



Bioplastics

(Bio-based and
Compostable Plastics)

John Harrold

Massachusetts Institute of Technology

Department of Materials Science and Engineering

Digital Learning Lab Fellow

Harvard Energy Journal Club

October 2, 2020

Bioplastics landscape

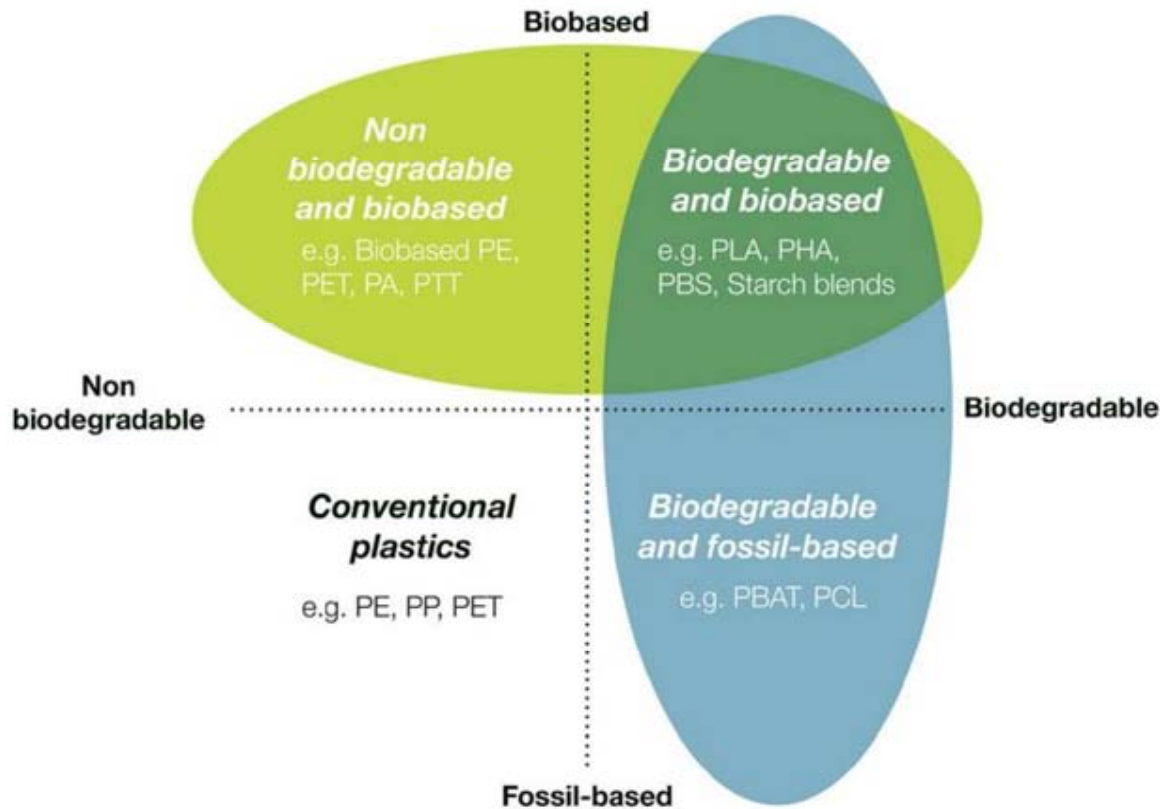
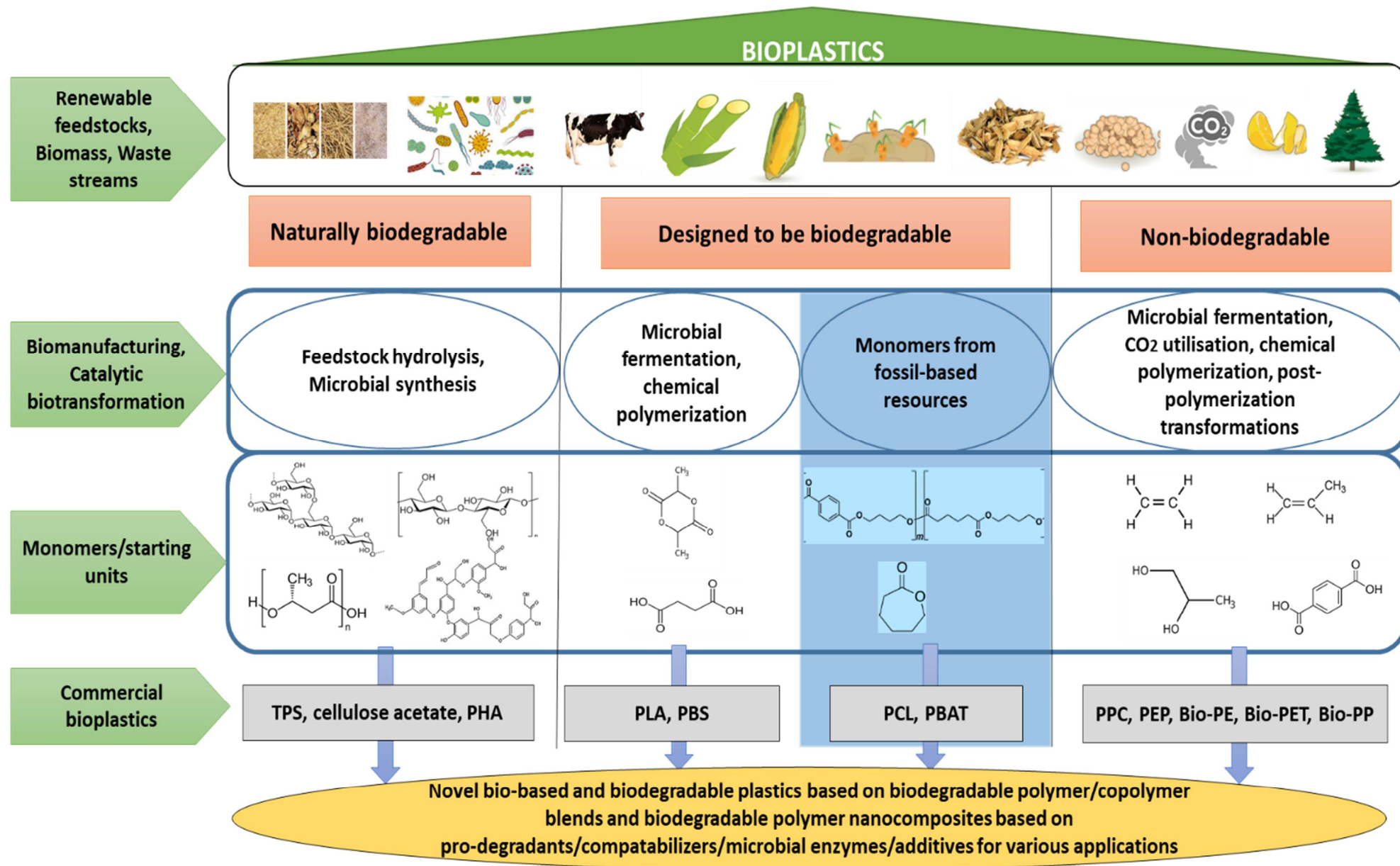


Figure 1. Understanding the three different categories of bioplastics [23].

PE	Polyethylene
PET	Polyethylene terephthalate
PA	Polyamine (Nylon)
PTT	Polytrimethylene terephthalate
PLA	Polylactic acid
PHA	Polyhydroxyalkanoates
PBS	Polybutylene succinate (polytetramethylene succinate)
PBAT	Polybutylene adipate terephthalate
PP	Polypropylene
PEF	Poly (Ethylene 2, 5-Furandicarboxylate)
PCL	Polycaprolactone
TPS	Thermoplastic Starch





Raw Materials

The process typically starts with growing plants such as sugar cane, corn and potatoes that are high in starches, the raw materials that replace petroleum products in bioplastics.



Extraction

The plant materials are harvested and processed to extract their starches.



Refining

The starches are processed further in bio-refineries through the use of special enzymes or fermentation (much as biofuels are made) to produce the chemical compounds that react to make plastics. The compounds can be refined to fit the specifications manufacturers need for different products.

The Life Cycle of Bioplastics

Some bioplastics decompose in a fairly short period of time, and the full life cycle of such products is shown here. Other bioplastics aren't biodegradable. But even in those cases, the use of plant-based raw materials means that pollution is being removed from the atmosphere while the plants grow, giving bioplastics a green appeal.

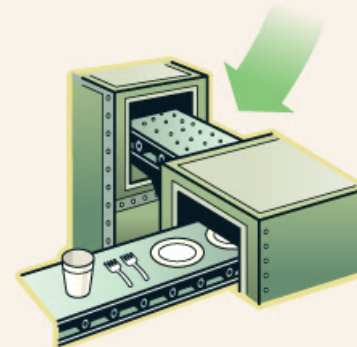


Compost and Renewal

The organic waste will compost and return to the earth as mulch to help new crops grow, completing the cycle.

Disposal

When disposing of a bioplastic product that is fully biodegradable, consumers can place it in an organic-waste collection bin.



Manufacturing

Bioplastics manufacturers use pellets or granules of the compounds to make utensils, plates, cup linings, carpeting and other products.

Industrial Composting vs Home Composting

	ANAEROBIC BACTERIA, NO FUNGI		AEROBIC BACTERIA AND FUNGI
50 – 60 °C	Chemical pulp Starch PLA Starch/PLA PHA	 THERMOPHILIC DIGESTION	INDUSTRIAL COMPOSTING Chemical pulp Mechanical pulp Starch PLA Starch/PCL PHA PBAT
≤ 35 °C	Chemical pulp Starch Starch/PCL PHA		HOME COMPOSTING Chemical pulp Mechanical pulp Starch Starch/PCL PHA PBAT

- Commercial composting can decompose meats, oils, and compostable plastics due to the higher heat and better aeration of the composting piles



Recycling

Single Stream

Single Stream makes recycling easy and convenient by allowing all recyclables to be collected in the same container. Here's how it works.



TRUCKS

are weighed and directed to the tip floor, where material is unloaded and inspected, then fed to a conveyor.



SORTERS

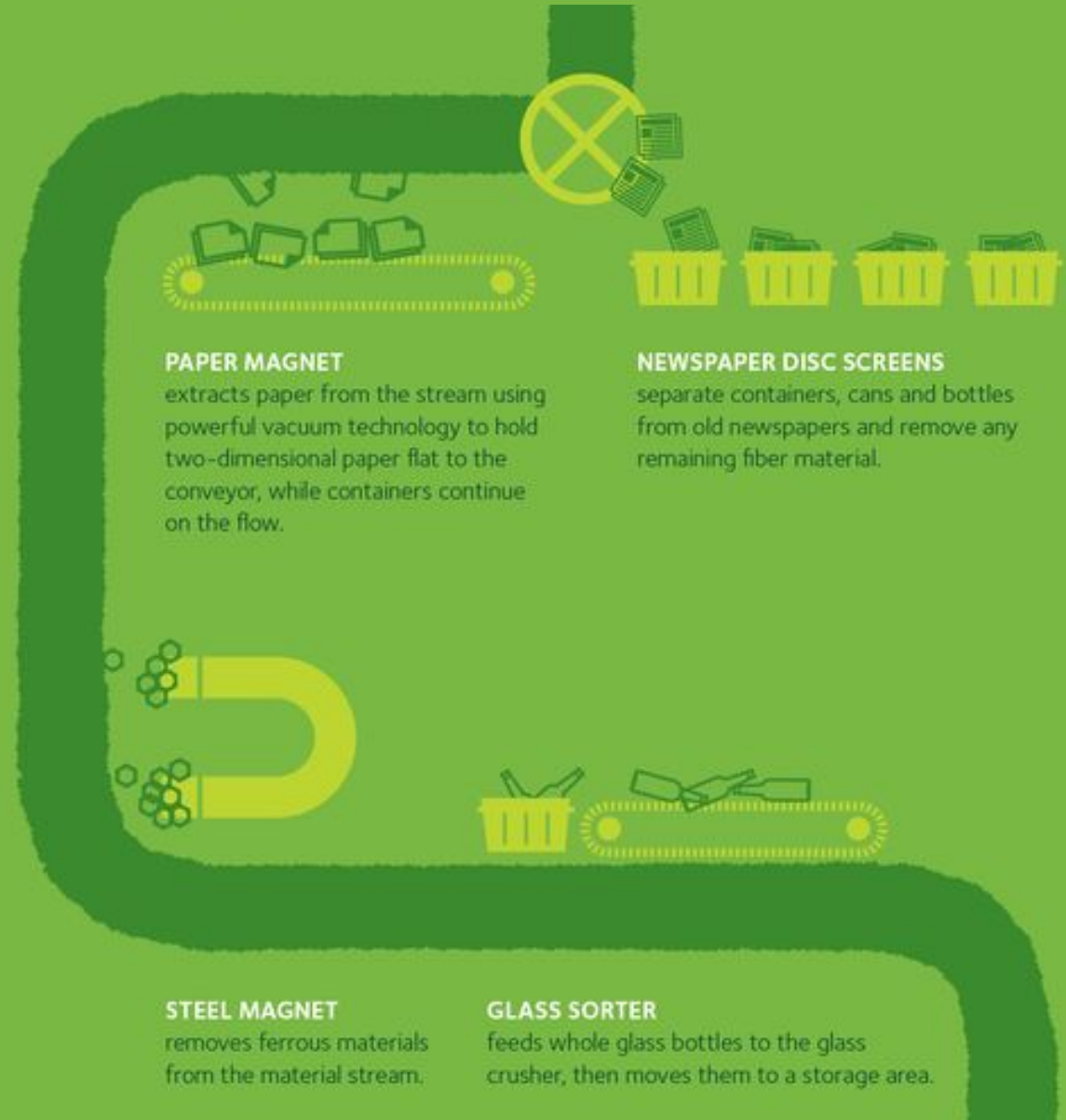
remove rejected items and film, which is vacuumed away. Bulky materials, inert materials and large pieces of plastic are also removed and in some cases sent for additional recycling.



CORRUGATED SCREENS

skim off old corrugated cardboard, which is inspected then conveyed to storage bunkers.

Recycling



Recycling



EDDY CURRENT

uses a rare earth electro current to repel aluminum over a baffle where it drops to a chute and is blown into a bunker for storage.



OPTICAL SCANNERS

separate out the last of the paper from the commingled stream, as well as PET soda/water bottles, HDPE milk/detergent bottles, and aseptic milk/juice cartons. Each are stored separately.



STORAGE BUNKERS

accumulate large quantities of each separated material stream, which are compacted into "bales" for shipment to end-use markets.

FORKLIFTS

move the bales to a finished product storage area where they are checked for quality.

BALES

are shipped via truck, rail or ship to end users around the world, where they are used as feedstock for new products.

General distribution and applications of plastics



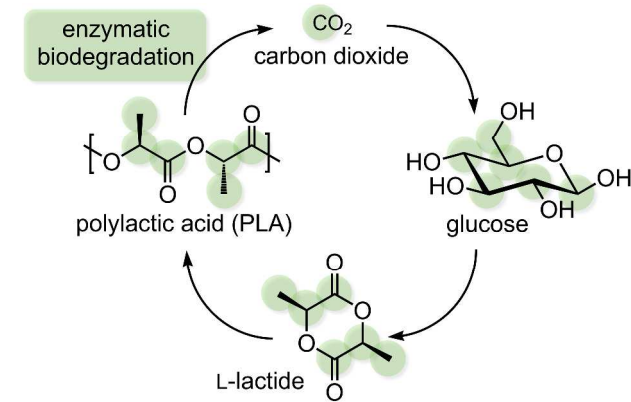
Biodegradable polymers Production

Polymer Name	Source/Feedstock	capacity (Kt/Year)	Sustainable end- of-life options
TPS, Cellulose, Cellulose acetate, Starch blends	Biomass, agro- residues, lignocellulosic derivatives	384	HC, IC, AD
PLA & PLA blends	Lactic acid from dairy whey, corn starch or organic residues	225	IC, MR, CR
PHA, PHB, PHO	Volatile fatty acids, glucose/glycerol from fermentation of municipal solid waste or any carbon feedstocks	30	HC, IC, AD, CR
PCL	Chiral hydroxy acids, lactones	--	HC, IC, CR
PBS	Succinic acid, 1,4- butanediol	97	CR, ED
PBAT & PBAT blends	Terephthalic acid, adipic acid hydroxymethyl furfurals (HMFs), butanediol	152	IC, CR

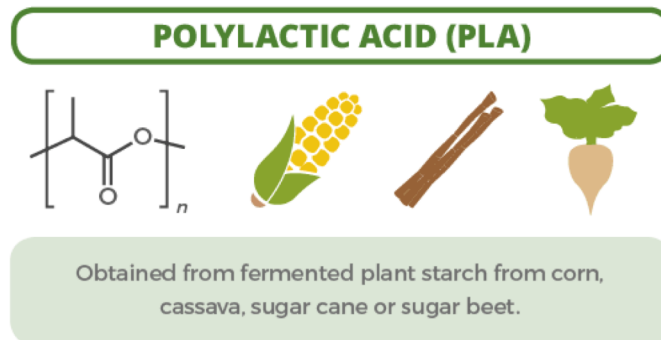
AD-Anaerobic Digestion; MR- Mechanical Recycling; CR-Chemical/catalytic Recycling;
ED- Enzymatic depolymerisation; IC- Industrial composting HC- Home composting

PLA & PLA blends

PLA is derived in a two step process that starts with fermenting the dextrose derived from a simple hydrolysis of corn starch. The product of the dextrose fermentation, lactic acid, is the basic building block of the Ingeo polylactide family of plastics. Lactic acid is further treated to create an intermediary monomer product called lactide, which is then polymerized through a process called ring opening polymerization to form PLA.



Scheme 1 The full lifecycle of polylactic acid (PLA) generally relies upon enzymatic biodegradation.



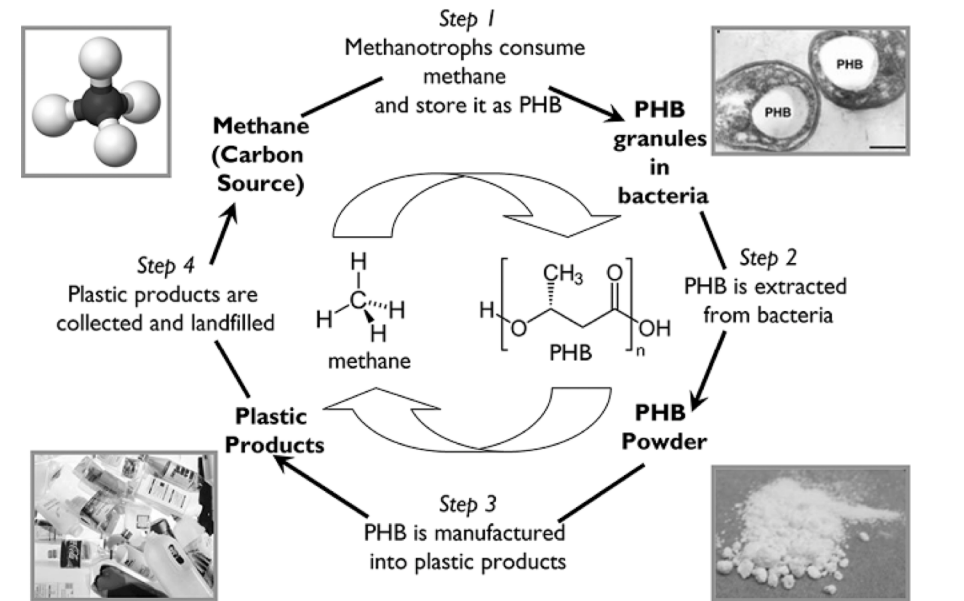
Biodegradable coffee cups are paper cups with a PLA lining to make the paper waterproof.



PLA has the second largest production volume of any biopolymer (behind TPS). It is also used in plastic films, bottles, and food containers.

PHA, PHB, PHO

Corn sugars are fed into commercial fermentation systems where a proprietary strain of microbes digest the sugar and produce Polyhydroxyalkanoates, or PHA. PHA is an intracellular byproduct of the bacteria, meaning the bacteria actually create the plastic within their cells. The PHA is then harvested through the destruction of the bacteria and is separated from the microbial cell matter and formulated into Mirel resin.



POLYHYDROXYALKANOATES (PHAs)

[*]OC(=O)C[C@H](C)O[*] ← poly-(R)-3-hydroxybutyrate (P3HB)

Extracted from bacteria, which produce it via the fermentation of sugar or lipids.

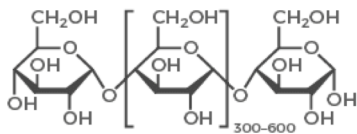


FIGURE 6. EXAMPLES OF MIREL/PHA PRODUCTS: BIOTUF BAGS, TARGET GIFT CARDS, SOILWRAP CONTAINER

TPS, Cellulose, Cellulose acetate, Starch blends

Much like PLA, or PHA, thermoplastic begins its life as starch. But instead of fermenting the starch, thermoplastics take advantage of starch plastic like polymer nature. The starch is first heated to destroy, or open up its inherently weak polymer structure. Then the starch is blended with complexing agents which are other polymers that reform with the starch creating a stronger biobased plastic.

THERMOPLASTIC STARCHES (TPS)



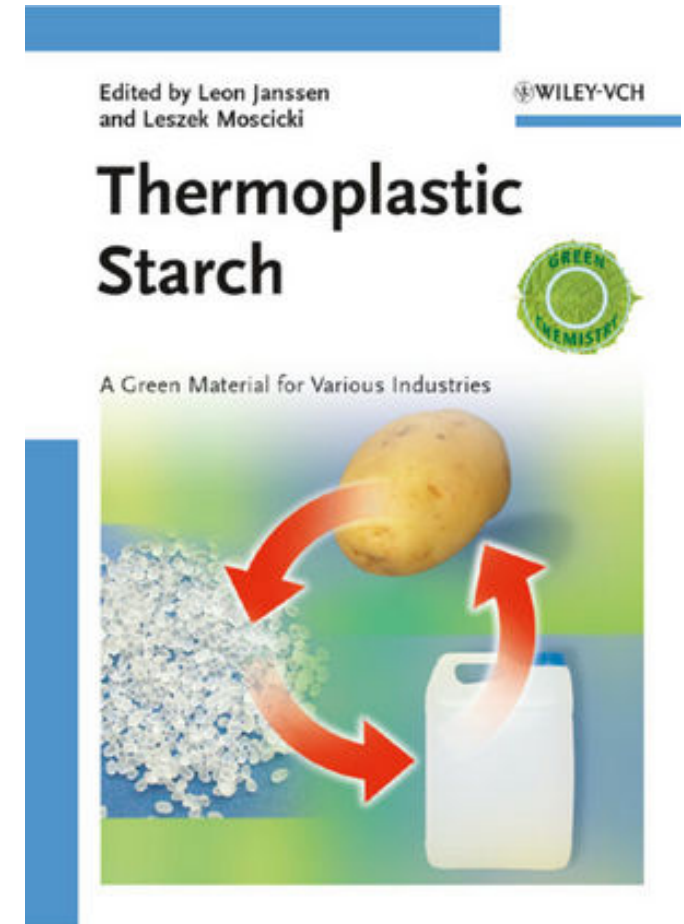
Starches from plant materials are heated with water, then mixed with plasticisers or other polymers.



PLA and TPS both find use in the manufacture of plastic cutlery that's biodegradable.



TPS is also used in food waste bags and some magazine wrappers. PHAs have fewer uses, but have medical uses such as in surgical sutures.

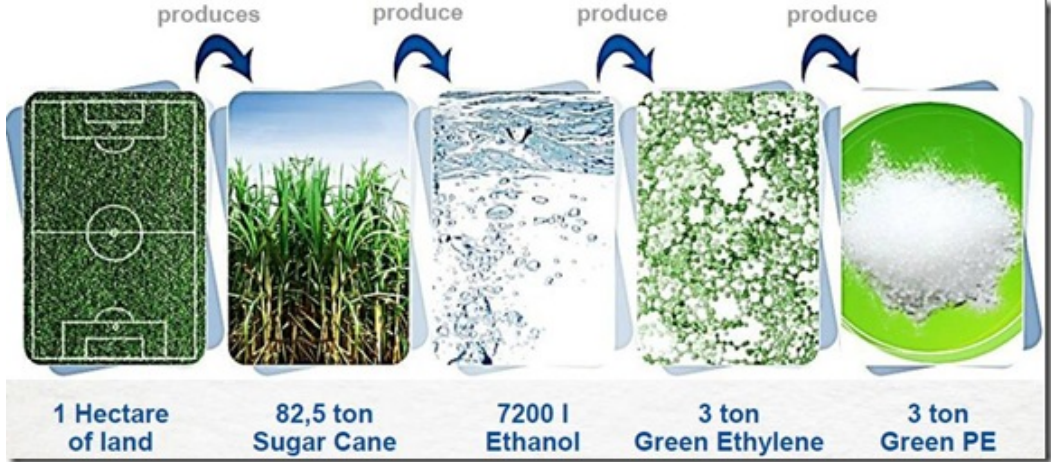
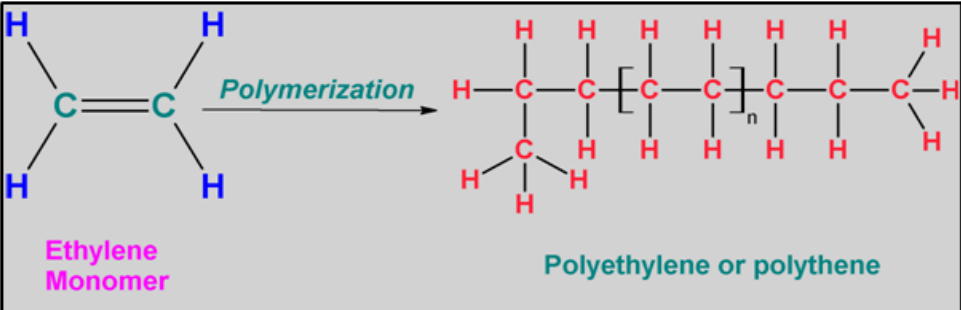


Bio-based and non-biodegradable polymers

Polymer Name	Source/Feedstock	capacity (Kt/Year)	Sustainable end- of-life options
Bio-PE	Bioethanol from sugarcane	200	MR
Bio-PET	Furan dicarboxylic acid from HMF's	560	MR, CR, ED
Bio-PTT	1, 3-propanediol	45	MR, CR
Bio-PEF	HMF's	--	ED
Bio-PP	Isobutanol	--	MR
Bio-PA	Volatile fatty acids, HMF's	--	MR, CR
Bio- polycarbonates	Bioethanol/dialkyl - carbonate/epoxides and carbon-dioxide	--	CR

AD-Anaerobic Digestion; MR- Mechanical Recycling; CR-Chemical/catalytic Recycling;
ED- Enzymatic depolymerisation; IC- Industrial composting HC- Home composting

Bio-Polyethene



Bio-Polyethene is considered a “Drop in replacement” for petroleum based PE and can be recycled, but not composted.

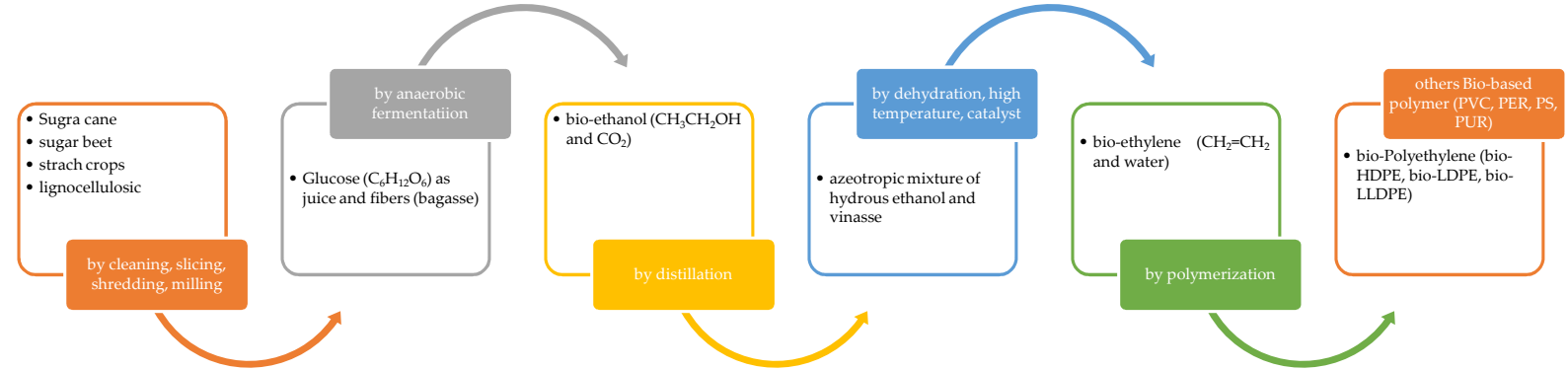
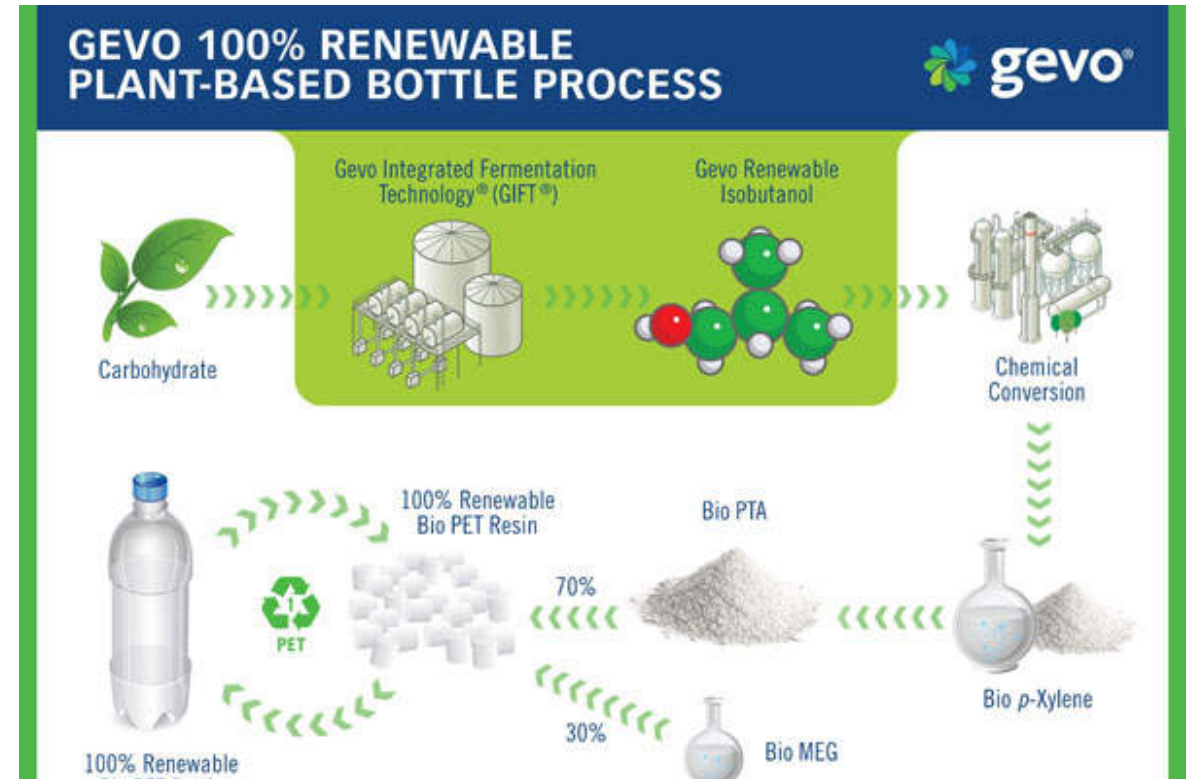


Figure 6. General scheme for Bio-PE production.

Siracusa, V. and Blanco, I., 2020. Bio-Polyethylene (Bio-PE), Bio-Polypropylene (Bio-PP) and Bio-Poly (ethylene terephthalate)(Bio-PET): Recent Developments in Bio-Based Polymers Analogous to Petroleum-Derived Ones for Packaging and Engineering Applications. *Polymers*, 12(8), p.1641.

BIO-PET

- Coca-Cola launched PlantBottle™, a fully-recyclable polyethylene terephthalate (PET) bottle made with 100% plant-based material, in June 2015,



Not biodegradable or compostable, recyclable .

Bio-Polypropylene

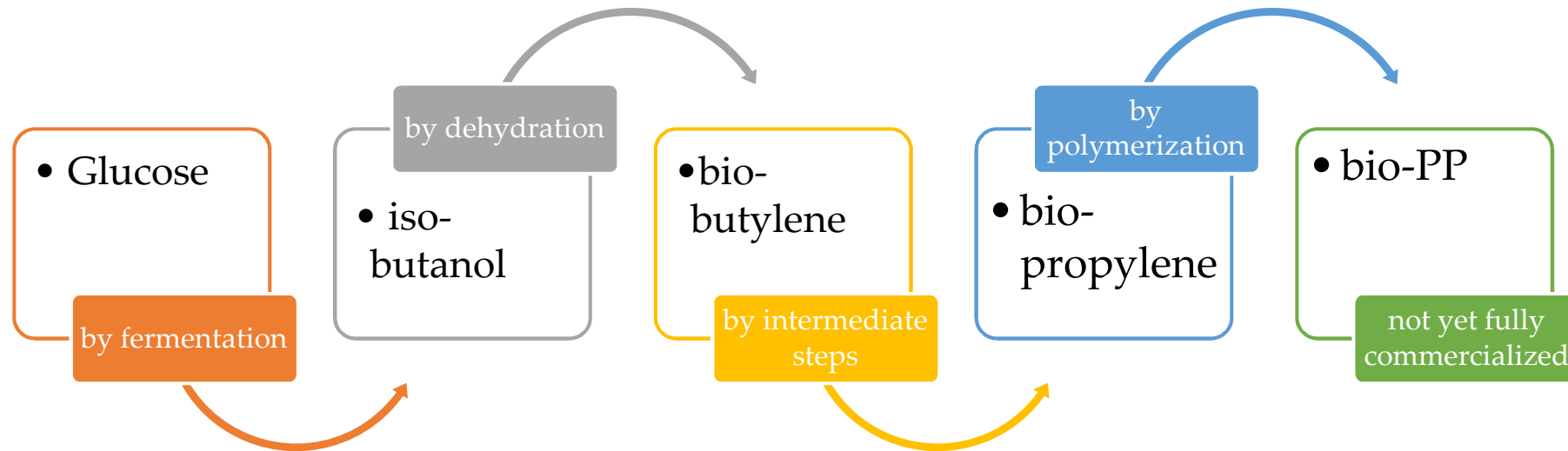
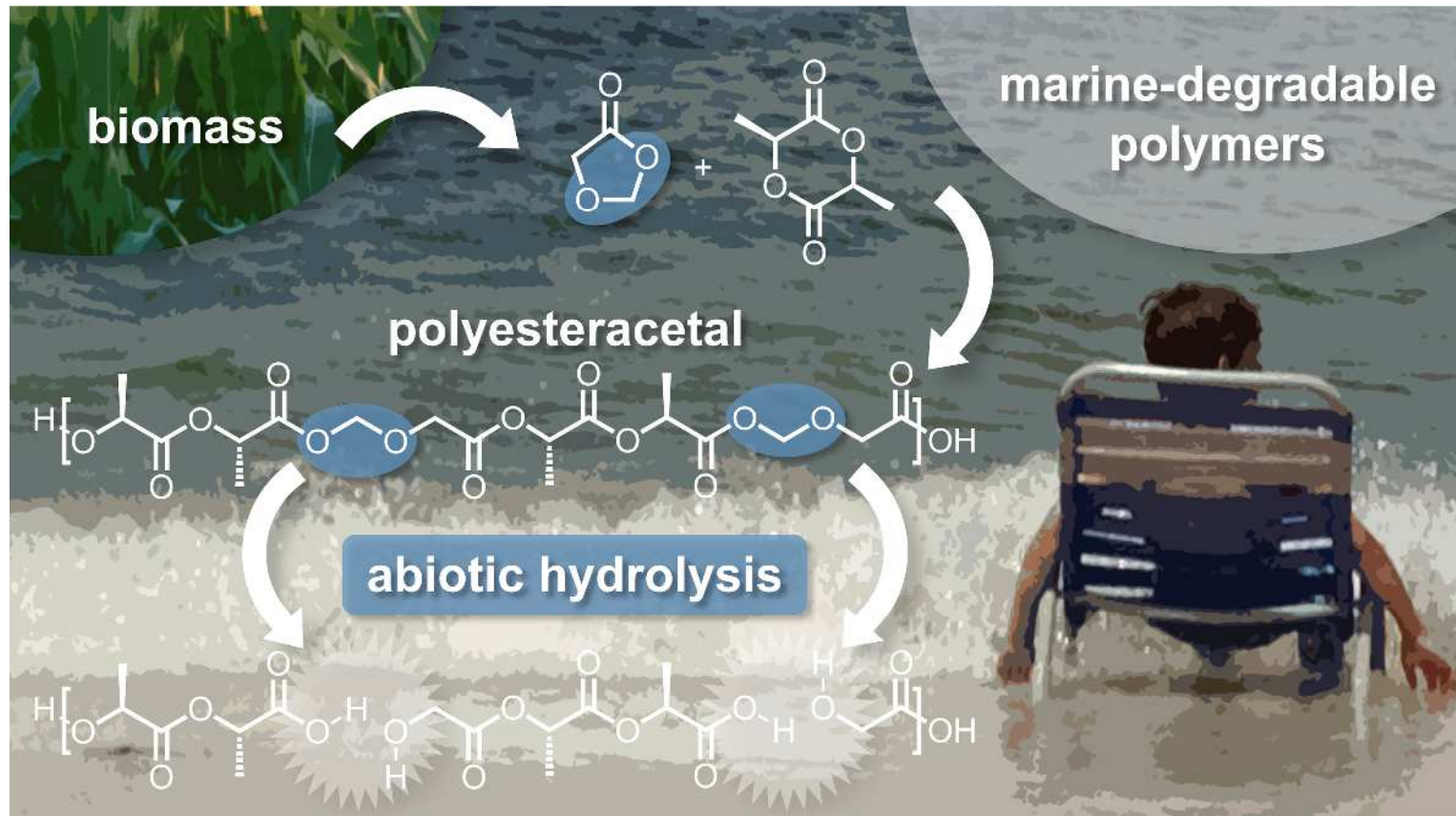


Figure 8. General scheme for Bio-PP.

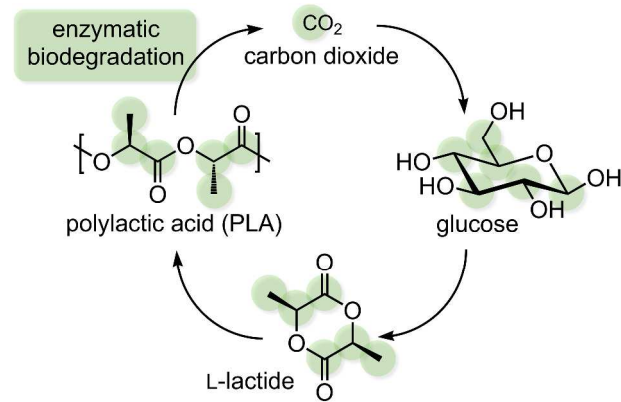
Polypropylene is often used to make more durable goods, this would lead to more carbon sequestration. PP is also highly recyclable.

Marine Degradable Plastics

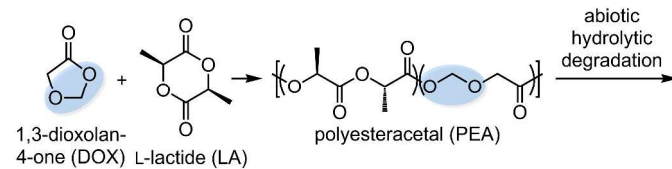


Marine-Degradable Polylactic Acid, Ryan T. Martin, Ludmila P. Camargo and Stephen A. Miller *Green Chemistry*, 2012, 00, 1-3

Marine Degradable Plastics

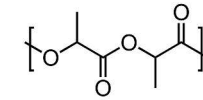


Scheme 1 The full lifecycle of polylactic acid (PLA) generally relies upon enzymatic biodegradation.



Scheme 3 Copolymerization strategy for synthesizing the polyesteracetal (PEA) copoly(lactide/1,3-dioxolan-4-one).

polylactic acid (PDLLA)



polyesteracetal (PEA)

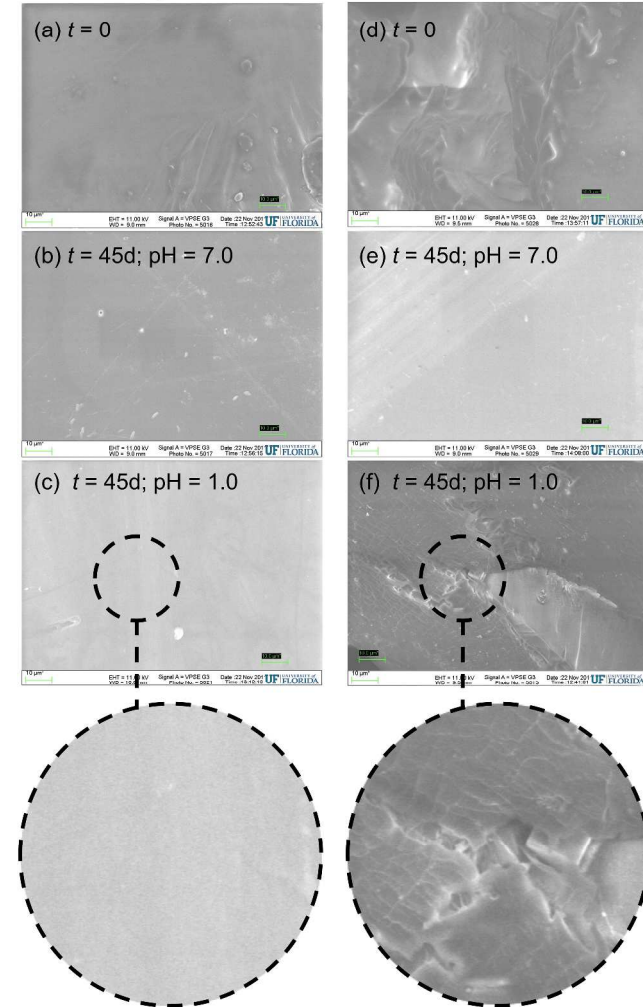
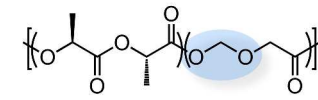


Figure 3 Under various aqueous conditions, surface erosion over 45 days is insignificant for poly(DL-lactide) (PDLLA) but is quite conspicuous for the polyesteracetal (4% DOX) when pH=1.

Plastic Precursors from Algae

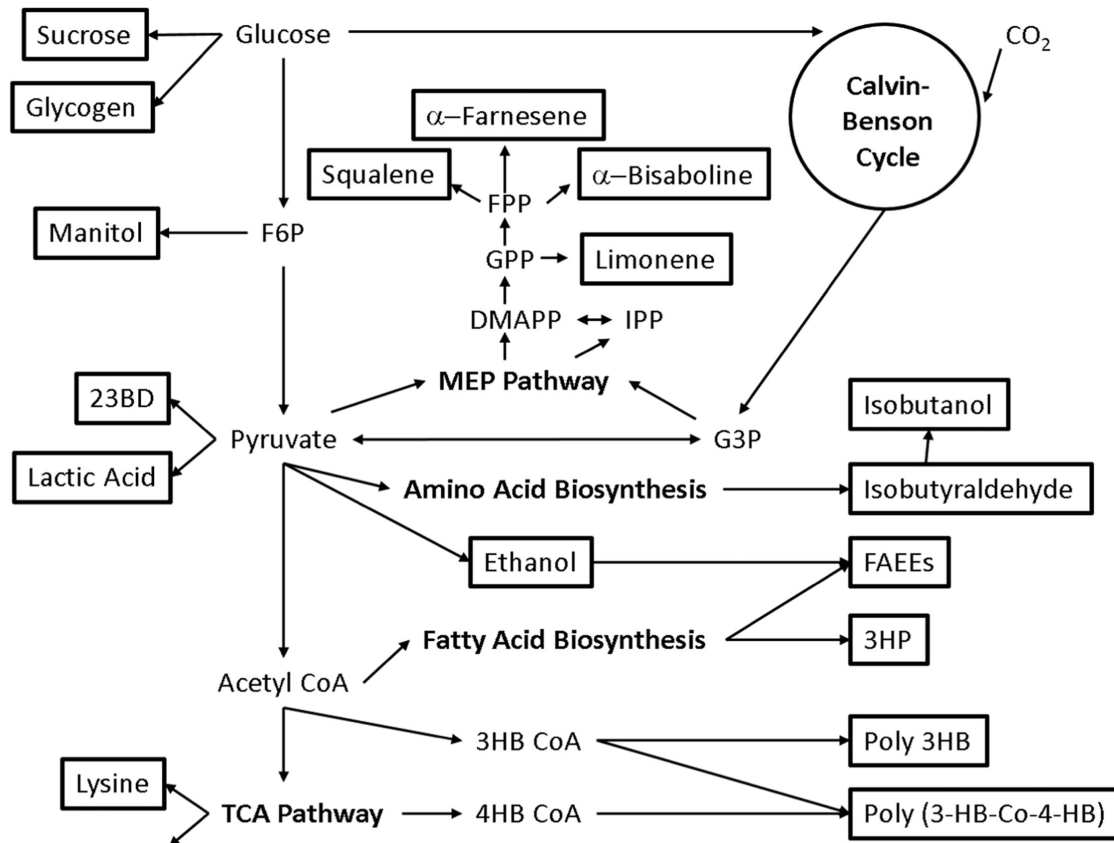


Fig. 1. Outline of metabolism and [metabolic engineering](#) in [cyanobacteria](#). Boxed chemicals are discussed in this review. Abbreviations: 23BD, 2,3-butanediol; 3HB, 3-hydroxybutyrate; 4HB, 4-hydroxybutyrate; DMAPP, dimethylallyl [pyrophosphate](#); F6P, [fructose-6-phosphate](#); FAEE, fatty acid ethyl ester; FPP, [farnesyl pyrophosphate](#); GPP, geranyl pyrophosphate; G3P, [glyceraldehyde-3-phosphate](#); IPP, [isopentenyl pyrophosphate](#); MEP, methylerythritol 4-phosphate; TCA, tricarboxylic acid.

Table 2

Cyanobacterial chemical production discussed in this review.

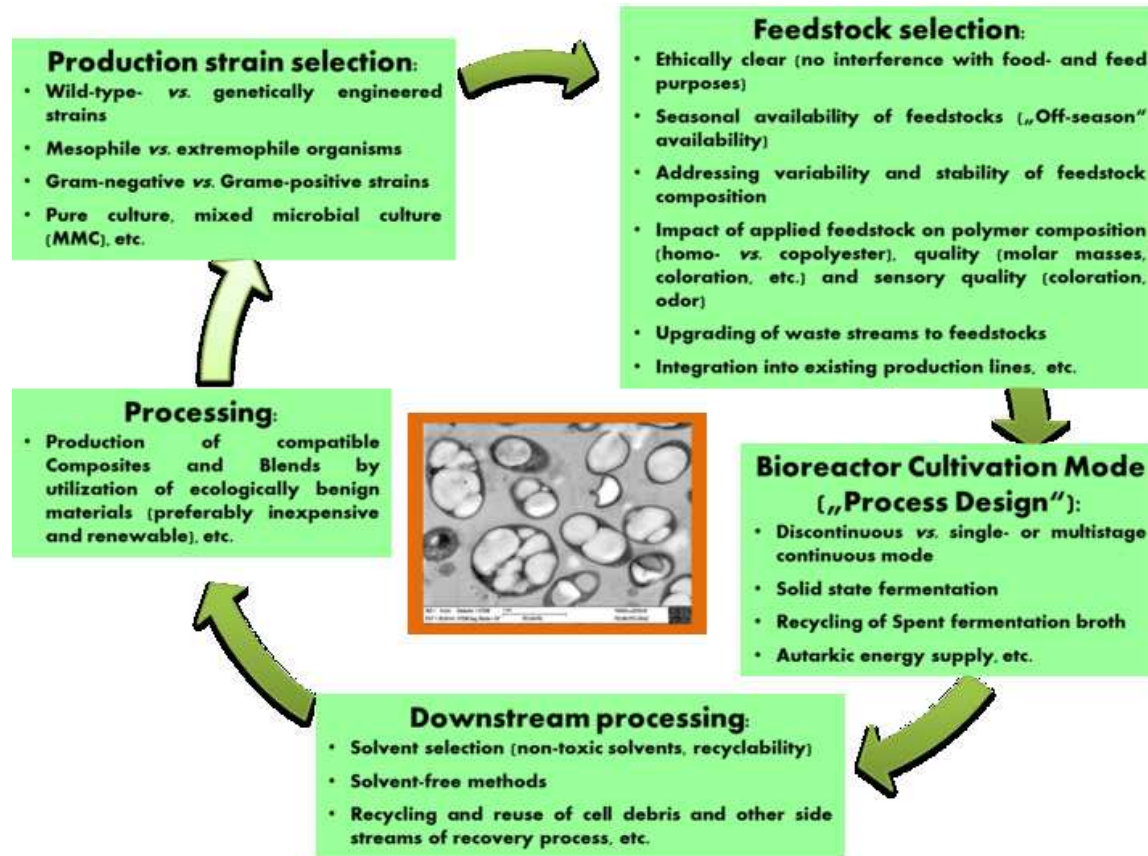
Strain	Compound	Titer (g/L)	References
2973	sucrose	3.3	Song et al., 2016
6803	3-hydroxypropionic acid	0.8	Wang et al., 2016b
	ethanol	5.5	Gao et al., 2012
	isobutanol	0.6	Miao et al., 2017
	lactic acid	0.8	Angermayr et al., 2014
	limonene	0.007	Lin et al., 2017
	2,3-butanediol	1.6	Nozzi et al., 2017
	alpha bisabolone	0.0006	Davies et al., 2014
	fatty acids	0.1	Ruffing, 2014
	glycogen	1.8	Aikawa et al., 2014
			3.0
		3.5	
	limonene	0.004	Davies et al., 2014
	lysine	0.4	Korosh et al., 2017
	mannitol	1.1	Jacobsen and Frigaard, 2014
	poly-3-hydroxybutyrate	0.05	Zhang et al., 2015
7942	2,3-butanediol	3.0 ^a	McEwen et al., 2016
		5.7 ^b	Kanno et al., 2017
		12.6 ^a	
	alpha-farnesene	0.005	Lee et al., 2017b
	ethanol	0.07	Deng and Coleman, 1999
	fatty acid ethyl esters	0.01	Lee et al., 2017a
	isobutyraldehyde	1.1	Atsumi et al., 2009
	isoprene	1.3	Gao et al., 2016
	limonene	0.005	Wang et al., 2016a
	squalene	0.05	Choi et al., 2017
	succinate	0.4	Lan and Wei, 2016
		7.3	Li et al., 2016b
	sucrose	2.6	Ducat et al. 2012
		0.8	Weiss et al., 2017

^a Photomixotrophic production under continuous lighting.

^b Photomixotrophic production under diurnal lighting.

Synechocystis sp. PCC 6803, *Synechococcus elongatus* PCC 7942, *Synechococcus* sp. PCC 7002, *Synechococcus elongatus* UTEX 2973

Plastic Precursors from Algae



Schematic illustration of factors impacting sustainability of PHA production

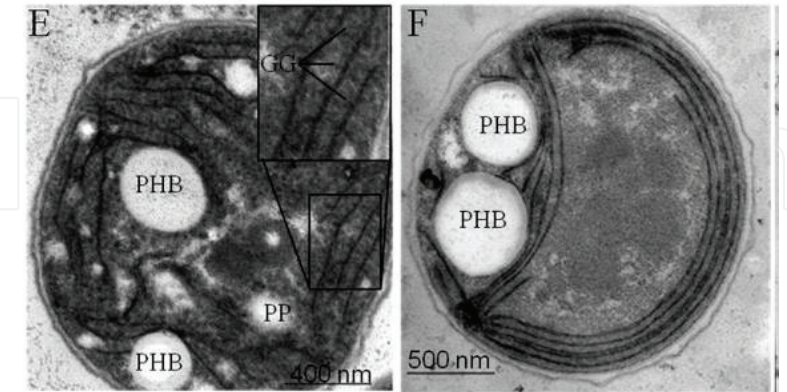


Figure 1. PHB granules in cyanobacteria. Left: Wild type. Right: Mutant (reproduced with permission from [22]).

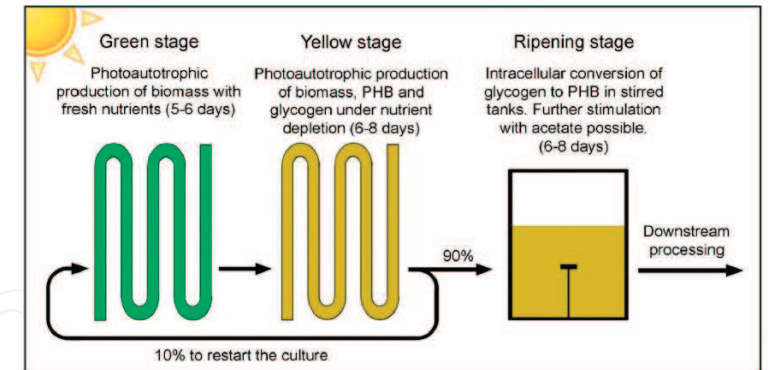
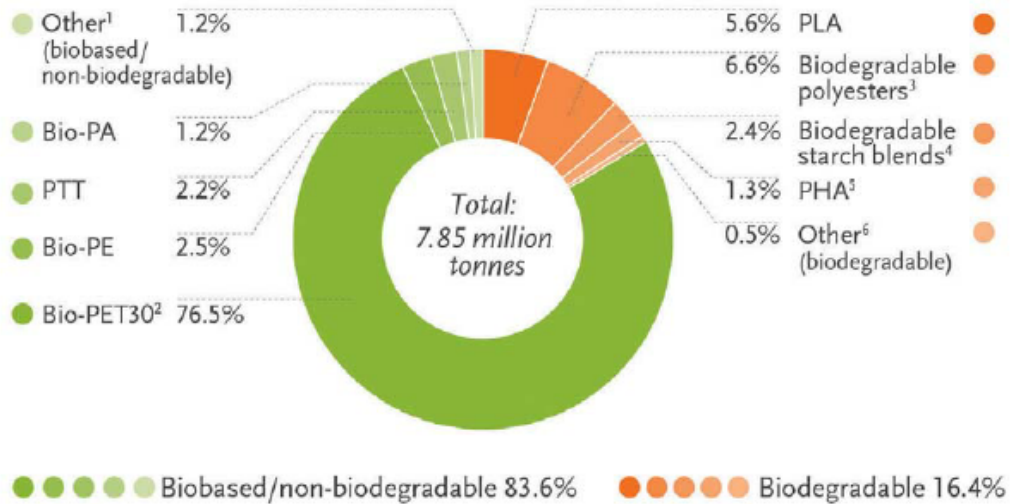


Figure 2. Operation mode for PHB production from cyanobacteria. The ripening tank is used for PHB production at a later stage, where no CO_2 is consumed, but glycogen gets converted into PHB (reproduced with permission from [18]).

Where do we use bioplastics?

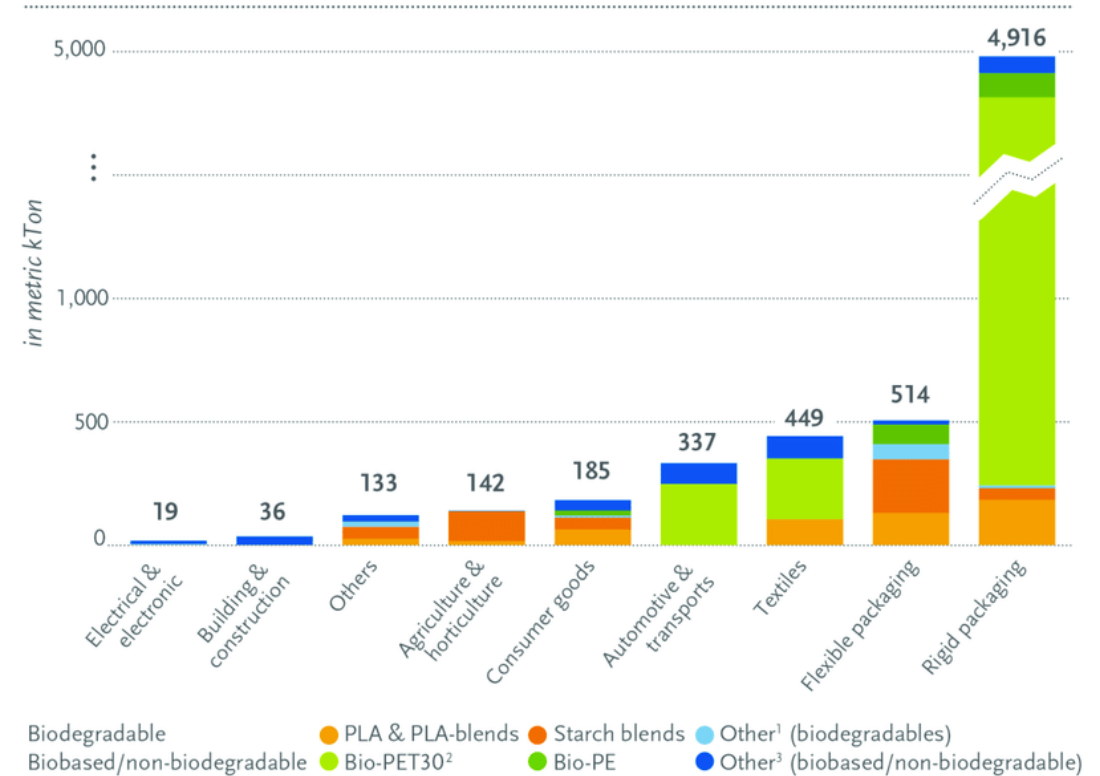
Global production capacities of bioplastics 2019
(by material type)



¹Contains durable starch blends, Bio-PC, Bio-TPE, Bio-PUR (except thermosets), PEF; ²Biobased content amounts to 30%, increase in volume subject to realisation of planned production facilities; ³Contains fossil-based PBAT, PBS, PCL; ⁴Blend components incl. in main materials; ⁵Incl. Newlight Technologies (CO₂-based); ⁶Contains regenerated cellulose (compostable hydrated cellulose foils) and biodegradable cellulose ester

Source: European Bioplastics, Institute for Bioplastics and Biocomposites, nova-Institute (2015).
More information: www.bio-based.eu/markets and www.downloads.ifbb-hannover.de

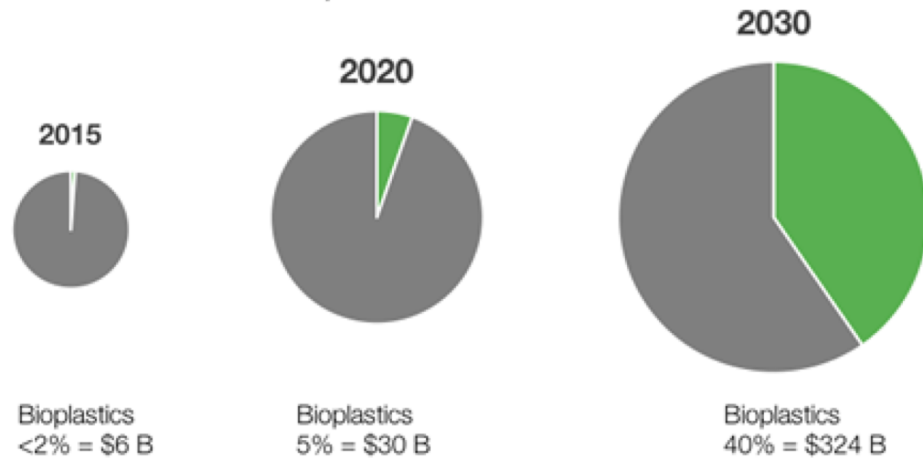
Global production capacities of bioplastics 2018 (by market segment)



Global production capacities of bioplastics 2018 (by market segments)
(European Bioplastics 2014)

Conclusions

Global Bioplastics Market



¹Source: Grand View Research 2014, European Bioplastics 2013, BCC Research 2017, Nexant Inc. 2012

²<https://www.alliedmarketresearch.com/press-release/bioplastics-market.html>

GLOBAL PLASTIC PRODUCTION



Use of bioplastics is increasing, but they still account for less than 1% of the global plastics market (as of 2018).

CONDITIONS FOR BIODEGRADING



Compostable plastics need specific conditions to break down – and take much longer to do so completely if they go to landfill instead of being recycled. However, they still break down faster than conventional plastics.



Biodegradable plastics are more expensive than plastics derived from fossil fuels on weight basis, and require land to grow raw materials. However, the greenhouse gas emissions associated with their production are lower.

References

Siracusa, V. and Blanco, I., 2020. Bio-Polyethylene (Bio-PE), Bio-Polypropylene (Bio-PP) and Bio-Poly (ethylene terephthalate)(Bio-PET): Recent Developments in Bio-Based Polymers Analogous to Petroleum-Derived Ones for Packaging and Engineering Applications. *Polymers*, 12(8), p.1641.

Marine-Degradable Polylactic Acid, Ryan T. Martin, Ludmila P. Camargo and Stephen A. Miller *Green Chemistry*, 2012, 00, 1-3

Shamsuddin, I.M., Jafar, J.A., Shawai, A.S.A., Yusuf, S., Lateefah, M. and Aminu, I., 2017. Bioplastics as better alternative to petroplastics and their role in national sustainability: a review. *Advances in Bioscience and Bioengineering*, 5(4), p.63.

Rameshkumar, S., Shaiju, P., O'Connor, K. E., & Babu P, R. (2019). *Bio-based and biodegradable polymers - State-of-the-art, Challenges and Emerging Trends. Current Opinion in Green and Sustainable Chemistry*. doi:10.1016/j.cogsc.2019.12.005

Carroll, A.L., Case, A.E., Zhang, A. and Atsumi, S., 2018. Metabolic engineering tools in model cyanobacteria. *Metabolic engineering*, 50, pp.47-56.

Compostable Plastics 101 California Organics Recycling Council Last Updated: 1/1/2011
[https://www.cptoolkit.org/Portals/0/Documents/Compostable Plastics 101 Paper.pdf](https://www.cptoolkit.org/Portals/0/Documents/Compostable%20Plastics%20101%20Paper.pdf)

Markl, E., Grünbichler, H. and Lackner, M., 2018. Cyanobacteria for PHB bioplastics production: a review. In *Algae*. IntechOpen.

Koller, M., Maršálek, L., de Sousa Dias, M.M. and Braunegg, G., 2017. Producing microbial polyhydroxyalkanoate (PHA) biopolyesters in a sustainable manner. *New biotechnology*, 37, pp.24-38.