/12/24/10449/htm

Biodegradation and bioremediation of floating plastic fragments from accumulated plastic waste in marine water with microalgae and cyanobacteria, via metabolic uptake or biosorption.

Engineered strains can be utilized, nowadays on a laboratory scale, utilizing macro-, micro- and nanoplastics as sources of carbons.

Biofuel (e.g., H_2 and isobutanol), biochemicals, lipids, and biomass can be products based on photosynthetic microbial growth on floating plastic wastes.

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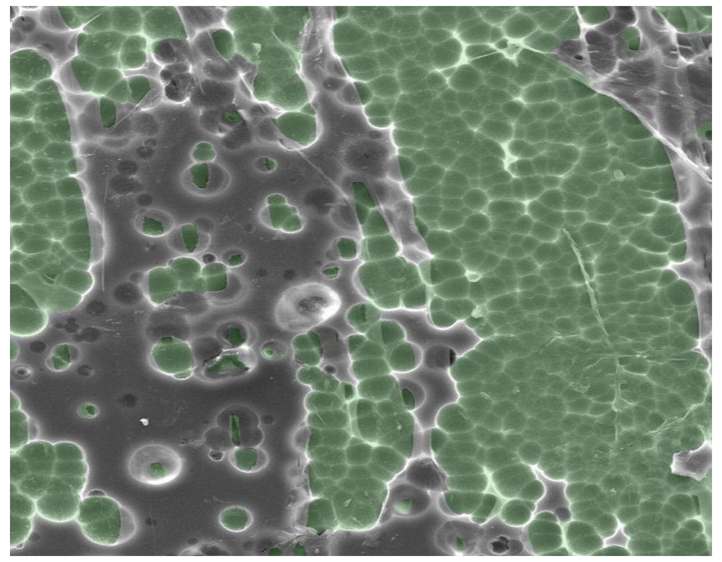
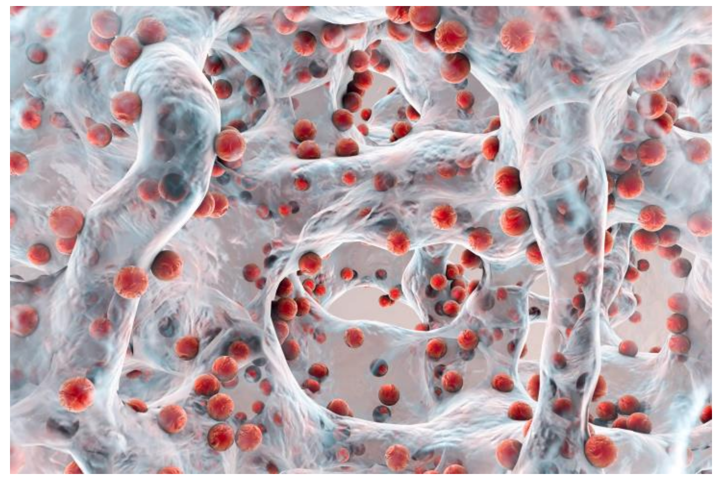
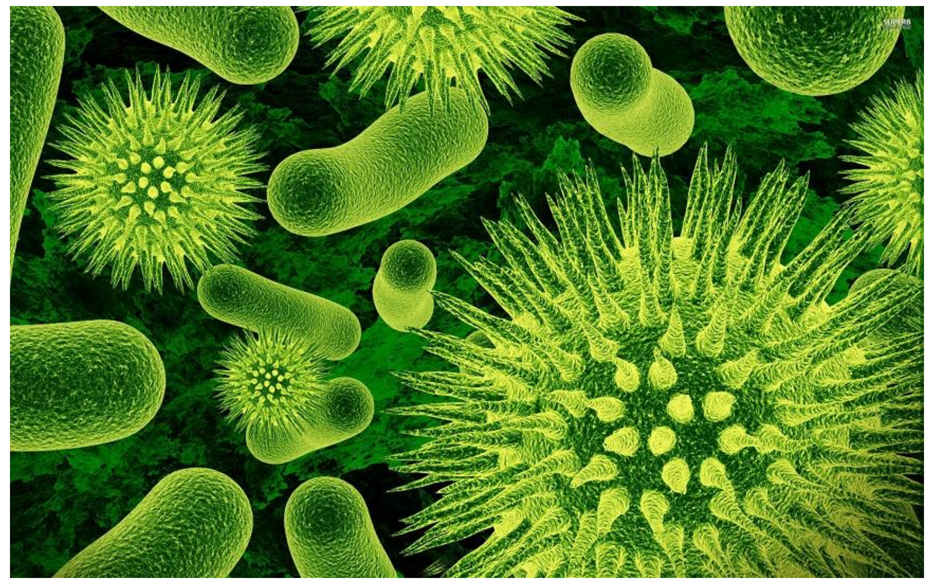
Microbial Degradation: *Ideonella sakaiensis*

Ideonella sakaiensis 201-F6 break PET down and use the plastic for energy

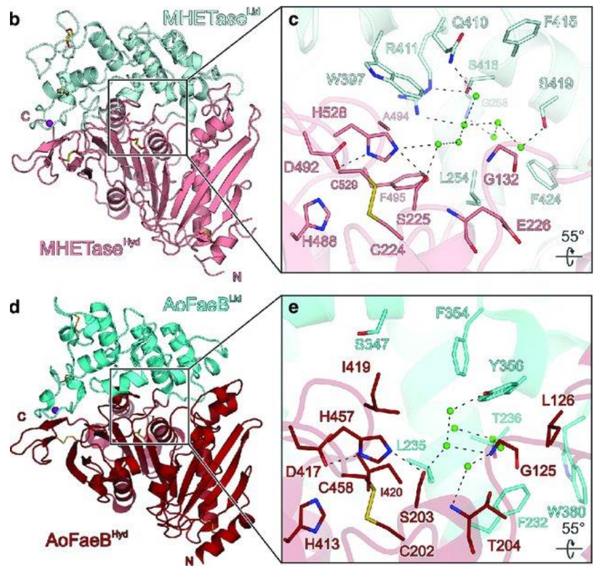




https://zap.aeiou.pt/

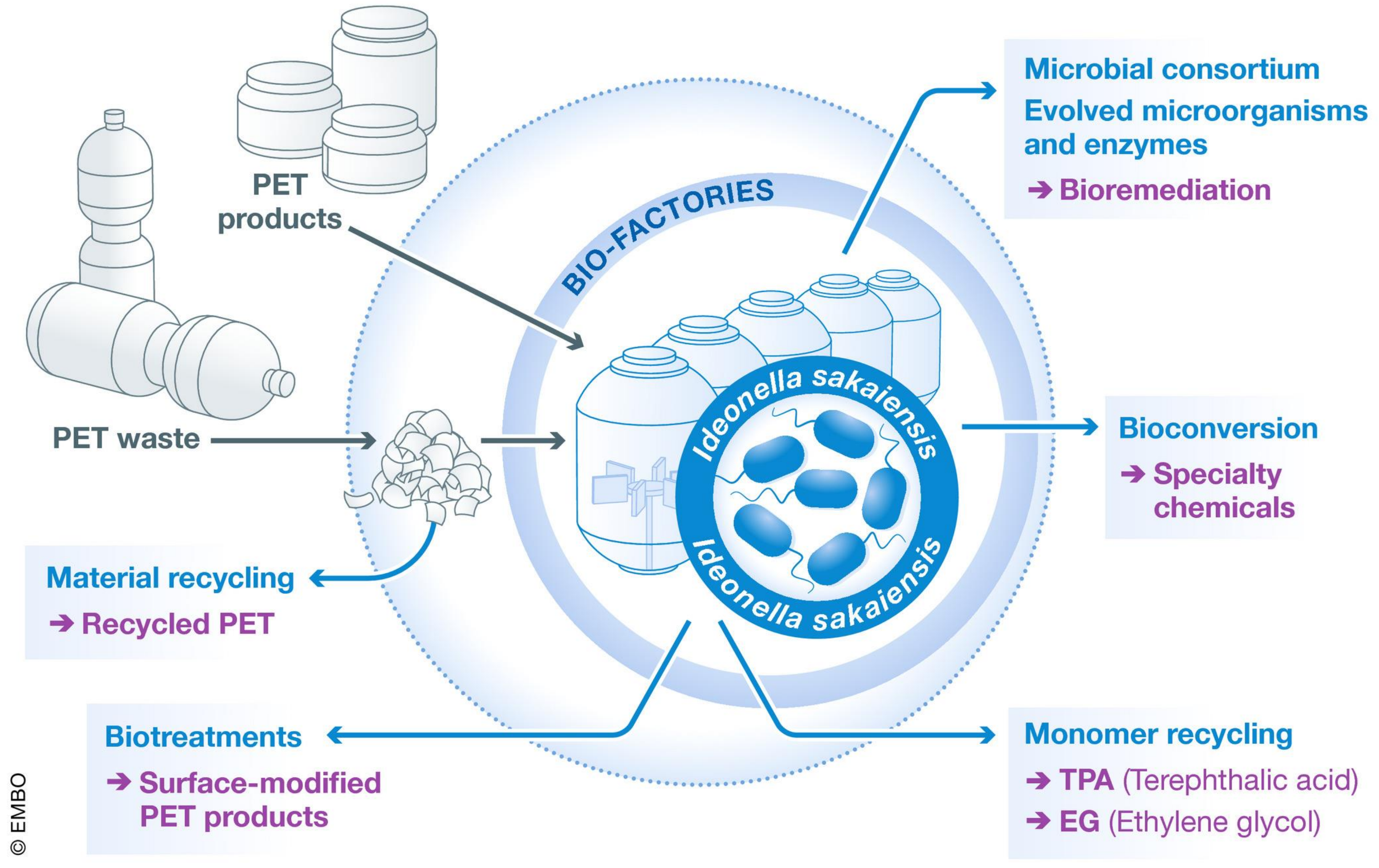


Mechanism:
Ideonella sakaiensis 201-F6 secrets the enzyme PETase.



https://www.journal/Nature-Communications-2041-1723

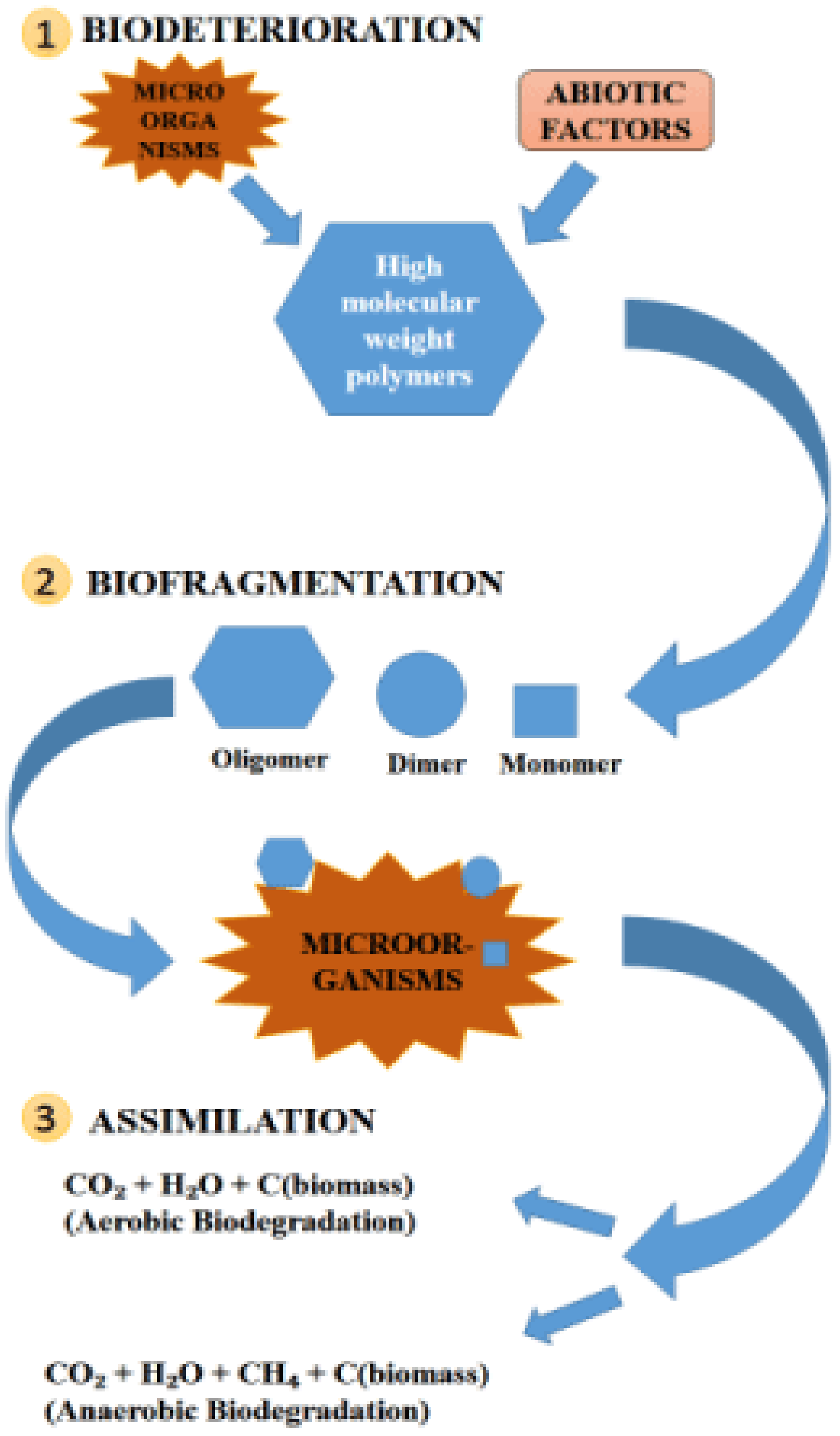
PETase splits the esters chemical bonds in PET, leaving smaller molecules that the bacteria absorb, using the carbon in them as a food source



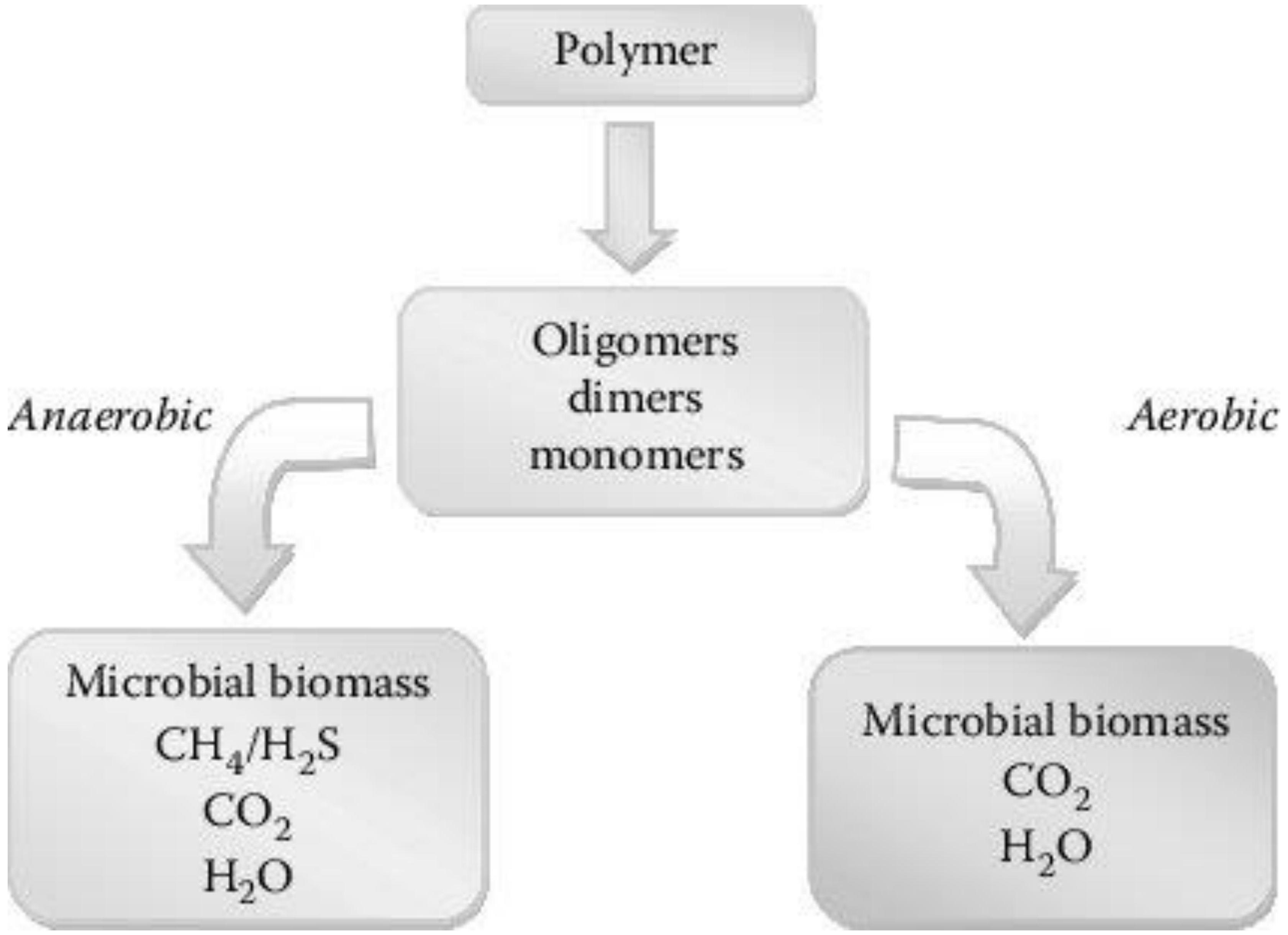
https://www.embopress.org/

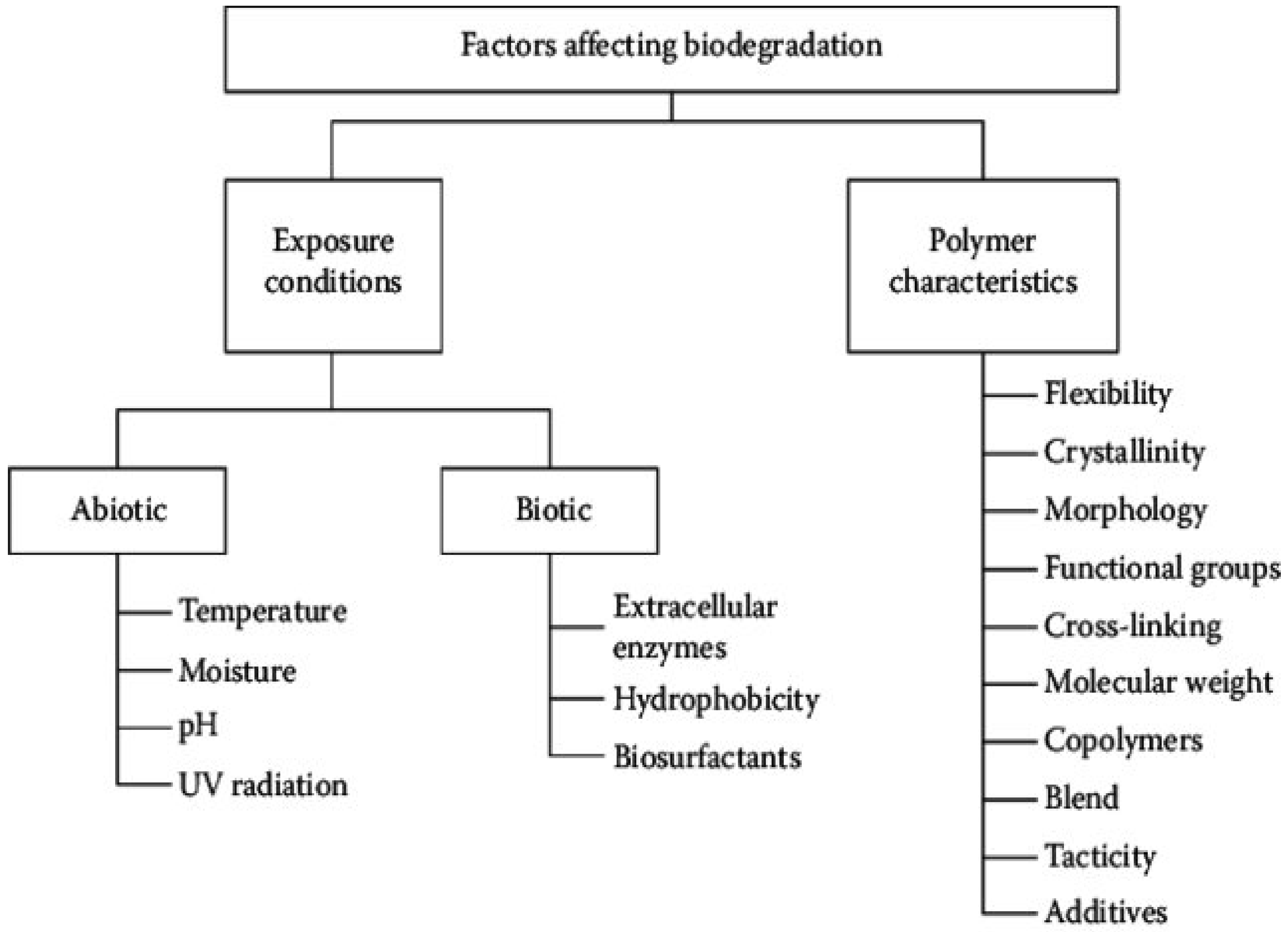
Microbial Degradation

Polymer biodegradation under aerobic and anaerobic conditions



https://www.Usage of Potential Micro-organisms for Degradation of Plastics (peertechzpublications.com)

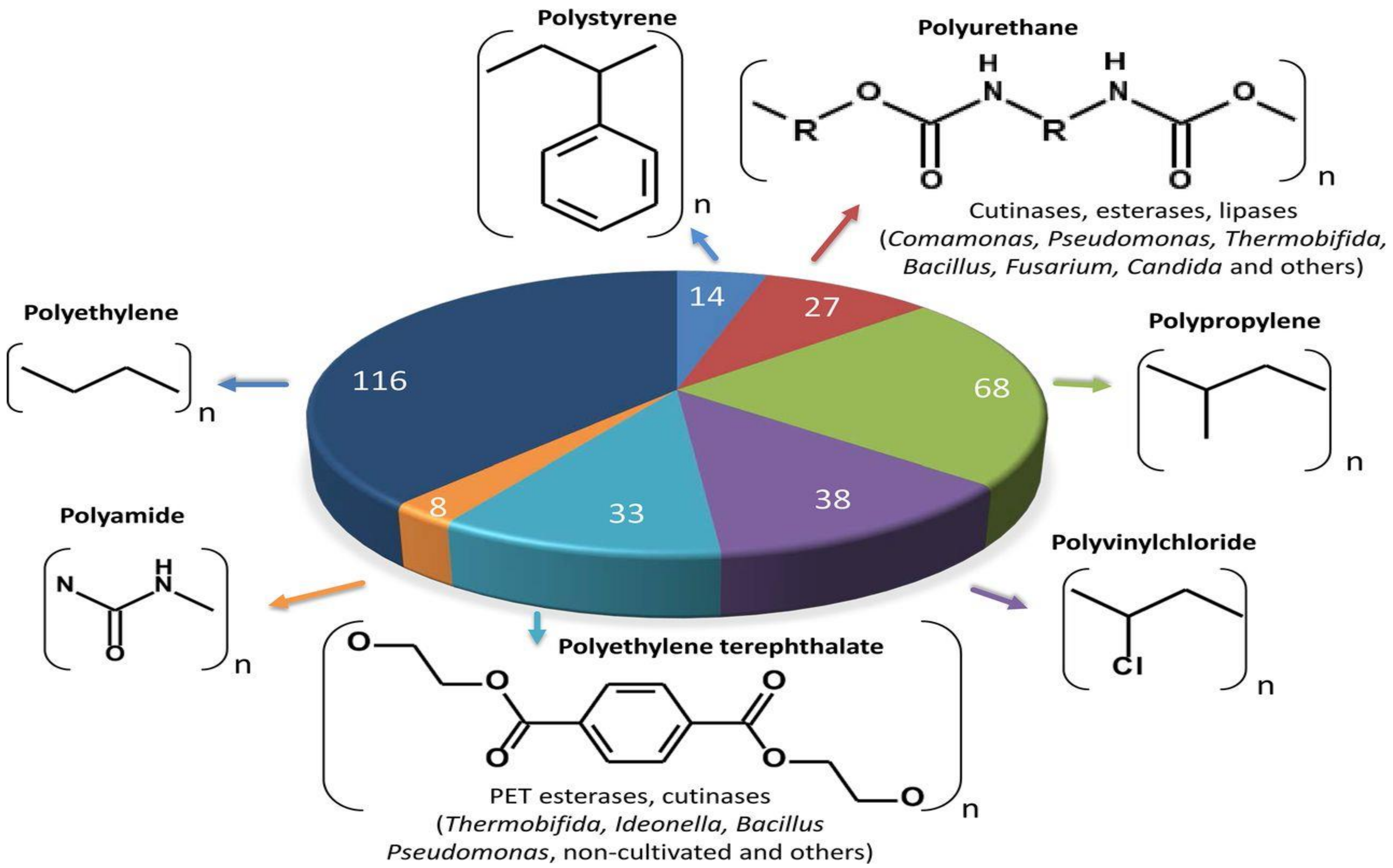




https://www.publication/296896016_The_Role_of_Microbes_in_Plastic_Degradation

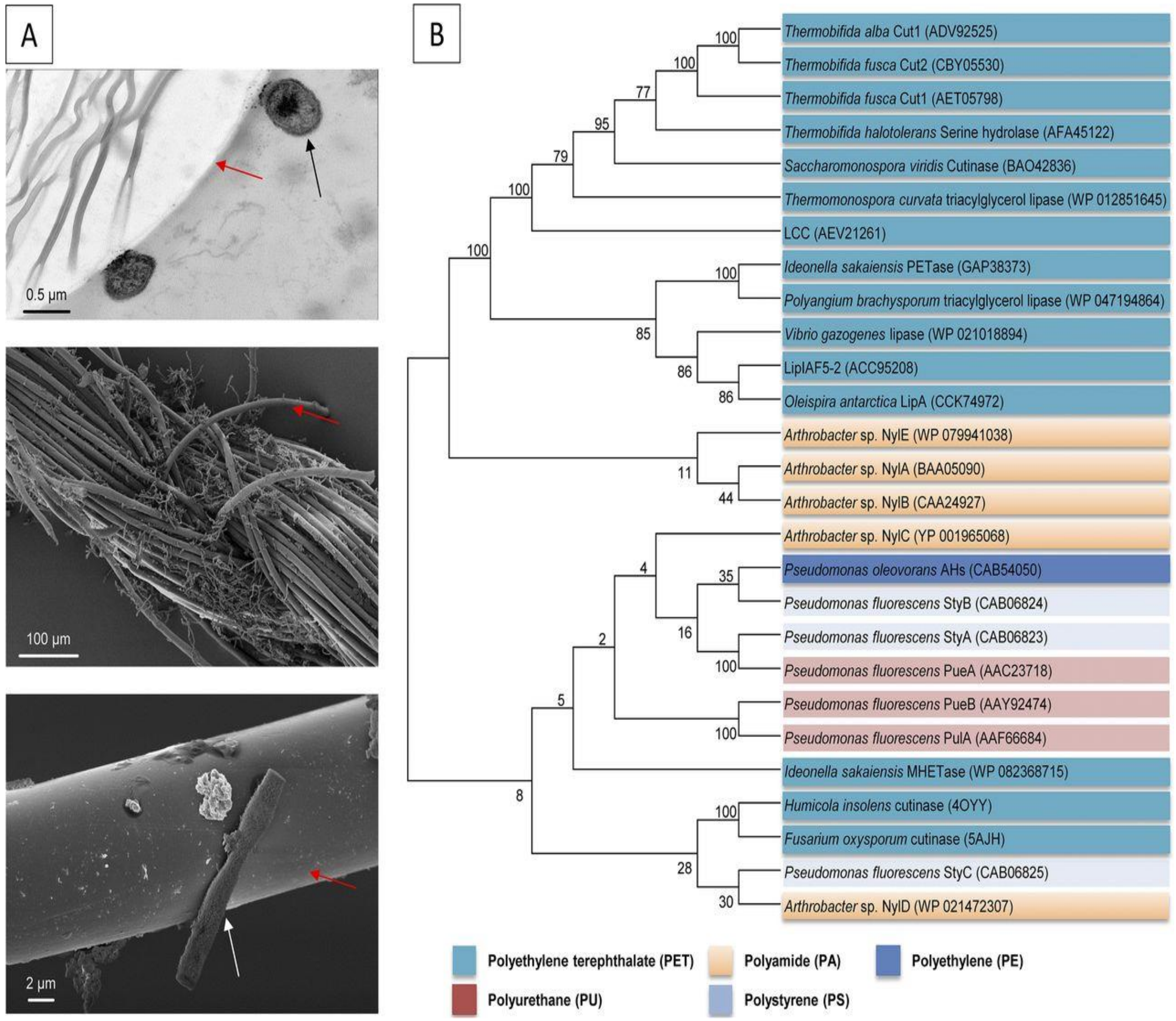
Enzymatic Degradation: Biocatalysis

Biocatalysis as an Emerging Solution for the Global Plastic Waste Challenge



Enzymatic Degradation: Source of enzymes

Microorganisms with their enzymatic capability for degradation of polymers



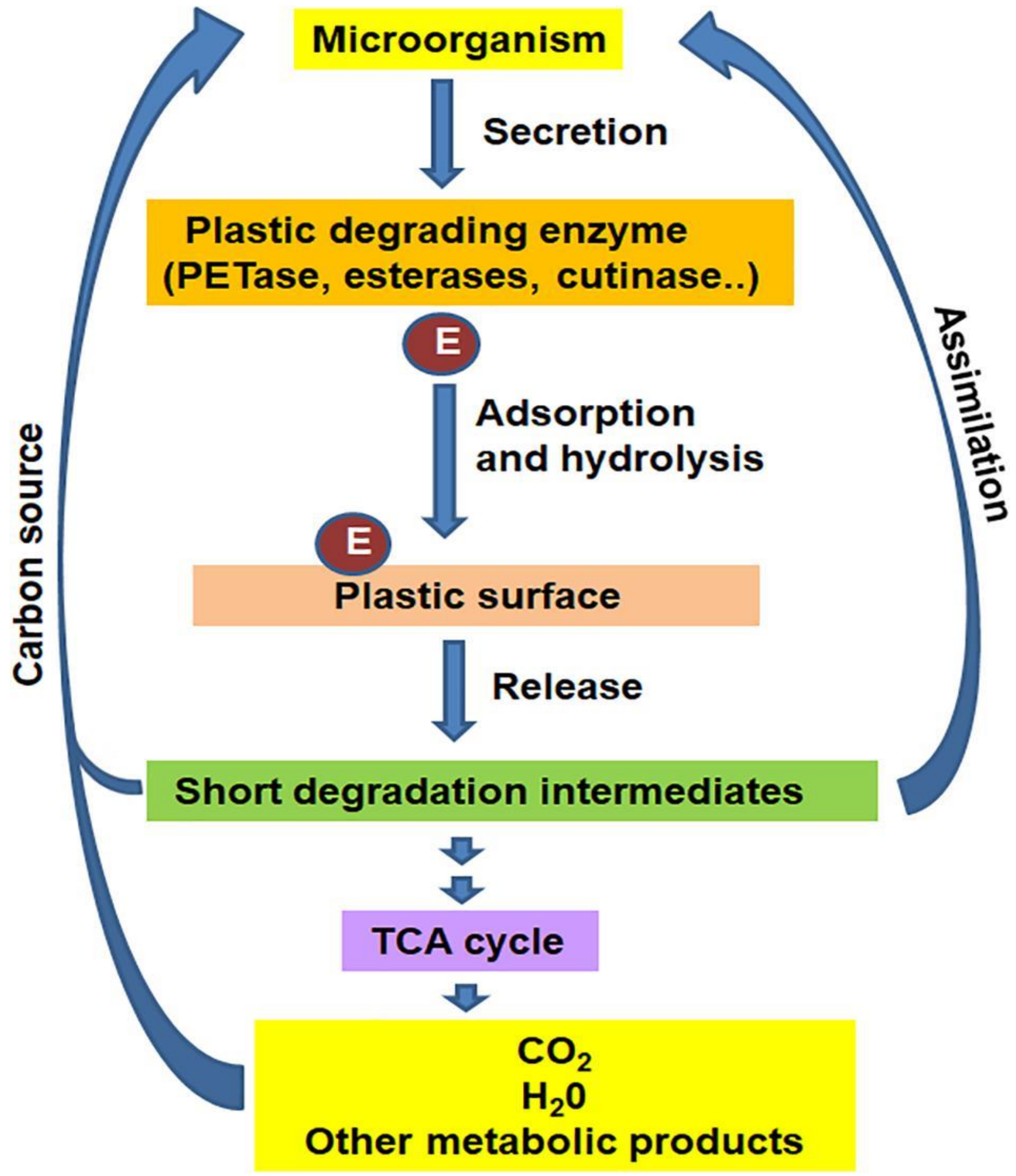
Microorganisms	Enzymes	Plastics
Bacteria		
Pseudomonas sp. E4	Alkane hydroxylase	LMWPE (Polyethylene)
P. putida AJ	Alkane hydroxylase	Vinyl Chloride (Polystyrene)
P. chlororaphis	Polyurethanase	Polyester (PUR)
P. aeruginosa	Esterase	Polyester (PUR)
P. protegens BC2 12	Lipase	Polyester (PUR)
P. fluorescen	Protease	Polyester (PUR)
Pseudomonas sp.	Lipase	PET
Pseudomonas sp. AKS2	Esterase	PES
P. stutzeri	PEG dehydrogenase	Polyethylene glycol (PEG)
P. vesicularis PD	Esterase	Polyvinyl alcohol (PVA)
R. arrizus	Lipase	PEA, PBS, and PCL
P. stutzeri	Serine hydrolase	PHA
Tremetesversicolor	Laccase	Nylon, PE
Rhodococcusequi	Aryl acylamidase	PUR

http/www.Sustainability | Free Full-Text | Hints at the Applicability of Microalgae and Cyanobacteria for the Biodegradation of Plastics (mdpi.com)

Enzymatic Degradation: Factors affecting

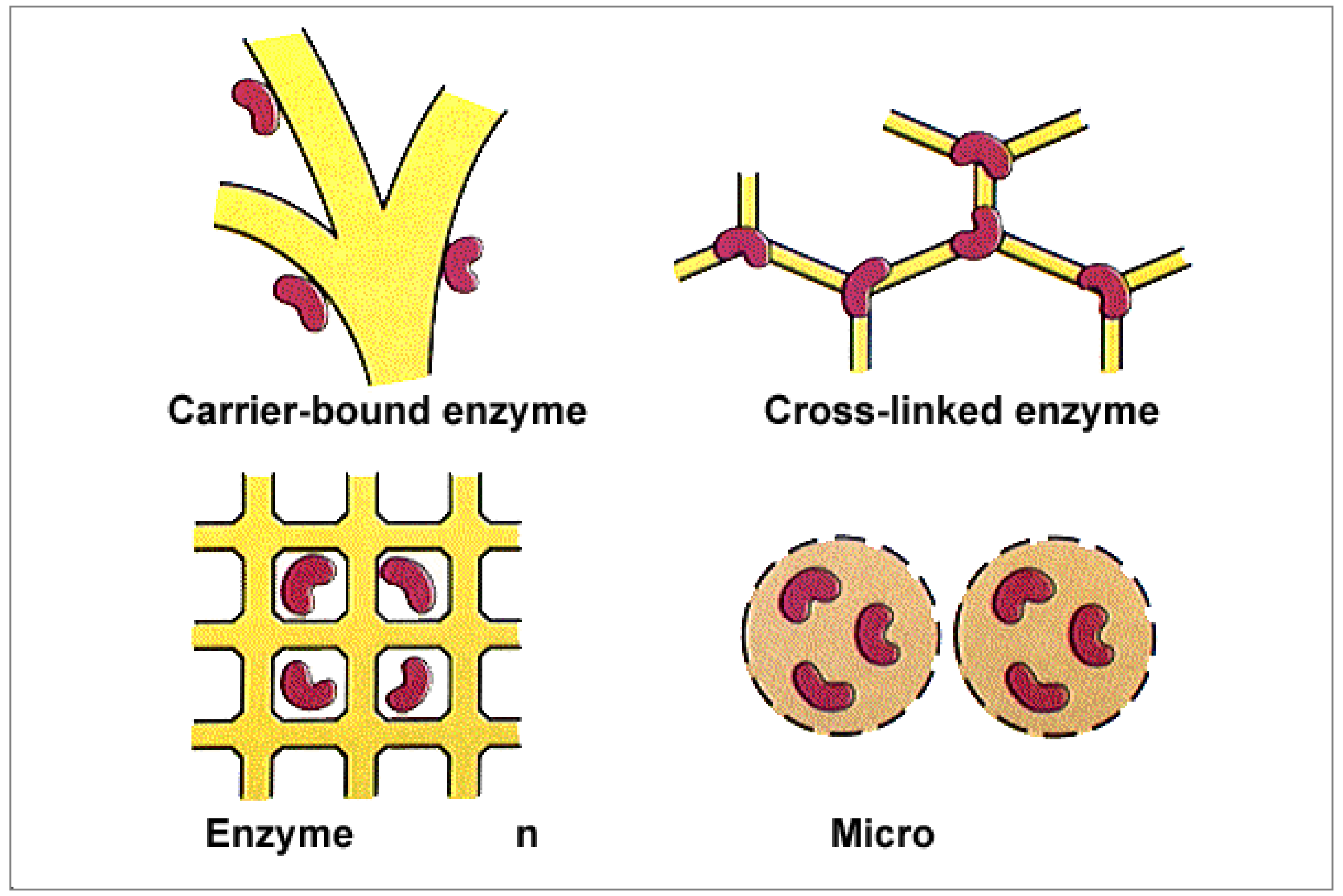
Factors affecting polymer biodegradation

- Enzyme expression can be induced by the presence of polymers to hydrolyze specific bonds
- Wild-type enzymes derived from different origins, and designer enzymes to specifically adsorb and attack certain man-made polymeric compounds
- Modification of the 3D structure of the enzyme is usually needed to improve their activity, stability, and specificity
- Due to the ability of cyanobacteria to be used as cell factories, they may be used to produce enzymes that can specifically degrade polymeric structures, in order to reduce the presence of micro- and nanoplastics in the environment



Approaches to improve enzyme activity and stability include:

Biocatalysts immobilization



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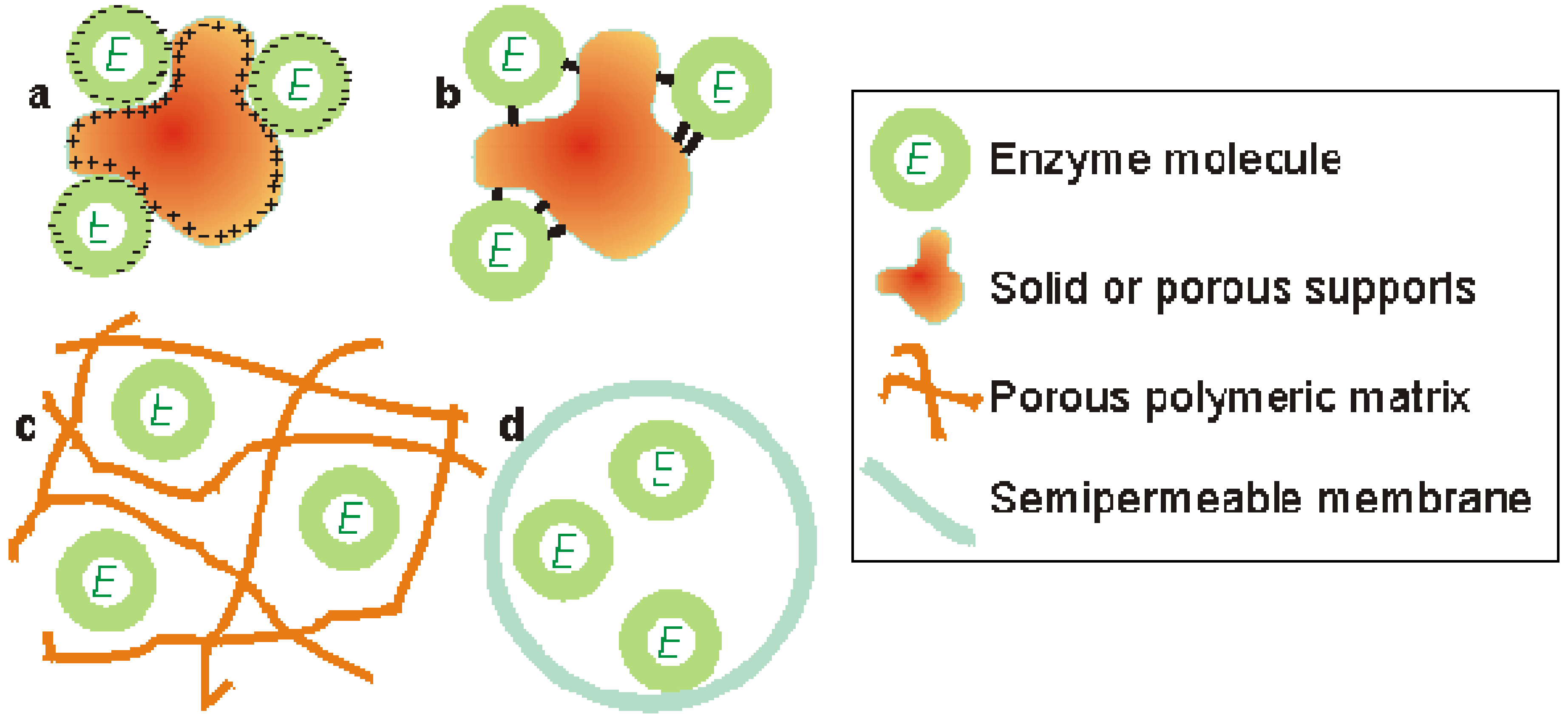
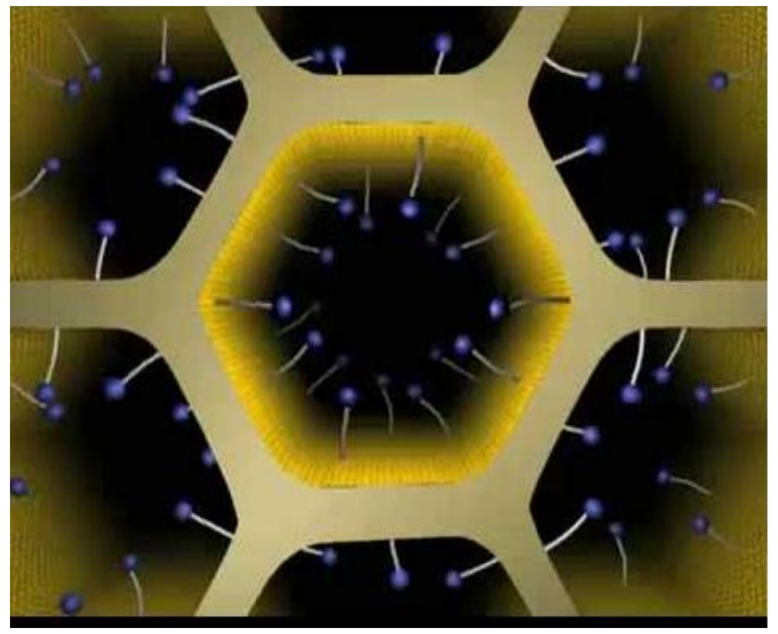
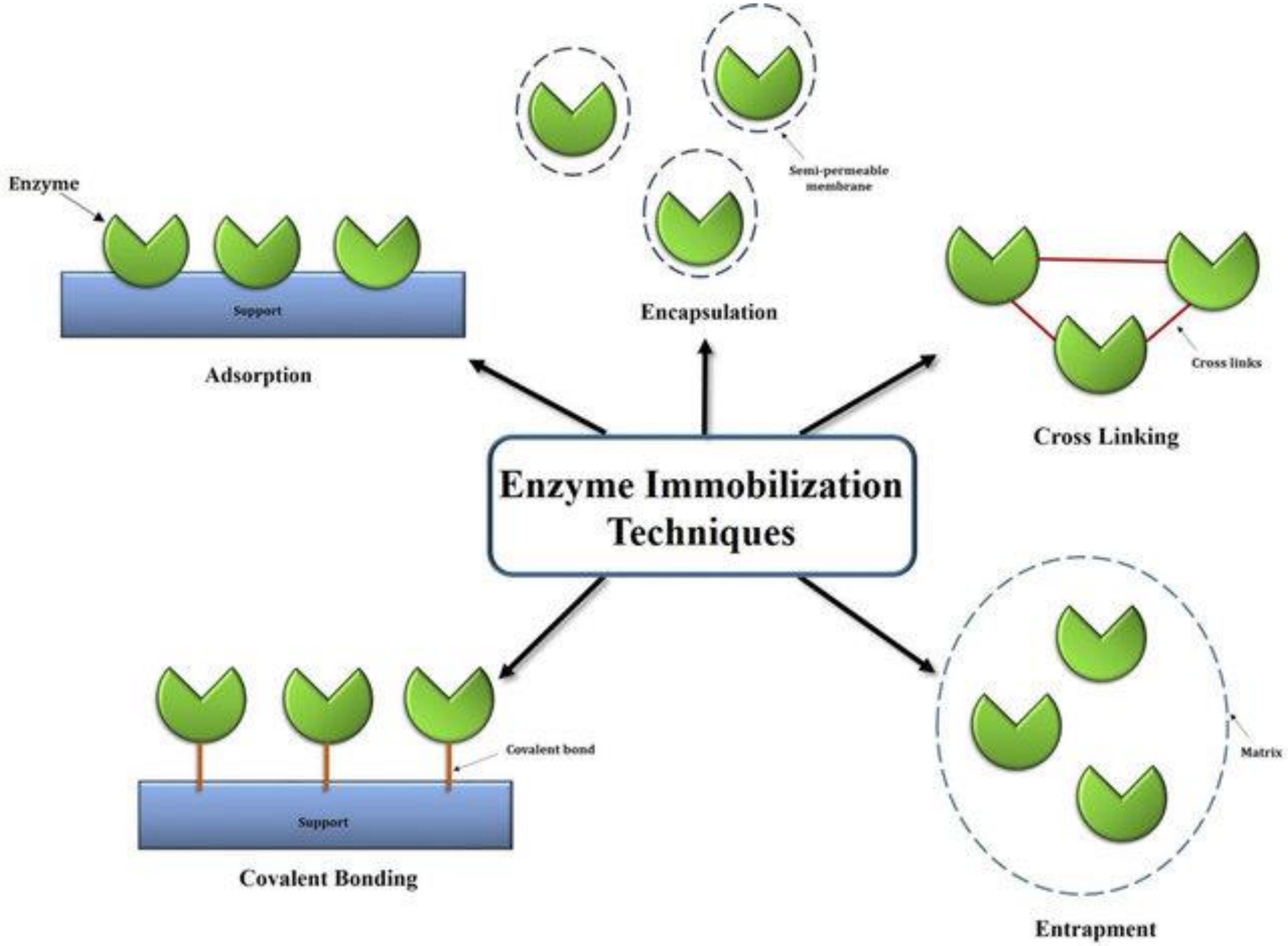
Methods of Enzymes Immobilization







http://www.publication/331104812_An_Overview_of_Immobilized_Enzyme_Technologies_

Enzymes Immobilization: Supports

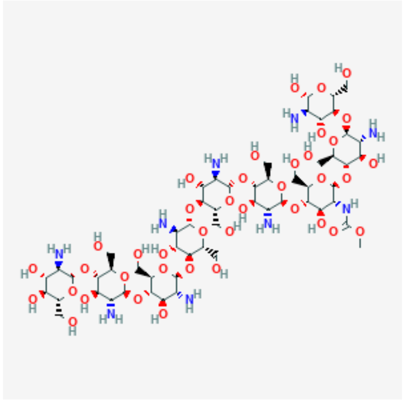
HYDROGELS

Marine origin (eg. Algae)

Alginates

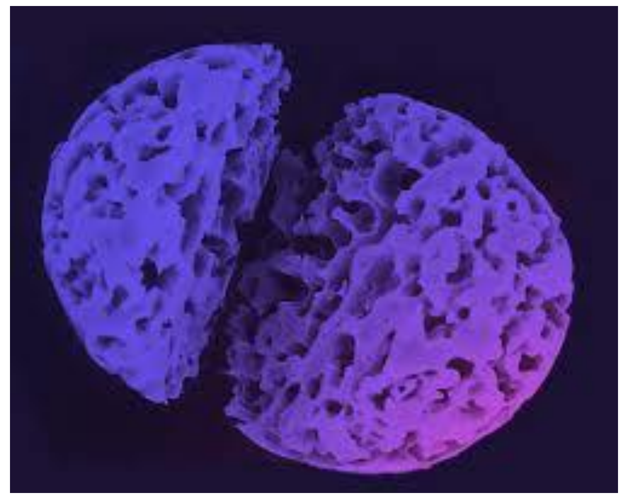
K-carragean

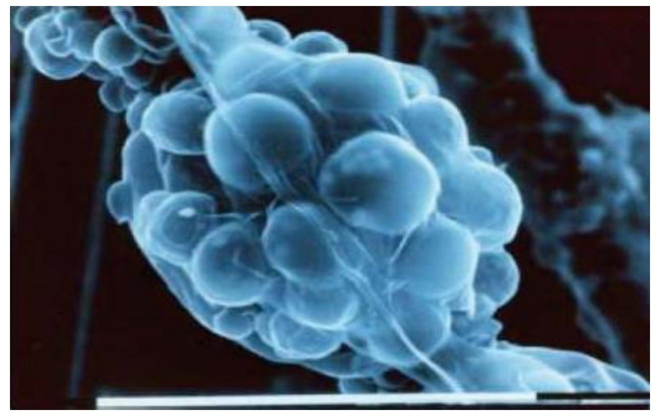
Chitosan



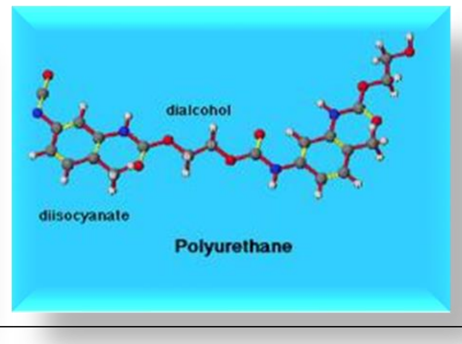
www.mpi-magdeburg.mpg.de

Microcarriers

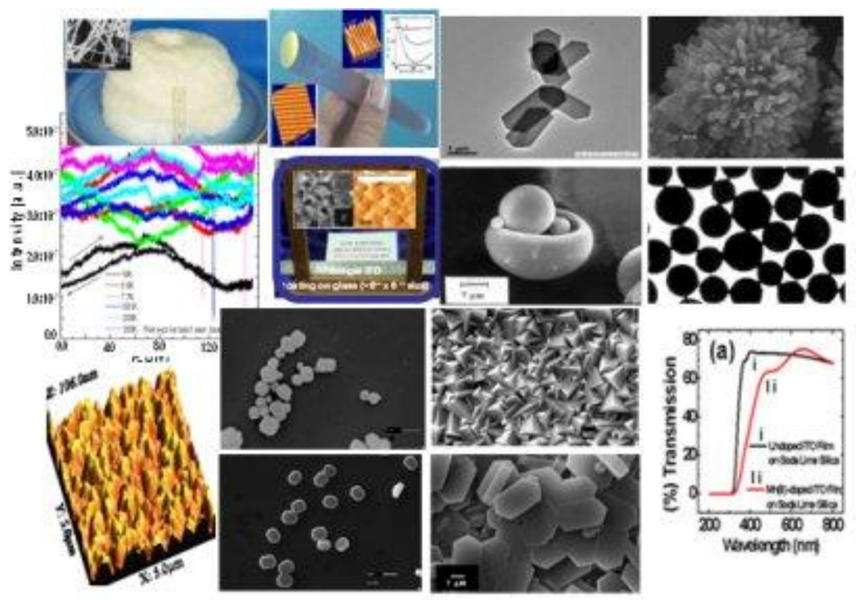




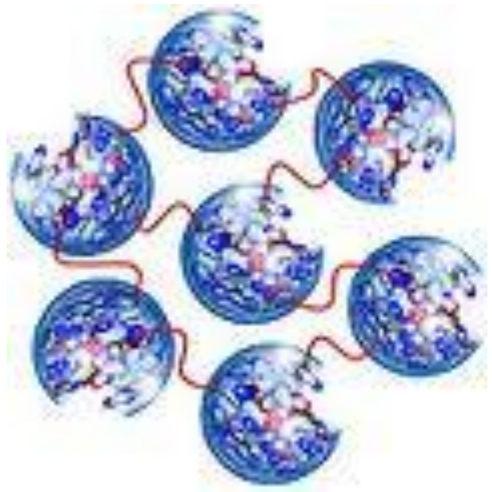
Poliurethans



Sol-gel

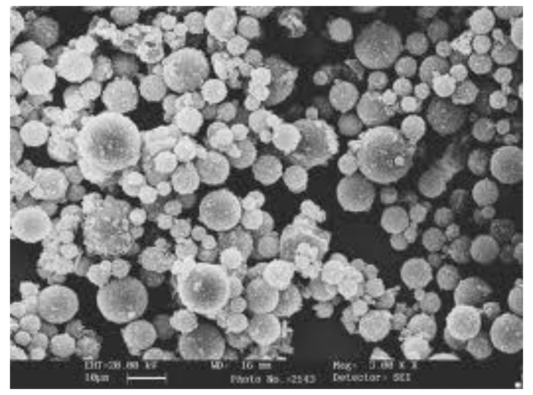


CLEAS

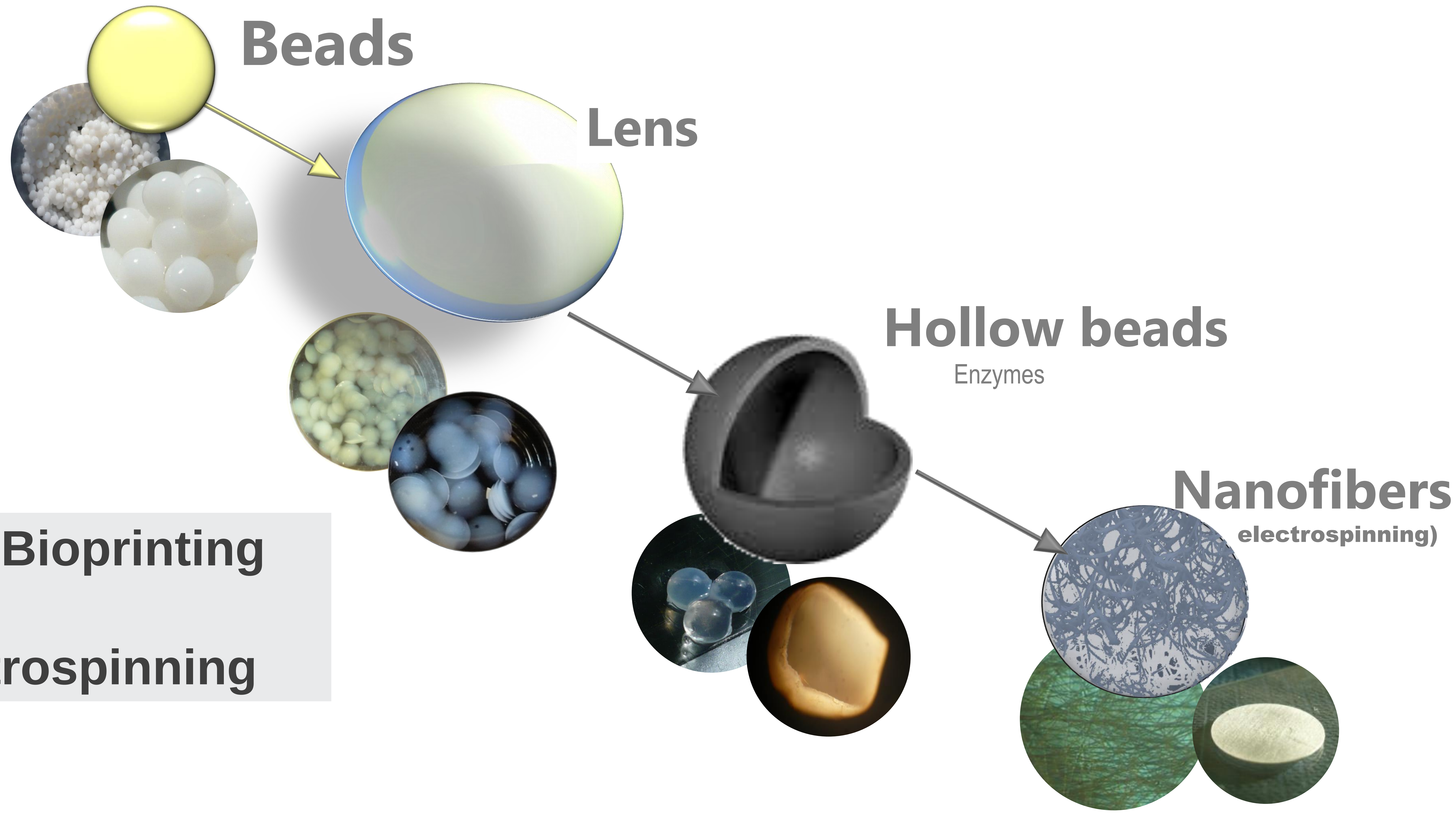


PVA

Microcapsules



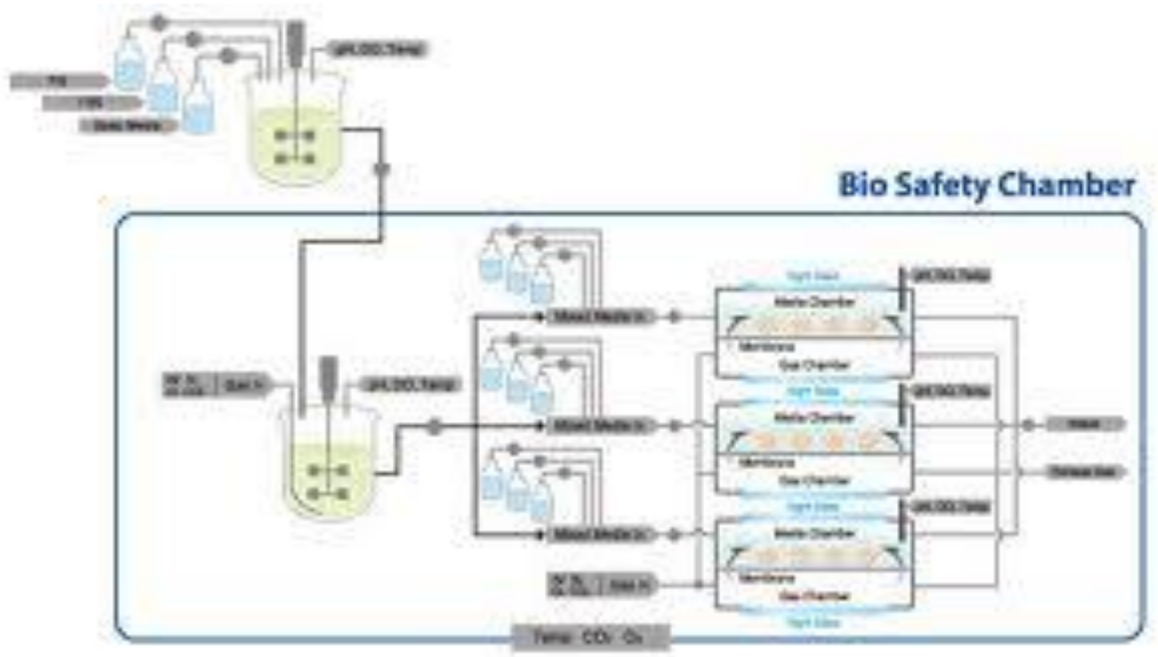
Enzymes Immobilization: Supports and Forms

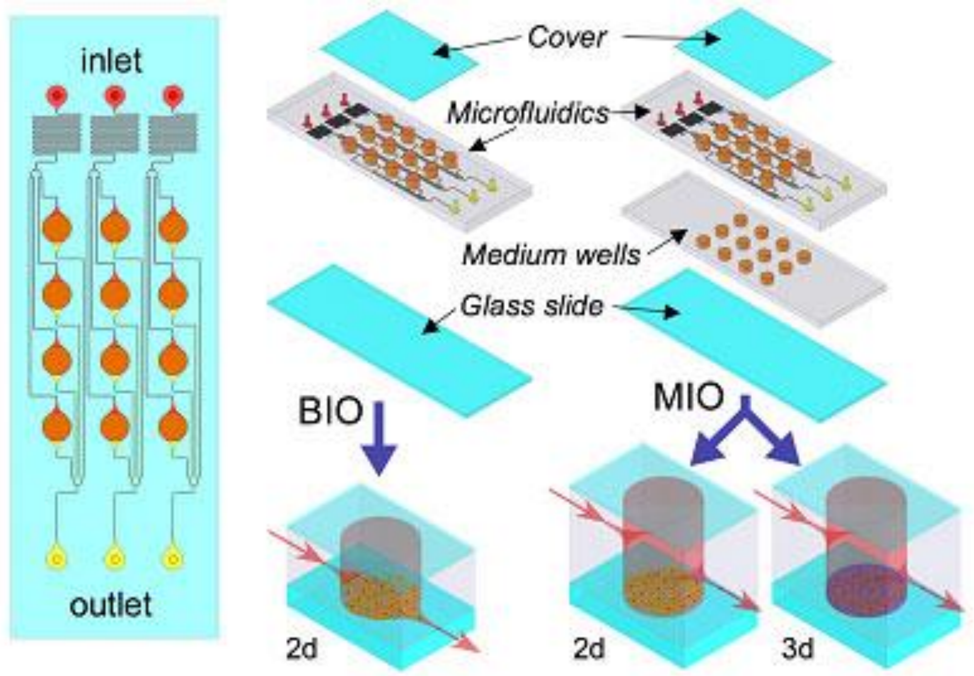


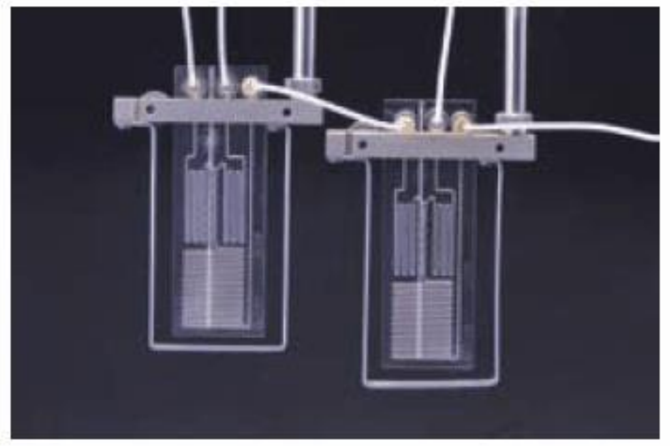
- **3D – Bioprinting**
- **Electrospinning**

Enzymes and Bioreactors

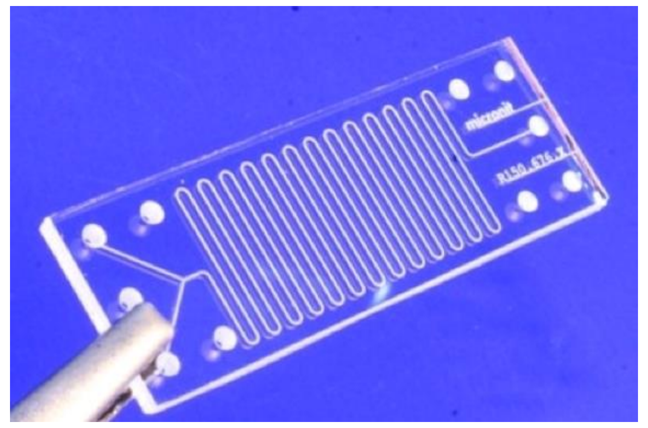
Microreactors







www.google.co.uk



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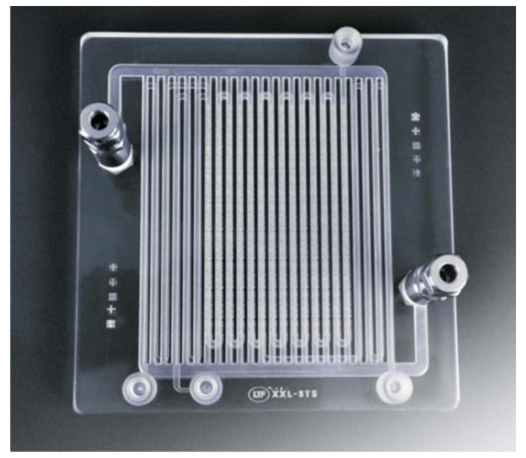
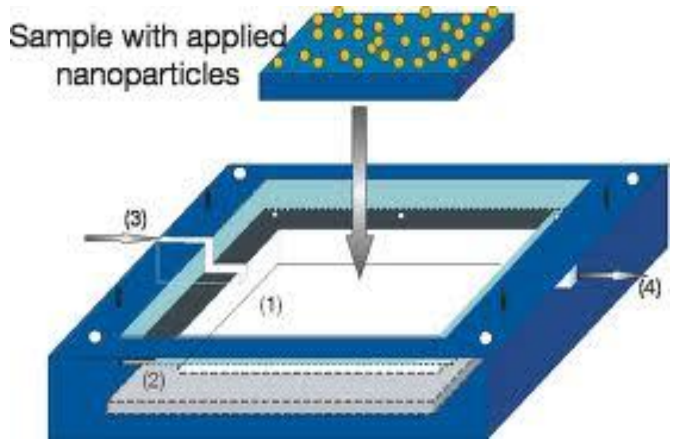


www.google.co.uk



Bioreactors

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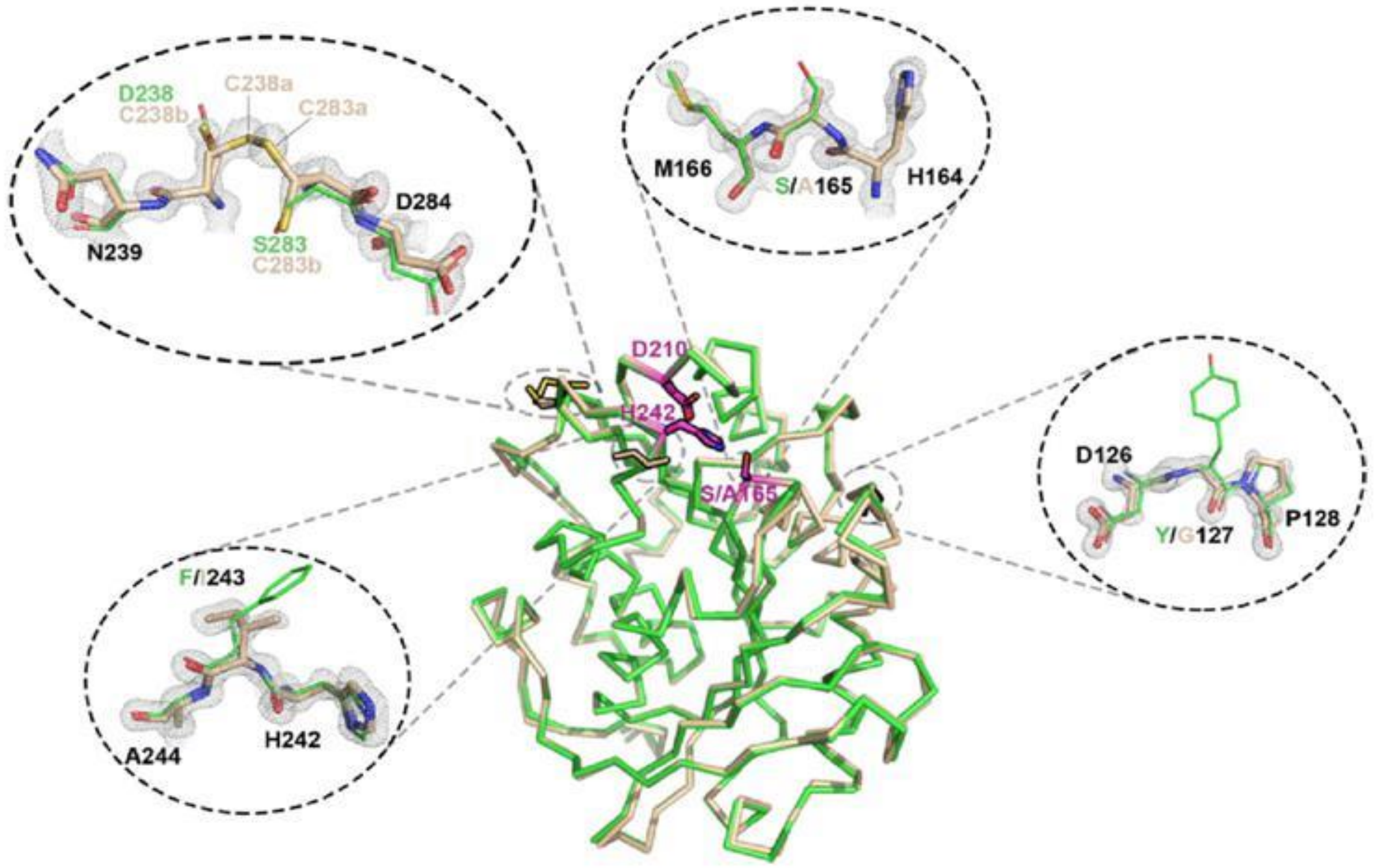
Case study: PET depolymerase

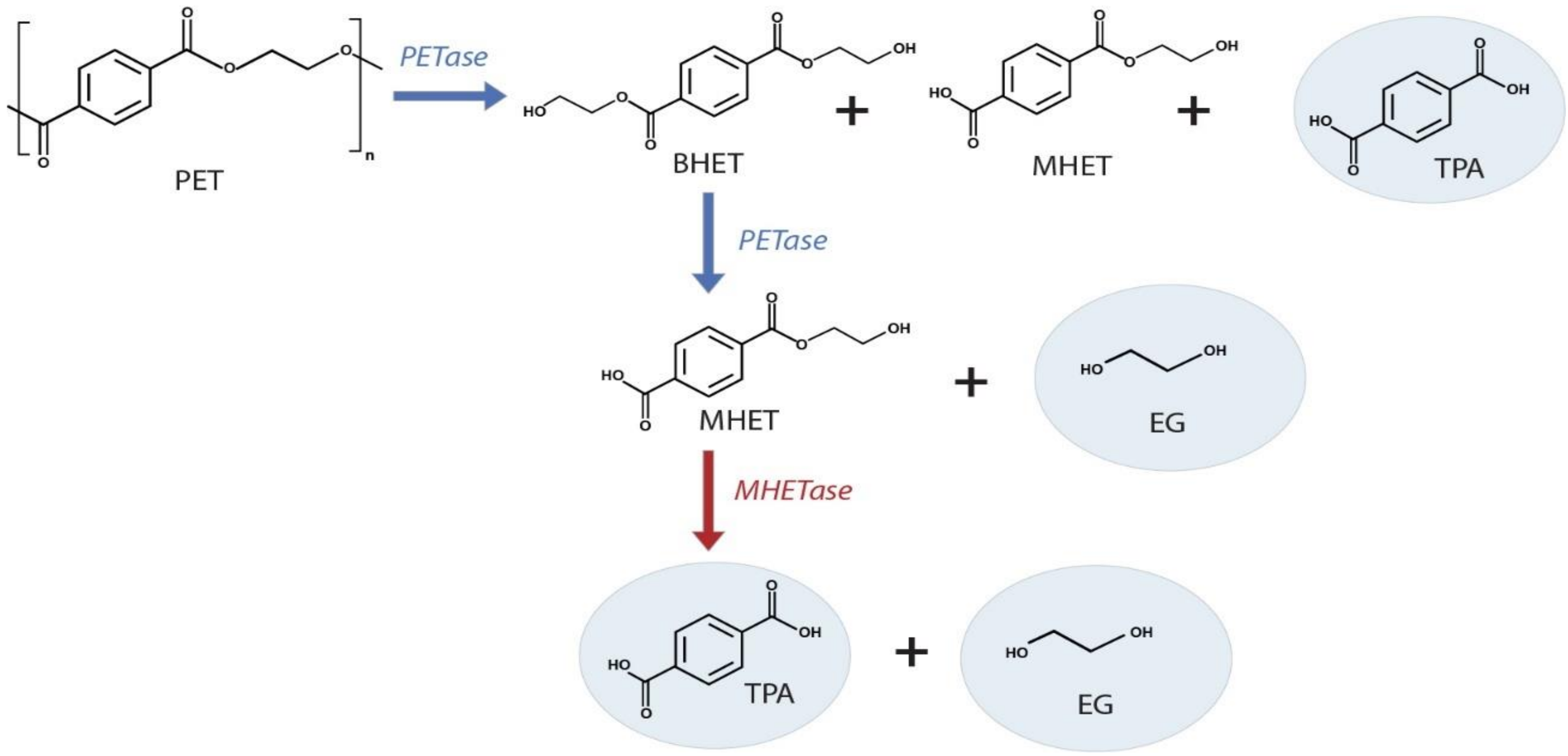
"After two years of the work of 20 scientists, we obtained this incredible enzyme able to deconstruct 90 percent of PET in less than 10 hours," Marty told *Forbes*.

An engineered PET depolymerase break down PET plastics



Case study: PET depolymerase

PET depolymerization scheme



PETase catalyzes the depolymerization of PET to bis(2-hydroxyethyl)-TPA (BHET), mono(2-hydroxyethyl) terephthalate (MHET), and terephthalic acid (TPA). MHETase converts MHET to monomers TPA and ethylene glycol (EG).

Case study: PET depolymerase

“French company **Carbios** has already demonstrated a bioreactor that can break apart PET plastics into their original components. This can then be used to make **new plastic**, obviating the need for fossil fuels and closing the production loop for plastic.
It’s still in its early stages, and it will likely be years before a commercial bioreactor comes online.”




https://www.carbios.com/wp-content/webp-express/webp-images/uploads/2021/03/ENZYMATIC-DEPOLYMERIZATION-OF-THE-POLYMERS-1.jpg.webp

Case study: PET depolymerase

https://www.carbios.com/wp-content/webp-express/webp-images/uploads/2021/03/ENZYMATIC-DEPOLYMERIZATION-OF-THE-POLYMERS-1.jpg.webp

Production of biodegradable plastics

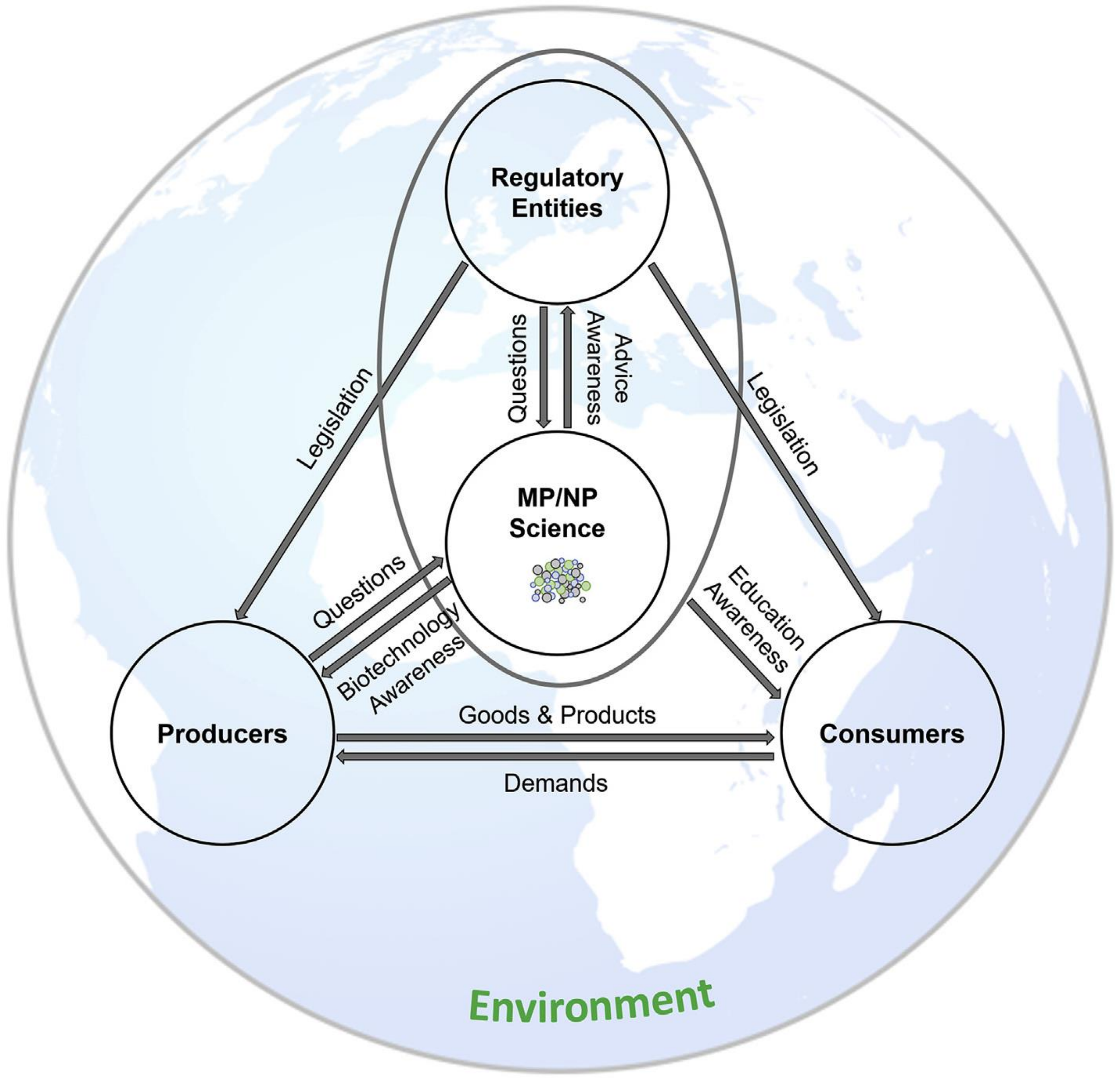
The process

The innovation of the biodegradation process consists of introducing enzymes into plastic and/or textile materials to make them biodegradable. These enzymes make it possible for PLA plastics to be 100% biodegradable under universal composting conditions (industrial, domestic or methanization.)

Development stage and outlooks

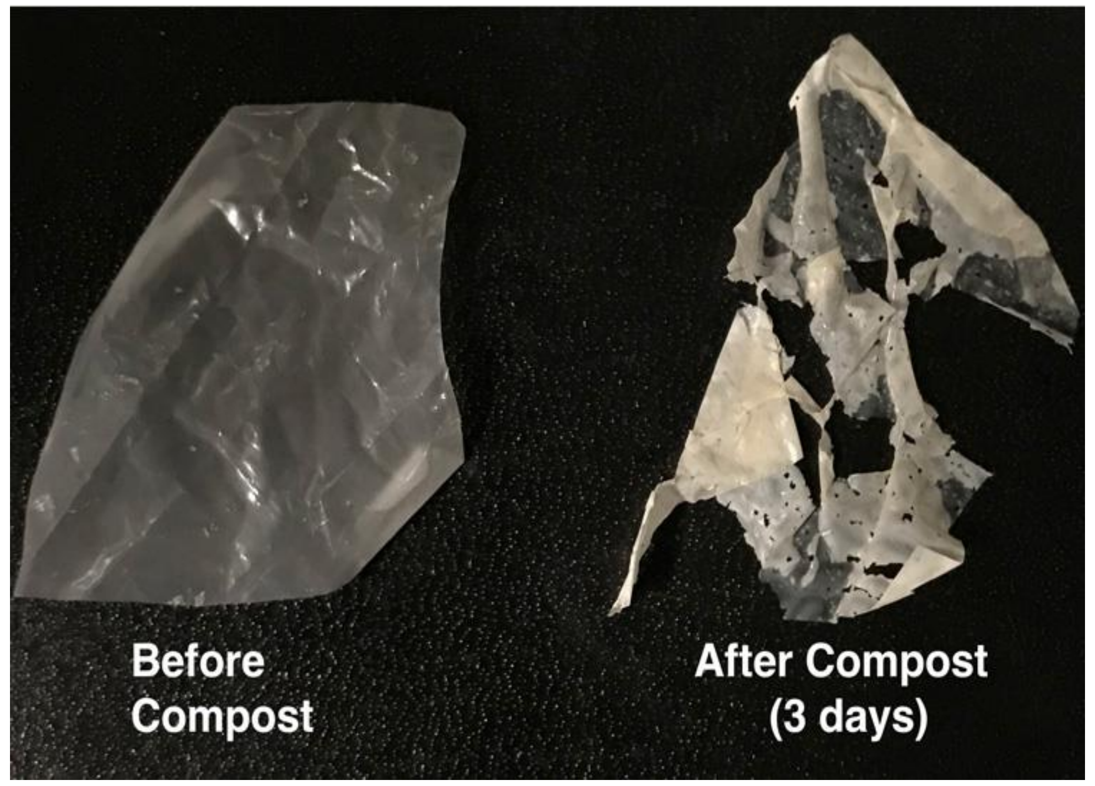
For PLA-based plastics (polylactic acid – polymer of biobased origin), this technology was licensed in 2016 to Carbiolice, currently jointly owned by Carbios and the SPI "Sociétés de Projets Industriels" fund operated by Bpifrance. This innovative solution is implemented in the form of an enzyme-based additive known as Evanesto®, which is easily integrated into conventional plastic and packaging manufacturing processes. Carbiolice offers an innovation capable of ensuring compostability of packaging with a high PLA content even under domestic conditions.

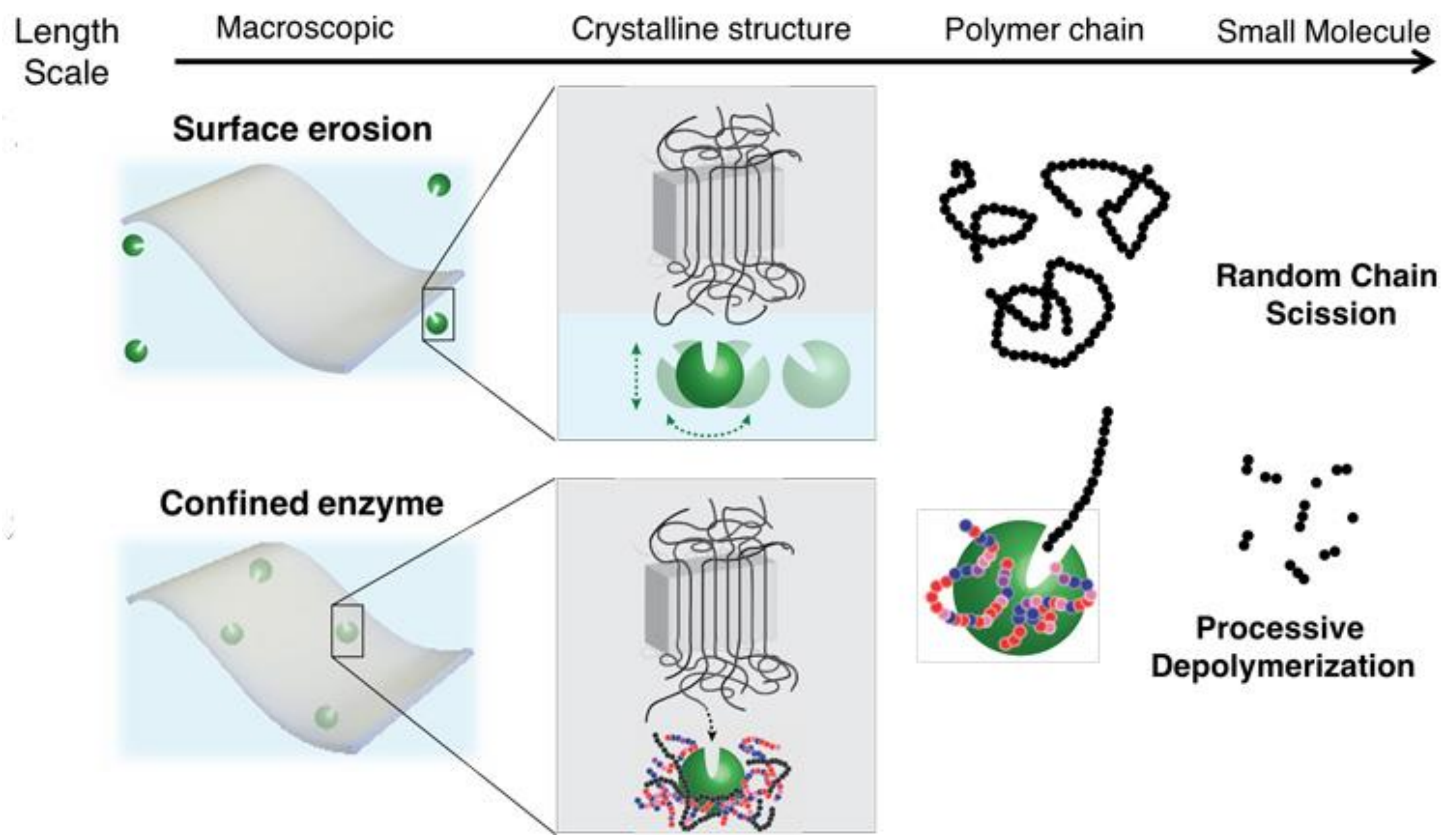
Through its production plant, Carbiolice expect to address different markets (flexible or rigid): the food industry (bags, trays, yoghurt pots, etc.), logistics (packaging bubbles, films) or agriculture (mulching films, horticultural pots, etc.)"



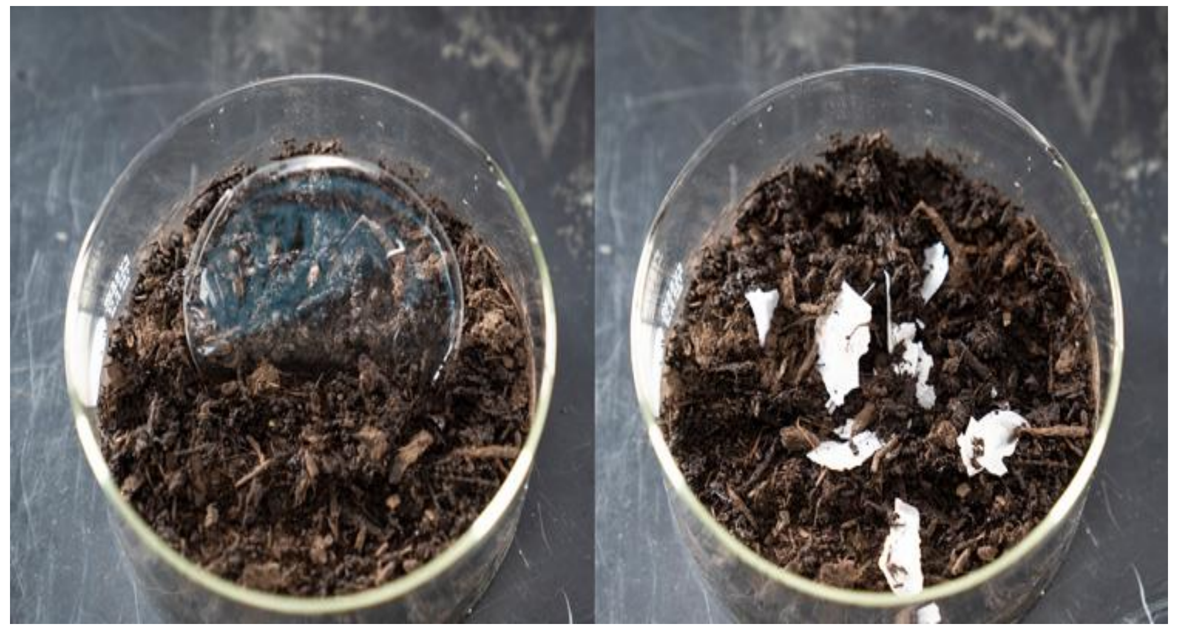
Current Opinion in Environmental Science & Health

Case study: Lipase in PLA





Enzymes such as lipase (green balls) can degrade plastic polymers from the surface, but they cut up the polymer randomly, leaving microplastics behind (top right).
A UC Berkeley group embedded enzyme nanoclusters throughout the plastic (lower left), protected by random heteropolymers (chains of colored balls).
The embedded enzymes were immobilized near the end of the polymer chains and, under the right conditions of heat and moisture, degrade polymer molecules primarily from the chain end.
This technique retains the plastic's integrity during use but, when the user triggers depolymerization, the plastic goes all the way down to recyclable small-molecule by-products.



A film of PLA (polylactic acid) plastic immediately after being placed in compost (left) and after one week in the compost (right). Embedded with an enzyme, the PLA plastic can biodegrade to simple molecules, making it promising as a future alternative to a non-degradable plastic.

https://news.berkeley.edu/2021/04/21/new-process-makes-biodegradable-plastics-truly-compostable/

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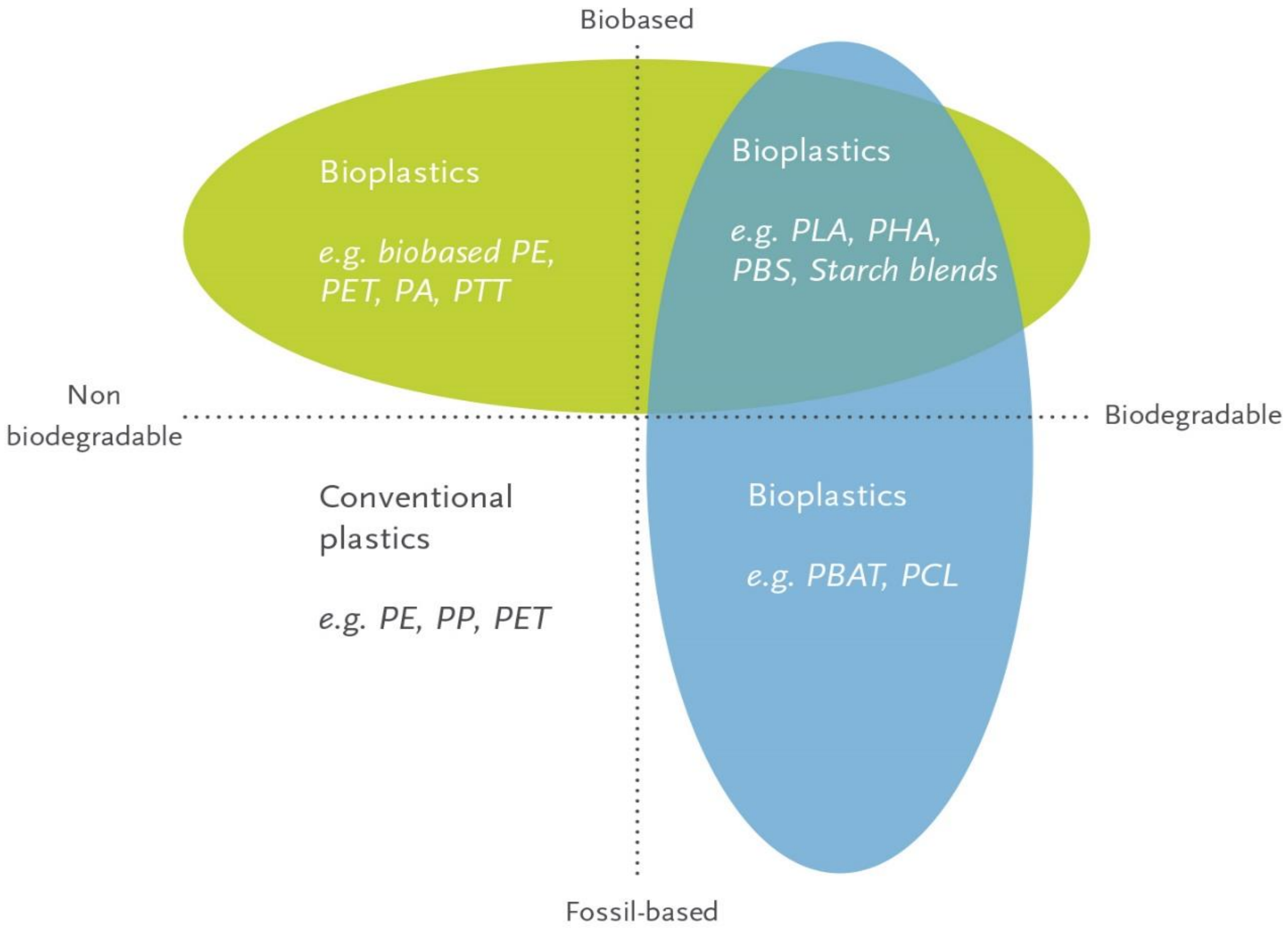
The drastically increasing amount of plastic waste is causing an environmental crisis that requires innovative technologies for recycling post-consumer plastics to achieve waste valorization while meeting environmental quality goals

- Biocatalytic depolymerization mediated by enzymes has emerged as an efficient and sustainable alternative for plastic treatment and recycling.
- A variety of plastic degrading enzymes have been discovered from microbial sources.
- Protein engineering has been exploited to modify and optimize plastic-degrading enzymes.
- Another goal is the Identification and optimization of new enzymes.
- Enzymatic recycling opens new ecological and competitive avenues for the virtuous management of the life cycle of plastic and textile materials
- Bioplastics improvement is another innovative approach.

Bioplastics

Bioplastic materials



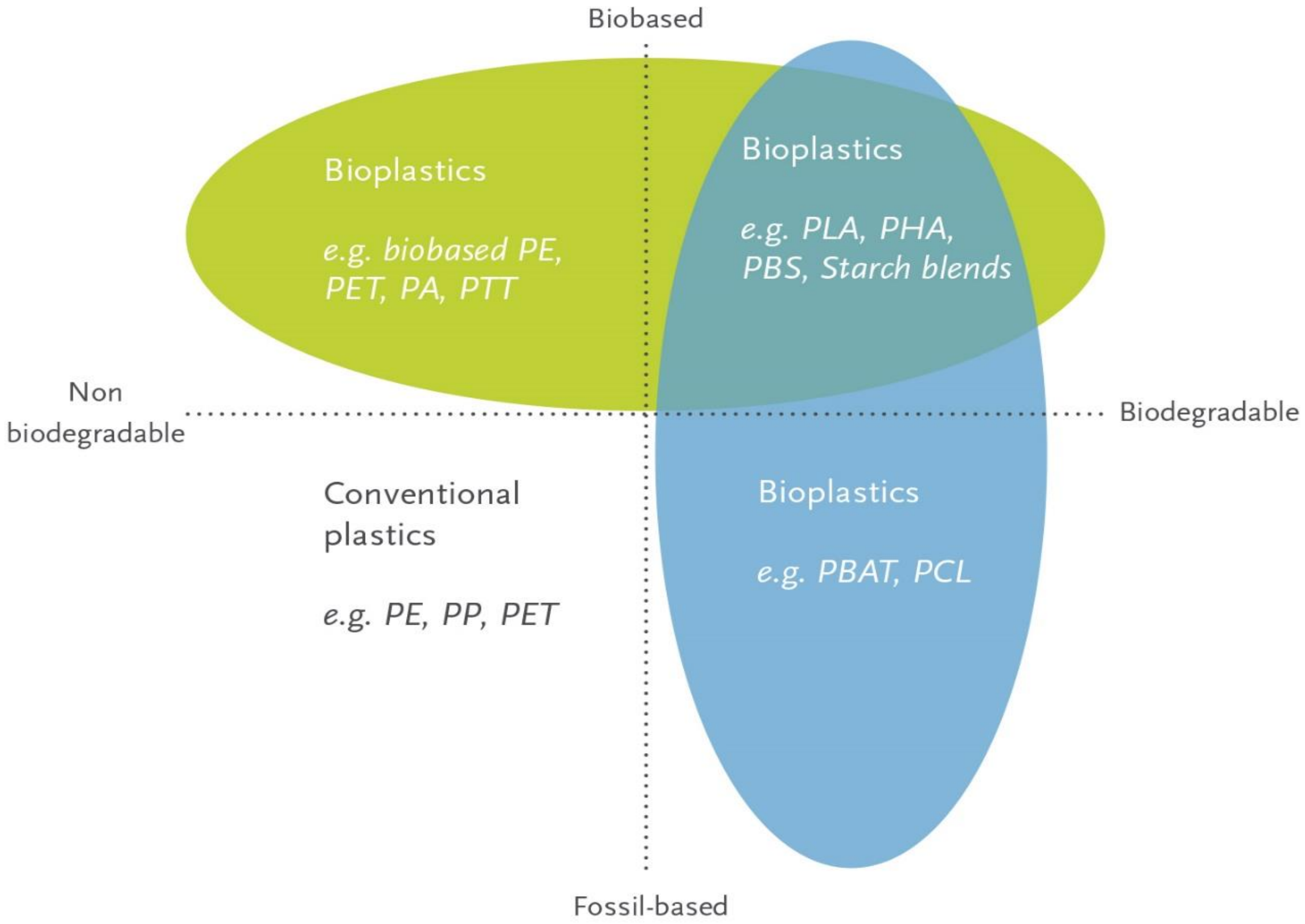
Bioplastic alternative for many conventional plastic material and corresponding application.

Bioplastics – plastics biobased, biodegradable, or both – have the same properties as conventional plastics and offer additional advantages.

Includesa reduced carbon footprint or additional waste management options, such as composting.

Bioplastics are an essential part of the bioeconomy and a fast-growing, innovative industry that has the potential to decouple economic growth from resource depletion and environmental impact.

Bioplastic materials



Bioplastics are a diverse family of materials with differing properties.

- Plastics that are based on fossil resources and are biodegradable, such as PBAT.
- TBio-based or partially bio-based non-biodegradable plastics, such as bio-based PE, PP, or PET (so-called drop-ins) and bio-based technical performance polymers, such as PTT or TPC-ET.
- Plastics that are both bio-based and biodegradable, such as PLA and PHA or PBS;

BIOPLASTICS

Bioplastics - **polymers that meet any of two criteria:**

- **Bio-based** and/or
- **Biodegradable**

Bio-based - the polymer is either entirely or partially obtained from biomass (organic renewable material of biological origin as well as organic waste)

Biodegradable - The material can break down into natural substances such as carbon dioxide, water and biomass, due to the action of biocatalysts.

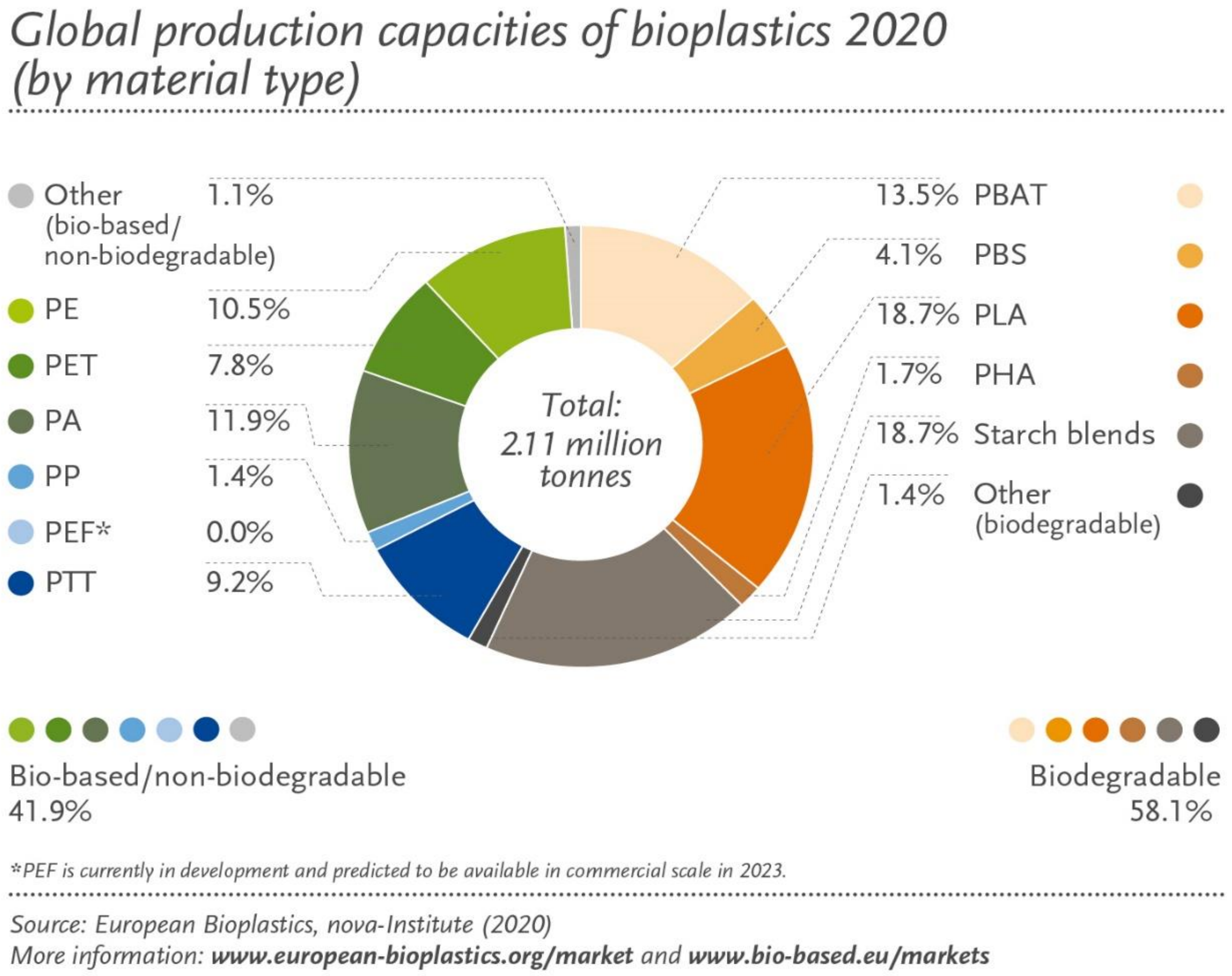
Bioplastics with indication of origin bio-based and biodegradability

(“y” means yes, “n” means no, and “y/n” refers to both statements being valid)

Polymer	Bio-Based	Biodegradable
Polylactic acid (PLA)	y	y
Starch blends, thermoplastic starch (TS)	y	y
Polyhydroxyalkanoates (PHAs)	y	y
Polybutylene succinate (PBS)	y/n	y
Polycaprolactone (PCL)	n	y
Polyurethanes (PURs)	y/n	y/n
Polyvinyl alcohol (PVA)	n	y
Polybutylene adipate terephthalate (PBAT)	n	y
Polyethylene Furanoate (PEF)	y	n
Bio-polypropylene (bio-PP)	y	n
Polytrimethylene terephthalate (PTT)	y	n
Bio-polyethylene terephthalate (bio-PET)	y	n
Bio-polyethylene (bio-PE)	y	n
Bio-polyamides (bio-PAs)	y	n

Polymers **2021**, *13*(8), 1229; https://doi.org/10.3390/polym13081229

Bioplastic Materials



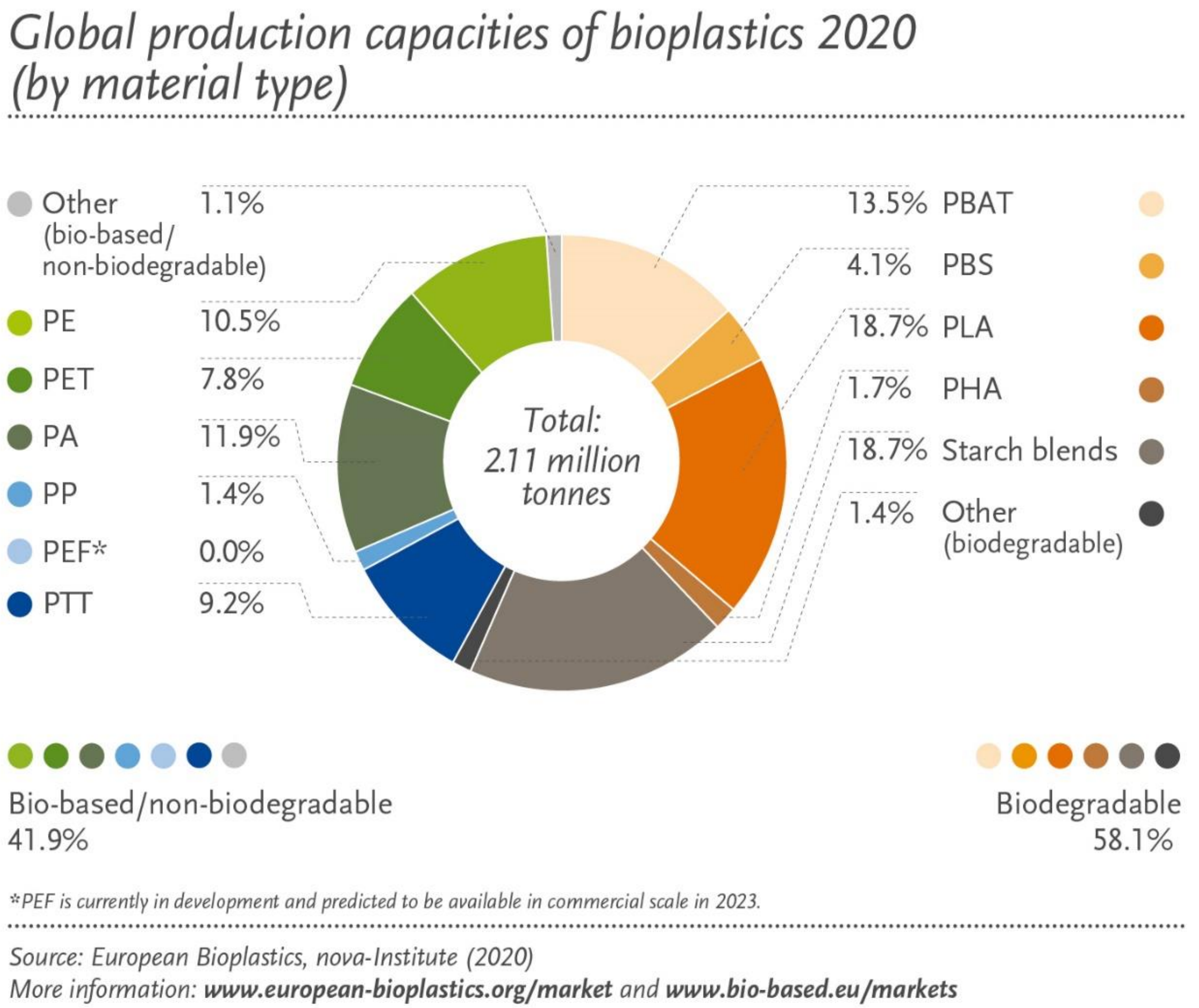
Currently, bioplastics represent about one per cent of the about 368 million tonnes of plastic produced annually.

But as demand is rising, and with more sophisticated materials, applications, and products emerging, the market is already growing very dynamically.

Additionally, new materials, such as PLA, PHA, cellulose or starch-based materials offer solutions with completely new functionalities, such as compostability and in some cases optimised barrier properties.

Along with the growth in variety of bioplastic materials, properties, such as flexibility, durability, printability, transparency, barrier, heat resistance, gloss and many more have been significantly enhanced.

Bioplastic Materials

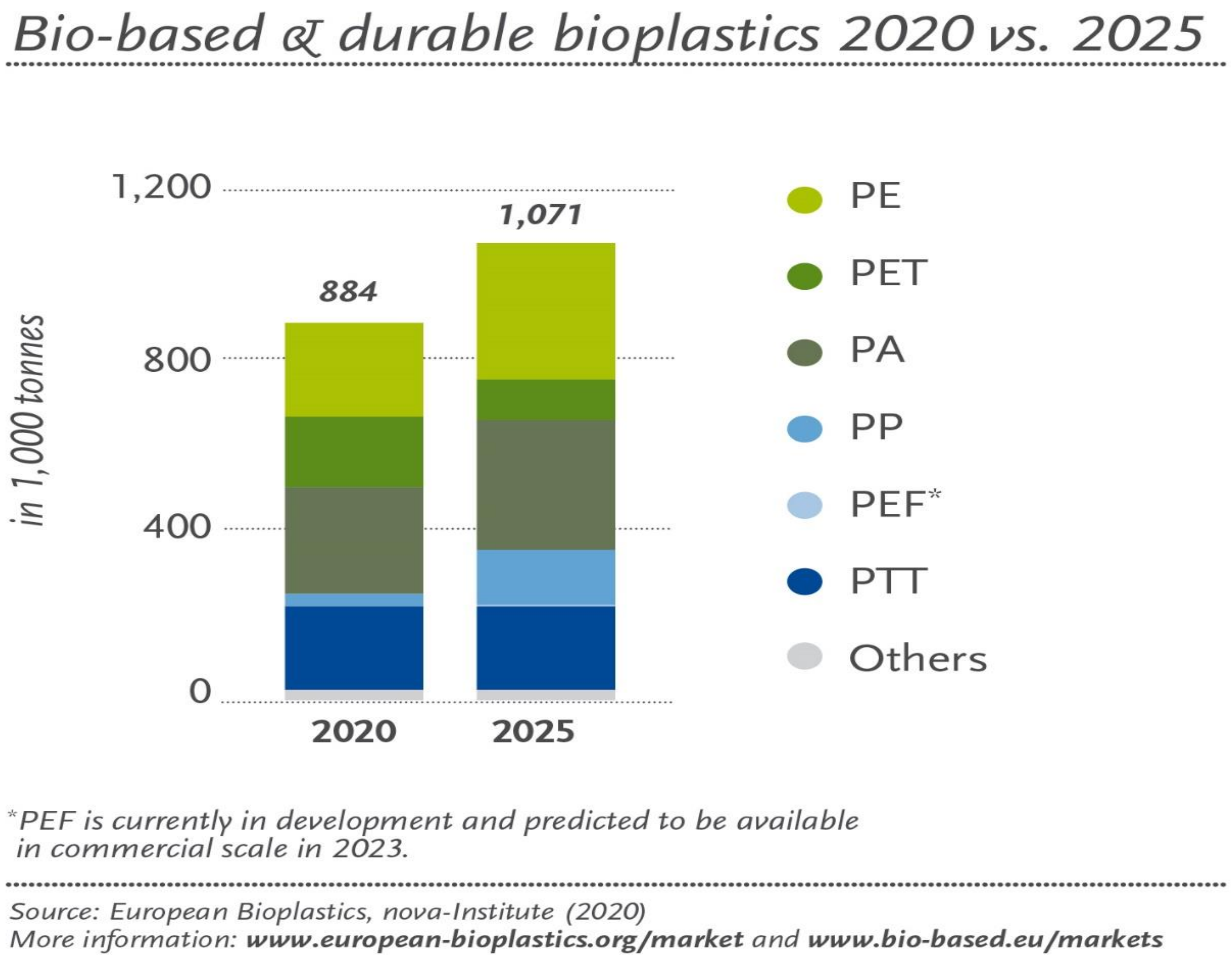


Environmental claims of bioplastics materials and products, such as biodegradability and the amount of biomass content, must always be specific, accurate, and ideally provide a third party substantiation for these claims.

A label awarded in accordance with independent certification based on acknowledged standards guarantees that the product fulfills the criteria claimed.

Reliable certification and labeling of bioplastics based on approved standards provided by CEN, ASTM, or ISO help the consumer to identify these products and inform about additional qualities the material or product possesses.

Bio-based Bioplastics

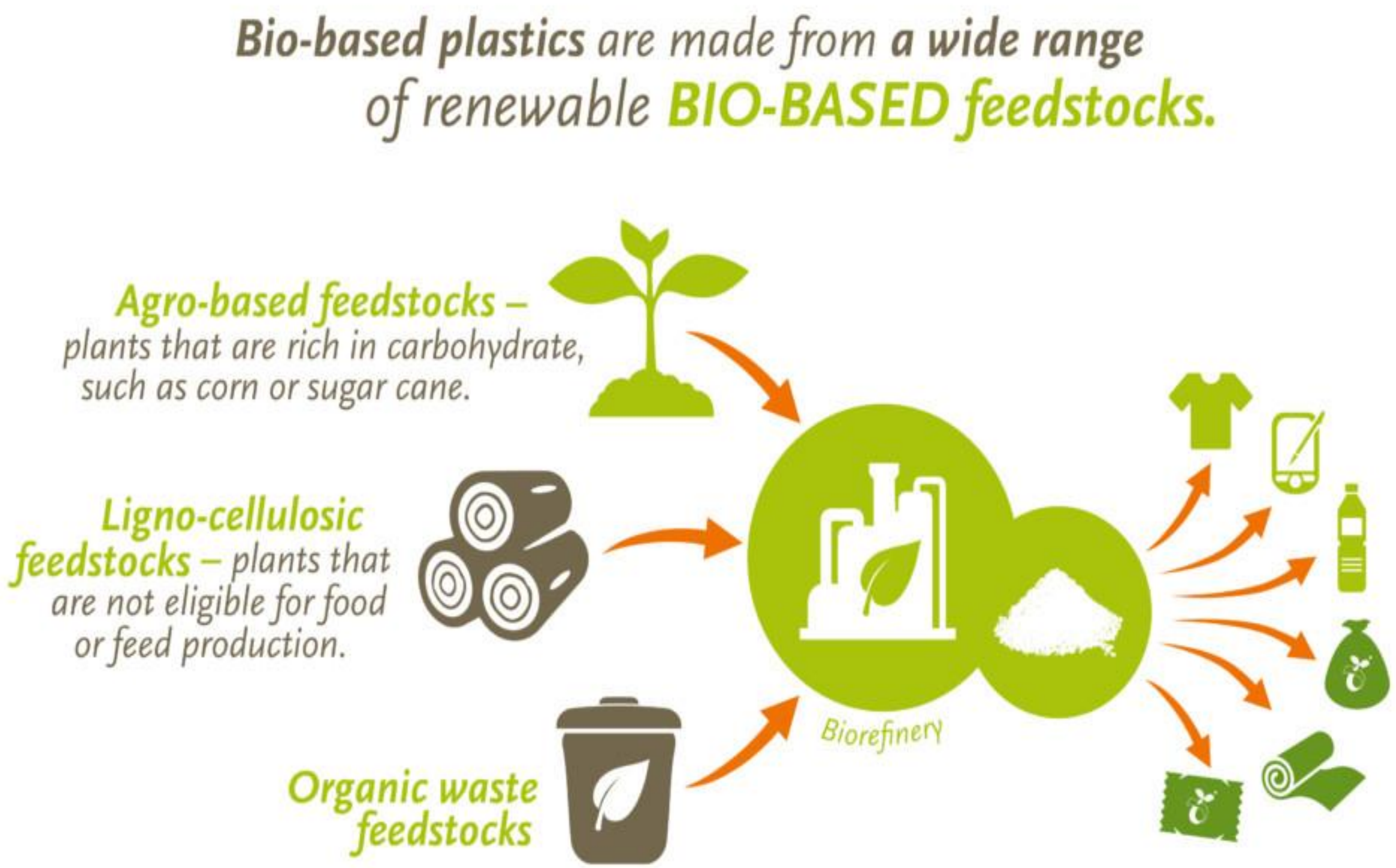


Biobased or partially biobased durable plastics, such as biobased or partially biobased PE, PET or PVC, possess properties, which are identical to their conventional versions.

These bioplastics are technically equivalent to their fossil counterparts; yet, they help to reduce a product’s carbon footprint.

Moreover, they can be mechanically recycled in existing recycling streams.

Bio-based Bioplastics



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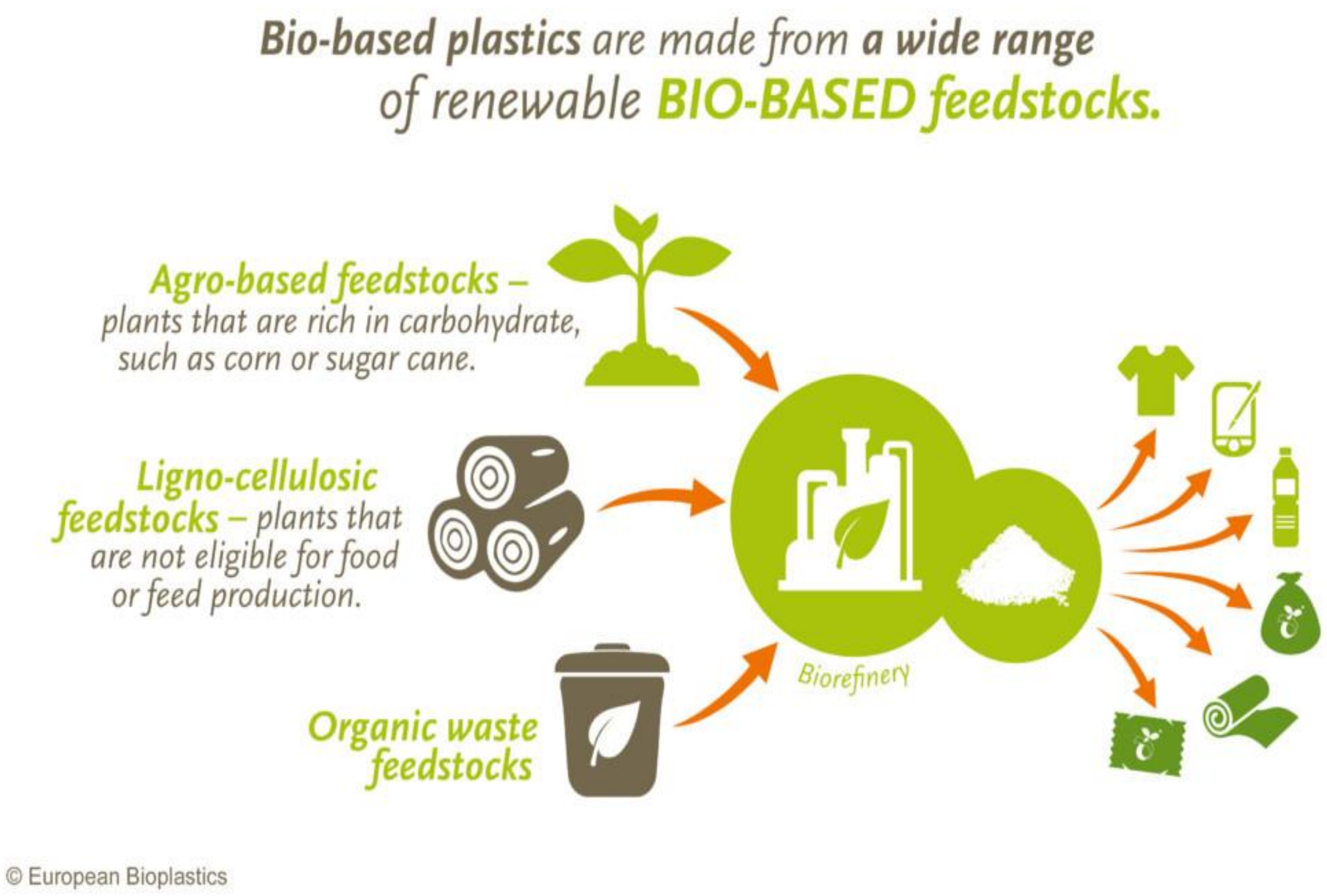
Bioplastics are mostly made of carbohydrate-rich plants such as corn or sugar cane, so called food crops or first generation feedstock.

First generation feedstock is currently the most efficient for the production of bioplastics, as it requires the least amount of land to grow and produces the highest yields

Bio-based Bioplastics

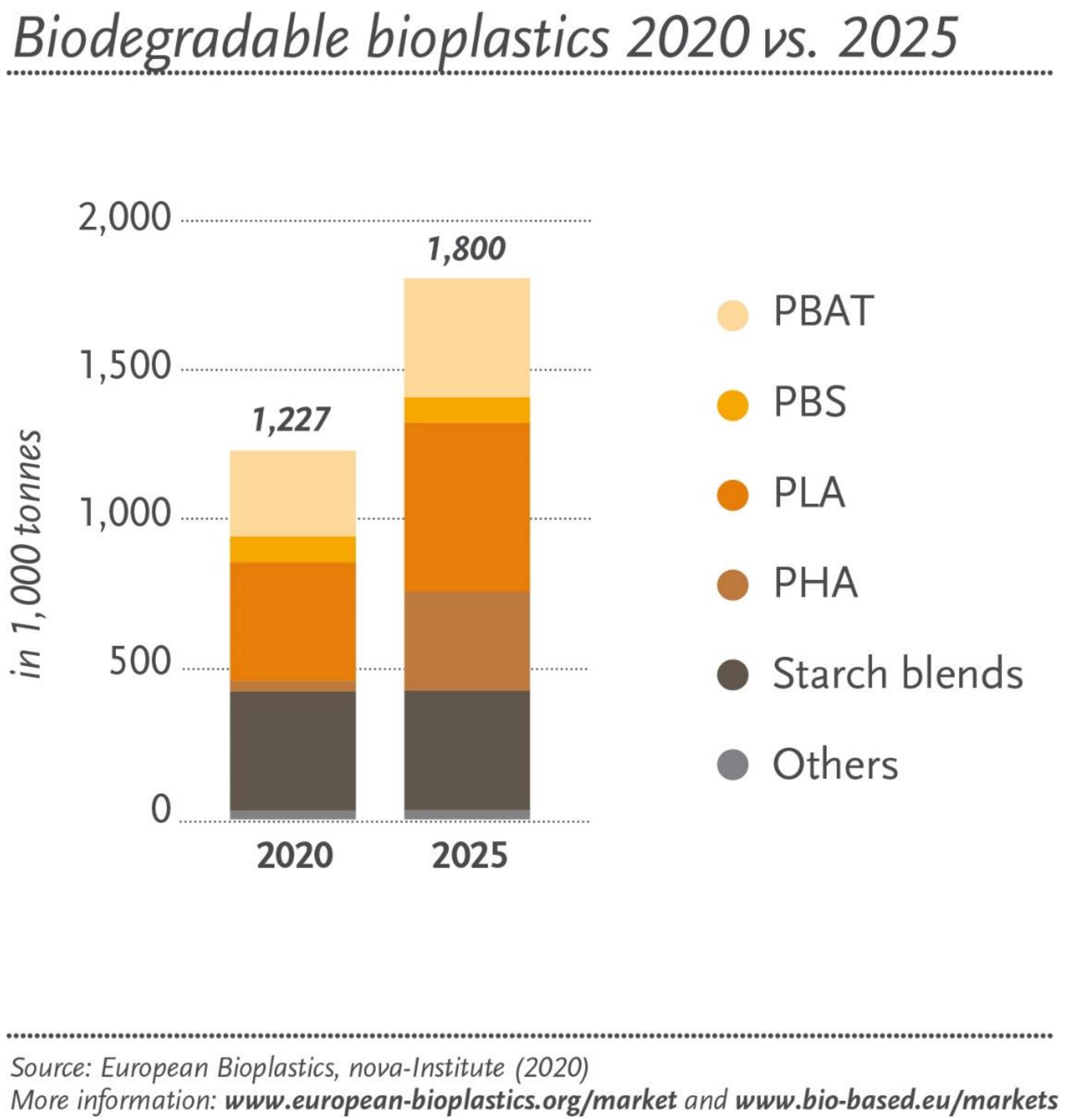


The bioplastics industry is also researching the use of non-food crops (second and third generation feedstock), such as cellulose and algae, with a view to its further use to produce bioplastics materials.

Innovative technologies focus on non-edible by-products of the production of food crops, which inevitably generate large amounts of cellulosic by-products, such as straw, corn stover or bagasse which are usually left on the field where they biodegrade at a quantity much higher than is necessary to restore the soil carbon pool.

This leaves significant potential for using biotechnological processes to create platform chemicals for industrial purposes – amongst them the production of bioplastics.

Biodegradable Plastics



Biodegradable plastics are often regarded as a possible solution to this problem as they can be decomposed by microrganisms without producing harmful or noxious residue during decomposition.

The process of biodegradation is dependent on environmental conditions.

Products suitable for industrial composting (as defined according to the EN 13432 standard) are fit for the conditions in a composting plant, but not for those outside in nature.

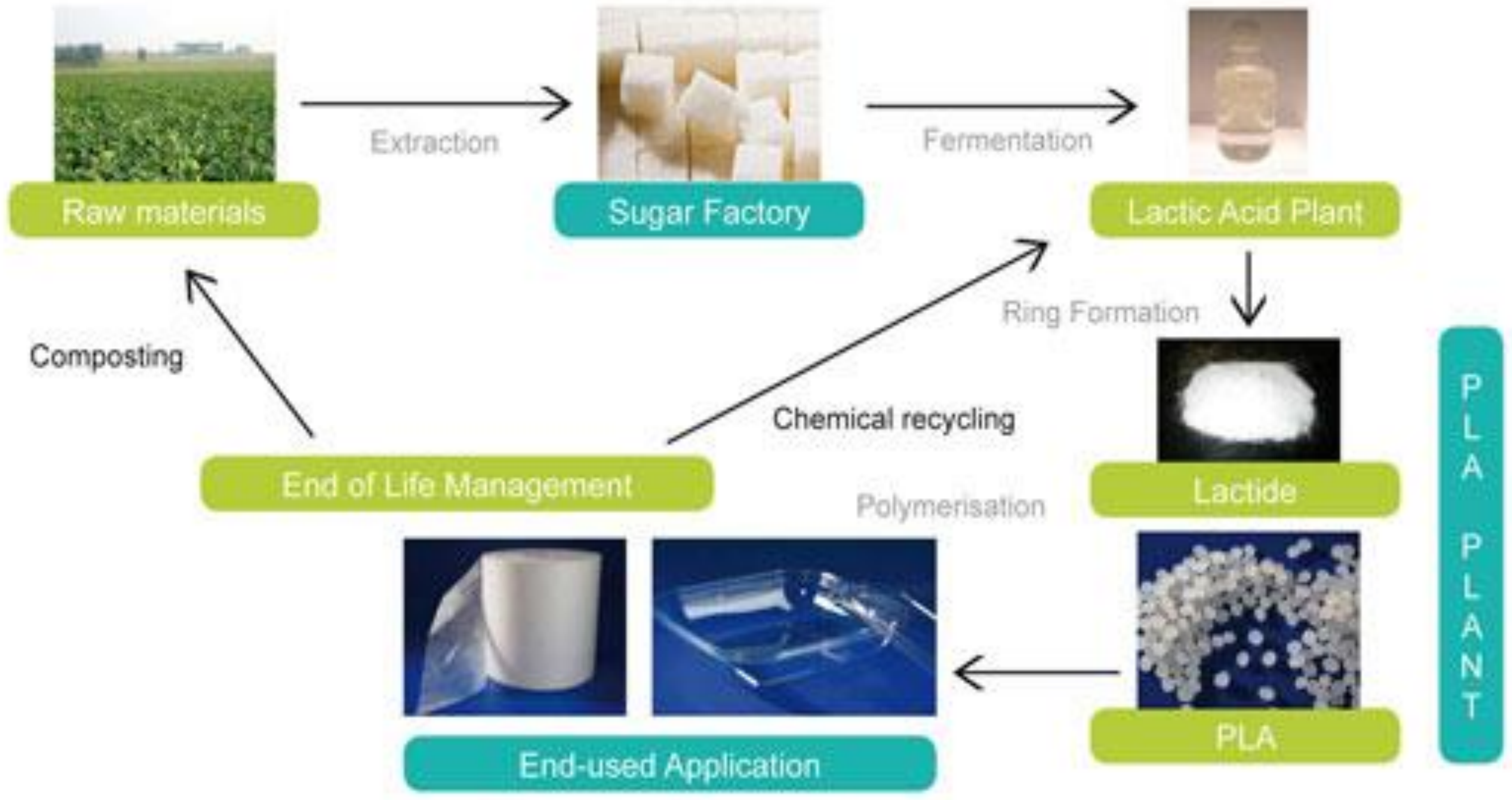
Bio-based/Biodegradable Bioplastics

Bio-based polymers and overview of their production

Polymer	Technology Overview
Polylactic acid (PLA)	Fermentation of carbohydrates (e.g., starch) yields lactic acid which polymerizes to low M_n PLA. This depolymerizes to lactide, which polymerizes to high M_n PLA.
Polybutylene succinate (PBS)	Bacterial fermentation of carbohydrates yields succinic acid, which is esterified to also obtain 1,4-butanediol. The two chemicals polymerize to PBS.
Polyurethanes (PUR)	Polyols from plant oils, reacted with isocyanates or bio-isocyanates to yield PUR.
Polyamides (PAs)	Diacids derived from castor oil reacted with a diamine to yield PAs. A typical pair is sebacic acid and decamethylenediamine (obtained from the acid).
Polyethylene (PE)	Fermentation of saccharides yields bioethanol, then dehydrated to ethylene. Polymerization yields bio-PE.
Thermoplastic starch	Typically obtained by gelatinization of starch (from corn, cassava, etc.) followed by casting or by extrusion of starch pellets and plasticizers.
Cellulose acetate	Cellulose from wood pulp converted to a triacetate form which is then hydrolyzed to cellulose acetate.
Regenerated cellulose	Cellulose converted to a soluble form, after regenerated to obtain a film (cellophane) or a fiber (rayon)
Polyhydroxyalkanoates	Intracellularly accumulated by different bacteria. Polyhydroxybutyrate was the first to be discovered.

Production of Bio-based/Biodegradable Bioplastics

Polylactic acid (PLA)



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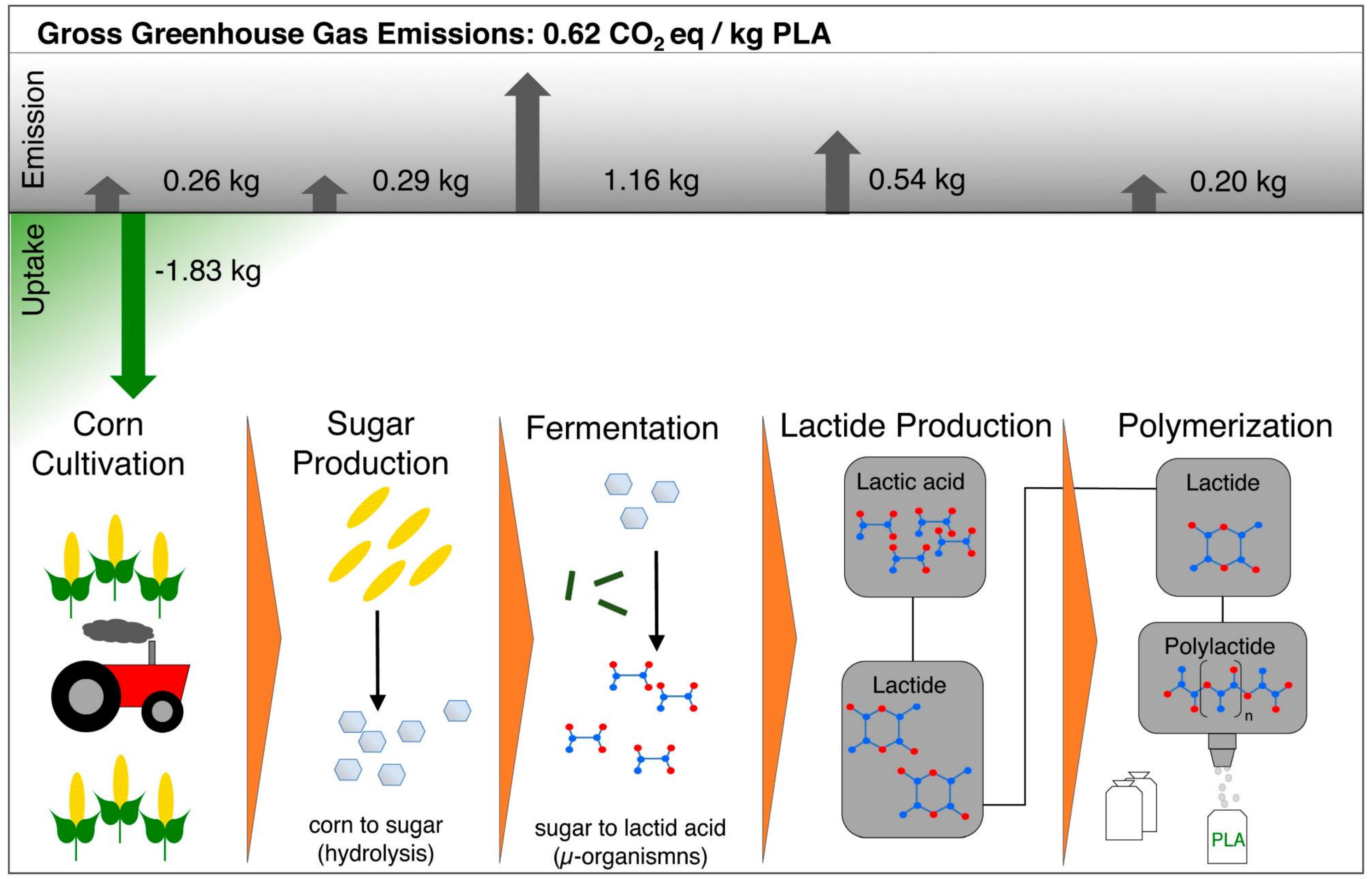
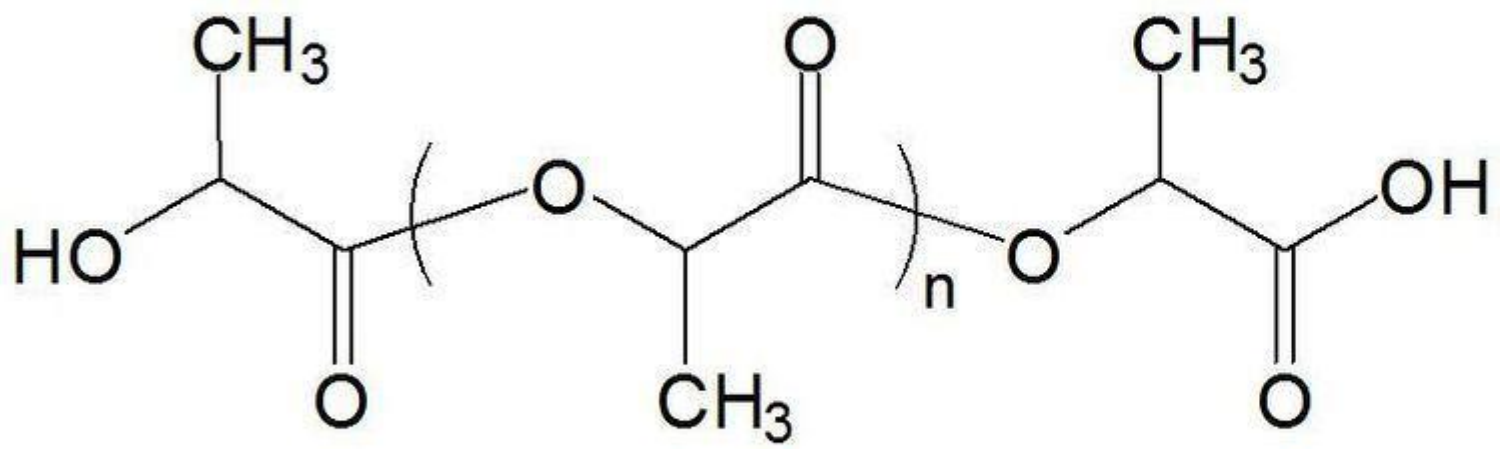
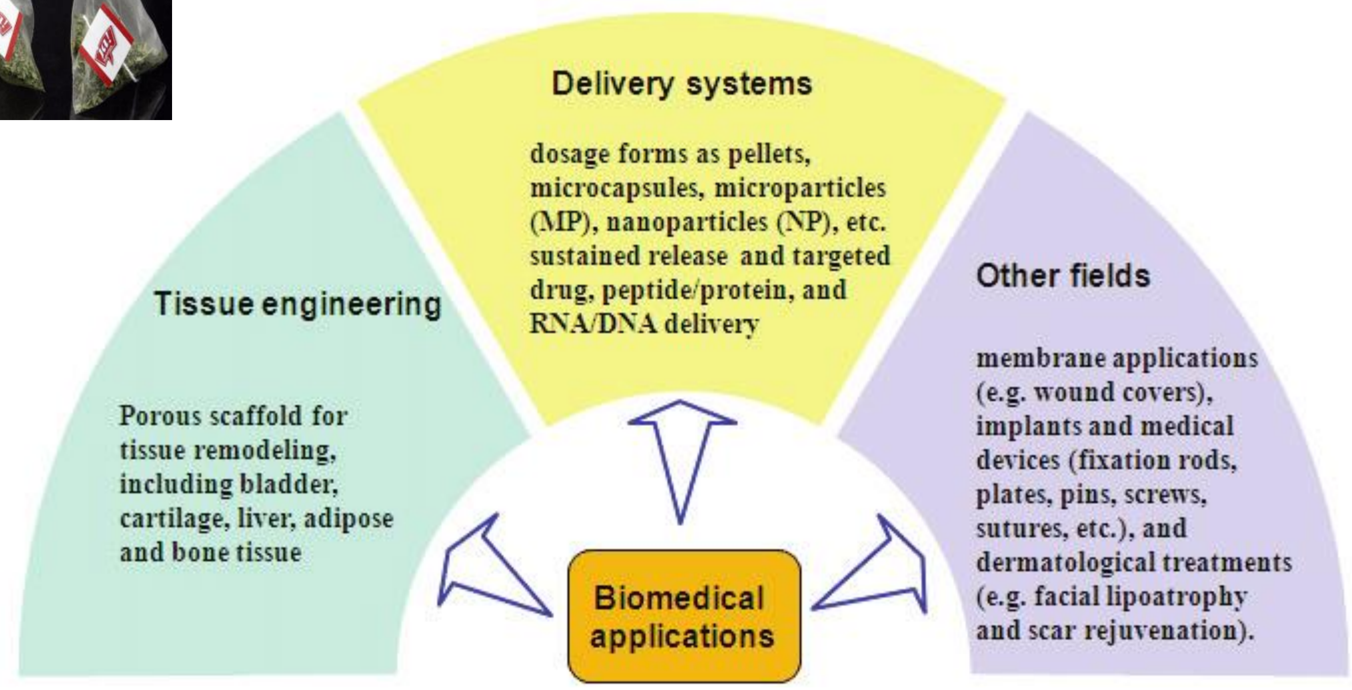


https://www.youtube.com/watch?v=CT3AvNqDVfE

2. PLA

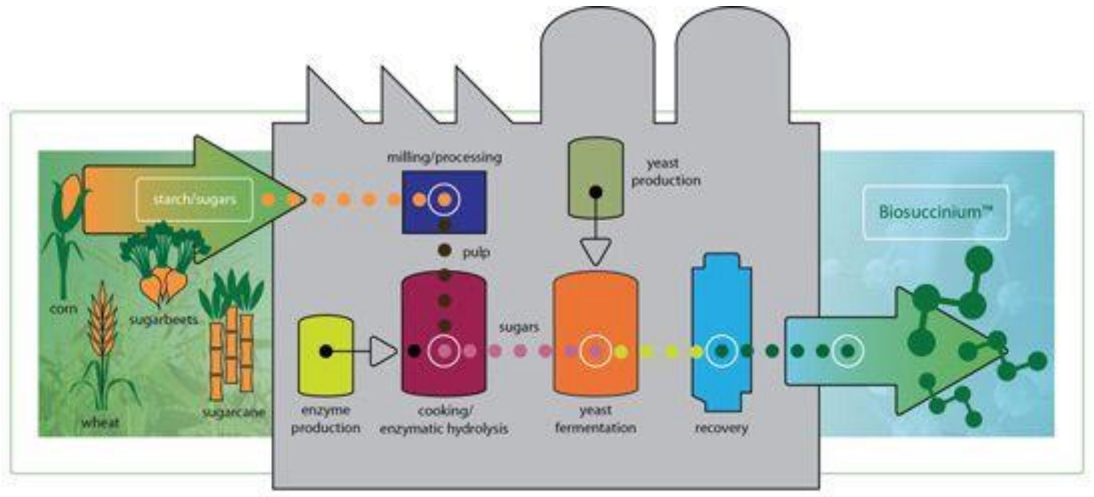


3. APPLICATIONS

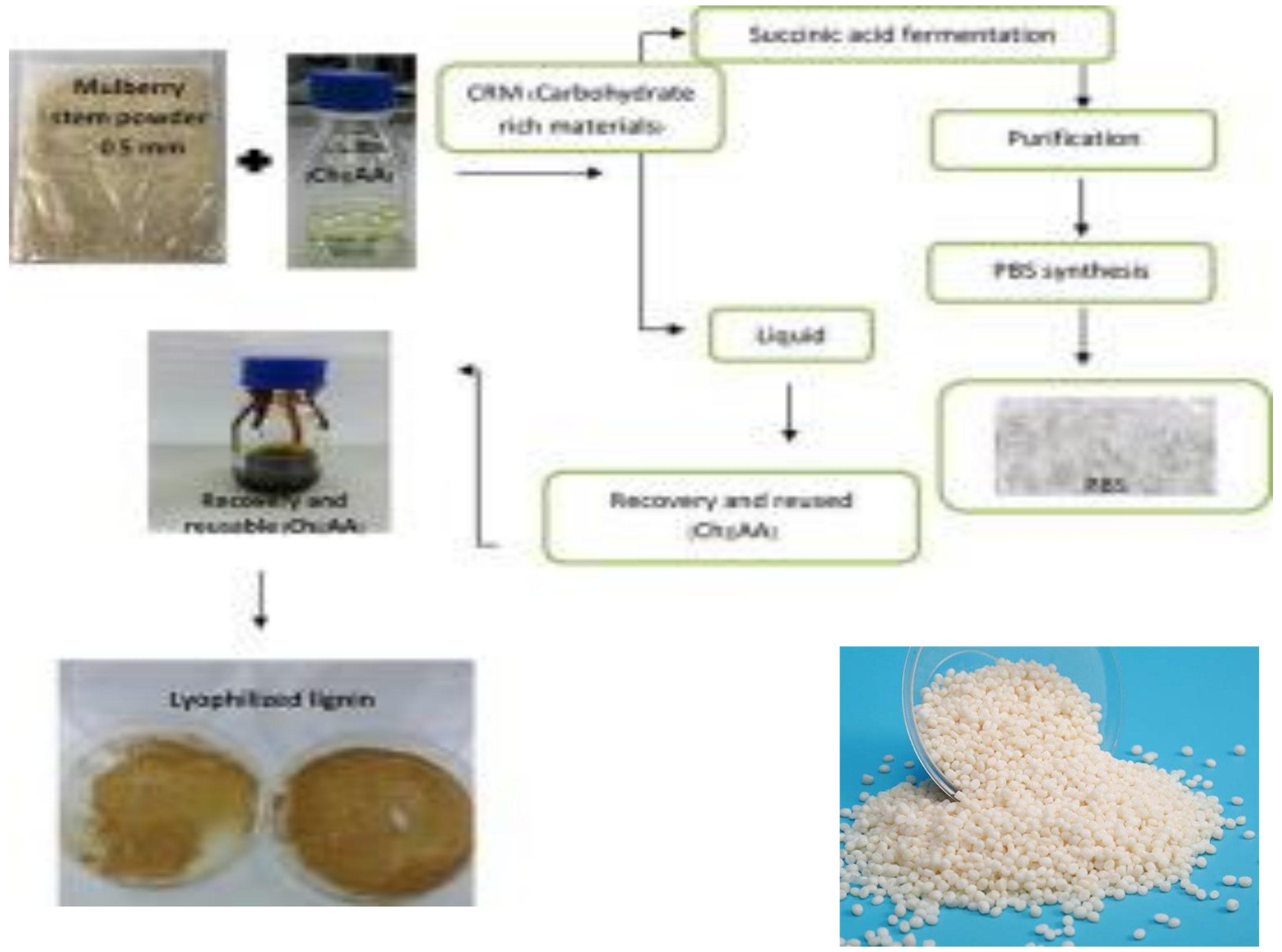


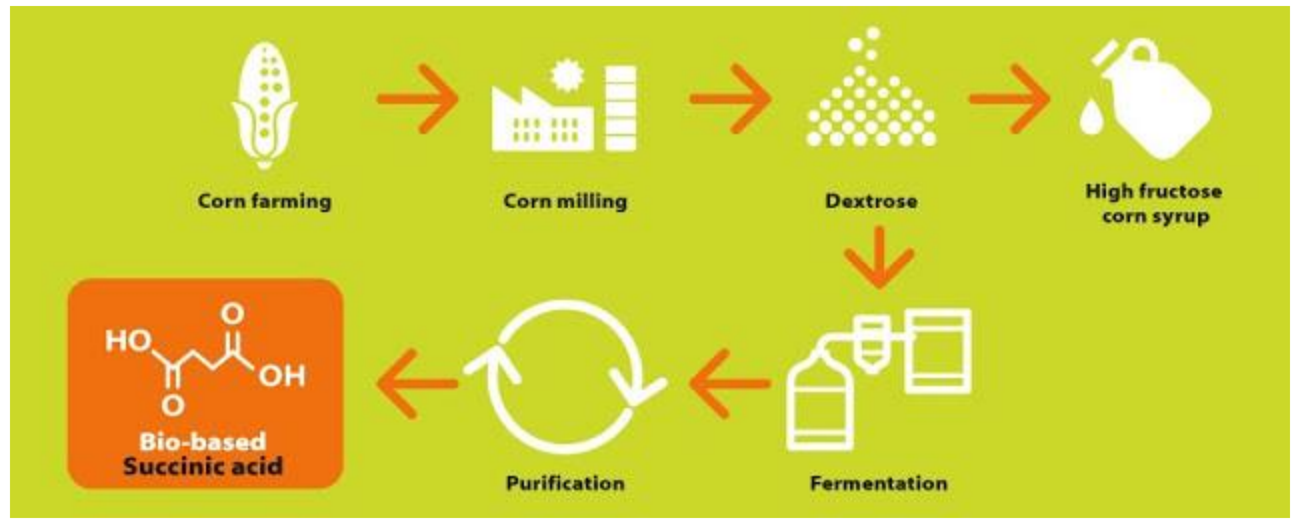
Production of Bio-based/Biodegradable Bioplastics

Polybutylene succinate (PBS)

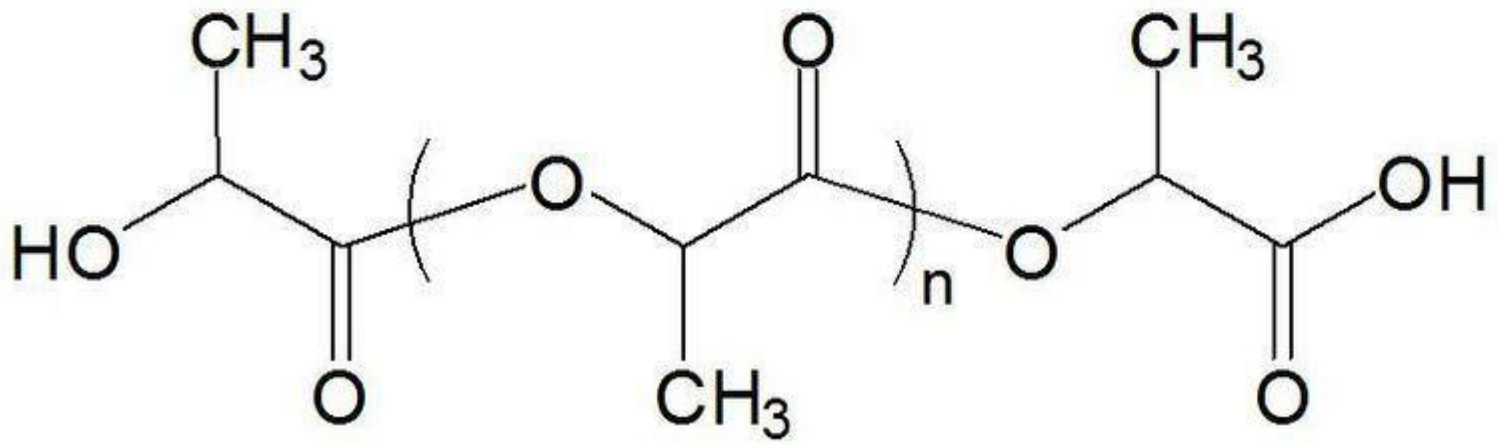


1. Production



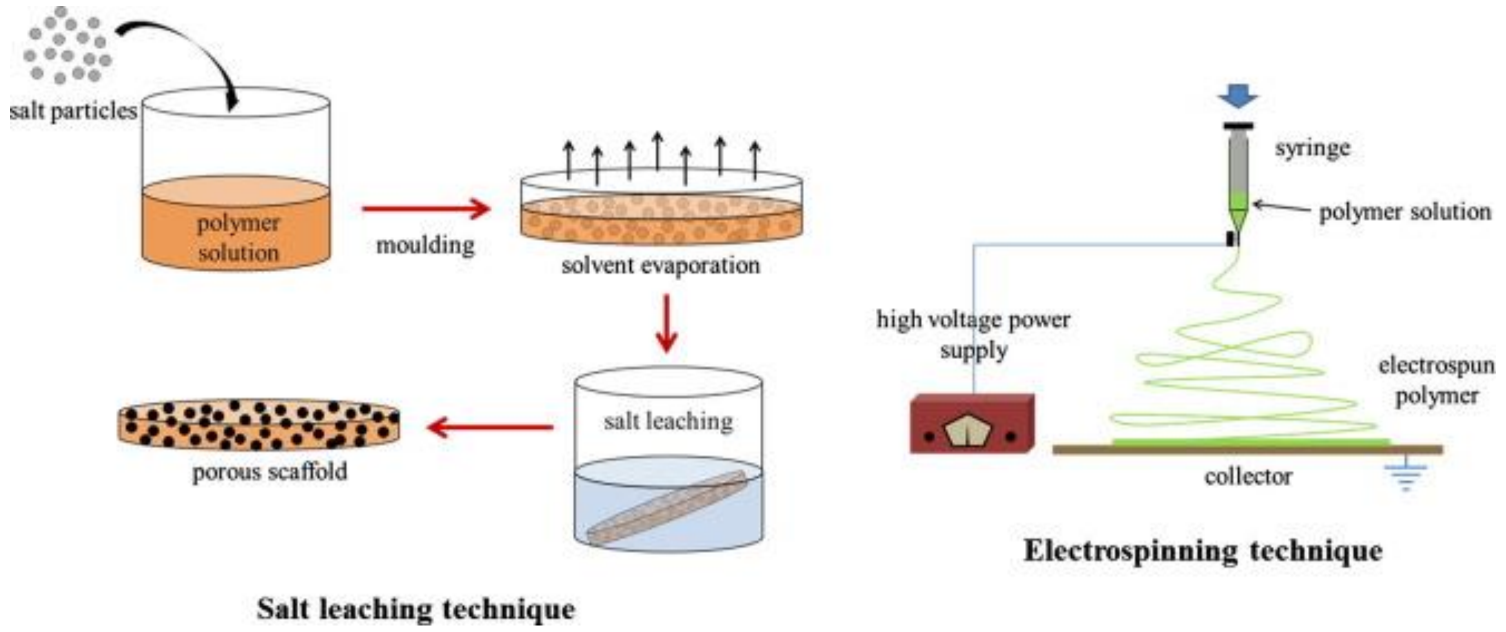


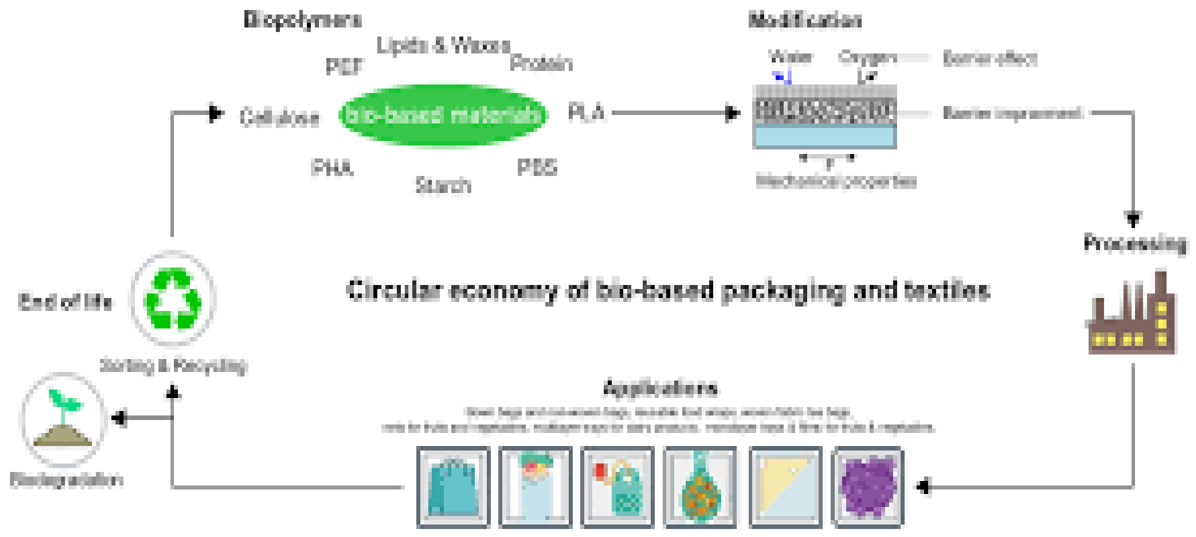
2. PBS



https://www.youtube.com/watch?v=CT3AvNqDVfE

3. APPLICATIONS

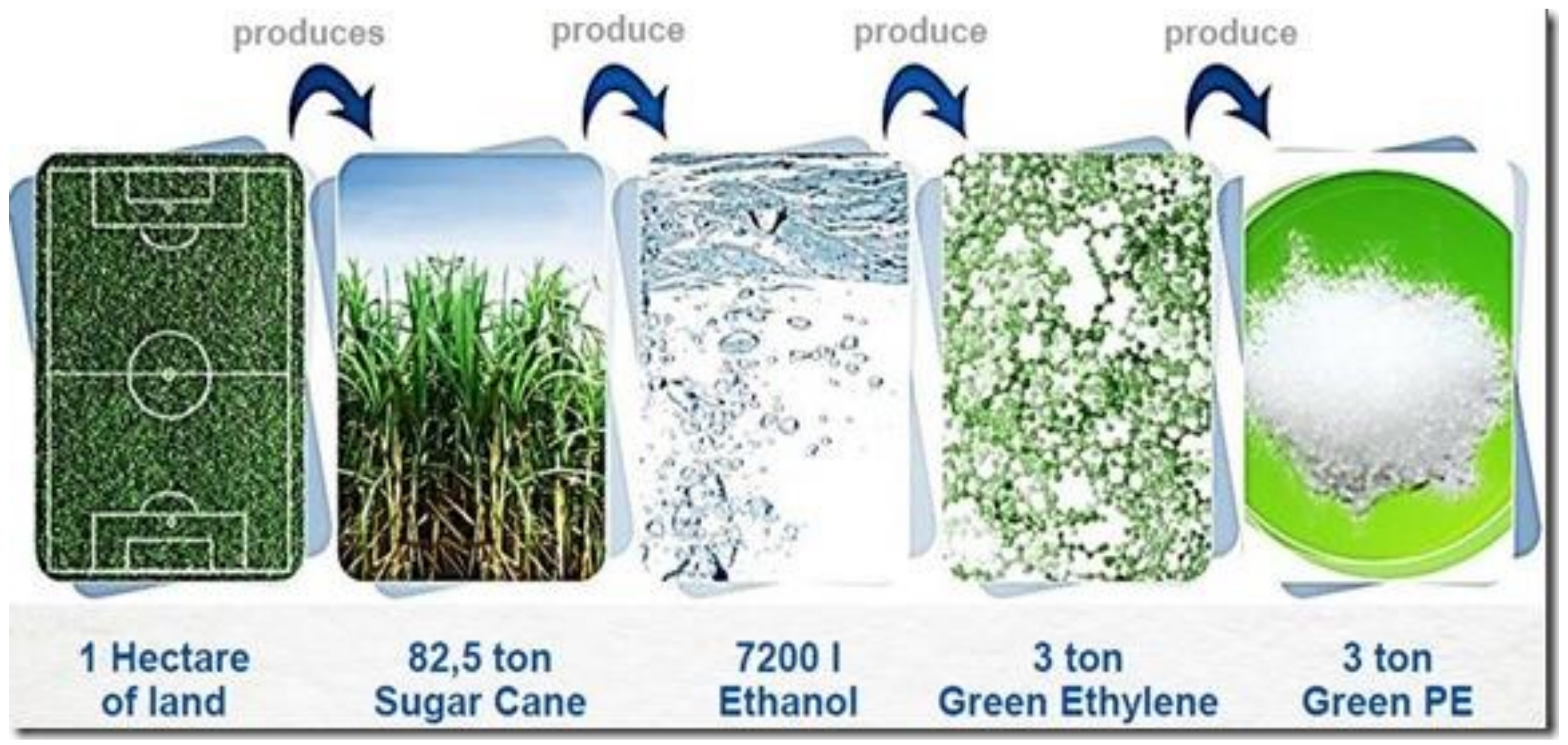


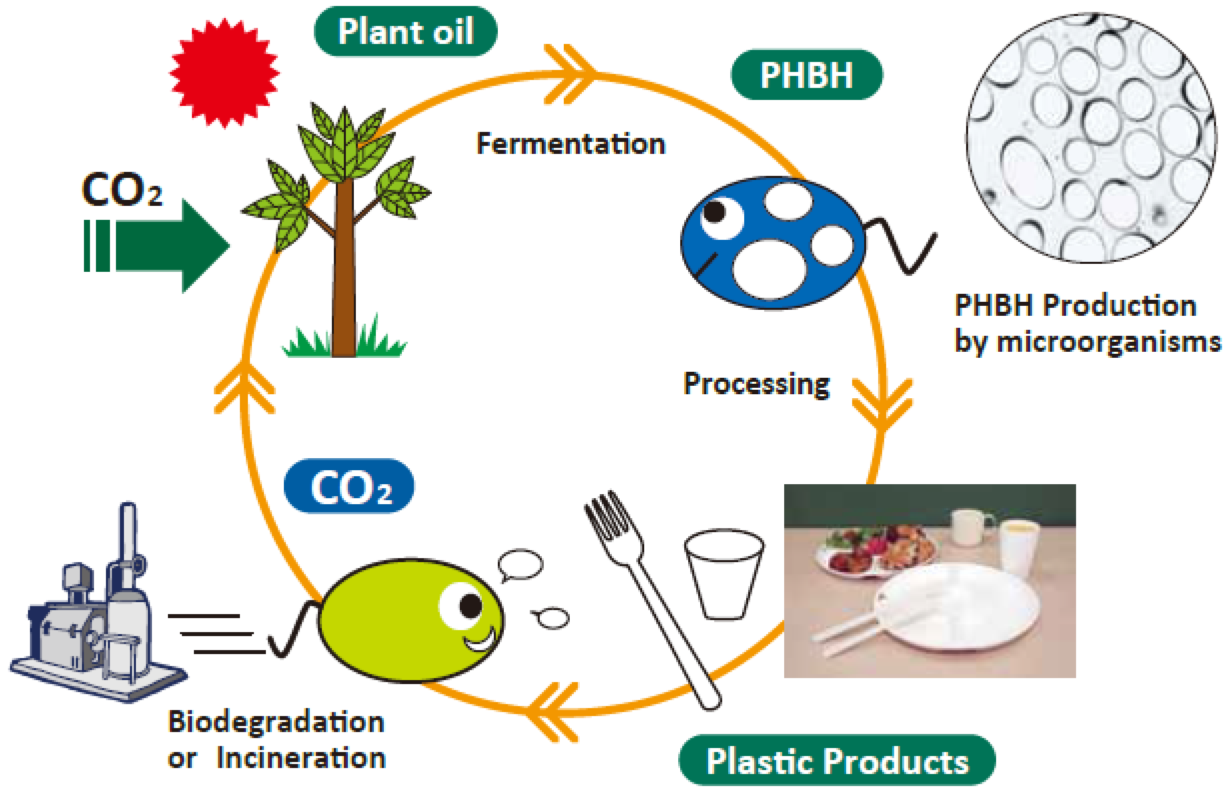


Production of Bio-based/Biodegradable Bioplastics

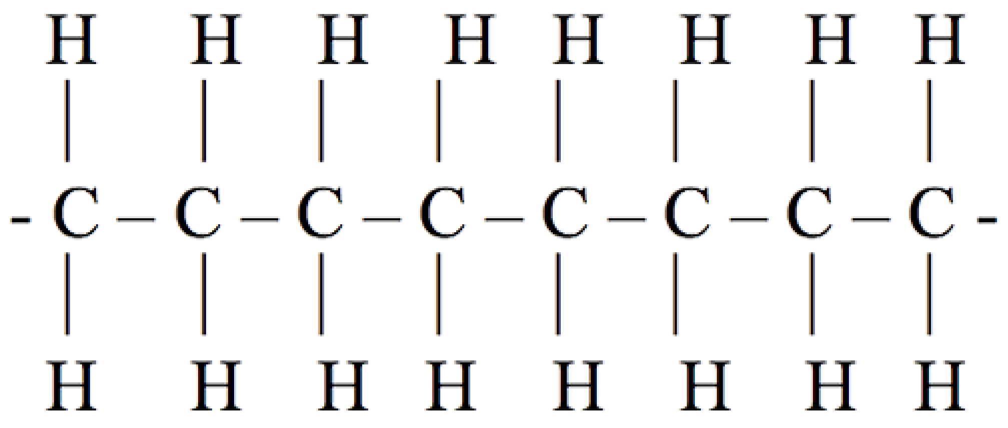
Polyethylene (PE)

1. Production





2. PE

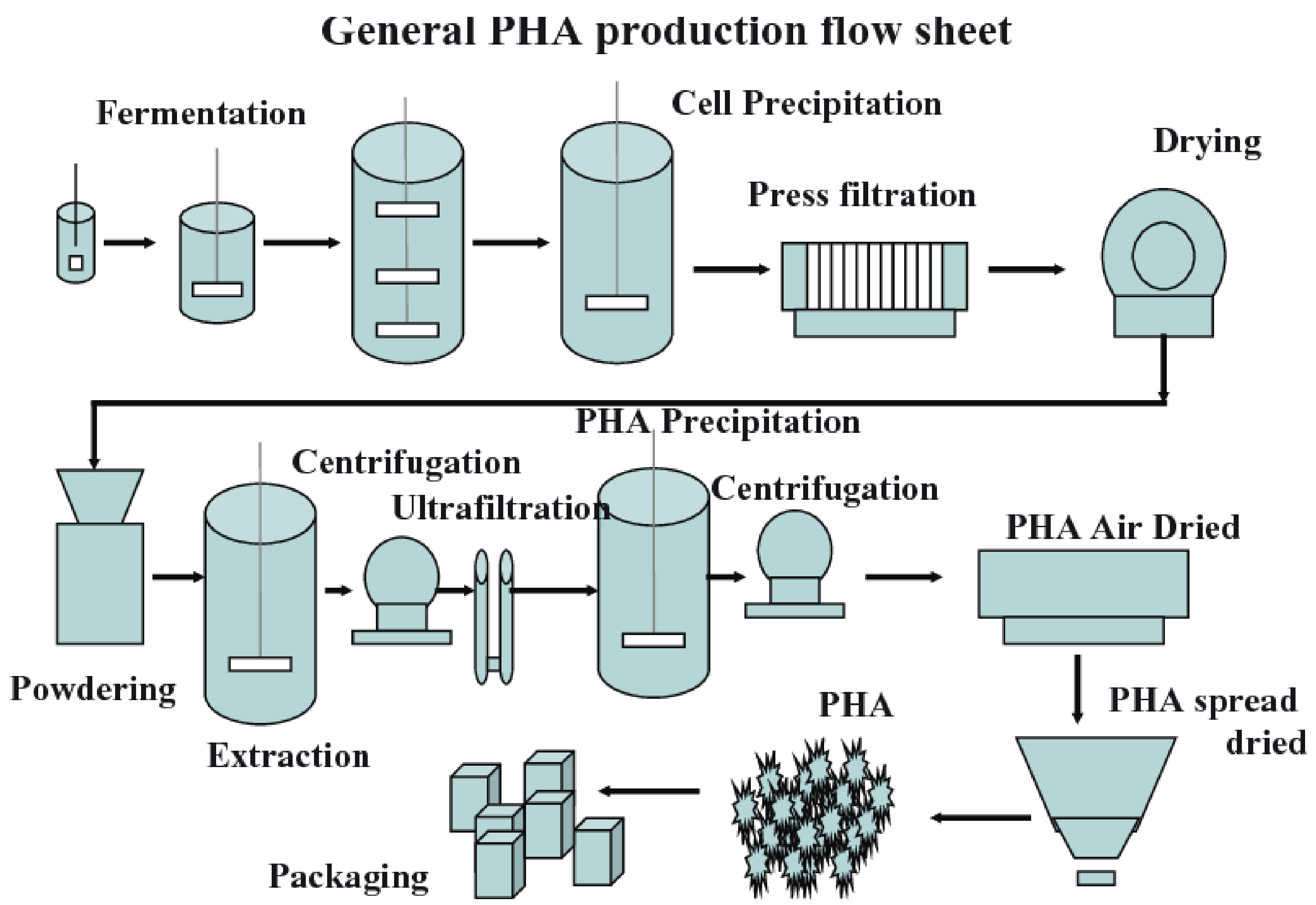


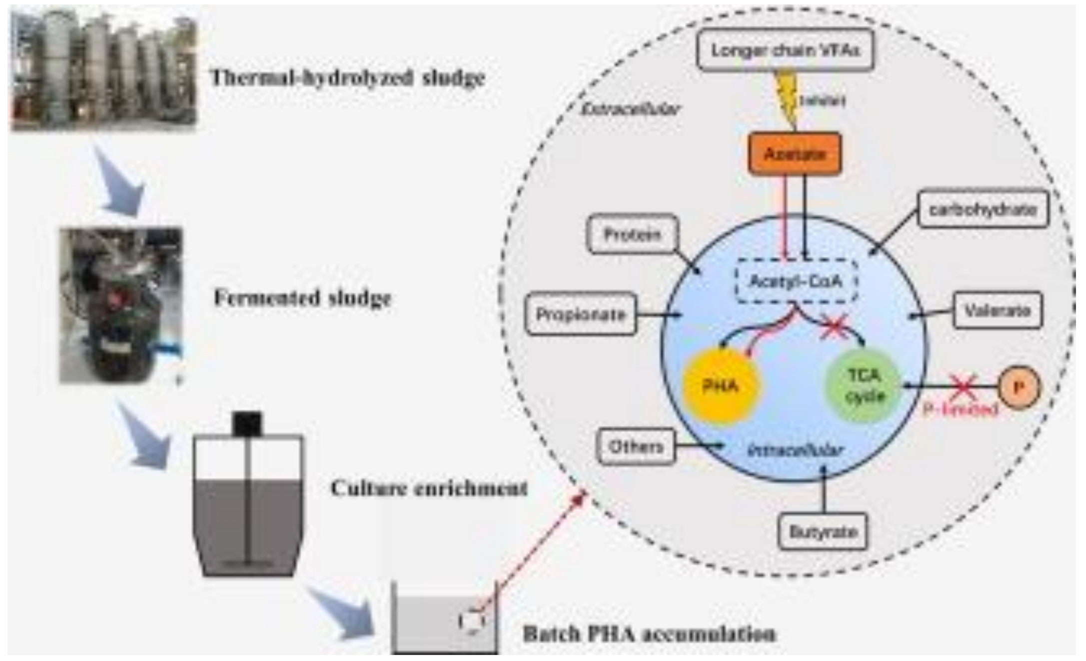
3. APPLICATIONS

Ulisses — Production of Bio-based/Biodegradable Bioplastics

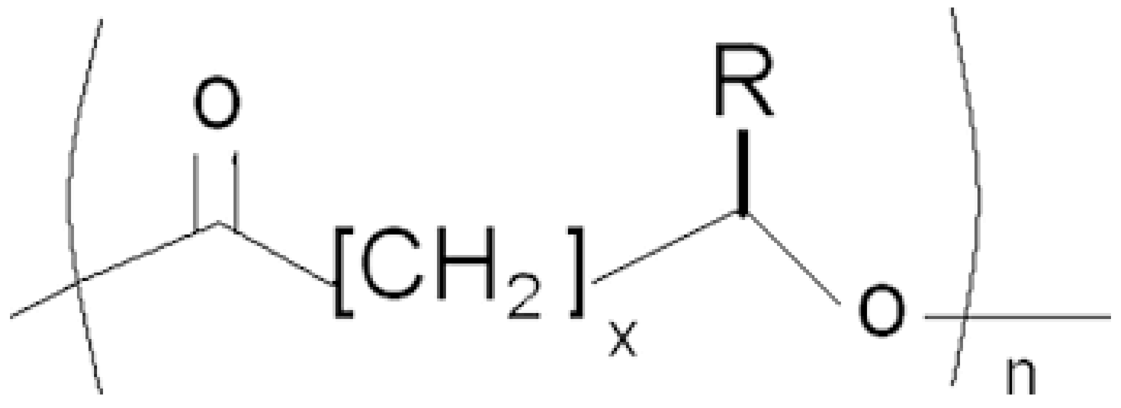
Polyhydroxyalkanoates

1. Production

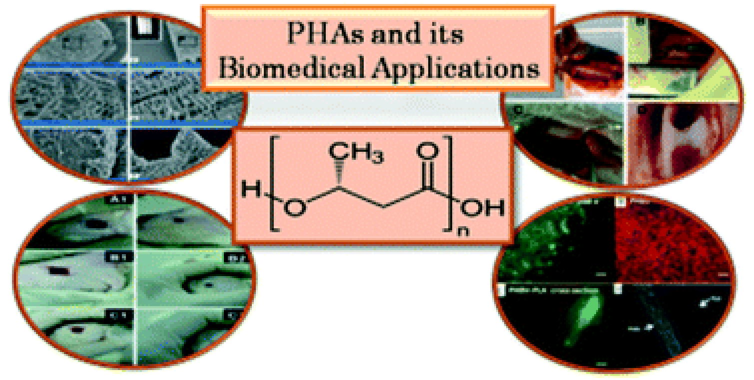


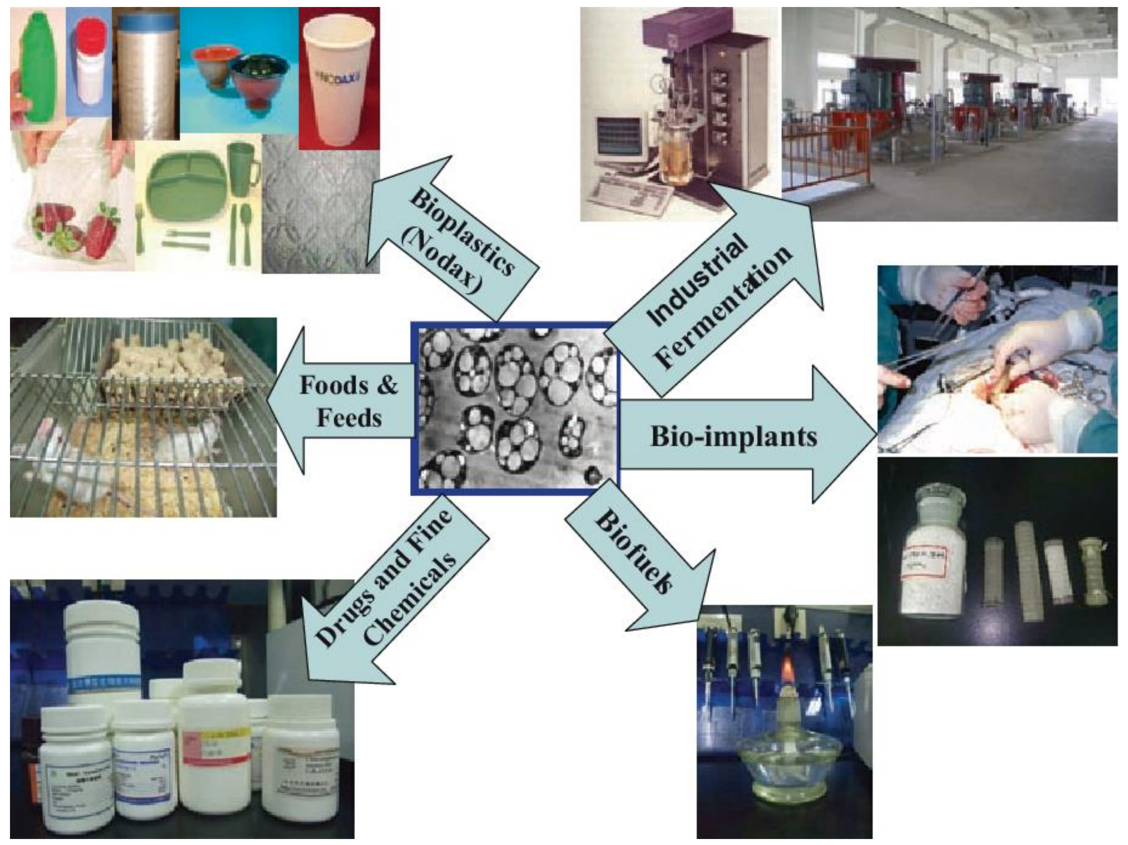


2. Polyhydroxyalkanoates



3. Applications





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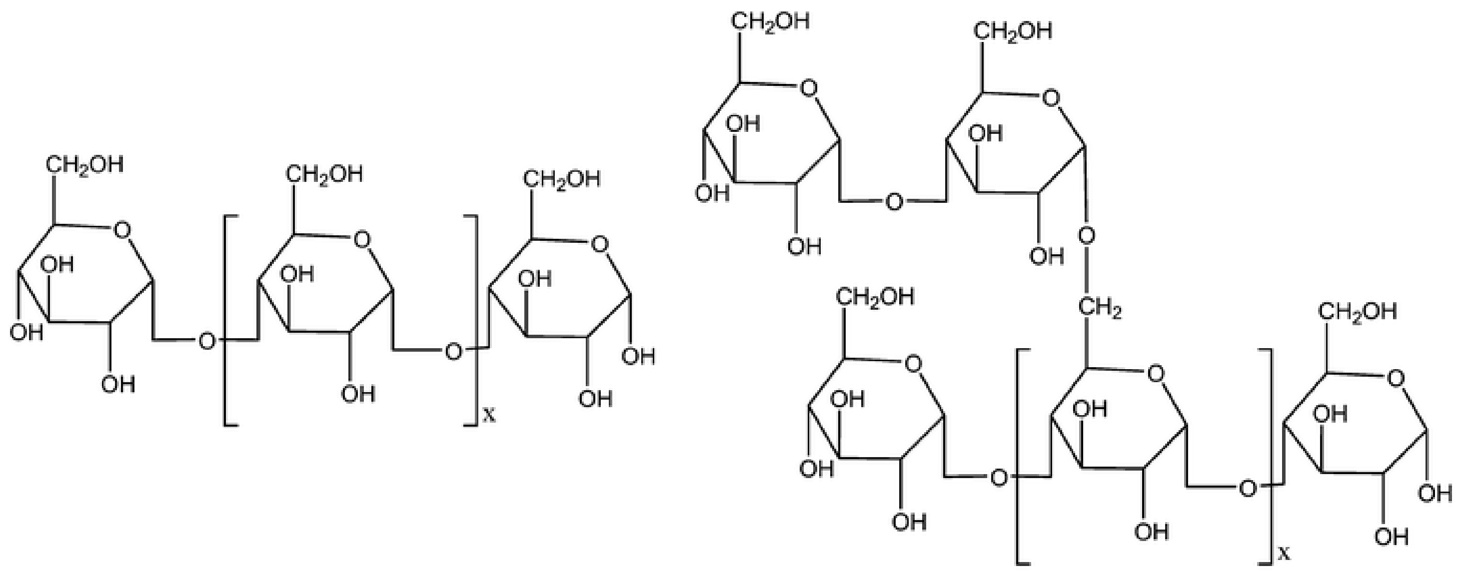
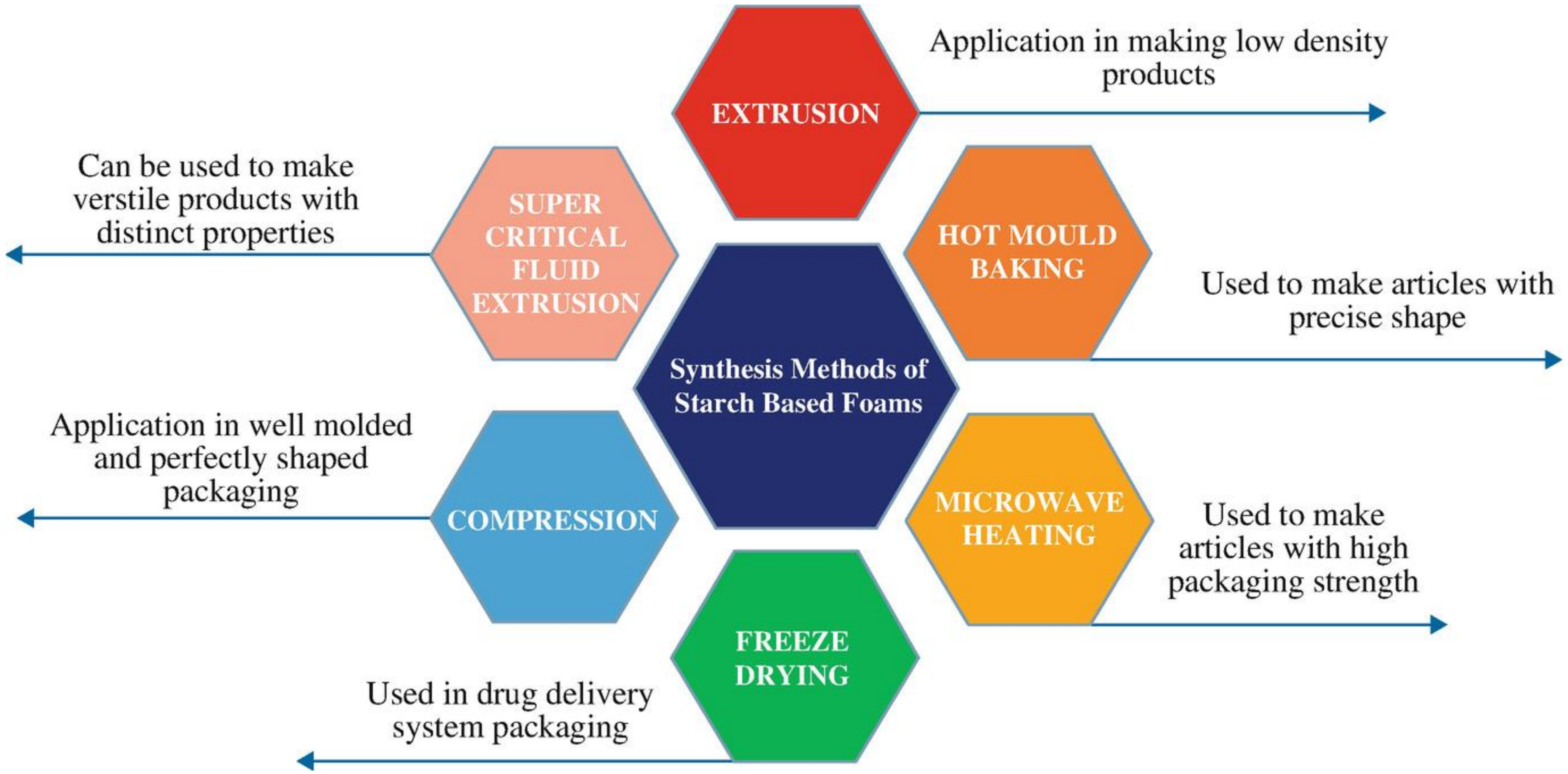
Starch-based polymers

Starch-based polymers form an important family of bioplastics on the market.

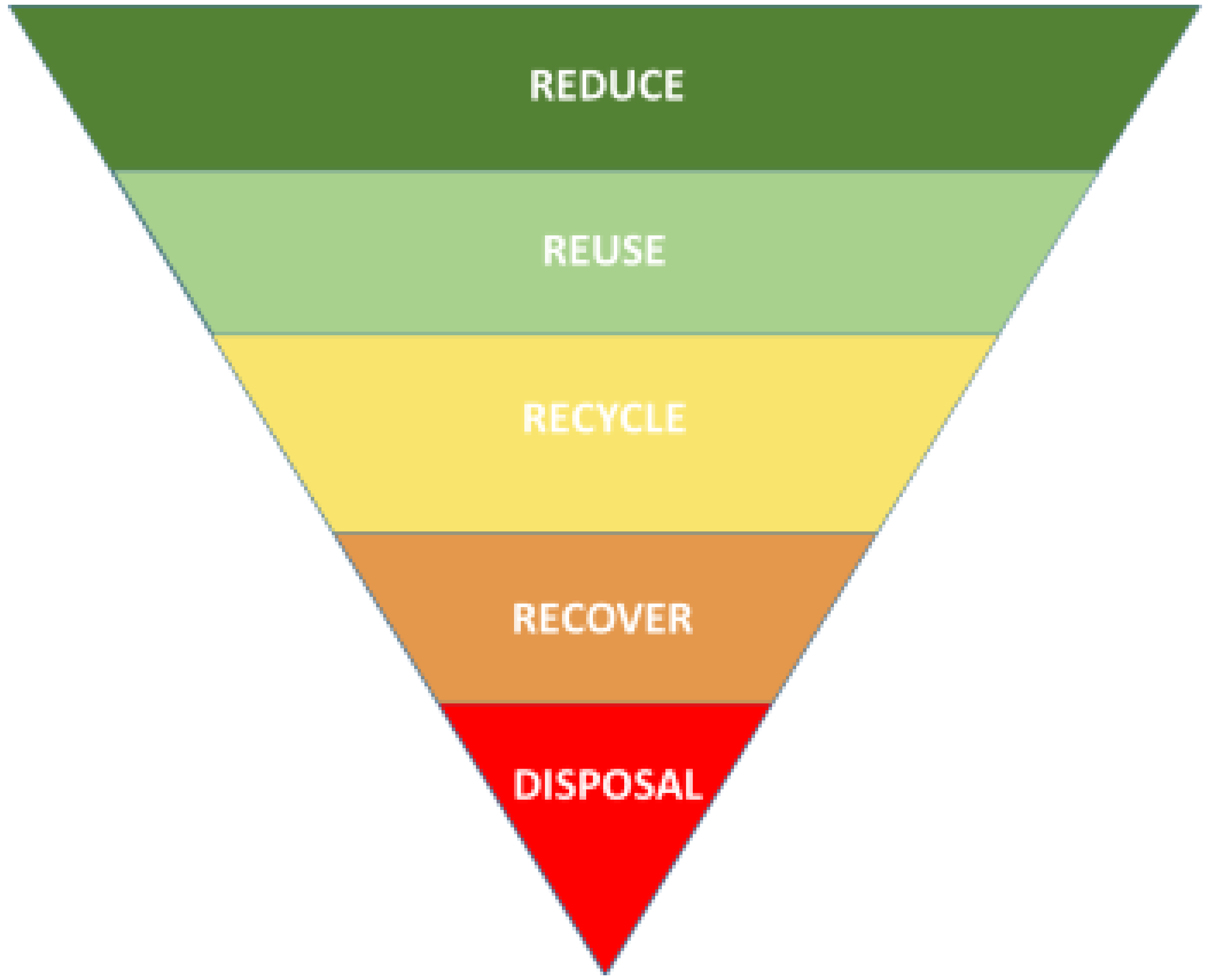


(a) (b)



Bioplastics – closing the loop

European waste hierarchy



The goal of this policy is to close the loop, meaning that the discarded product or material should be used again after its intended use. For bio-based plastics, there are two preferable ways to close the loop: recycling and composting.

Assuming continued strong growth of the bioplastics market based on the current stage of technological development, a market of 2.87 million tonnes could be achieved by the year 2025, accounting for about 1.1 million hectares, or 0.02 percent of the global agricultural area.

This estimation does not include the expected increased share of food residues, non-food crops or cellulosic biomass, which will lead to a smaller land use demand for bioplastics than the predicted amount mentioned above.

(European Bioplastics (2020) www.european.pioplastics.org

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UNIVERSITY OF LISBON
INTERDISCIPLINARY STUDIES
ON SUSTAINABLE ENVIRONMENT AND SEAS

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