BioPlastics

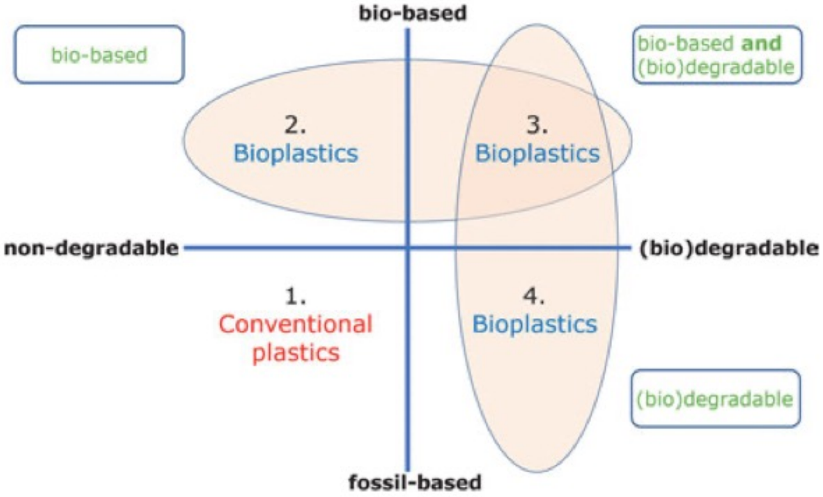
BioPlastics

Bio-based Corn ethanol => Ethylene => Polyethylene
Corn ethanol=> Ethylene glycol => PET
Biorefining

Biodegradable

Compostable

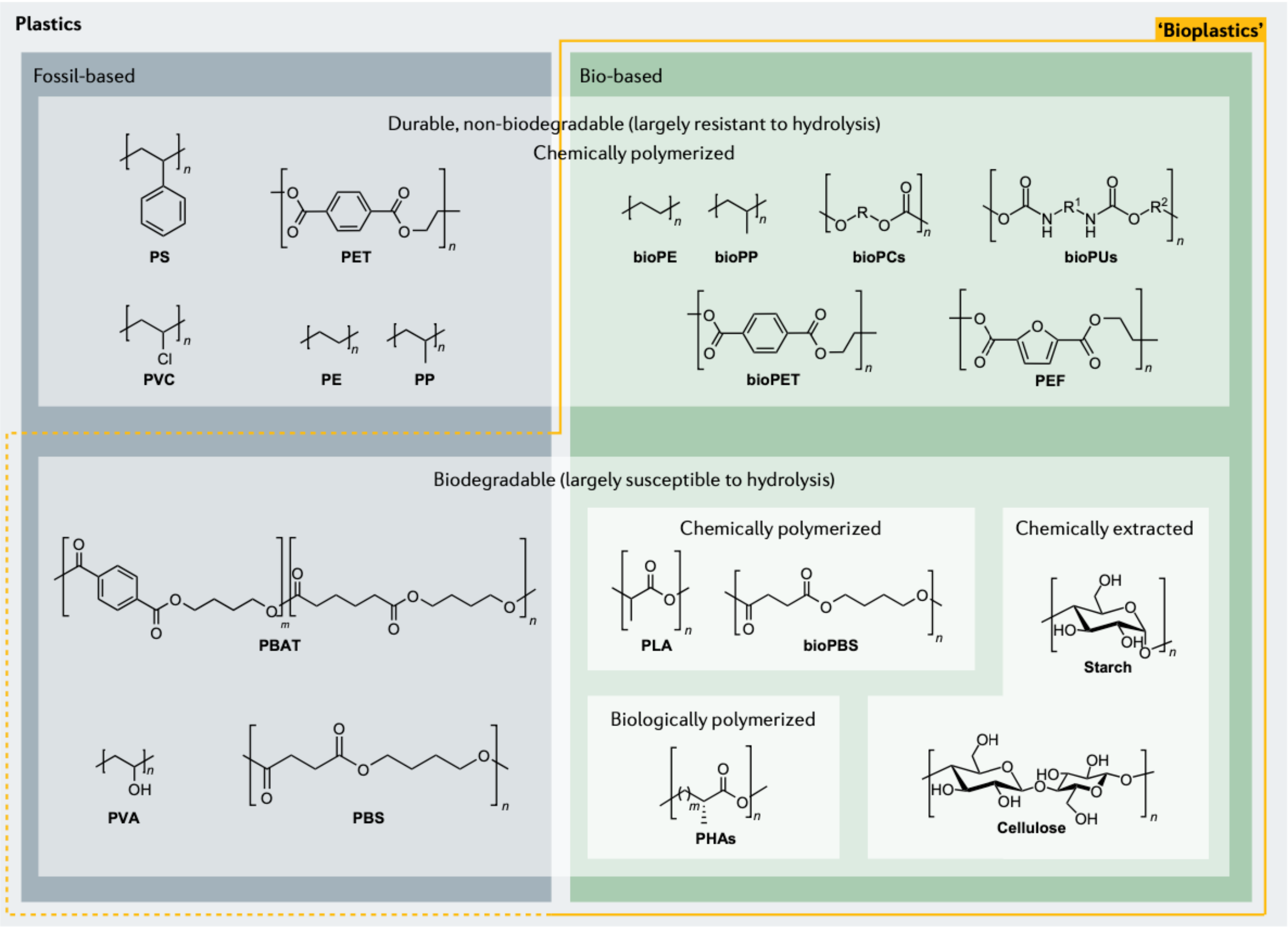
Industrially Compostable



BioPlastics

An Ideal BioPlastic:

- 100% properties until planned degradation lifetime when it totally degrades
- Degradation products are non-toxic and non-eutrophic
- (Degrades into O_2 and N_2 for instance)
- Costs less than petrochemical plastics
- Manufactured from a renewable resource (sunlight or seaweed)
- Doesn’t compete with food production
- Tunable properties such as barrier for films, modulus for injection molding Crack resistance, Temperature Use Range -50°C to 100°C
- Totally interchangeable with existing plastics processing with no adjustment of processing equipment (plug and play)
- Doesn’t require additives or non-toxic, biodegradable additives exist



PbaT, polybutylene adipate-*co*-terephthalate; PC, polycarbonate; Pe, polyethylene; PeF, polyethylene furanoate; PeT, polyethylene terephthalate; Pla, polylactic acid; PP, polypropylene; PS, polystyrene; Pu, polyurethane; Pva, polyvinyl alcohol; PvC, polyvinylchloride; PBS poly(butylene succinate)

Bio-based What is the goal:

Mass-Balance Accounting of Monomers

Make Plastics from Crops

Make Plastics from Agricultural Waste (Fermentation/Separation)

Make Monomer from Fermentation & Industrial Polymerization

Biodegradable by genetic selection/engineering of microbes

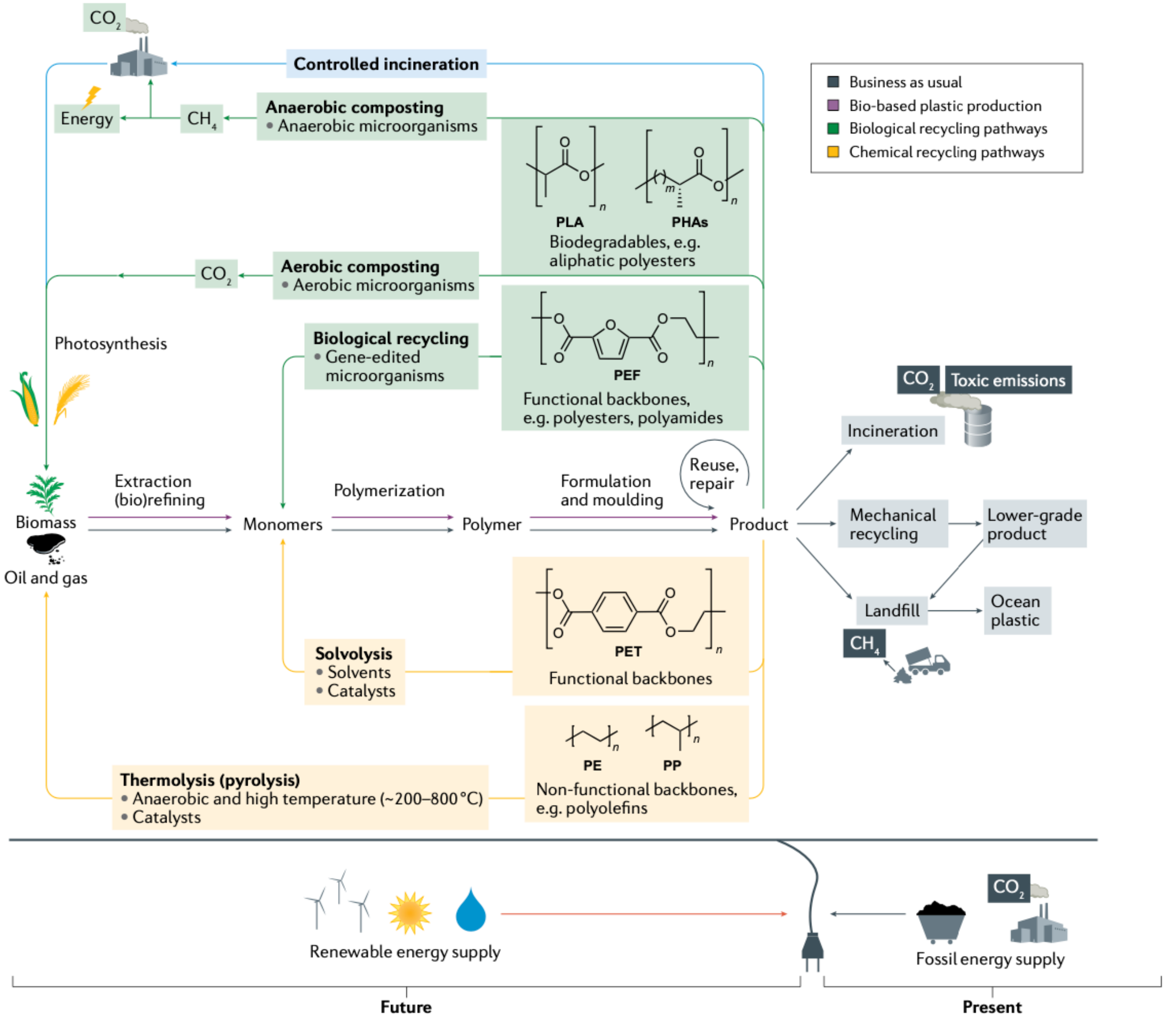
Natural Biodegradation

Industrial Biodegradation

Degradable into small pieces (starch filler)

Plastics Life-Cycle

Start



⬛ Business as usual
🟪 Bio-based plastic production
🟩 Biological recycling pathways
🟨 Chemical recycling pathways

CO_2

Controlled incineration

Energy

CH_4

Anaerobic composting
- Anaerobic microorganisms

PLA

PHAs

Biodegradables, e.g. aliphatic polyesters

CO_2

Aerobic composting
- Aerobic microorganisms

Photosynthesis

Biological recycling
- Gene-edited microorganisms

PEF

Functional backbones, e.g. polyesters, polyamides

Biomass

Oil and gas

Extraction (bio)refining

Monomers

Polymerization

Polymer

Formulation and moulding

Reuse, repair

Product

CO_2 Toxic emissions

Incineration

Mechanical recycling

Lower-grade product

Landfill

Ocean plastic

CH_4

Solvolysis
- Solvents
- Catalysts

PET

Functional backbones

Thermolysis (pyrolysis)
- Anaerobic and high temperature (~200–800 °C)
- Catalysts

PE

PP

Non-functional backbones, e.g. polyolefins

Renewable energy supply

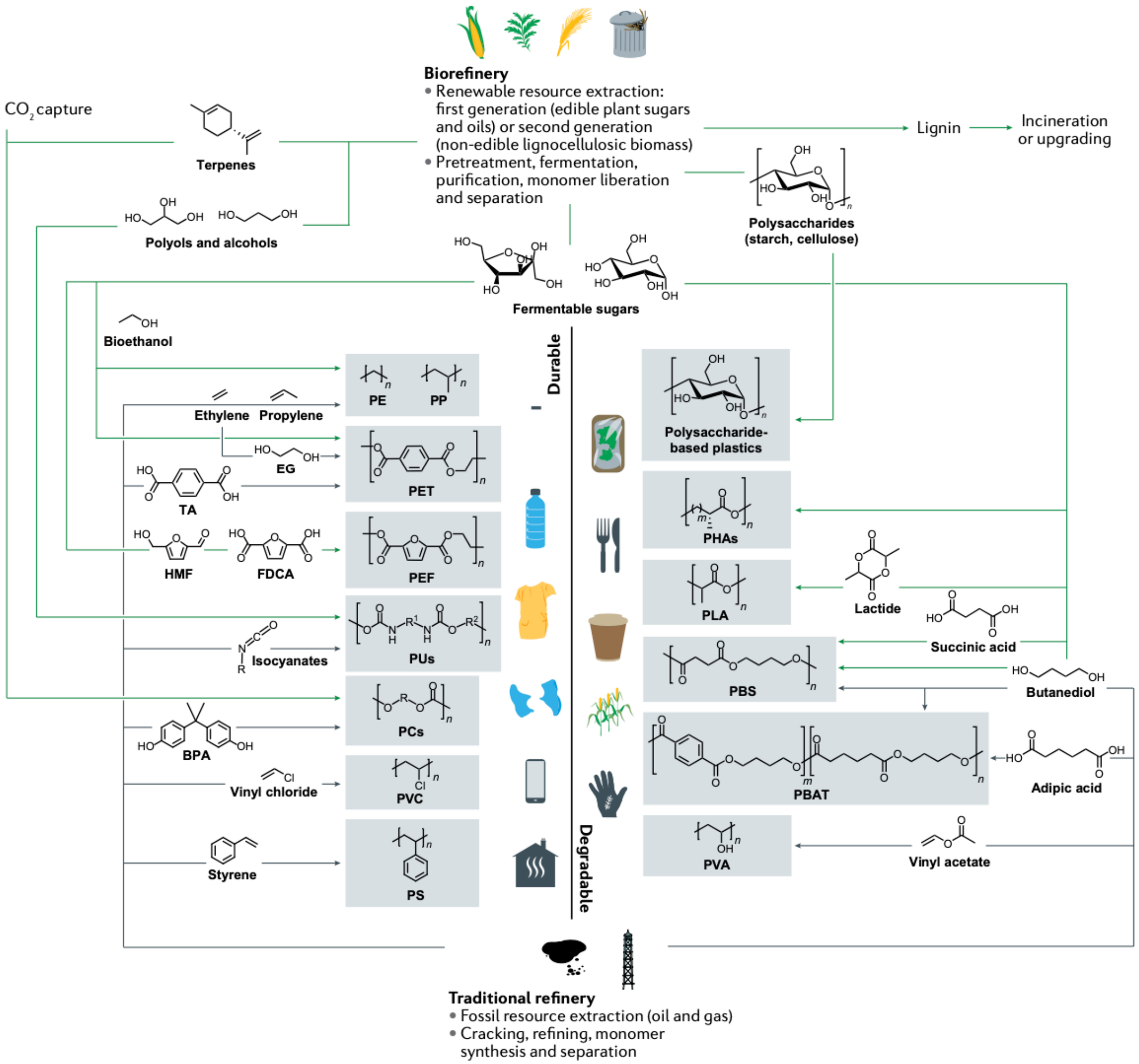
CO_2

Fossil energy supply

Future

Present

Biorefinery vs Fossil Refinery



Biorefinery

- Renewable resource extraction: first generation (edible plant sugars and oils) or second generation (non-edible lignocellulosic biomass)
- Pretreatment, fermentation, purification, monomer liberation and separation

Traditional refinery

- Fossil resource extraction (oil and gas)
- Cracking, refining, monomer synthesis and separation

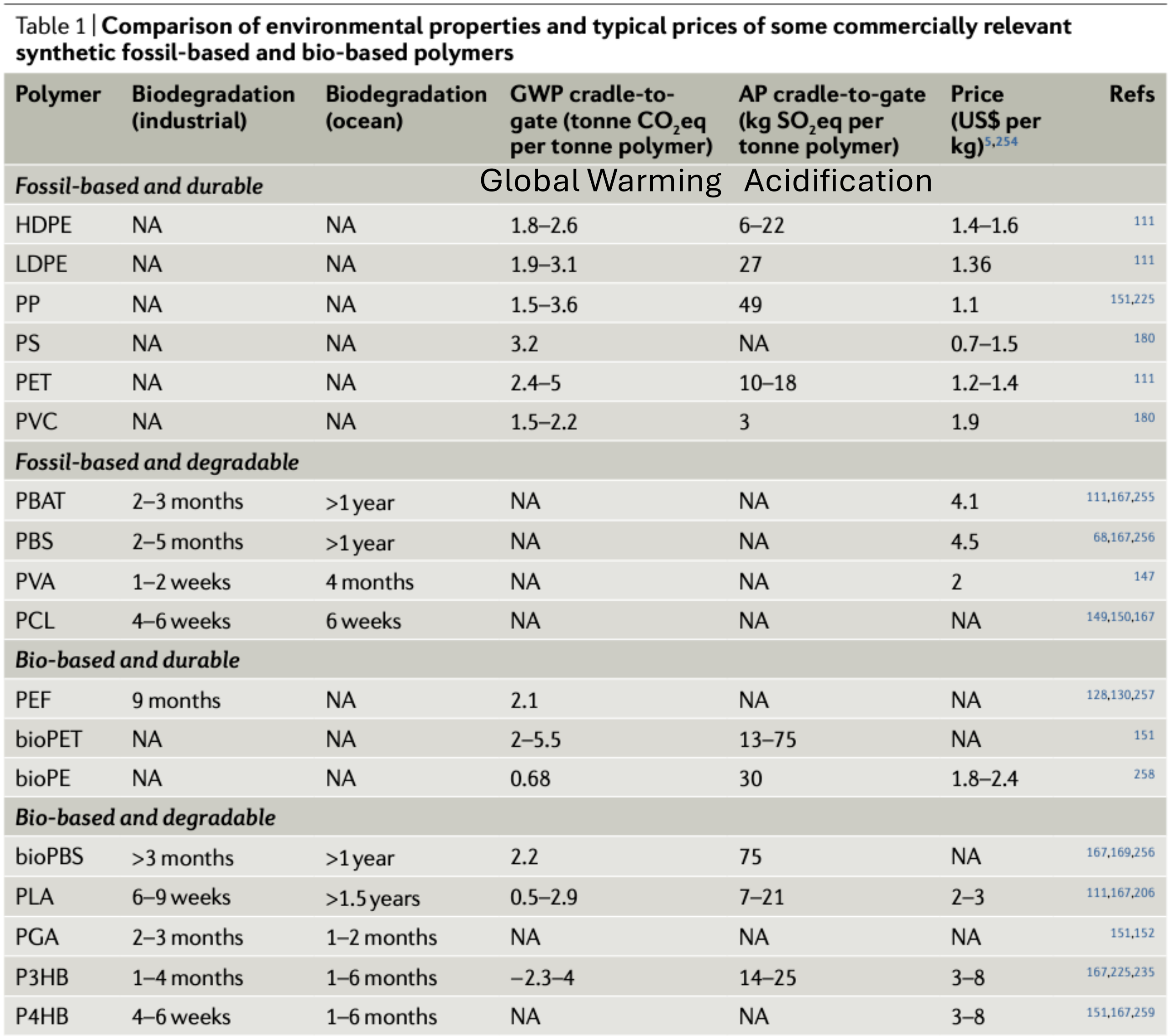
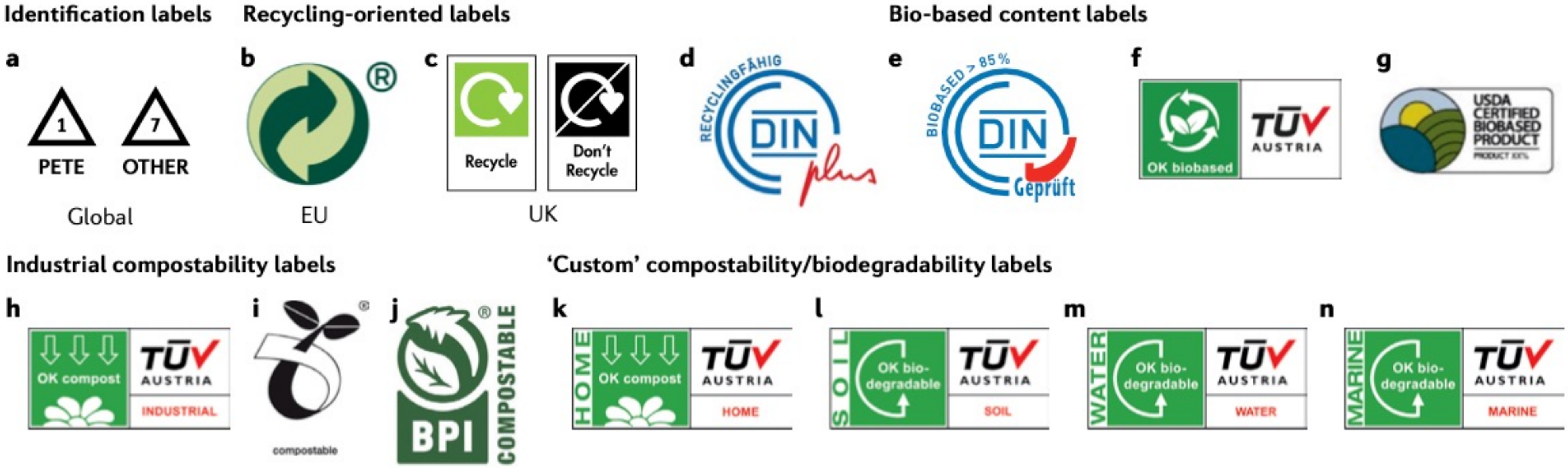


Table 1 | **Comparison of environmental properties and typical prices of some commercially relevant synthetic fossil-based and bio-based polymers**

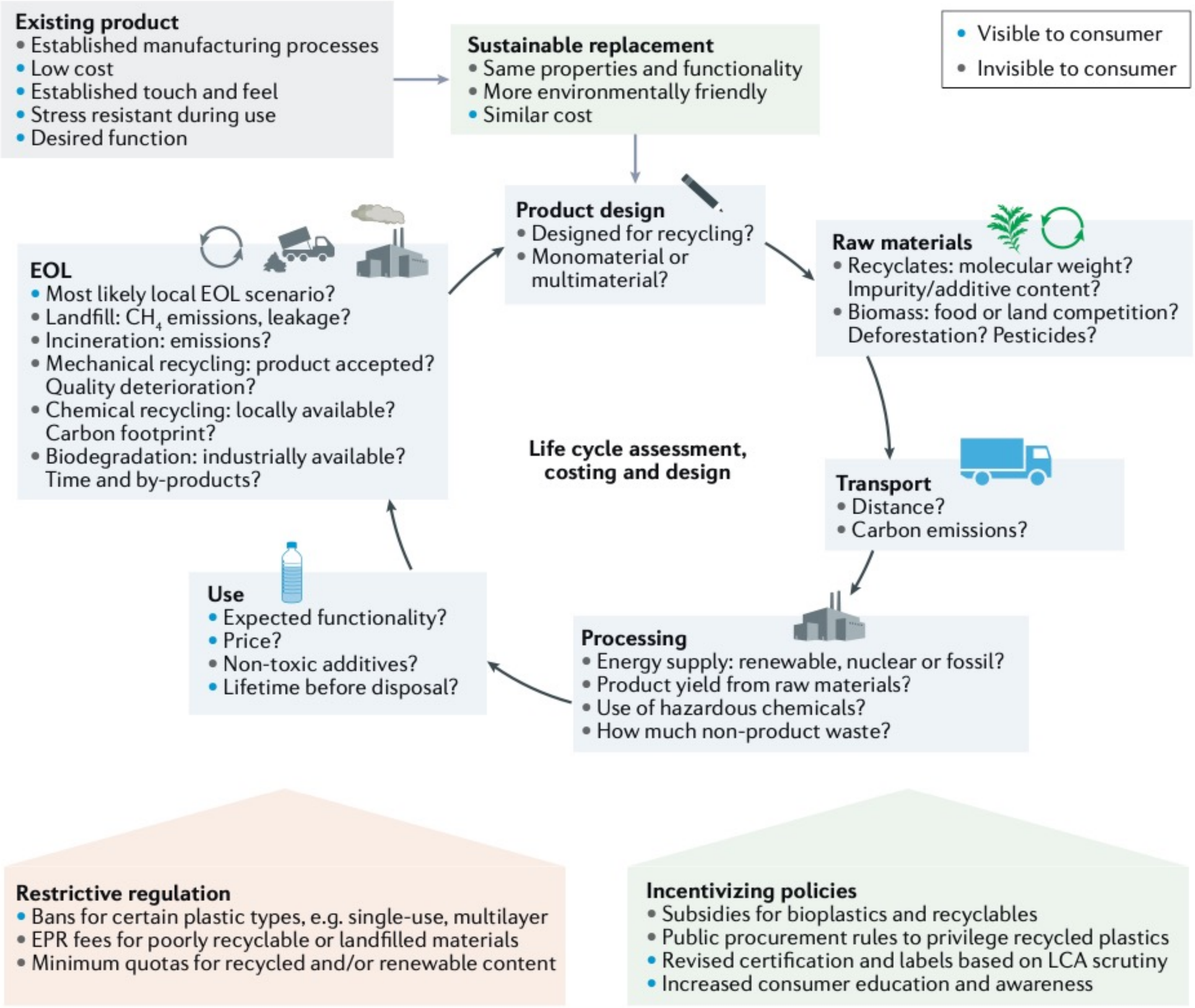
Polymer	Biodegradation (industrial)	Biodegradation (ocean)	GWP cradle-to-gate (tonne CO_2eq per tonne polymer)	AP cradle-to-gate (kg SO_2eq per tonne polymer)	Price (US$ per kg)[5,254]	Refs
Fossil-based and durable			Global Warming	Acidification		
HDPE	NA	NA	1.8–2.6	6–22	1.4–1.6	111
LDPE	NA	NA	1.9–3.1	27	1.36	111
PP	NA	NA	1.5–3.6	49	1.1	151,225
PS	NA	NA	3.2	NA	0.7–1.5	180
PET	NA	NA	2.4–5	10–18	1.2–1.4	111
PVC	NA	NA	1.5–2.2	3	1.9	180
Fossil-based and degradable						
PBAT	2–3 months	>1 year	NA	NA	4.1	111,167,255
PBS	2–5 months	>1 year	NA	NA	4.5	68,167,256
PVA	1–2 weeks	4 months	NA	NA	2	147
PCL	4–6 weeks	6 weeks	NA	NA	NA	149,150,167
Bio-based and durable						
PEF	9 months	NA	2.1	NA	NA	128,130,257
bioPET	NA	NA	2–5.5	13–75	NA	151
bioPE	NA	NA	0.68	30	1.8–2.4	258
Bio-based and degradable						
bioPBS	>3 months	>1 year	2.2	75	NA	167,169,256
PLA	6–9 weeks	>1.5 years	0.5–2.9	7–21	2–3	111,167,206
PGA	2–3 months	1–2 months	NA	NA	NA	151,152
P3HB	1–4 months	1–6 months	−2.3–4	14–25	3–8	167,225,235
P4HB	4–6 weeks	1–6 months	NA	NA	3–8	151,167,259

Degradable polymers are those that contain readily hydrolysable aliphatic ester bonds in their backbone and polyvinyl alcohol (PVA), whose degradation follows a diketone pathway. Durable polymers are those with a backbone that is typically more resistant to enzymatic and non-enzymatic hydrolysis, such as aromatic esters, amides and those with C–C bonds. Note that non-zero degradation may occur in any polymer. Biodegradation refers to industrial compostability under EN 13432 or ASTM D6400 conditions or degradation in ocean water according to the references. The values or ranges, where available, for global warming potential (GWP) and acidification potential (AP) are taken from a 2020 review of cradle-to-gate life cycle assessments6 or from other references, where indicated. HDPE, high-density polyethylene; LDPE, low-density polyethylene; NA, not available; P3HB, poly(3-hydroxybutyrate); P4HB, poly(4-hydroxybutyrate); PBAT, polybutylene adipate-*co*-terephthalate; PBS, polybutylene succinate; PCL, polycaprolactone; PE, polyethylene; PEF, polyethylene furanoate; PET, polyethylene terephthalate; PGA, polyglycolic acid; PLA, polylactic acid; PP, polypropylene; PS, polystyrene; PVA, polyvinyl alcohol; PVC, polyvinylchloride.

Bio-Based Plastics



Issues for Implementation of Bioplastics



Existing product
- Established manufacturing processes
- Low cost
- Established touch and feel
- Stress resistant during use
- Desired function

Sustainable replacement
- Same properties and functionality
- More environmentally friendly
- Similar cost

- Visible to consumer
- Invisible to consumer

Product design
- Designed for recycling?
- Monomaterial or multimaterial?

Raw materials
- Recyclates: molecular weight? Impurity/additive content?
- Biomass: food or land competition? Deforestation? Pesticides?

Transport
- Distance?
- Carbon emissions?

Processing
- Energy supply: renewable, nuclear or fossil?
- Product yield from raw materials?
- Use of hazardous chemicals?
- How much non-product waste?

Use
- Expected functionality?
- Price?
- Non-toxic additives?
- Lifetime before disposal?

EOL
- Most likely local EOL scenario?
- Landfill: CH_4 emissions, leakage?
- Incineration: emissions?
- Mechanical recycling: product accepted? Quality deterioration?
- Chemical recycling: locally available? Carbon footprint?
- Biodegradation: industrially available? Time and by-products?

Life cycle assessment, costing and design

Restrictive regulation
- Bans for certain plastic types, e.g. single-use, multilayer
- EPR fees for poorly recyclable or landfilled materials
- Minimum quotas for recycled and/or renewable content

Incentivizing policies
- Subsidies for bioplastics and recyclables
- Public procurement rules to privilege recycled plastics
- Revised certification and labels based on LCA scrutiny
- Increased consumer education and awareness

Bio-Based Plastics

Polyhydroxybutyrate

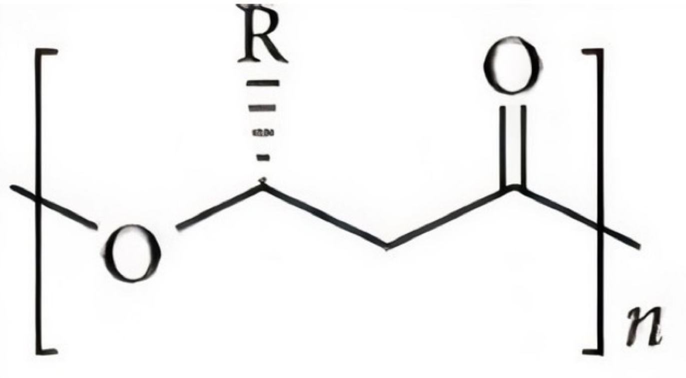


Figure 1. Typical chemical structure of polyhydroxyalkanoate (PHA) molecules [5].

Table 1. Summary of mechanical properties of P3(HB) and petrochemical based (PP, PET, PE) and bio-based polymers (PLA).

Mechanical Property	P3HB	PP	PET	LDPE	HDPE	PLLA	PDLLA
Tensile modulus (GPa)	3–3.5	1.95	9.35	0.26–0.5	0.5–1.1	2.7–4.14	1–3.45
Tensile Strength (MPa)	20–40	31–45	62	30	30–40	15.5–150	27.6–50
Elongation at break (%)	5–10	50–145	230	200–600	500–700	20–30	1.5–20
Degree of Crystallinity (%)	50–60	42.6–58.1	7.97	25–50	60–80	13.94	3.5
Melting Temperature (°C)	165–175	160–169.1	260	115	135	170–200	amorphous
Glass Transition Temperature (°C)	5–9	−20–−5	67–81	−130–100	−130–100	50–60	50–60

Polyhydroxybutyrate

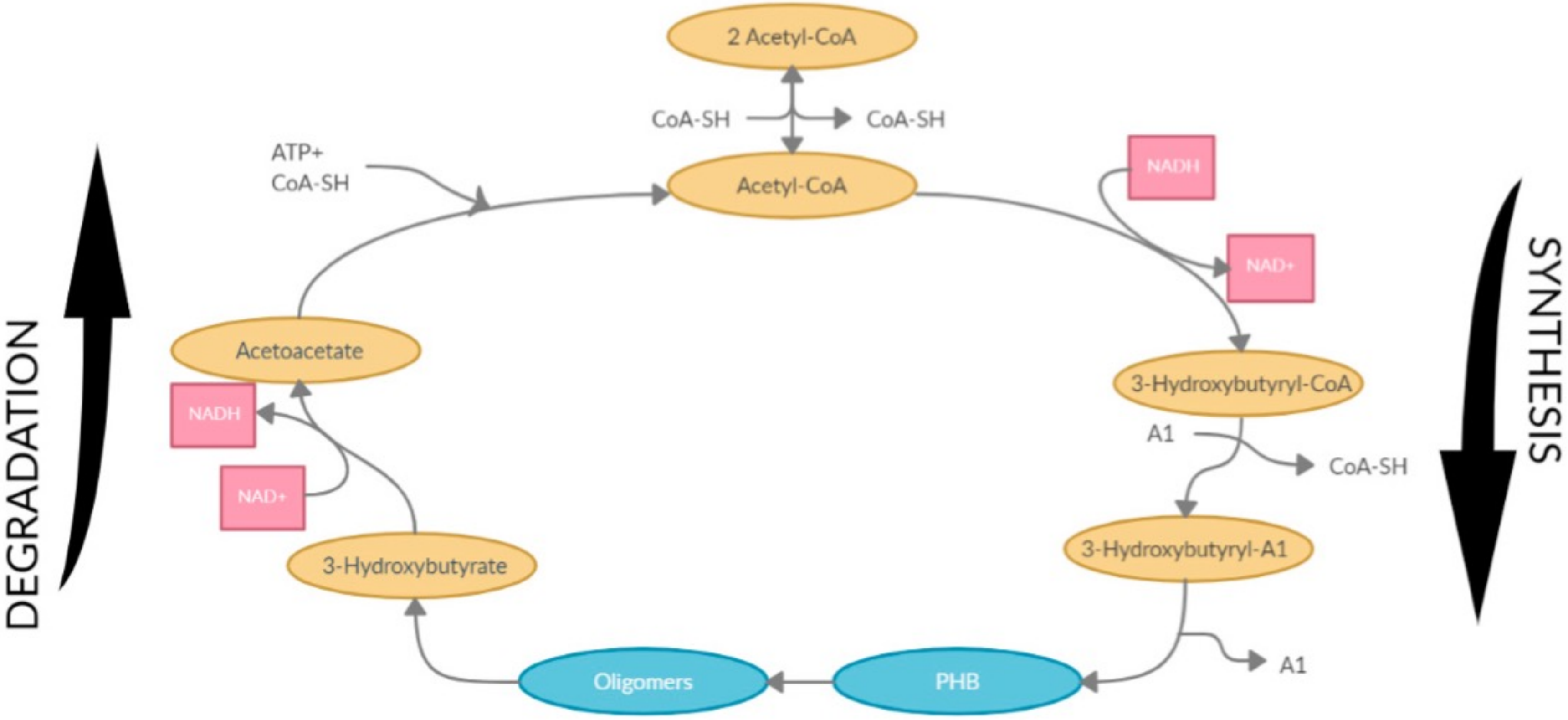


Figure 3. Polyhydroxybutyrate (PHB) synthesis and degradation process.

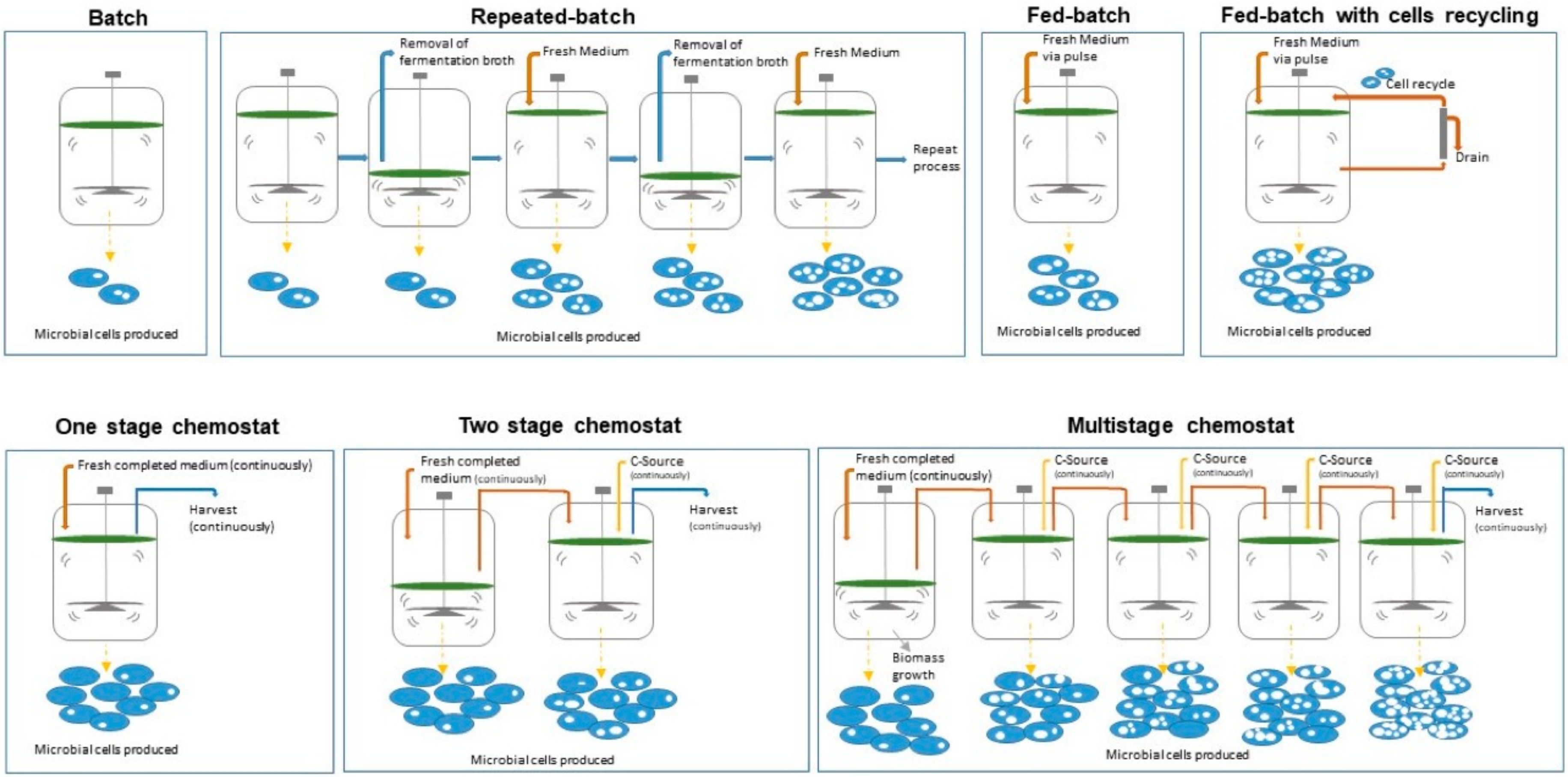


Figure 4. Fermentation processes commonly used for PHA biosynthesis [3].

Table 2. Comparison of PHB materials' thermal properties produced by different bacterial strains with literature values (Xc—degree of crystallinity, Tm—melting temperature, Tg—glass transition temperature).

Mechanical Property	**Literature Values**	**PHB from *Bacillus megaterium***	**PHB from *C. nector***
Xc (%)	53.4	23–37	46–53
Tm (°C)	169	151–176	169–175
Tg (°C)	1.1	−1–4	−0.2–0.6

Table 3. Summary of the results obtained when different fermentation mediums were used for PHB production (Xc—degree of crystallinity, Tm—melting temperature, Tg—glass transition temperature) [73,74].

Carbon Source	**Fermentation Medium**	**Tg (°C)**	**Tm (°C)**	**Xc (%)**
Soy Cake	Batch SSF in non-supplemented medium	−0.3	170.4	46
Soy Cake	Batch SSF in supplemented medium	−0.2	169.5	45
Soy Cake	Batch Submerged	1.1	173	53
Glucose/Fructose	Batch Submerged (0% oleic acid)	−4	173	70
Glucose/Fructose	Batch Submerged (0.9% oleic acid)	0	172	62
Glucose/Fructose	Batch Submerged (3.0% oleic acid)	−10	149	53

Polyhydroxybutyrate

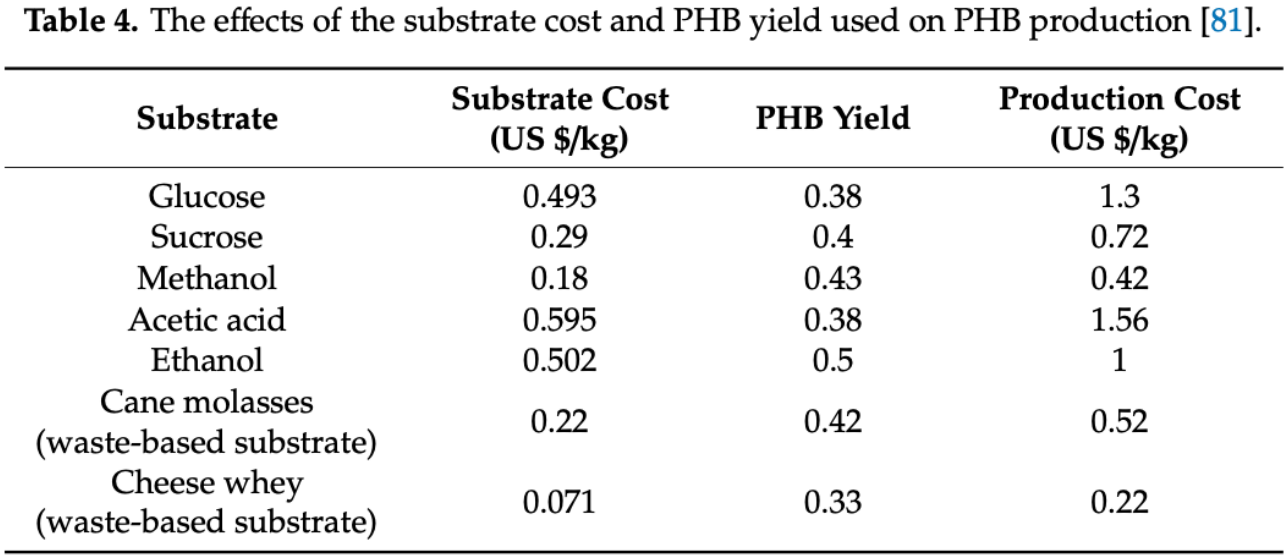


Table 4. The effects of the substrate cost and PHB yield used on PHB production [81].

Substrate	Substrate Cost (US $/kg)	PHB Yield	Production Cost (US $/kg)
Glucose	0.493	0.38	1.3
Sucrose	0.29	0.4	0.72
Methanol	0.18	0.43	0.42
Acetic acid	0.595	0.38	1.56
Ethanol	0.502	0.5	1
Cane molasses (waste-based substrate)	0.22	0.42	0.52
Cheese whey (waste-based substrate)	0.071	0.33	0.22

Polyhydroxybutyrate

Polyhydroxy Butyrate Companies

AGRANA

green dot BIOPLASTICS

TianAn Biopolymer

Nature's Eco-Friendly Solution

Cardia bioplastics

Full Cycle

BASF

We create chemistry

kaneka

BIOME TECHNOLOGIES

Disclaimer: List of key companies in no particular order

Polyhydroxybutyrate

Bio-Innovation Pioneers: Giants like NatureWorks and Mitsubishi Chemical Corporation invest heavily in R&D, developing new strains of bacteria and fermentation processes to optimize PHB production, improve its properties, and reduce costs. Think genetically engineered bacteria that produce PHB with enhanced strength and flexibility, or innovative fermentation technologies that utilize waste materials as feedstock.

Cost-Conscious Champions: Regional players like Tianjin Green Bio and Zhejiang Hisun Biomaterials focus on affordability, utilizing efficient production processes and readily available feedstocks like corn and cassava starch to cater to price-sensitive segments and emerging markets. This strategy ensures their PHB solutions reach a wider audience.

Niche Specialists: Smaller players carve out their niches by specializing in specific applications or industries. Some focus on high-performance PHB for medical devices or drug delivery systems, while others cater to the growing demand for sustainable packaging solutions in the food & beverage industry. This targeted approach allows them to excel in specialized areas.

Polyhydroxybutyrate

- **Sustainability Spotlight:** Consumer and regulatory pressure is pushing manufacturers towards eco-friendly solutions. PHB's biodegradability, compostability, and low carbon footprint resonate with environmentally conscious consumers and align with regulations promoting sustainable packaging and materials.
- **Performance Prowess:** PHB boasts impressive properties like excellent biocompatibility, strength, and water resistance, making it suitable for diverse applications from medical implants to food packaging.
- **Technological Advancements:** Advancements in fermentation technologies, genetic engineering, and material science are driving down production costs and enhancing PHB's performance, making it a more competitive alternative to traditional plastics.
- **Circular Economy Aspirations:** PHB's ability to be biodegraded and recycled into new products aligns with the goals of a circular economy, further enhancing its appeal in a resource-constrained world.

Polyhydroxybutyrate

- AGRANA Beteiligungs-AG (Austria)
- Green Dot Bioplastics (USA)
- TianAn Biologic Materials Co., Ltd. (China)
- Tianjin GreenBio Materials Co., Ltd. (China)
- Cardia Bioplastics (Australia)
- FULL CYCLE BIOPLASTICS (USA)
- PolyFerm Canada (Canada)
- BASF SE (Germany)
- Kaneka Corporation (Japan)
- Biome Technologies PLC (UK)

Polyhydroxybutyrate

Recent Developments:

October 2023: NatureWorks unveils a new grade of PHB with enhanced heat resistance, opening doors for its use in automotive and electronics applications.

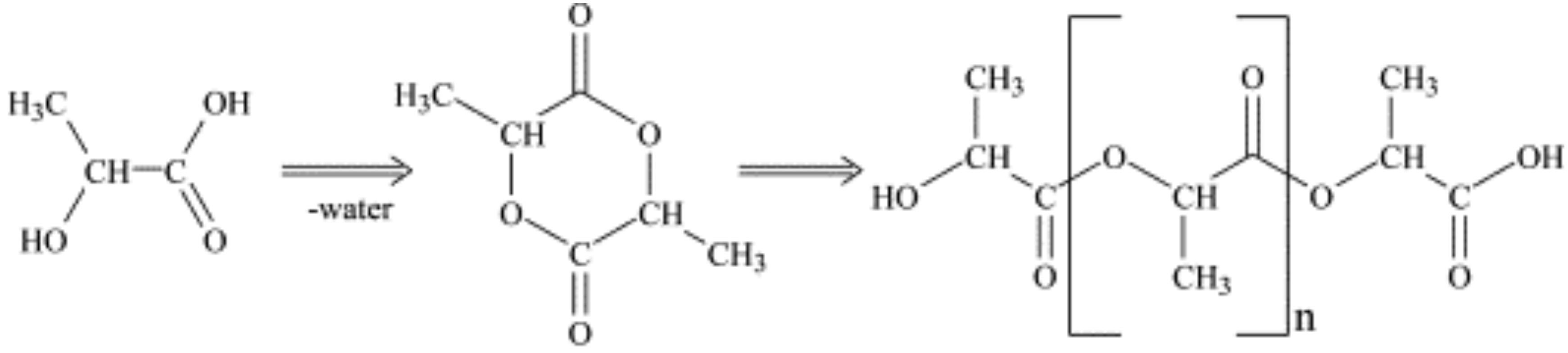
November 2023: Mitsubishi Chemical Corporation partners with a startup to develop PHB production technologies that utilize food waste as feedstock, promoting resource efficiency and circularity.

December 2023: Tianjin Green Bio expands its production capacity and establishes a new research facility dedicated to optimizing PHB production processes.

January 2024: Zhejiang Hisun Biomaterials enters into a collaboration with a major food packaging manufacturer to develop and supply PHB-based food trays and containers.

Polylactic Acid

Industrial composting



Lactic Acid

cyclic lactide monomer

Poly (Lactic Acid)

Polylactic Acid

Total Corbian PLA

Total Corbion was founded in 2017. It is a global technological leader in the PLA and acticide monomers based in Thailand. The corporation is a subsidiary of TotalEnergies, Corbion. They provide innovative solutions by producing materials that can be used in fresh food, packaging, consumer goods, fibers, food service ware and 3D printing.

Evonik is a German based chemical company. It was founded in 2007. Evonik Operations GmbH is a subsidiary and RAG – Stiftung its parent organization. It is one of the leading names among polyactic acid manufacturers. They specialize in production of specialty chemicals. It is headquartered from Essen, North Rhine-Westphalia, Germany.

Natureworks PLA

It is an international chemical manufacturing company that produces bioplastics as an alternative to conventional plastic that is made from petroleum. It has its headquarters in Minnetonka, Minnesota, United States. The **NatureWorks** corporation was founded in 1898. Cargill, PTT Public Company Limited, PTT Chemical International Private Limited are the parent organizations of the firm while Natureworks B.V is its esteemed subsidiary. They specialize in manufacturing Ingeo brand polylactic acid.

Futerro PLA

Futerro is a private plastic fabrication company. It is a Belgian based company that was founded in 1992. They develop lactic acid and polylactic acid. They envision offering ecological alternatives to conventional plastic; a sustainable future. This company has made its mark in the industry because of its futuristic vision.

Industrial Composting in Cincinnati (doesn’t seem to exist, despite claims)

Queen City Commons (not industrial composting, doesn’t take PLA)

GoZERO Services (doesn’t seem to be functional, they sell composted dirt for $20 a gallon?)

Grind the waste (trees, bones, meat, fish, and “normal” compost)

Monitor humidity and especially temperature to about 150°F (70°C)
Enough to kill bad bacteria but cool enough for good bacterial and fungi to work at high rates (4 months)

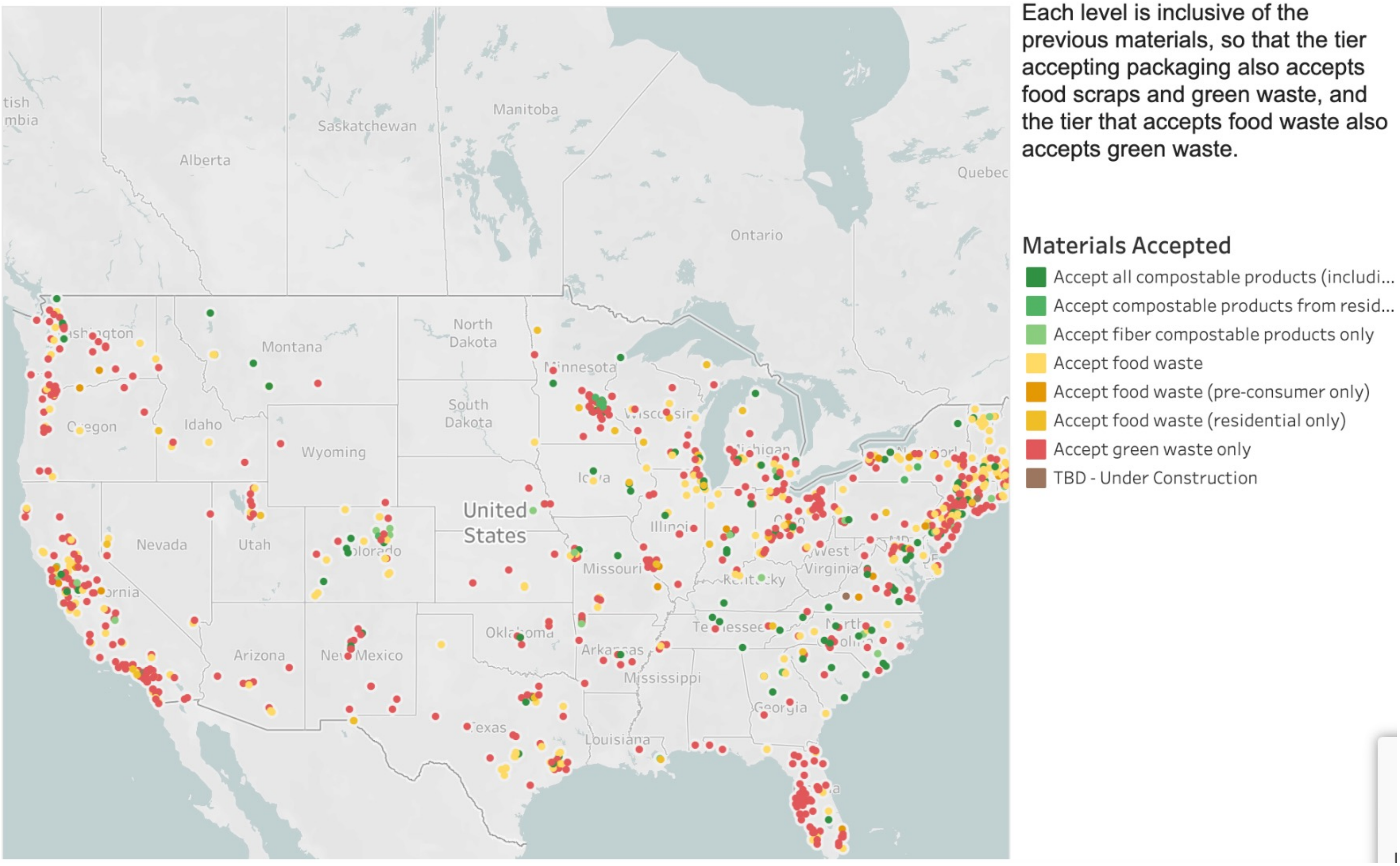
Home composting doesn’t grind and about 100°F slower rate (two years)

PLA only degrades in industrial compost

Polylactic Acid

Industrial composting

Each level is inclusive of the previous materials, so that the tier accepting packaging also accepts food scraps and green waste, and the tier that accepts food waste also accepts green waste.



Industrial production of monomers from methane
Methane can come from compost or fossil source

India Biogas Reactor (https://www.youtube.com/watch?v=9kKRdlAFuZw)

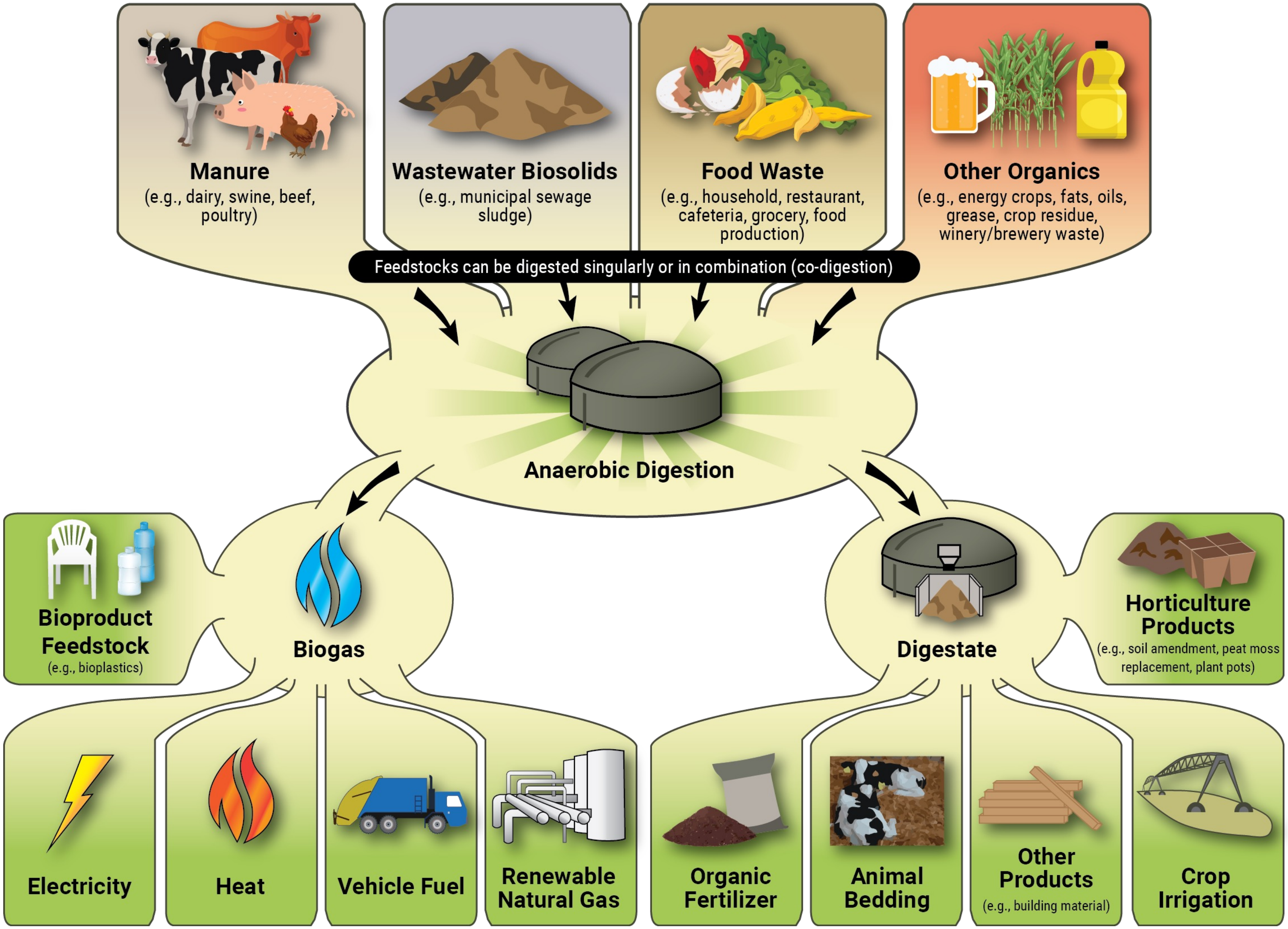
Biogas Reactor for the Developing World (https://www.youtube.com/watch?v=Cwm5Rm8uIsk)

Biomass/Syngas

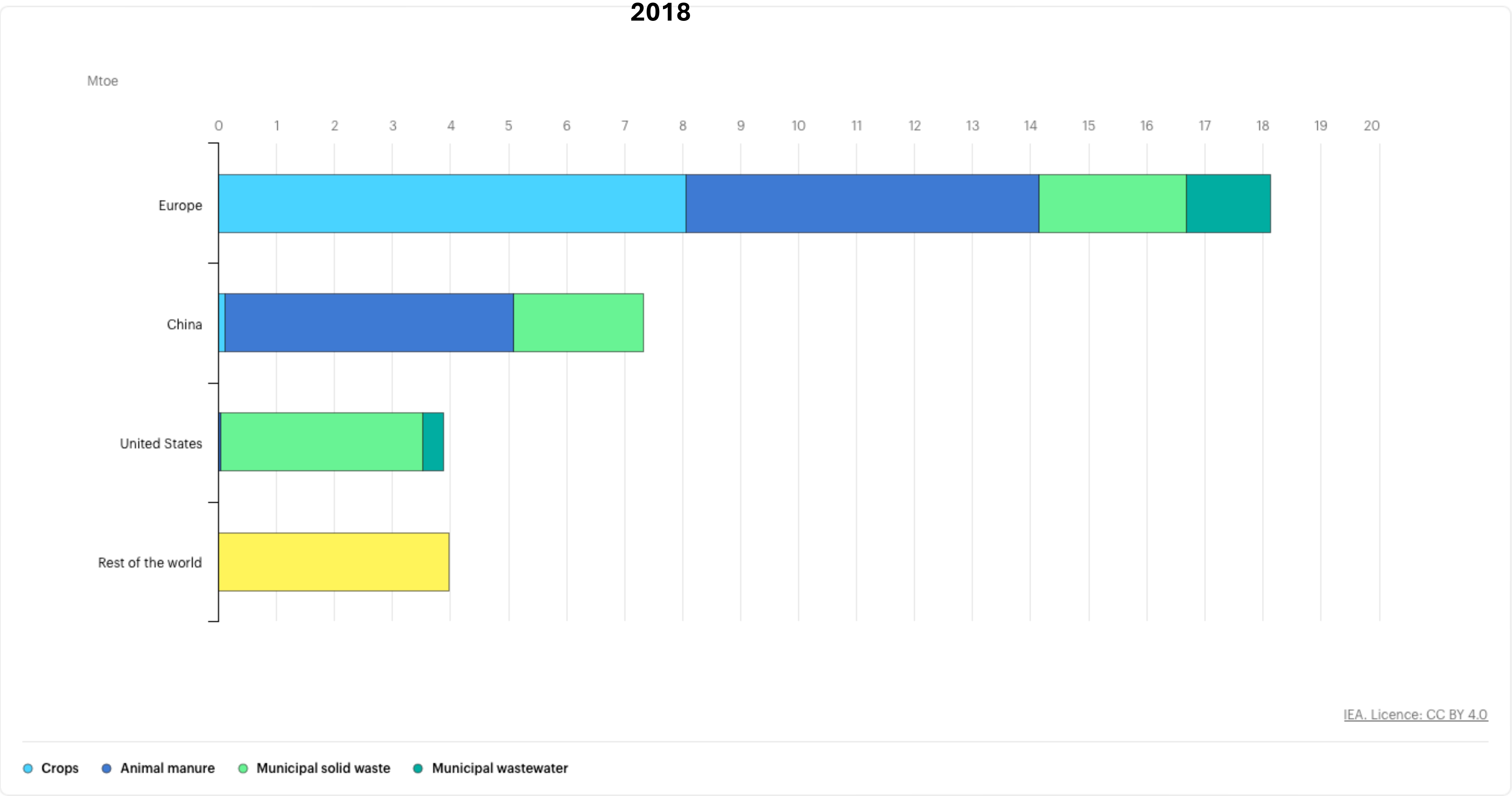
Single House Biogas (http://www.youtube.com/watch?v=3th2bcqHbsk)

Biomass/Syngas

Biogas in Kenya (http://www.youtube.com/watch?v=qh3mmgiybTw)


Manure
(e.g., dairy, swine, beef, poultry)
Wastewater Biosolids
(e.g., municipal sewage sludge)
Food Waste
(e.g., household, restaurant, cafeteria, grocery, food production)
Other Organics
(e.g., energy crops, fats, oils, grease, crop residue, winery/brewery waste)
Feedstocks can be digested singularly or in combination (co-digestion)
Anaerobic Digestion
Biogas
Digestate
Bioproduct Feedstock
(e.g., bioplastics)
Horticulture Products
(e.g., soil amendment, peat moss replacement, plant pots)
Electricity
Heat
Vehicle Fuel
Renewable Natural Gas
Organic Fertilizer
Animal Bedding
Other Products
(e.g., building material)
Crop Irrigation

2018



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The development of biogas has been uneven across the world, as it depends not only on the availability of feedstocks but also on policies that encourage its production and use. Europe, the People's Republic of China (hereafter, "China") and the United States account for 90% of global production.

Europe is the largest producer of biogas today. Germany is by far the largest market, and home to two-thirds of Europe's biogas plant capacity. Energy crops were the primary choice of feedstock that underpinned the growth of Germany's biogas industry, but policy has recently shifted more towards the use of crop residues, sequential crops, livestock waste and the capture of methane from landfill sites. Other countries such as Denmark, France, Italy and the Netherlands have actively promoted biogas production.

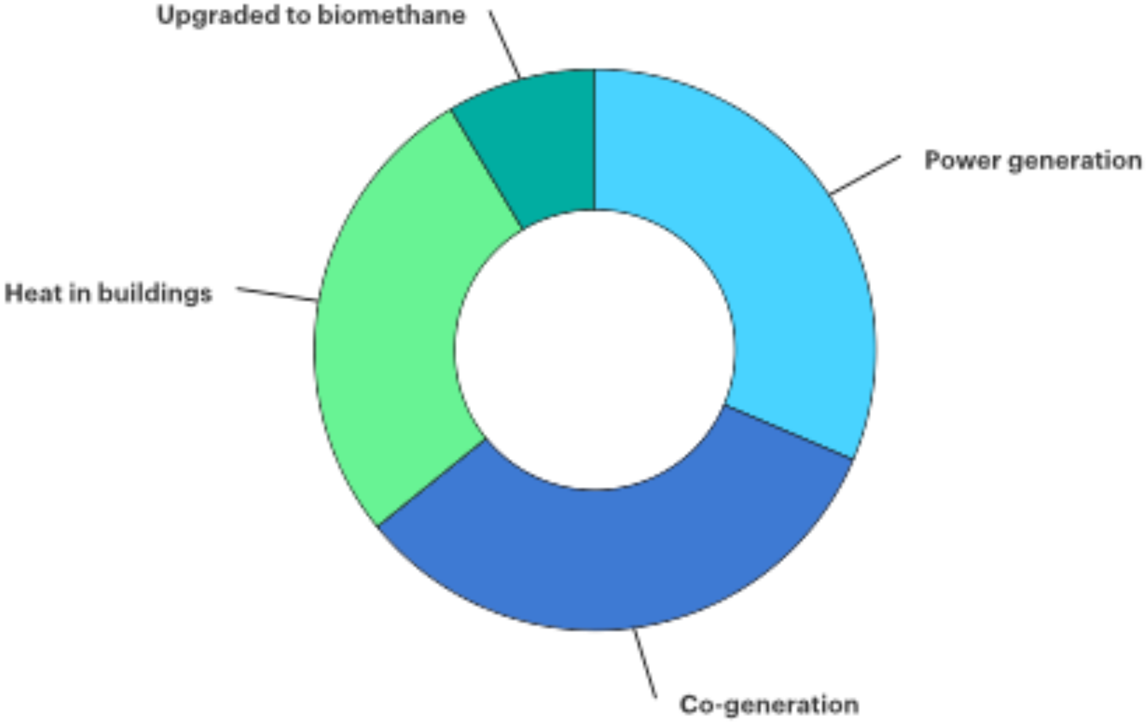
In **China**, policies have supported the installation of household-scale digesters in rural areas with the aim of increasing access to modern energy and clean cooking fuels; these digesters account for around 70% of installed biogas capacity today. Different programmes have been announced to support the installation of larger-scale co-generation plants (i.e. plants producing both heat and power). Moreover, the Chinese National Development and Reform Commission issued a guidance document in late 2019 specifically on biogas industrialisation and upgrading to biomethane, supporting also the use of biomethane in the transport sector.

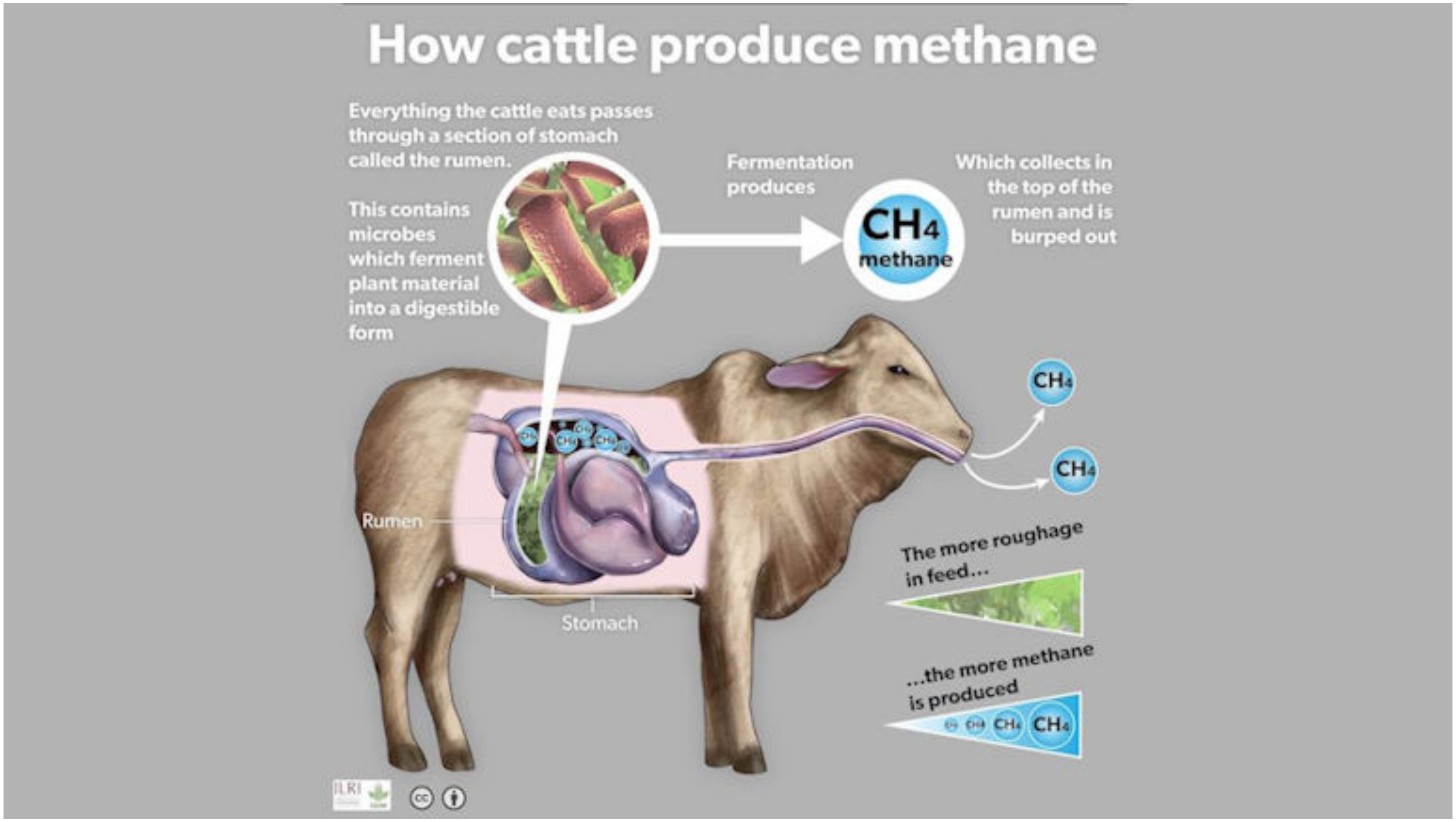
In the **United States**, the primary pathway for biogas has been through landfill gas collection, which today accounts for nearly 90% of its biogas production. There is also growing interest in biogas production from agricultural waste, since domestic livestock markets are responsible for almost one-third of methane emissions in the United States (USDA, 2016). The United States is also leading the way globally in the use of biomethane in the transport sector, as a result of both state and federal support.

Around half of the remaining production comes from developing countries in Asia, notably **Thailand** and **India**. Remuneration via the Clean Development Mechanism (CDM) was a key factor underpinning this growth, particularly between 2007 and 2011. The development of new biogas projects fell sharply after 2011 as the value of emission reduction credits awarded under the CDM dropped. Thailand produces biogas from the waste streams of its cassava starch sector, biofuel industry and pig farms. India aims to develop around 5 000 new compressed biogas plants over the next five years (GMI, 2019). **Argentina** and **Brazil** have also supported biogas through auctions; Brazil has seen the majority of production come from landfills, but there is also potential from vinasse, a by-product from the ethanol industry.

A clear picture of today's consumption of biogas in **Africa** is made more difficult by a lack of data, but its use has been concentrated in countries with specific support programmes. Some governments, such as Benin, Burkina Faso and Ethiopia, provide subsidies that can cover from half to all of the investment, while numerous projects promoted by non-governmental organisations provide practical know-how and subsidies to lower the net investment cost. In addition to these subsidies, credit facilities have made progress in a few countries, notably a recent lease-to-own arrangement in Kenya that financed almost half of the digester installations in 2018 (ter Heegde, 2019)

Biogas consumption by end use, 2018





How cattle produce methane

Everything the cattle eats passes through a section of stomach called the rumen.

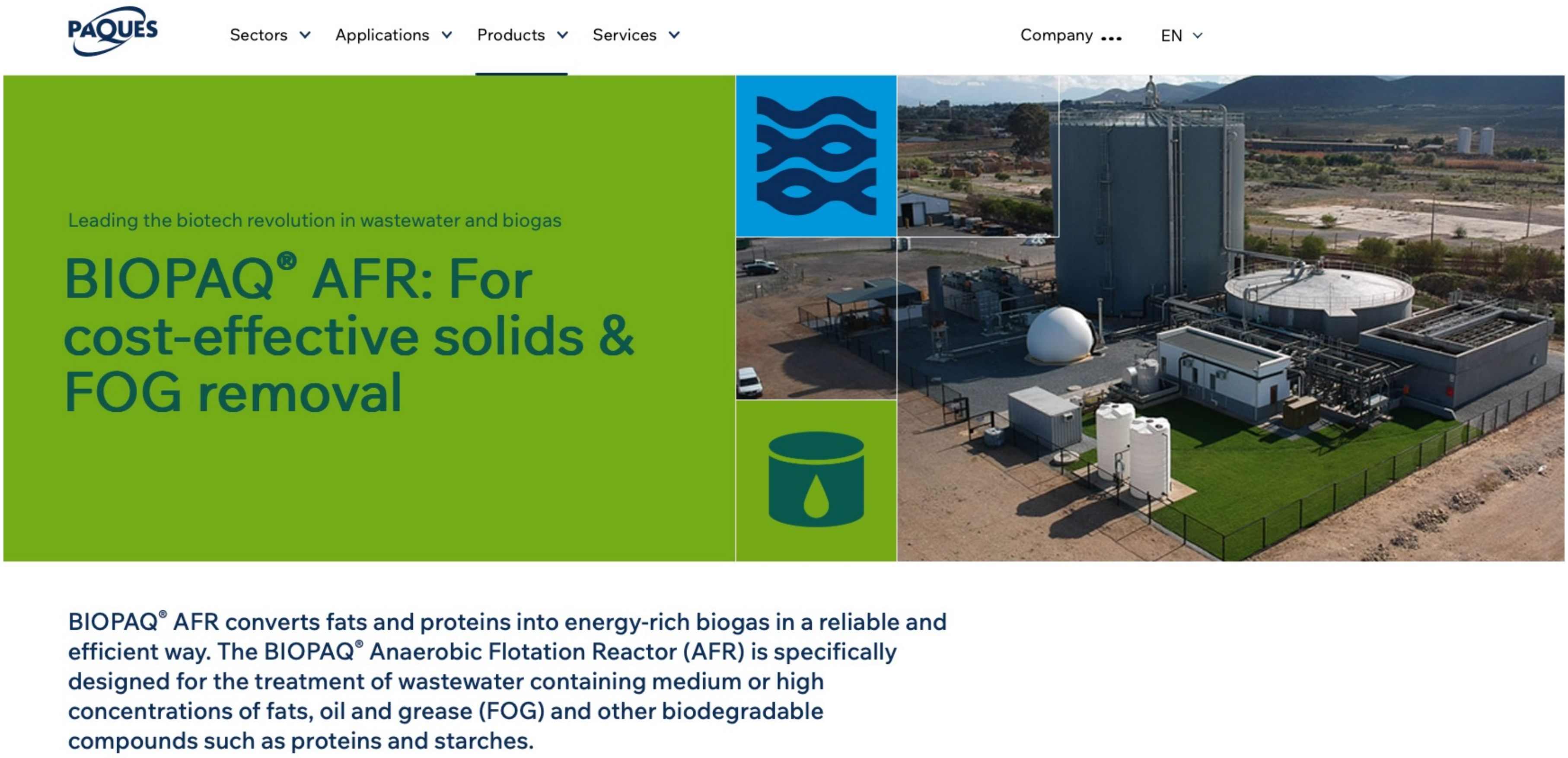
This contains microbes which ferment plant material into a digestible form

Fermentation produces

Which collects in the top of the rumen and is burped out

The more roughage in feed…

…the more methane is produced



Leading the biotech revolution in wastewater and biogas

BIOPAQ® AFR: For cost-effective solids & FOG removal

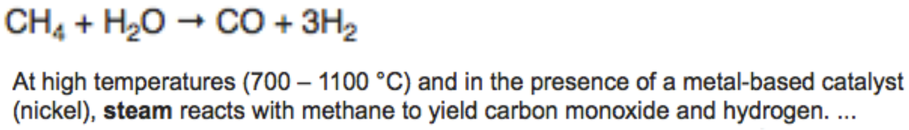
BIOPAQ® AFR converts fats and proteins into energy-rich biogas in a reliable and efficient way. The BIOPAQ® Anaerobic Flotation Reactor (AFR) is specifically designed for the treatment of wastewater containing medium or high concentrations of fats, oil and grease (FOG) and other biodegradable compounds such as proteins and starches.

[AFR Process Video for Methane Production]

Methane from Cows, Sewage, Compost, Landfill, etc.

Steam Reforming Reaction: CH_4 to H_2 and CO

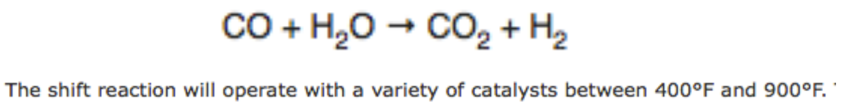
Biomass/Syngas



$$CH_4 + H_2O \rightarrow CO + 3H_2$$

At high temperatures (700 – 1100 °C) and in the presence of a metal-based catalyst (nickel), **steam** reacts with methane to yield carbon monoxide and hydrogen. ...

Water Shift Gas Reaction: CO to H_2



$$CO + H_2O \rightarrow CO_2 + H_2$$

The shift reaction will operate with a variety of catalysts between 400°F and 900°F.

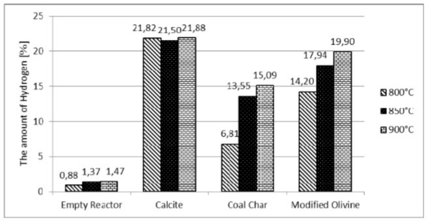
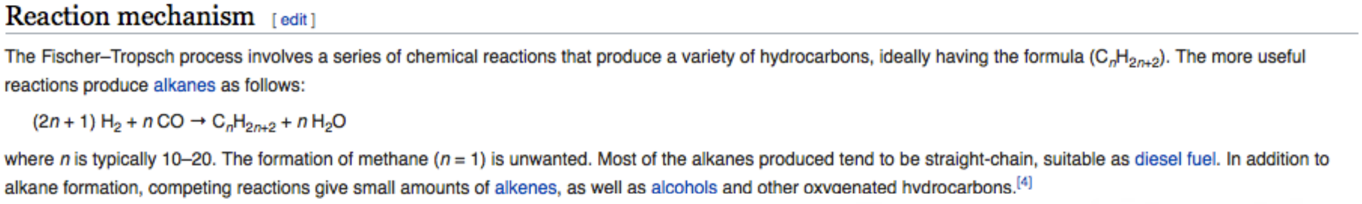


Fig. 3. Average percentage representation of hydrogen for the studied catalysts at t=800, 850 and 900°C

Fischer-Tropsch Reaction: H_2 and CO to Liquid Fuel

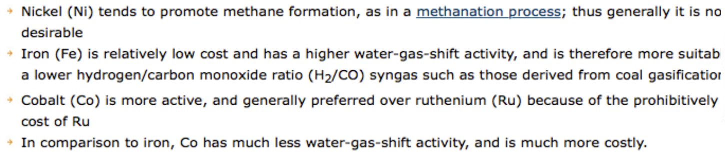


Reaction mechanism [edit]

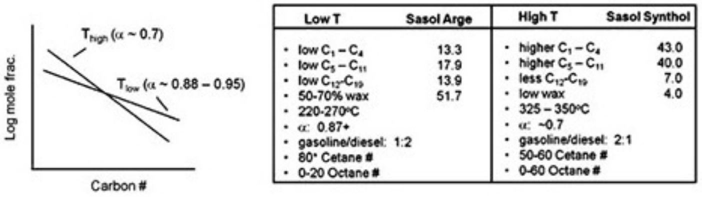
The Fischer–Tropsch process involves a series of chemical reactions that produce a variety of hydrocarbons, ideally having the formula (C_nH_{2n+2}). The more useful reactions produce alkanes as follows:

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$$

where n is typically 10–20. The formation of methane ($n = 1$) is unwanted. Most of the alkanes produced tend to be straight-chain, suitable as diesel fuel. In addition to alkane formation, competing reactions give small amounts of alkenes, as well as alcohols and other oxygenated hydrocarbons.[4]

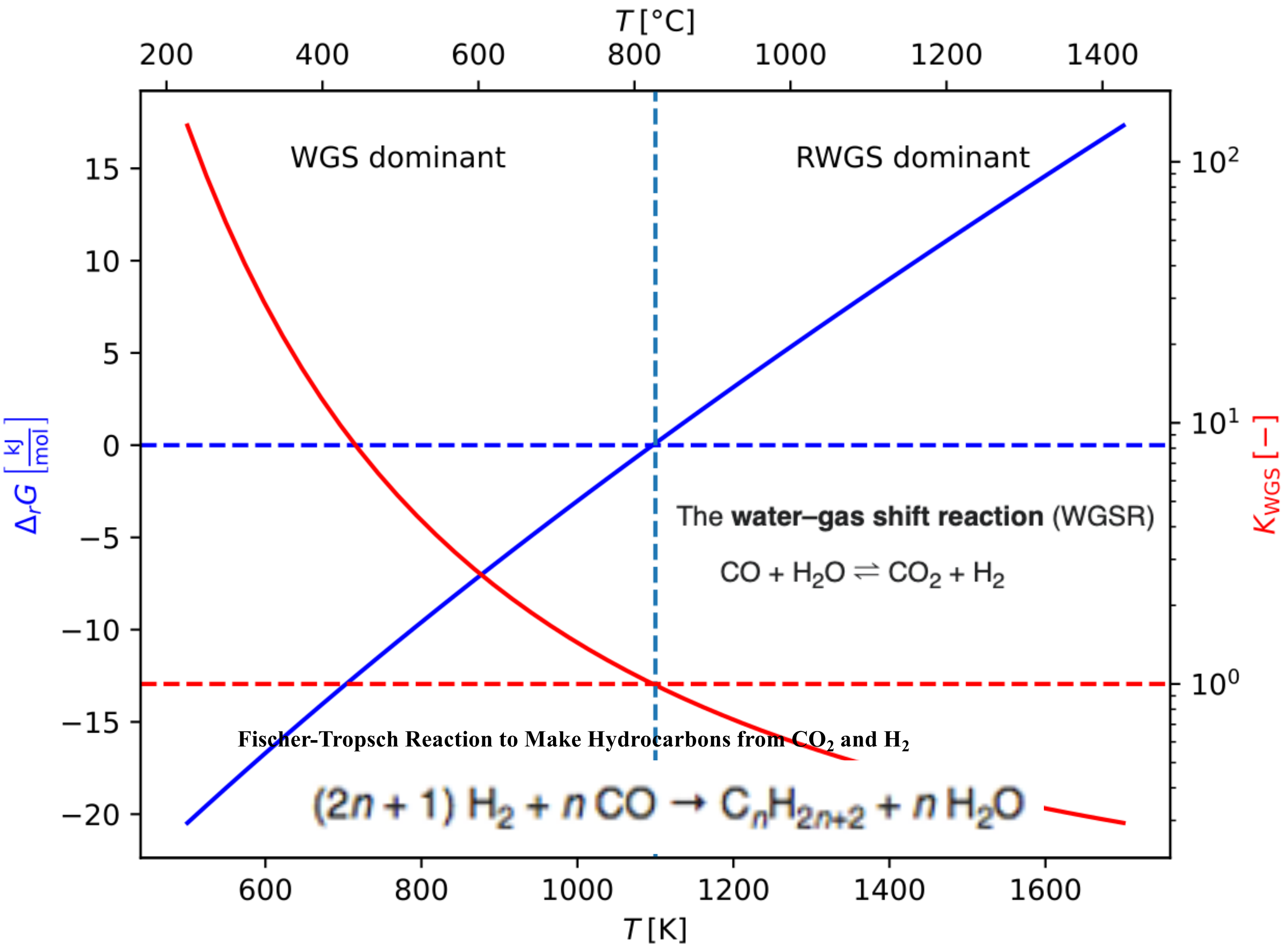


- Nickel (Ni) tends to promote methane formation, as in a methanation process; thus generally it is no desirable
- Iron (Fe) is relatively low cost and has a higher water-gas-shift activity, and is therefore more suitab a lower hydrogen/carbon monoxide ratio (H_2/CO) syngas such as those derived from coal gasificatio
- Cobalt (Co) is more active, and generally preferred over ruthenium (Ru) because of the prohibitively cost of Ru
- In comparison to iron, Co has much less water-gas-shift activity, and is much more costly.



Low T	Sasol Arge	High T	Sasol Synthol
low $C_1 - C_4$	13.3	higher $C_1 - C_4$	43.0
low $C_5 - C_{11}$	17.9	higher $C_5 - C_{11}$	40.0
low C_{12}-C_{19}	13.9	less C_{12}-C_{19}	7.0
50-70% wax	51.7	low wax	4.0
220-270°C		325 – 350°C	
α: 0.87+		α: ~0.7	
gasoline/diesel: 1:2		gasoline/diesel: 2:1	
80* Cetane #		50-60 Cetane #	
0-20 Octane #		0-60 Octane #	

Dependency of Fischer–Tropsch synthesis ASF distribution on temperature. Product selectivities (in %) of the Sasol Arge (220 °C)



The **water–gas shift reaction** (WGSR)

$CO + H_2O \rightleftharpoons CO_2 + H_2$

Fischer-Tropsch Reaction to Make Hydrocarbons from CO_2 and H_2

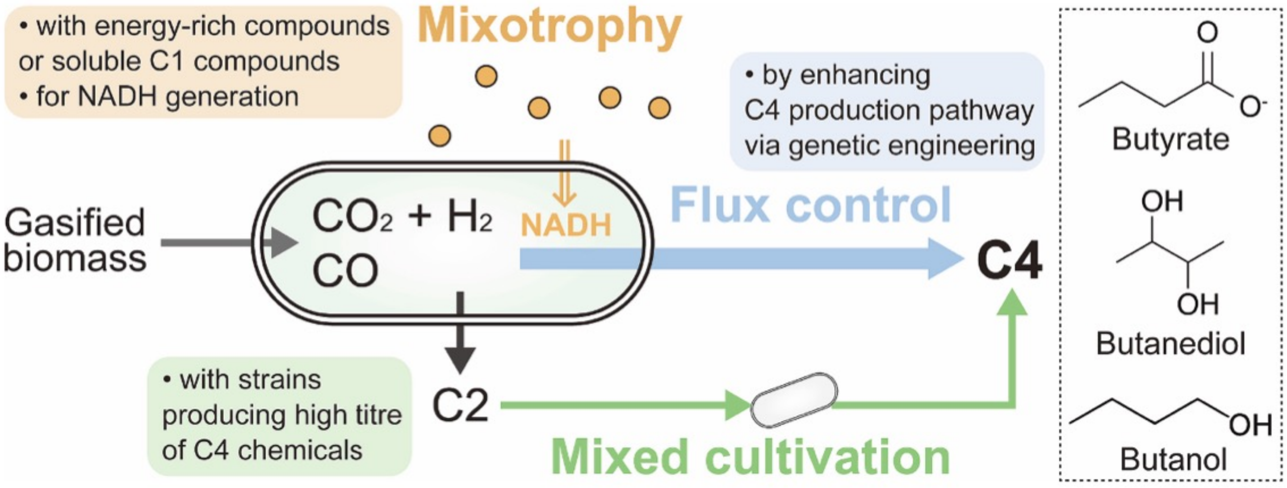
$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$

Fermentation of Syngas

Syngas can also be fermented to give ethanol (CH_3CH_2OH), 1-propanol ($CH_3CH_2CH_2OH$), 1-butanol ($CH_3CH_2CH_2CH_2OH$), acetic acid (CH_3COOH), butyric acid ($CH_3CH_2CH_2COOH$), or other chemical building blocks.

Acetogens.

In the past few years, US-based company Lanzatech developed processes for the production of bio-based 2,3-butanediol ($CH_3CHOHCHOHCH_3$) and ethanol (CH_3CH_2OH). Also, US-based **Synata Bio** invested in pilot plant facilities to produce ethanol (CH_3CH_2OH) and 1-butanol ($CH_3CH_2CH_2CH_2OH$), starting from *syngas* feedstock.



Pyrolysis Oil, biocrude or bio-oil

Anaerobic heat wood

- water driven off 100°C
- dry wood
- 270°C decomposition and heat
- 450°C charcoal and tar
- 600°C biochar

- Remain at 400-500°C makes mostly biochar in hours

- Above 700°C liquid and gas in seconds
  Bio-oil and syngas

15% of the energy is consumed by the process

Pyrolysis Oil, biocrude or bio-oil

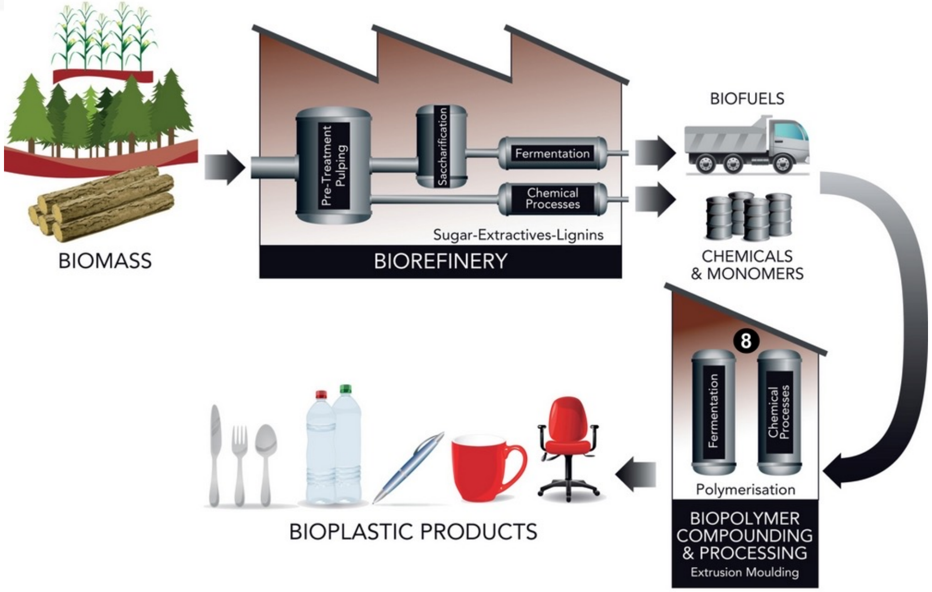
Hydrothermal liquification

- Wet biomass
- 350°C and 21 MPa
- Bio-oil with twice the energy density of pyrolysis oil

Related materials:

- Black Liquor (pulp mill lignin)
- Rubber Oil (tires)

Use Pyrolysis Oil to make ”bio-plastic” by bio-refining

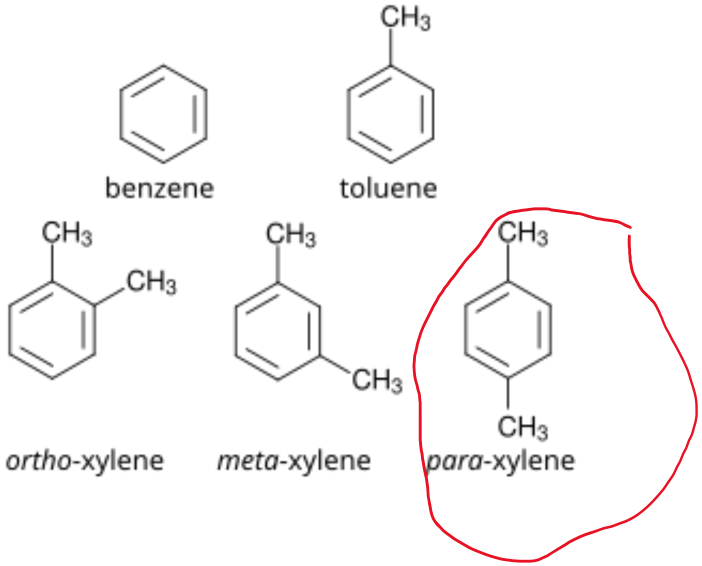


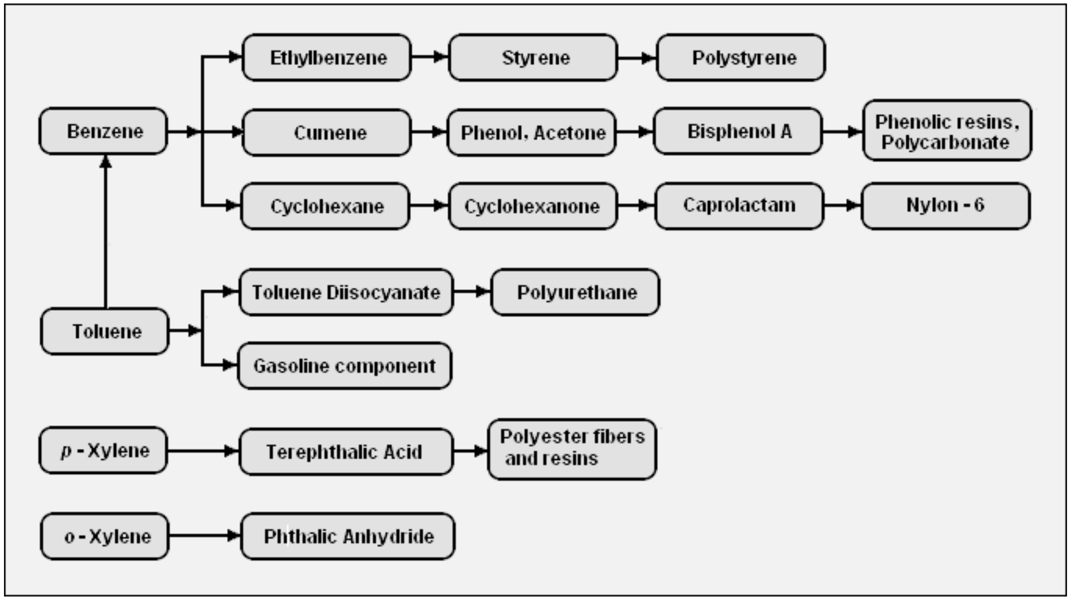
Bio-based Terephthalic Acid for biobased PET

Pyrolysis of organic matter.
Low Temperature/Slow Heating (<450°C) => Biochar
Intermediate Temperature/Rapid Heating=> **Pyrolysis Oil**
High Temperature/Rapid Heating (>800°C) => Gasses (CH_4, H_2, CO, and CO_2)

Bio-oil + Zeolite ($Na_2Al_2Si_3O_{10} \cdot 2\ H_2O$) => ***bioBTX***

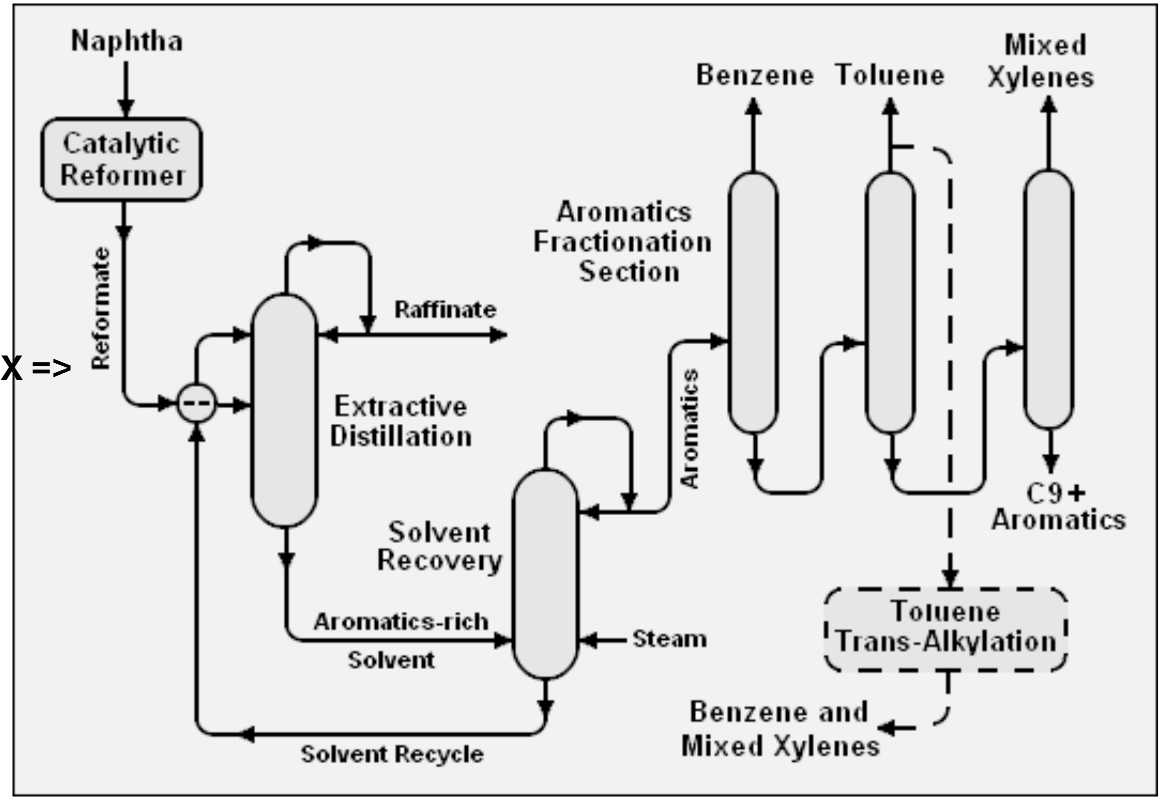
BTX





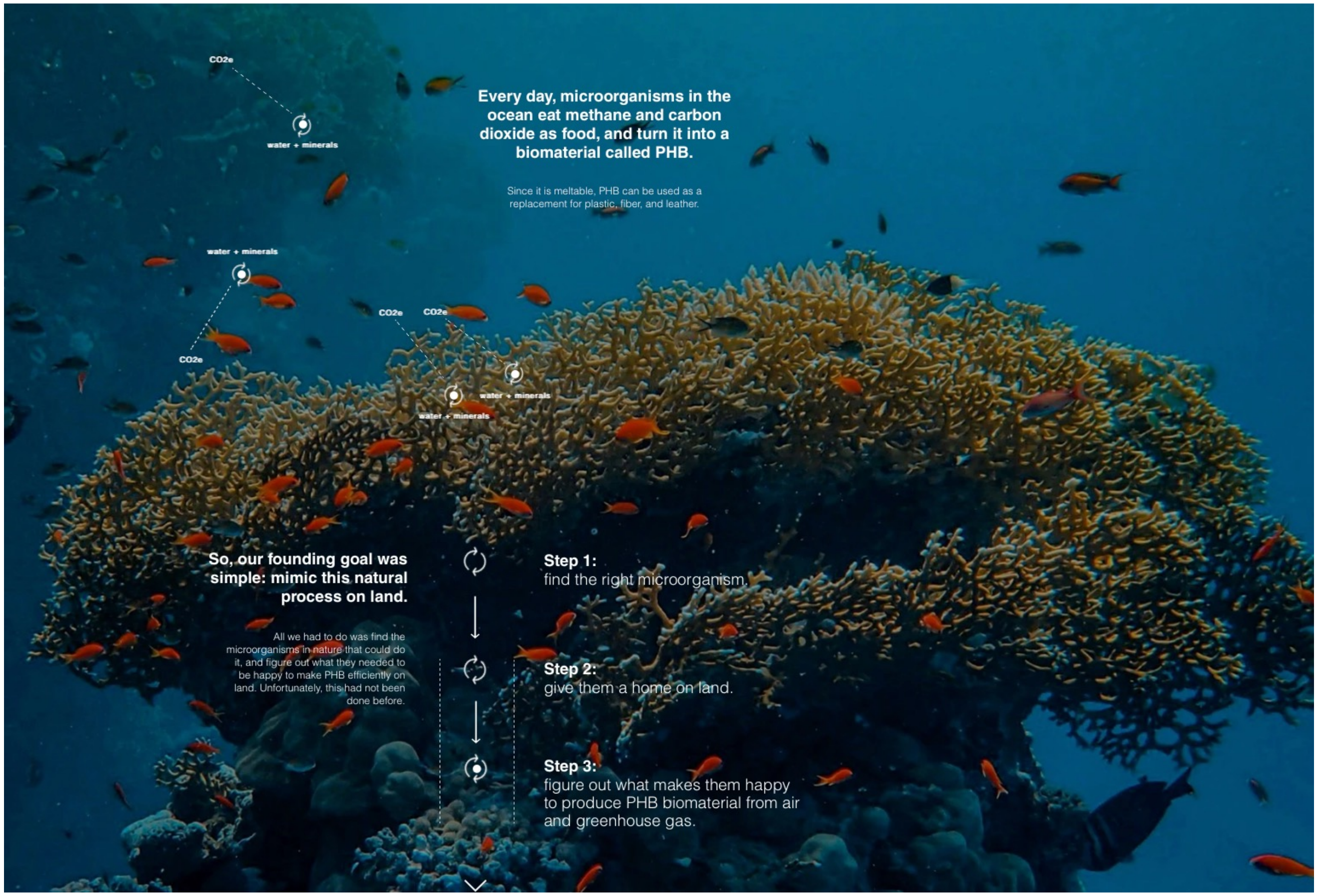
Bio-based Terephthalic Acid for biobased PET

Bio-BTX =>



Methane from Cows, Sewage, Compost, Landfill, etc.

PHB from Methane (Newlight, Huntington Beach CA)



Every day, microorganisms in the ocean eat methane and carbon dioxide as food, and turn it into a biomaterial called PHB.

Since it is meltable, PHB can be used as a replacement for plastic, fiber, and leather.

So, our founding goal was simple: mimic this natural process on land.

All we had to do was find the microorganisms in nature that could do it, and figure out what they needed to be happy to make PHB efficiently on land. Unfortunately, this had not been done before.

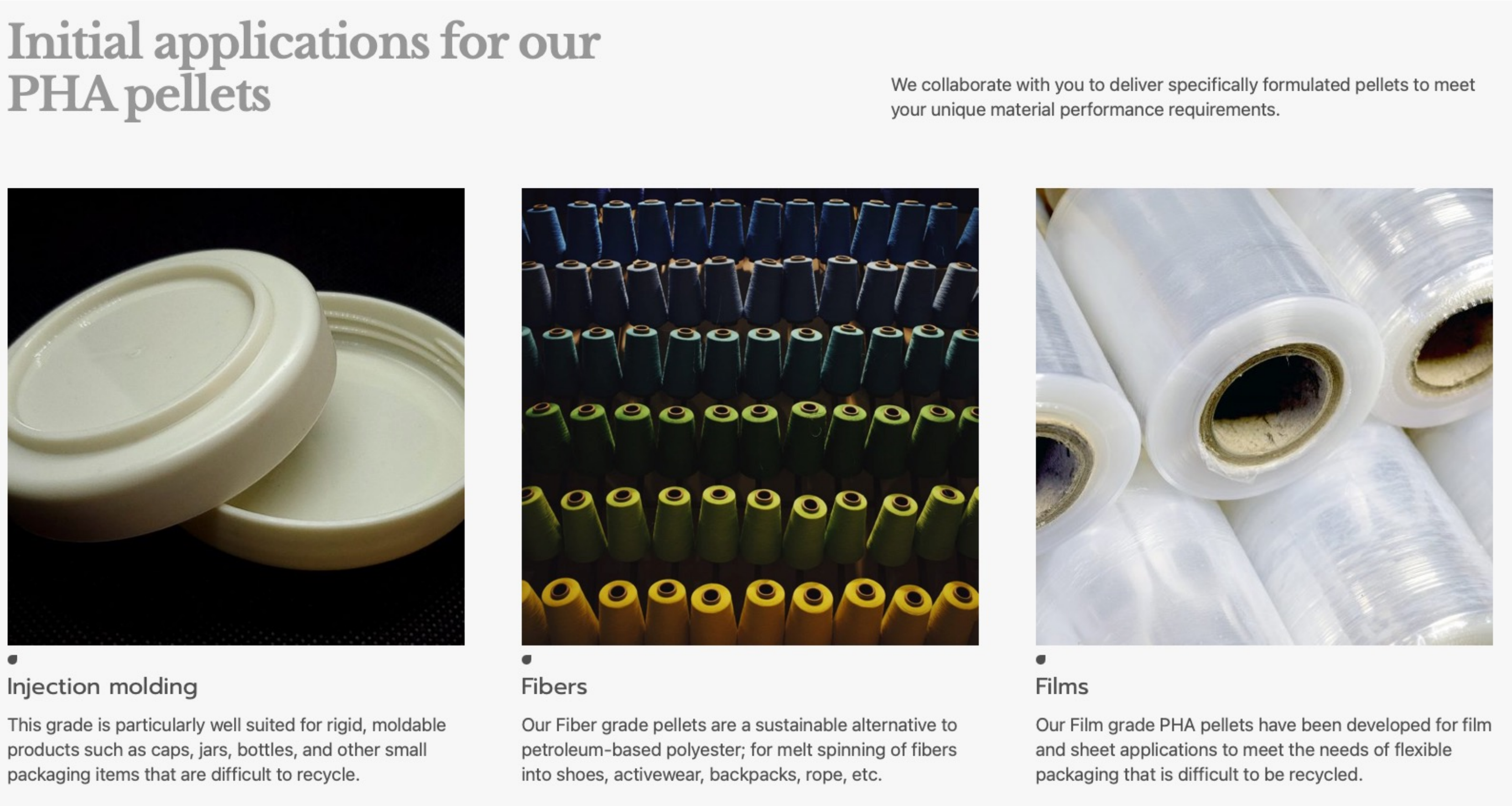
Step 1:
find the right microorganism.

Step 2:
give them a home on land.

Step 3:
figure out what makes them happy to produce PHB biomaterial from air and greenhouse gas.

PHB from Methane (Newlight, Hunington Beach CA)

PHB from Methane (Mango Materials Berkley CA)



Initial applications for our PHA pellets

We collaborate with you to deliver specifically formulated pellets to meet your unique material performance requirements.

Injection molding

This grade is particularly well suited for rigid, moldable products such as caps, jars, bottles, and other small packaging items that are difficult to recycle.

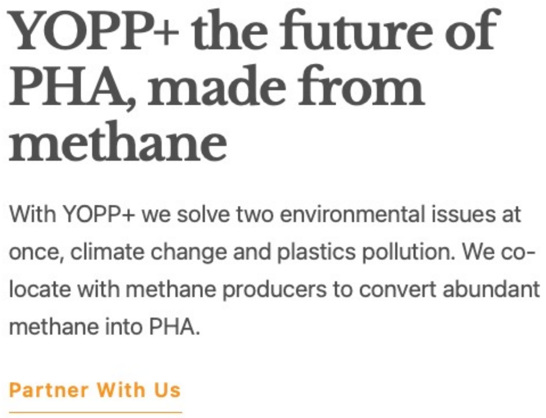
Fibers

Our Fiber grade pellets are a sustainable alternative to petroleum-based polyester; for melt spinning of fibers into shoes, activewear, backpacks, rope, etc.

Films

Our Film grade PHA pellets have been developed for film and sheet applications to meet the needs of flexible packaging that is difficult to be recycled.

PHB from Methane (Mango Materials Berkley CA)



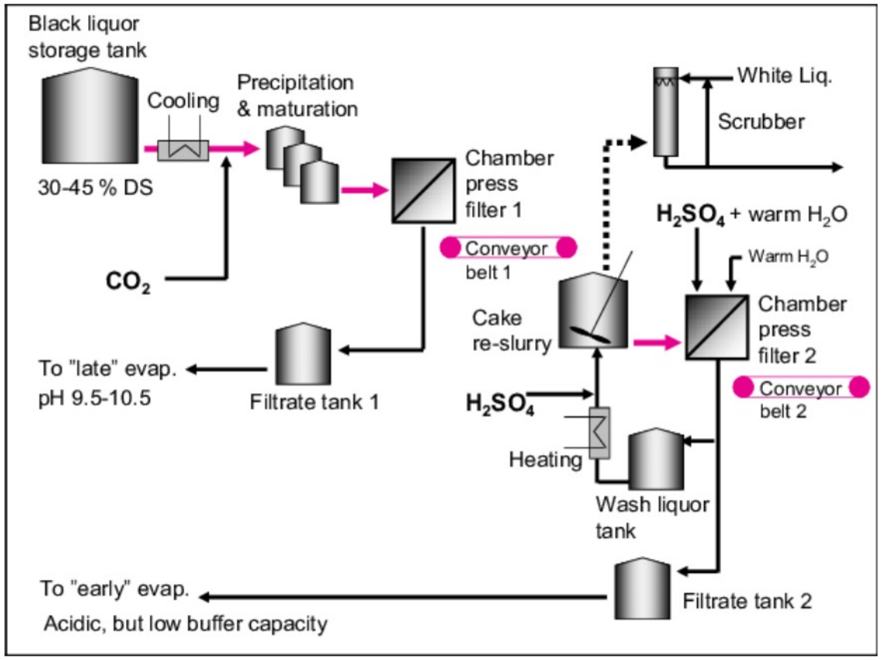
YOPP+ the future of PHA, made from methane

With YOPP+ we solve two environmental issues at once, climate change and plastics pollution. We co-locate with methane producers to convert abundant methane into PHA.

Lignin

LignoBoost (Sweden) and LignoForce (Canada)

a renewable source of aromatic compounds



General layout of the LignoBoost lignin removal process (post-treatment, drying and pulverizing are excluded)

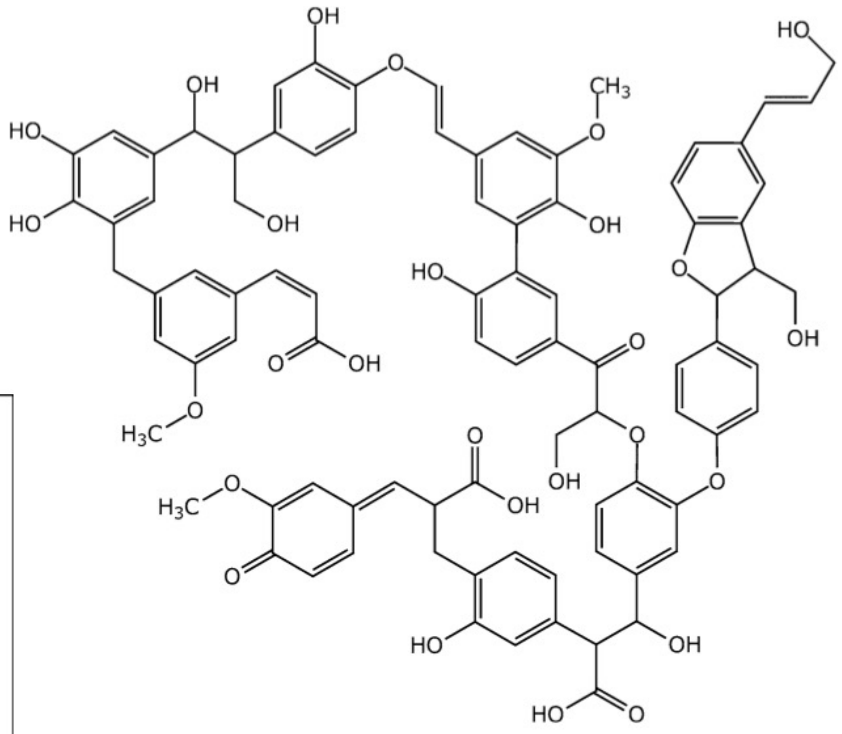
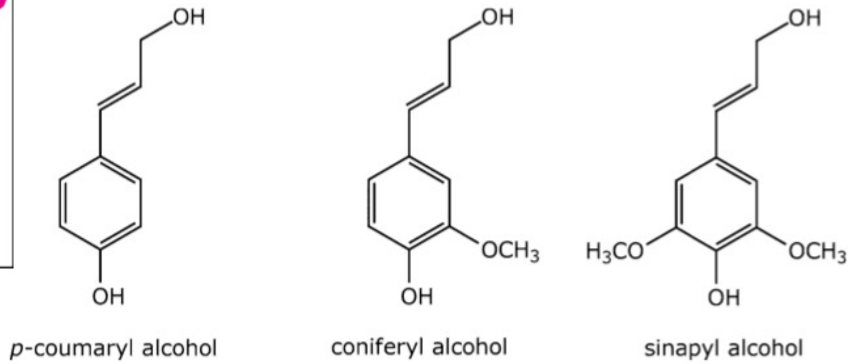


Figure 3.5: Proposed chemical structure of lignin.



p-coumaryl alcohol

coniferyl alcohol

sinapyl alcohol

Figure 3.6: Chemical structures of lignin buildings blocks (monolignols).

Starch, Cellulose and Glucose

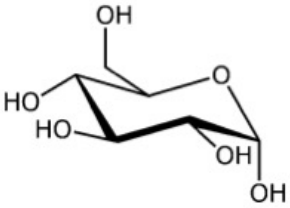


Figure 3.7: Chemical structure of glucose.

β-1,4-glycosidic linkages

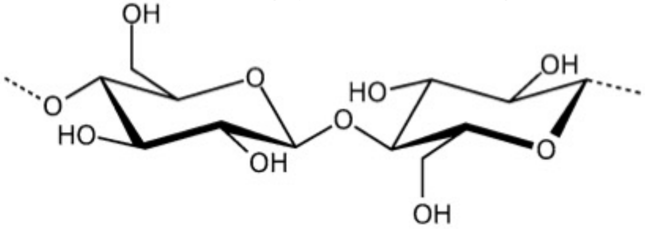


Figure 3.9: Chemical structure of cellulose.

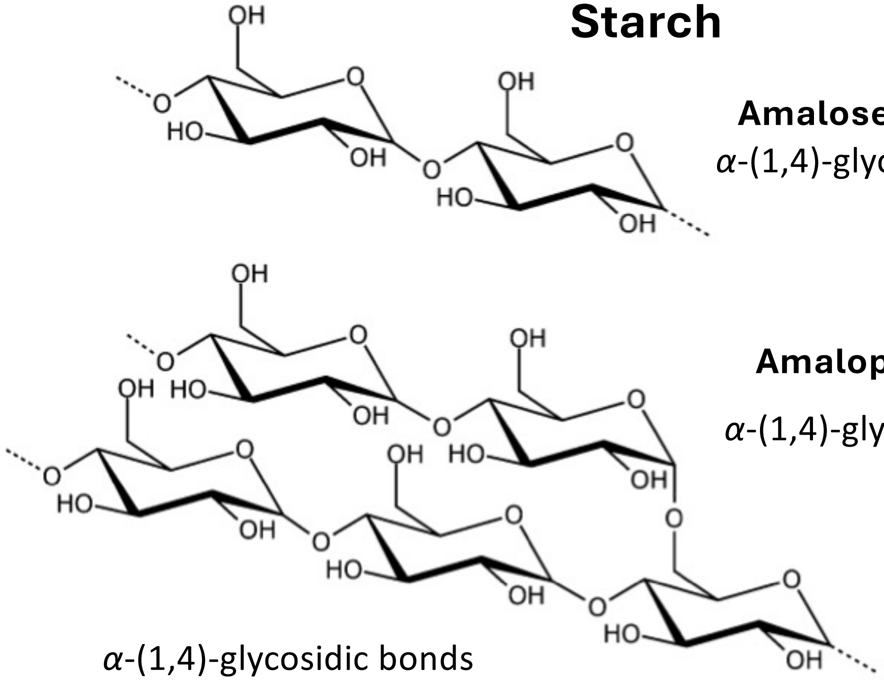
Starch

Amalose

α-(1,4)-glycosidic linkages

Amalopectin

α-(1,4)-glycosidic linkages



α-(1,4)-glycosidic bonds
occasionally (1,6) (branches)

Figure 3.8: Chemical structures of amylose (top) and amylopectin (bottom).

Starch, Cellulose and Glucose

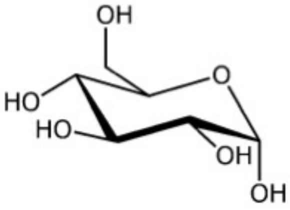


Figure 3.7: Chemical structure of glucose.

β-1,4-glycosidic linkages

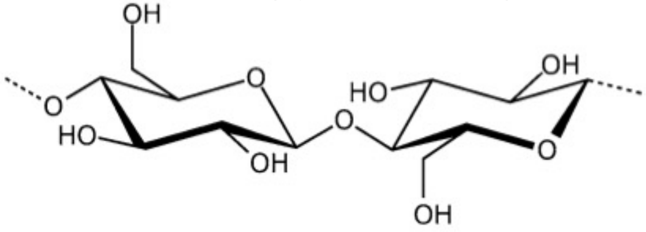


Figure 3.9: Chemical structure of cellulose.

Only glucose and no branching

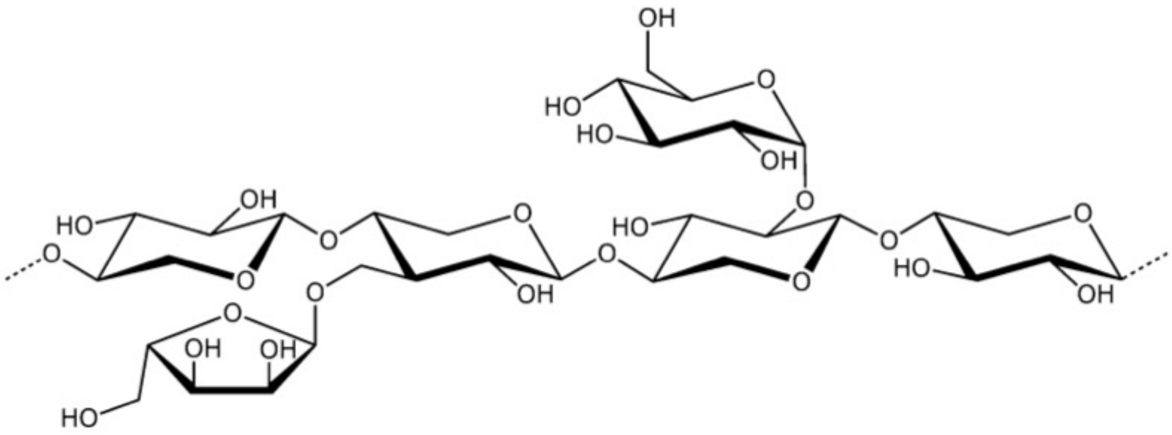
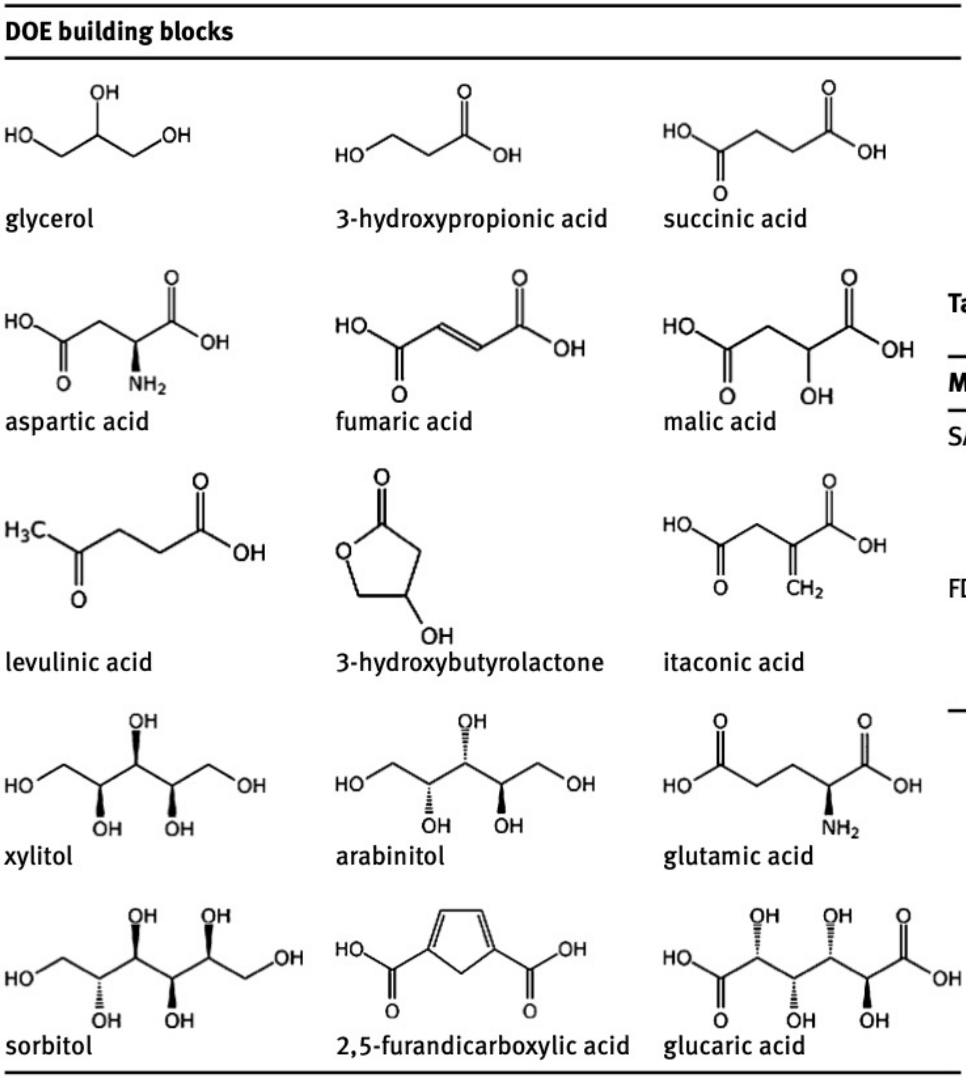


Figure 3.10: Chemical structure of hemicellulose.

Different sugars and branching

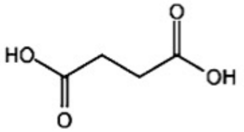
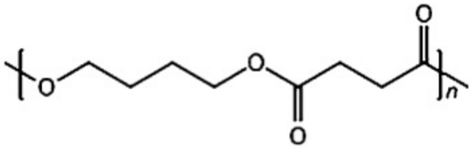
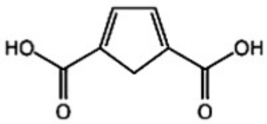
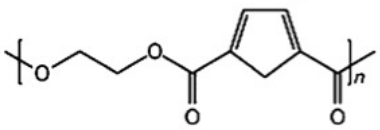
Sugar-based Feedstock

Table 3.2: DOE top value added sugar-based building blocks (biochemicals).



DOE building blocks		
glycerol	3-hydroxypropionic acid	succinic acid
aspartic acid	fumaric acid	malic acid
levulinic acid	3-hydroxybutyrolactone	itaconic acid
xylitol	arabinitol	glutamic acid
sorbitol	2,5-furandicarboxylic acid	glucaric acid

Table 3.3: Polybutylene succinate (PBS) and polyethylene furanoate (PEF).

Monomer	Chemical structure	Polymer	Chemical structure
SA		PBS	
FDCA		PEF	

Bio-Based Oils

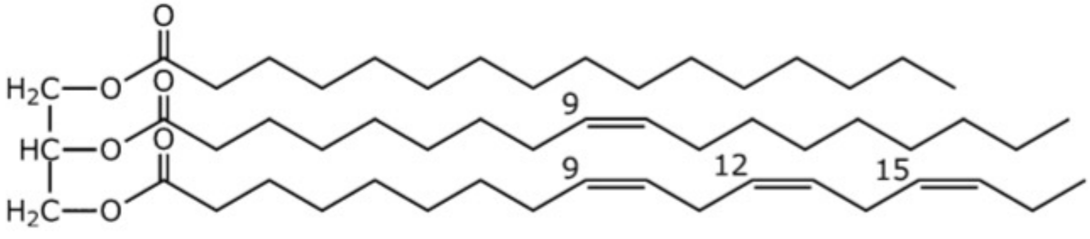


Figure 3.11: Chemical structure of a triglyceride with C16:0, C18:1, and C18:3 fatty acids.

Glycerol	$CH_2OHCHOHCH_2OH$
Fatty Acids	(C:D) C = number of carbons, D = unsaturated bonds Saturated: palmitic (16:0), stearic acid (18:0) Unsaturated oleic acid (18:1), linoleic acid (18:1), and α-linoleic acid (18:3)

Bio-Based Oils

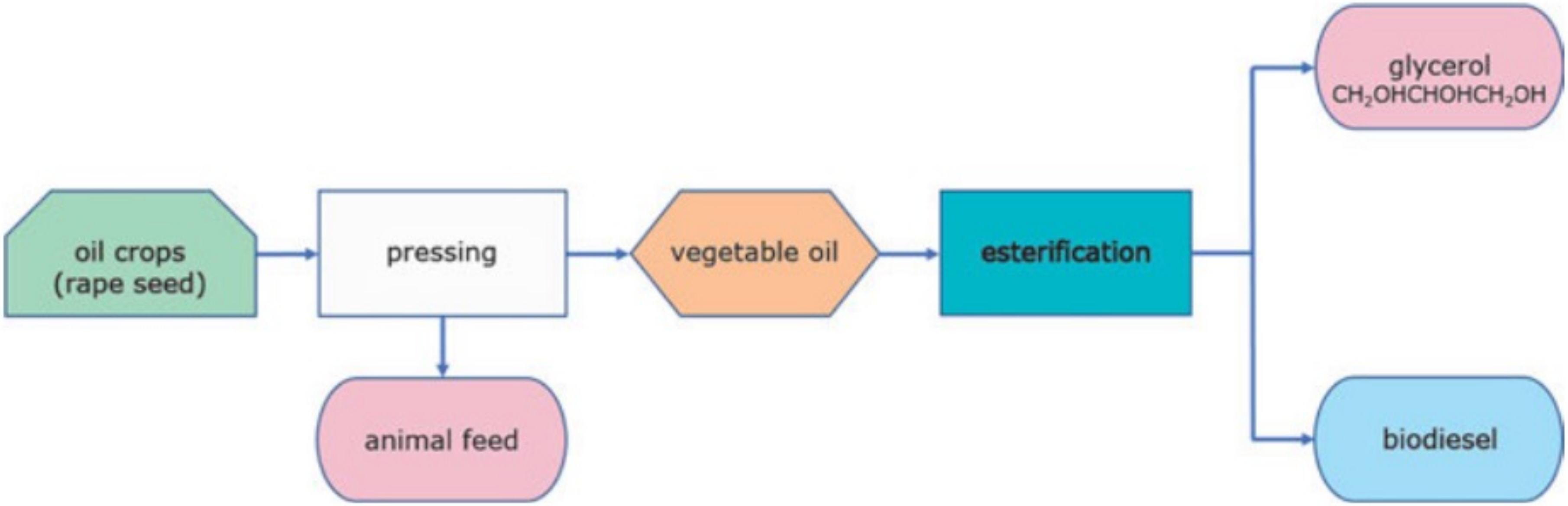


Figure 3.25: Process flow diagram for the production of biodiesel.

Bio-Based Oils

Glycerol can be transformed into bio-based propylene in a one- step catalytic process using molybdenum-based catalysts.

The glycerol-to-propylene (GTP) process was first introduced by Quattor Petrochimica, headquartered in Rio de Janeiro (Brazil). In 2009, this company was incorporated by the Brazilian-based company Braskem.

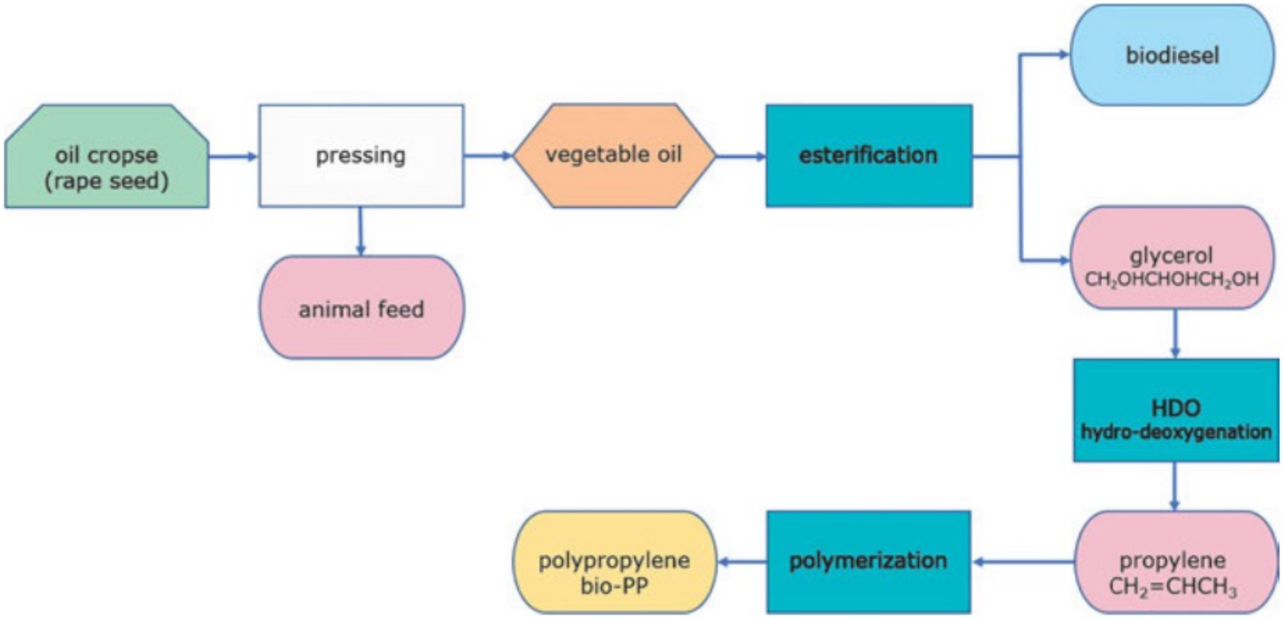


Figure 3.26: Process flow diagram for the production of bio-PP (route 2).

Bio-Based Plastics

Primary feedstocks
Primary feedstocks include primary biomass that is harvested from forest or agricultural land.

Secondary feedstocks
Secondary feedstocks are process residues, such as sawmill residues or black liquor generated by the forests products industry.

Tertiary feedstocks
Tertiary feedstocks are postconsumer wastes or residues (such as waste waters or municipal solid waste).

Bio-Based Plastics

Renewable Feedstocks:

Dedicated feedstocks

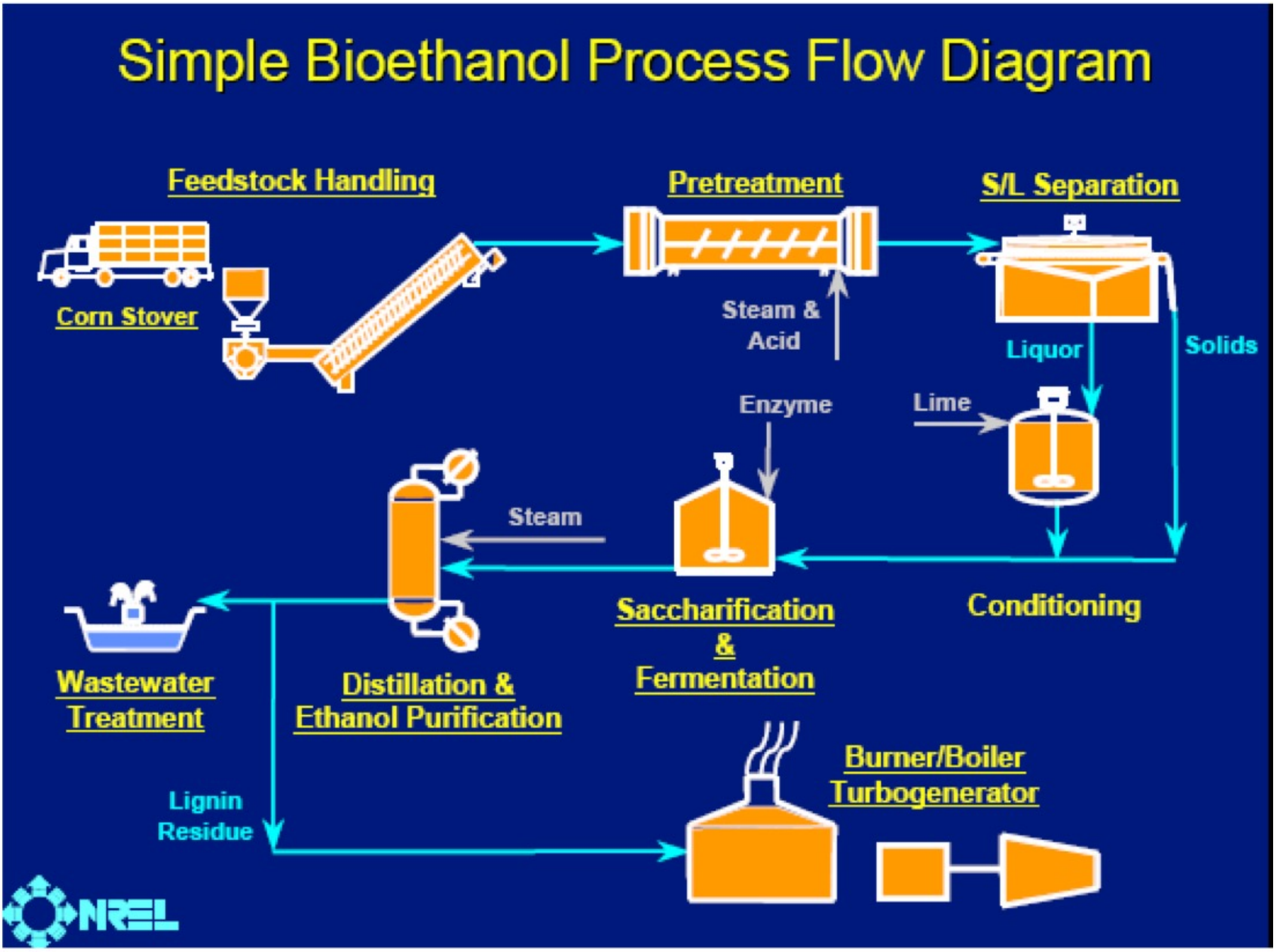
– Sugar crops (e. g., sugar beet or sugar cane).
– Starch crops (e. g., wheat or corn).
– Lignocellulosic crops (e. g., wood or miscanthus).
– Oil-based crops (e. g., rape seed oil, soya oil, palm oil, or jatropha). – Grasses (e. g., green plant materials).
– Marine biomass (e. g., micro and macro algae).

Residues

- – Oil-based residues (e. g., animal fat from food industries or used cooking oil from restaurants, households, and other sources).
- – Lignocellulosic residues (e. g., crop residues or saw mill residues).
- – Organic residues (e. g., organic urban waste or household waste).

Table 3.1: Type of processes related to biorefinery.

Process	Description	Examples
Thermochemical	In thermochemical processes renewable feedstock undergoes extreme conditions (high temperature and/or pressure, with or without the use of a catalyst.	– Combustion – Gasification – Hydrothermal upgrading – Pyrolysis – Aqueous Phase Reforming (APR)
Biochemical	Biochemical processes occur at mild conditions (low temperature and pressure) using microorganisms or enzymes.	– Aerobic fermentation – Anaerobic fermentation – Enzymatic processes
Chemical	In chemical processes, well-known chemical reactions take place.	– Esterification – Hydrogenation – Dehydrogenation – Hydration – Dehydration – Dimerization – Oxidation – Reduction – Hydrolysis – Polymerization
Mechanical/physical	In mechanical/physical processes, mechanical or physical treatments of materials are carried out.	– Extraction – Separation – Fractionation – Filtration – Pre-treatment – Milling – Distillation – Crystallisation – Purification



Simple Bioethanol Process Flow Diagram

Feedstock Handling

Corn Stover

Pretreatment

Steam & Acid

S/L Separation

Liquor

Solids

Lime

Enzyme

Conditioning

Steam

Saccharification & Fermentation

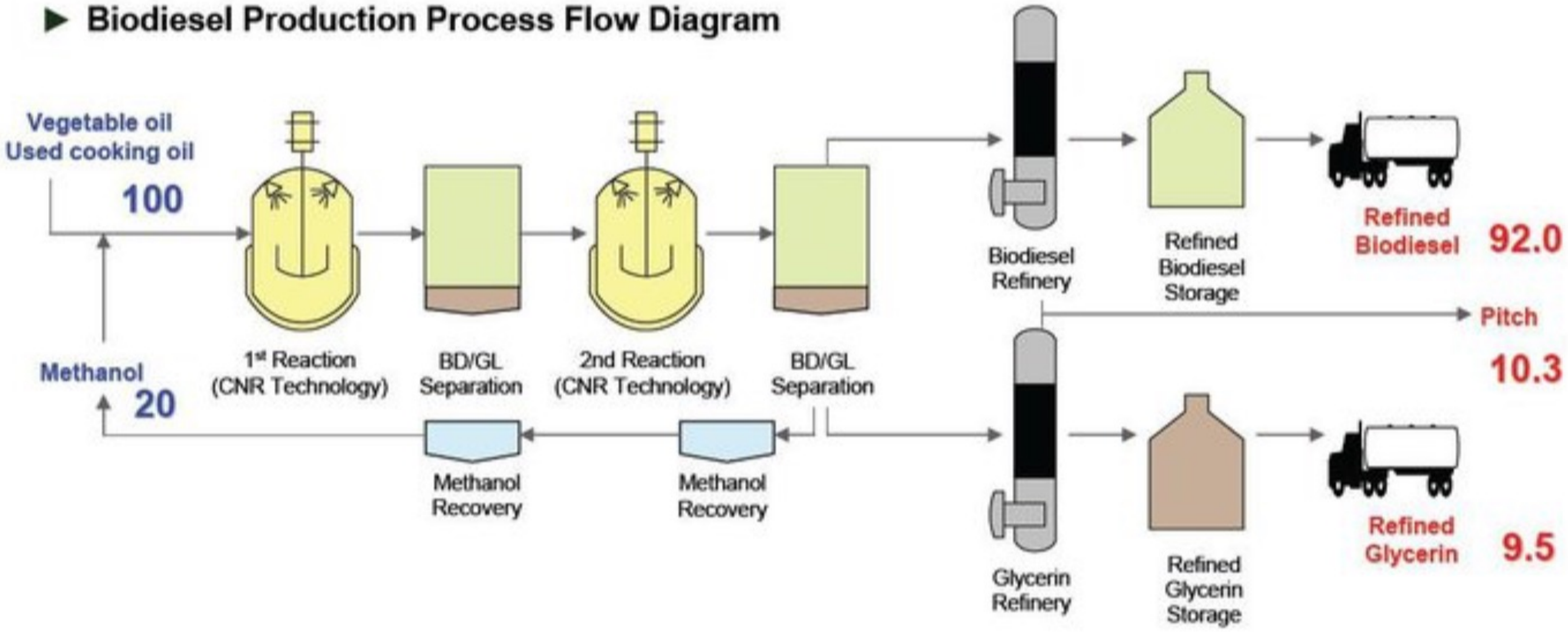
Distillation & Ethanol Purification

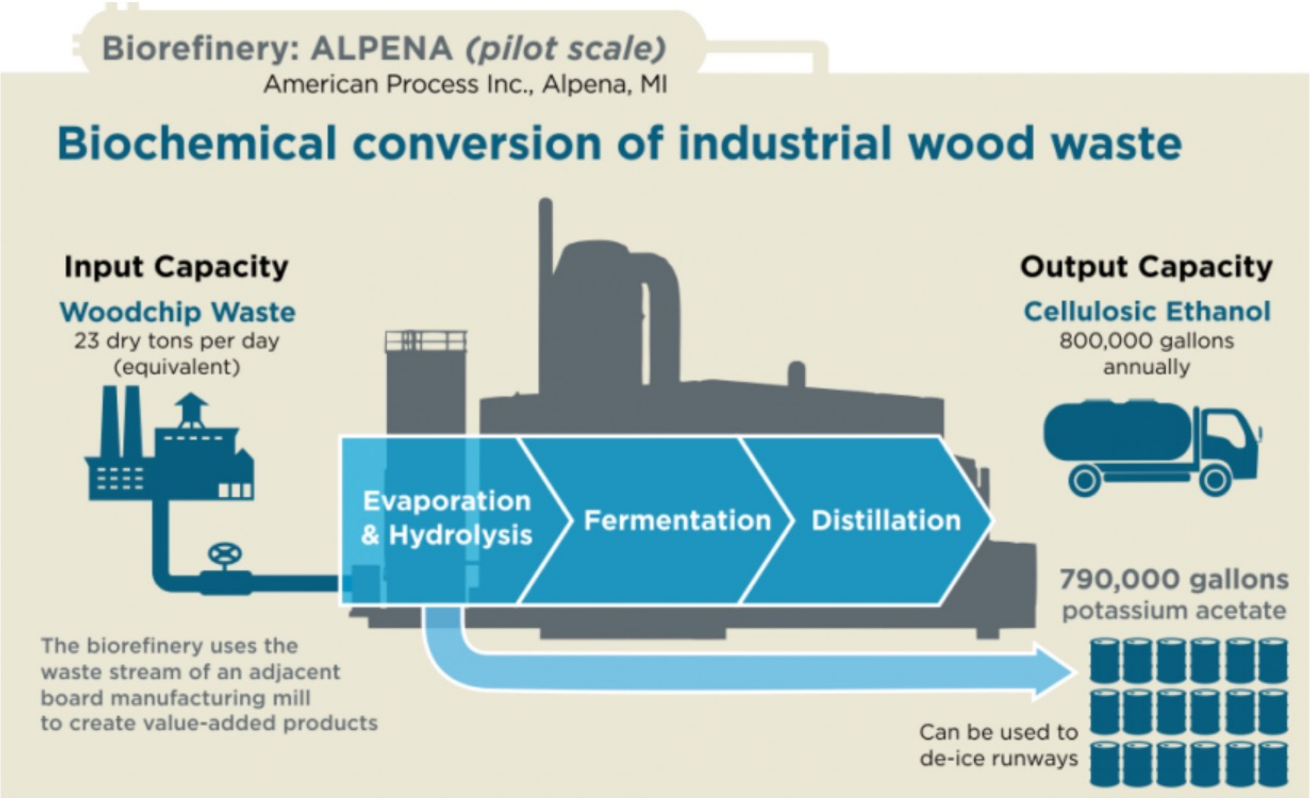
Wastewater Treatment

Lignin Residue

Burner/Boiler Turbogenerator

► Biodiesel Production Process Flow Diagram





Biorefinery: ALPENA *(pilot scale)*

American Process Inc., Alpena, MI

Biochemical conversion of industrial wood waste

Input Capacity

Woodchip Waste

23 dry tons per day
(equivalent)

The biorefinery uses the waste stream of an adjacent board manufacturing mill to create value-added products

Output Capacity

Cellulosic Ethanol

800,000 gallons
annually

790,000 gallons
potassium acetate

Can be used to
de-ice runways

Bio-Based Plastics

– *Bio-based* (or partly bio-based), non-biodegradable plastics, such as bio-based polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) (so-called drop-in solutions)

– Bio-based and *biodegradable plastics*, such as polylactic acid (PLA), polyhydroxyalkanoates (PHA), polybutylene succinate (PBS), and starch blends

– Plastics that are based on fossil resources (*fossil-based*) and biodegradable, such as poly(butylene-*co*-adipate-*co*-terephthalate) (PBAT)

Sugar based
type 3

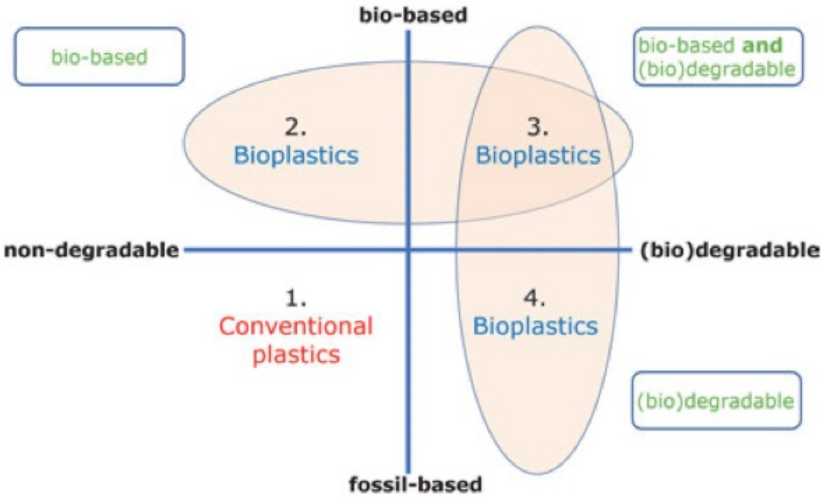
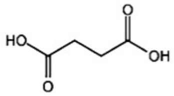
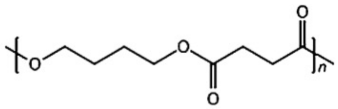
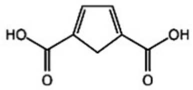
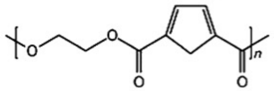
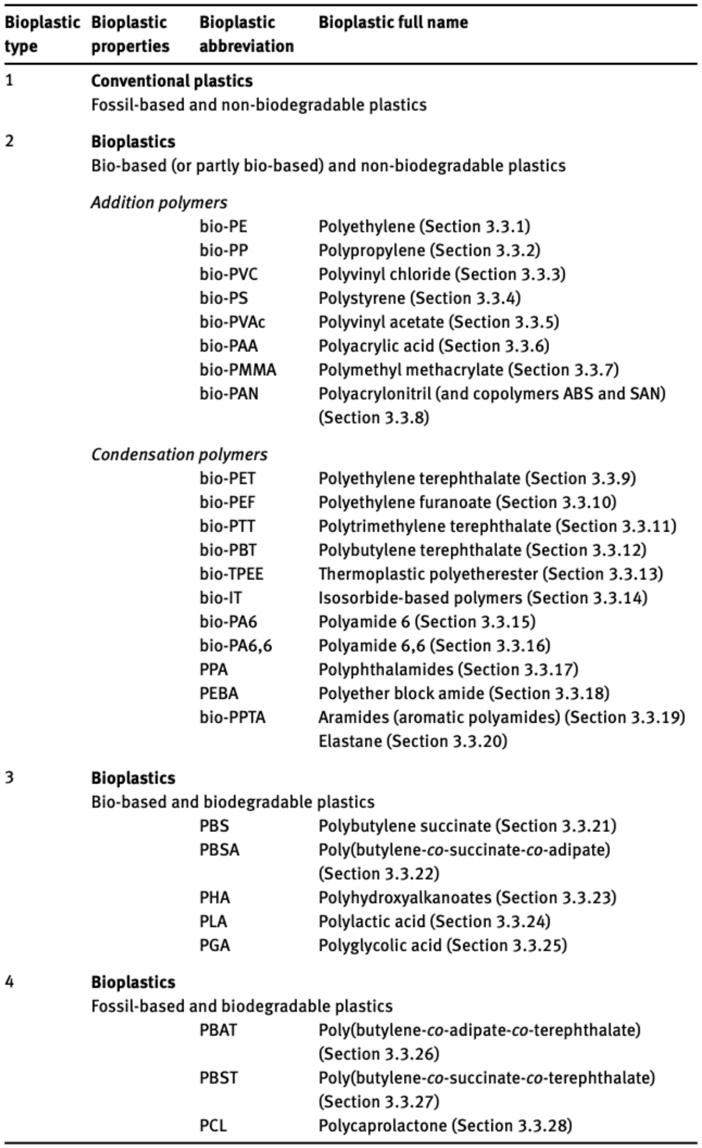
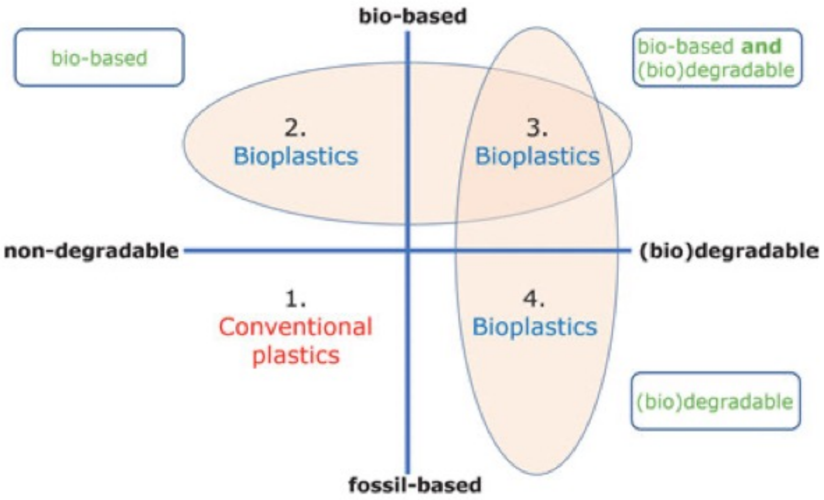


Table 3.3: Polybutylene succinate (PBS) and polyethylene furanoate (PEF).

Monomer	Chemical structure	Polymer	Chemical structure
SA		PBS	
FDCA		PEF	



Bioplastic type	Bioplastic properties	Bioplastic abbreviation	Bioplastic full name
1	**Conventional plastics** Fossil-based and non-biodegradable plastics		
2	**Bioplastics** Bio-based (or partly bio-based) and non-biodegradable plastics		
	Addition polymers		
		bio-PE	Polyethylene (Section 3.3.1)
		bio-PP	Polypropylene (Section 3.3.2)
		bio-PVC	Polyvinyl chloride (Section 3.3.3)
		bio-PS	Polystyrene (Section 3.3.4)
		bio-PVAc	Polyvinyl acetate (Section 3.3.5)
		bio-PAA	Polyacrylic acid (Section 3.3.6)
		bio-PMMA	Polymethyl methacrylate (Section 3.3.7)
		bio-PAN	Polyacrylonitril (and copolymers ABS and SAN) (Section 3.3.8)
	Condensation polymers		
		bio-PET	Polyethylene terephthalate (Section 3.3.9)
		bio-PEF	Polyethylene furanoate (Section 3.3.10)
		bio-PTT	Polytrimethylene terephthalate (Section 3.3.11)
		bio-PBT	Polybutylene terephthalate (Section 3.3.12)
		bio-TPEE	Thermoplastic polyetherester (Section 3.3.13)
		bio-IT	Isosorbide-based polymers (Section 3.3.14)
		bio-PA6	Polyamide 6 (Section 3.3.15)
		bio-PA6,6	Polyamide 6,6 (Section 3.3.16)
		PPA	Polyphthalamides (Section 3.3.17)
		PEBA	Polyether block amide (Section 3.3.18)
		bio-PPTA	Aramides (aromatic polyamides) (Section 3.3.19)
			Elastane (Section 3.3.20)
3	**Bioplastics** Bio-based and biodegradable plastics		
		PBS	Polybutylene succinate (Section 3.3.21)
		PBSA	Poly(butylene-*co*-succinate-*co*-adipate) (Section 3.3.22)
		PHA	Polyhydroxyalkanoates (Section 3.3.23)
		PLA	Polylactic acid (Section 3.3.24)
		PGA	Polyglycolic acid (Section 3.3.25)
4	**Bioplastics** Fossil-based and biodegradable plastics		
		PBAT	Poly(butylene-*co*-adipate-*co*-terephthalate) (Section 3.3.26)
		PBST	Poly(butylene-*co*-succinate-*co*-terephthalate) (Section 3.3.27)
		PCL	Polycaprolactone (Section 3.3.28)



Polyethylene

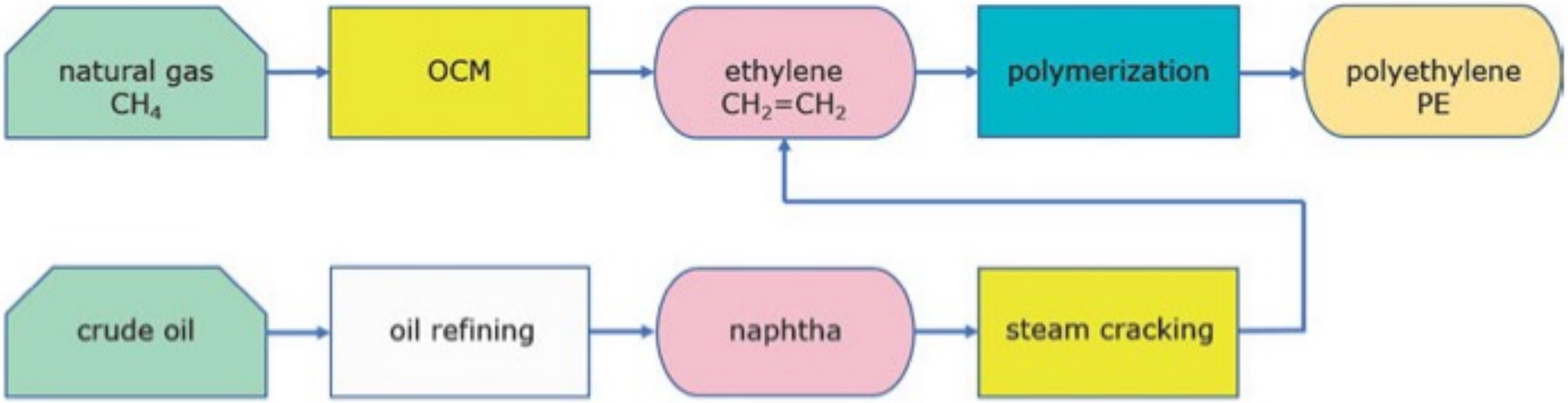
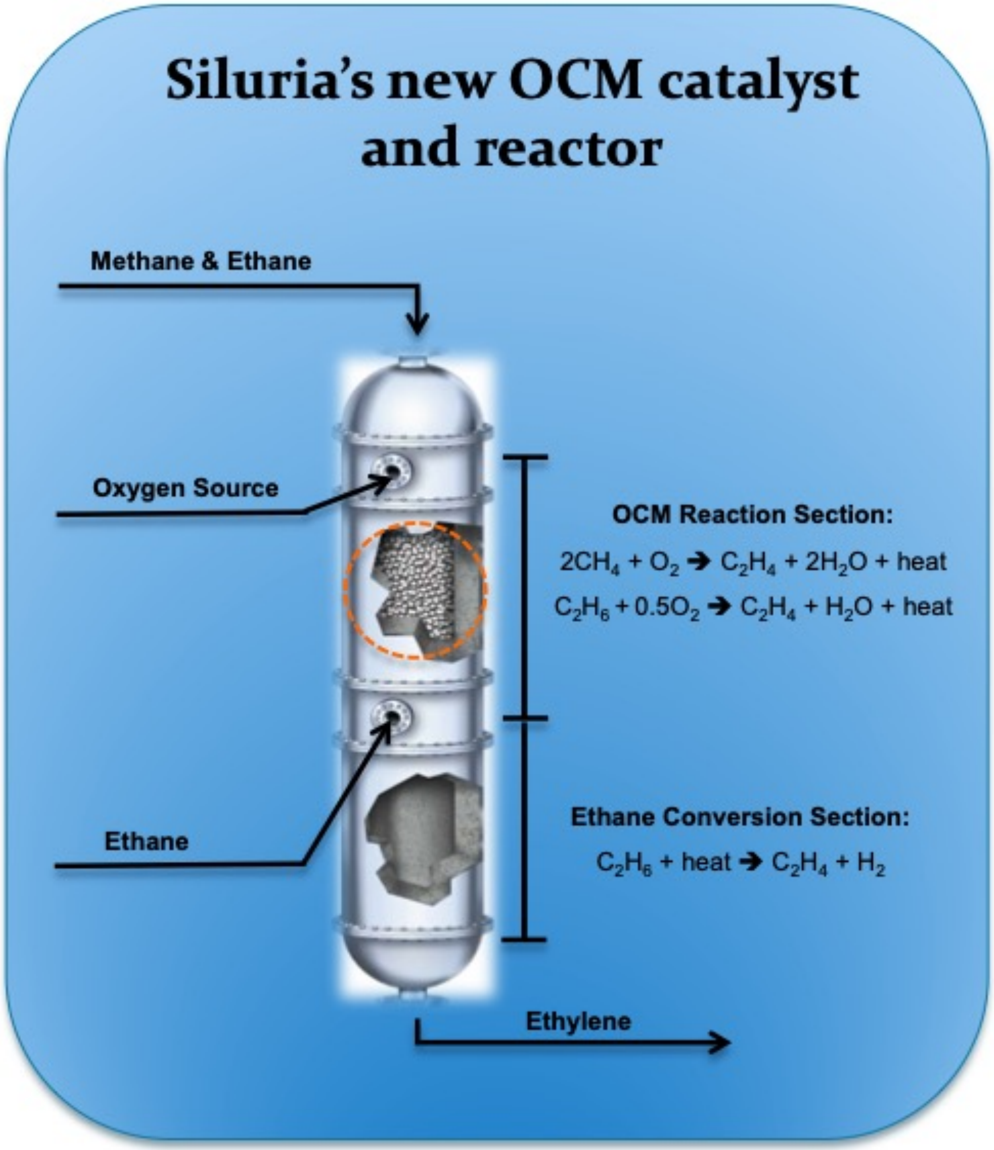


Figure 3.17: Process flow diagram for production of PE.

Oxidative coupling of methane (OCM) uses special developed nanowire OCM catalysts.
The OCM process, also called the Gemini technology, was developed by Siluria Technologies.



Siluria's new OCM catalyst and reactor

OCM Reaction Section:

$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O + \text{heat}$

$C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O + \text{heat}$

Ethane Conversion Section:

$C_2H_6 + \text{heat} \rightarrow C_2H_4 + H_2$

Process starts with methane to produce ethylene

NGL Supply Map- New Sources are Physically Removed from Demand

Source: EPRINC

Bio-Based Polyethylene (Bio-PE)

Dehydrate bio-ethanol (bio-based ethanol, CH_3CH_2OH) to bio-based ethylene ($CH_2=CH_2$) and subsequently polymerizing bio-based ethylene into *bio-based polyethylene* (bio-PE).

1G feedstocks: 85% or bioethanol comes from sugar cane (in Brazil) or corn starch (in USA).

2G feedstocks: Lignocellulose. Low-cost crop and forest residues, wood process waste, and the organic fraction of municipal solid waste can all be used as lignocellulosic feedstocks

Ethylene from lignocellulose by 2 methods: 1) biochemical route and 2) acid hydrolysis route

Lignocellulose to ethylene

Biochemical route:
Enzymes and micro-organisms convert cellulose or hemicellulose to complex sugars.

- Saccharification: A cellulase enzyme breaks down the cellulose molecule into monosaccharides such as glucose, or shorter polysaccharides and oligosaccharides.
- Because cellulose molecules bind strongly to each other, cellulose breakdown is relatively difficult compared to the breakdown of other polysaccharides such as starch.
- The sugars are further fermented to produce bio-ethanol.

Acid hydrolysis route:

- Lignocellulosic feedstock is pretreated and,
- Subsequently, acid hydrolysis (using either dilute acid or concentrated acid) breaks down cellulose to glucose,
- Fermentation to produce bio-ethanol.

- Yeasts are added to convert the sugars to bio-ethanol,
- which is then distilled off to obtain bio-ethanol up to 96 % in purity.
- One glucose molecule ($C_6H_{12}O_6$) is fermented into two molecules of bio-ethanol (CH_3CH_2OH) and two molecules of carbon dioxide (CO_2)

POET-DSM Advanced Biofuels Project LIBERTY

- First commercial scale demonstration of technology
- Currently being constructed in Emmetsburg, Iowa
- DSM and POET 50% share
- Total investment $250 million
- Designed to produce more than 20 million gallons
- Replicate technology throughout POET’s existing network of 27 corn ethanol plants

PROJECT UNDER CONSTRUCTION

ABENGOA BIOENERGY

Using an innovative process, Abengoa Bioenergy's cellulosic ethanol plant will convert non-edible crop residue into clean fuel.

U.S. DEPARTMENT OF ENERGY LOAN PROGRAMS OFFICE

INVESTING *in* AMERICAN ENERGY

PROJECT SUMMARY

In September 2011, the Department of Energy issued a $132.4 million loan guarantee to finance Abengoa Bioenergy Biomass of Kansas (ABBK), one of the first commercial-scale biofuel plants in the United States, located about 90 miles southwest of Dodge City, Kansas.

- In 2015, DuPont Industrial Biosciences opened the doors to the largest cellulosic ethanol plant in the world.
- The DuPont biorefinery, located in Nevada, Iowa (USA), is powered by corn stover and produces 115 million liters of bio-ethanol a year.
- By the end of 2018, it was announced that the German-based firm VERBIO acquired DuPont’s cellulosic 2G bio- ethanol plant and a portion of its corn stover inventory.
- VERBIO installed additional facilities to produce renewable natural gas (RNG) made from corn stover and other cellulosic crop residues at the site.
- VERBIO has two other cellulosic 2G bio-ethanol production facilities in Schwedt (Germany) and in Pinnow (Germany).

Generations 1 and 2 bio-ethanol
Route 2 Acid hydrolysis
Route 1 Biochemical

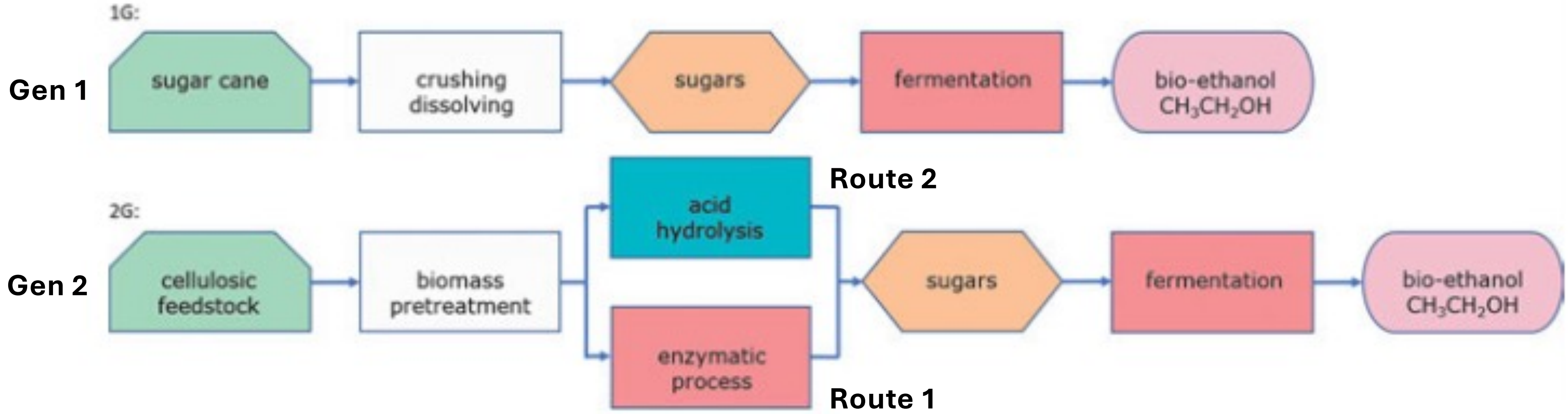


Figure 3.19: Process flow diagram for production of bio-ethanol (route 1).

Generation 1 Bio-Plastics

Braskem (Brazil) 200,000 metric tons a year

30 bio-based HDPE, LDPE, and LLDPE grades

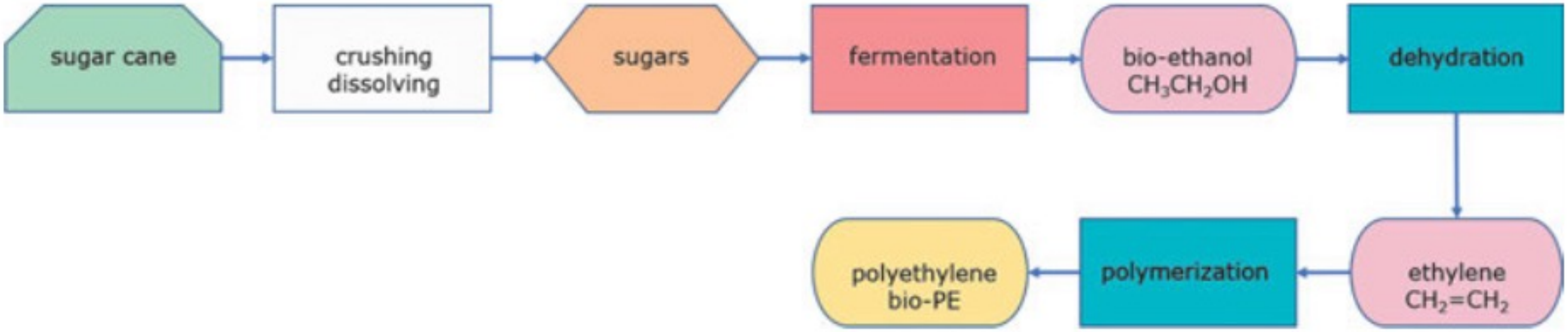


Figure 3.21: Process flow diagram for production of bio-PE.

Tetra Rex® cartons from Tetra Pak
Danone with Activia
Proctor and Gamble Pantene bottles.
LEGO Group “botanical” elements range, prepared from Braskem’s I’m GreenTM bio-PE

Generation 2 bio-ethanol
Acid Hydrolysis Route 2

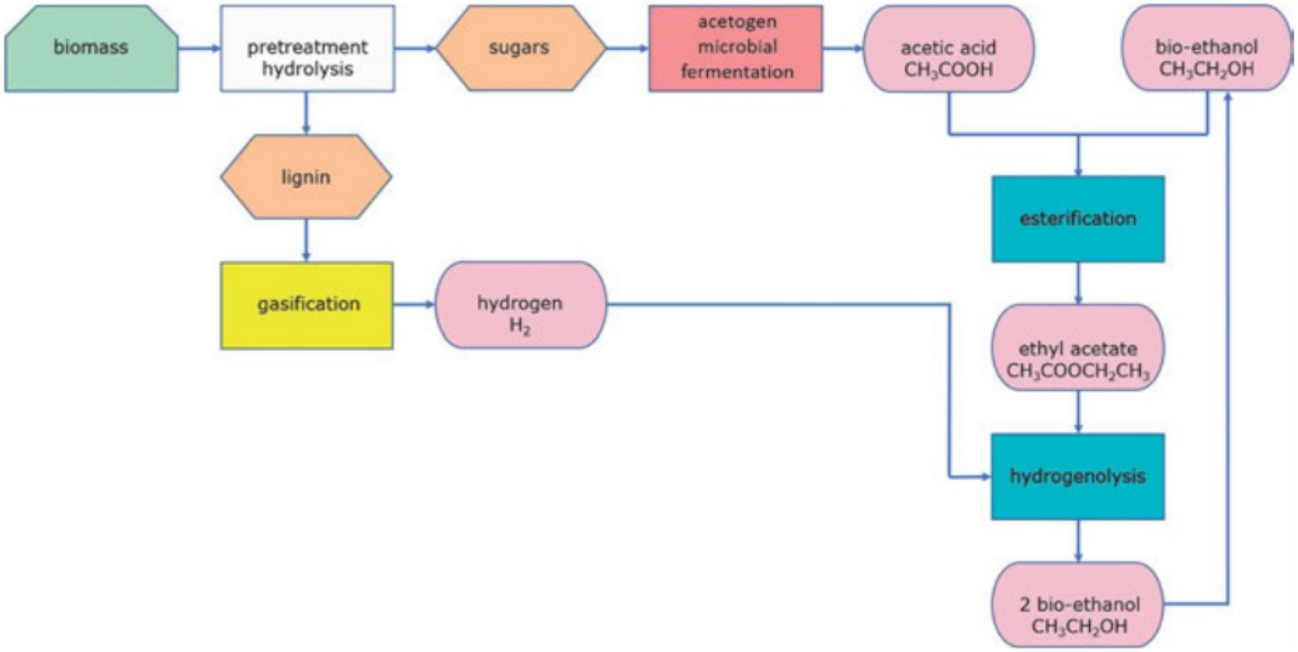
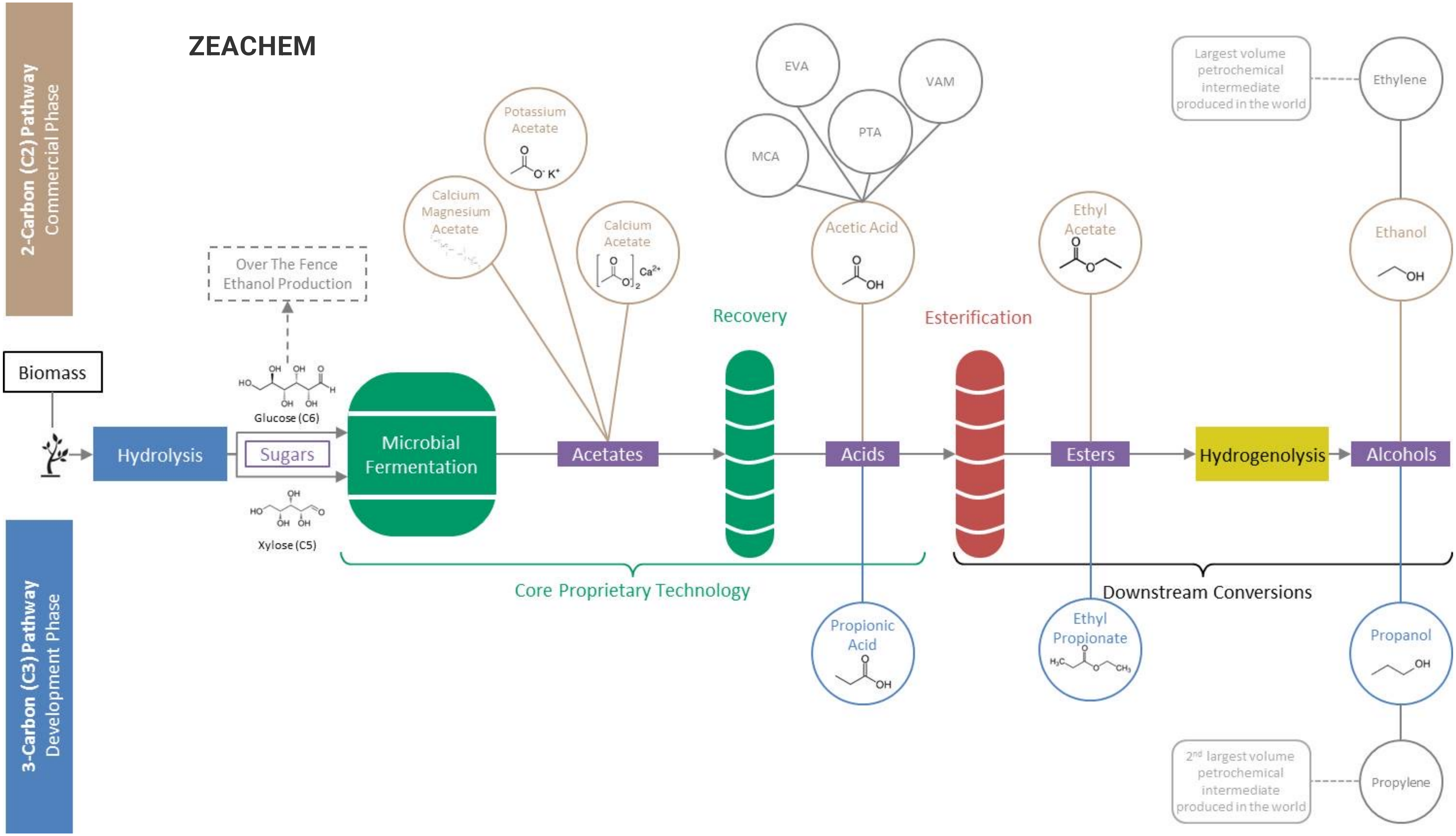


Figure 3.20: Process flow diagram for production of bio-ethanol via Zea2 LLC technology (route 2).

ZEACHEM



2-Carbon (C2) Pathway
Commercial Phase

3-Carbon (C3) Pathway
Development Phase

Biomass

Hydrolysis

Sugars

Glucose (C6)

Xylose (C5)

Over The Fence
Ethanol Production

Microbial
Fermentation

Acetates

Calcium
Magnesium
Acetate

Potassium
Acetate

Calcium
Acetate

Recovery

Acids

Acetic Acid

MCA

EVA

PTA

VAM

Propionic
Acid

Core Proprietary Technology

Esterification

Esters

Ethyl
Acetate

Ethyl
Propionate

Hydrogenolysis

Alcohols

Ethanol

Ethylene

Largest volume
petrochemical
intermediate
produced in the world

Propanol

Propylene

2^{nd} largest volume
petrochemical
intermediate
produced in the world

Downstream Conversions

Bio-Based Polypropylene

Since 2019, the Finnish group Neste has been providing its partners LyondellBasell in Wesseling (D) and Borealis in Kallo and Beringen (B) with so-called “bio-naphtha” (hydrogenated vegetable oils, largely from used fats or non-food oils).

LyondellBasell offers potential customers an approx. 30% bio-based PP variant produced from this (scale: 5-10 kt per year).

Borealis launched a PP containing a percentage of bio-based materials at the end of 2019.

Bio-based percentages of up to about 75% are possible.

A significant price premium (in the order of 50–100%).

Bio-Based Polypropylene

Mitsui's process, Route 1

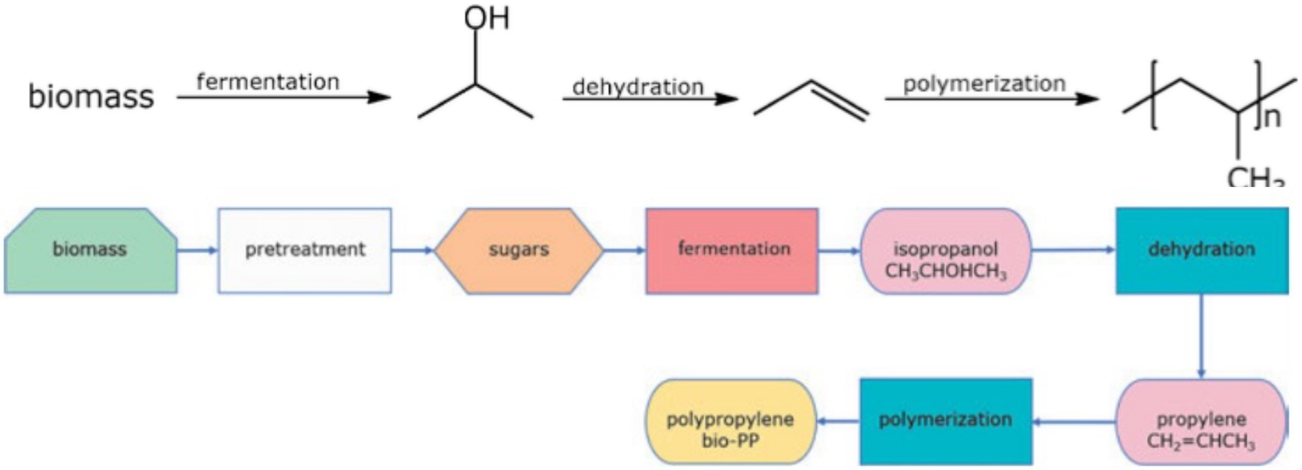


Figure 3.24: Process flow diagram for production of bio-PP (route 1).

Bio-Based Polypropylene

Braskem Process

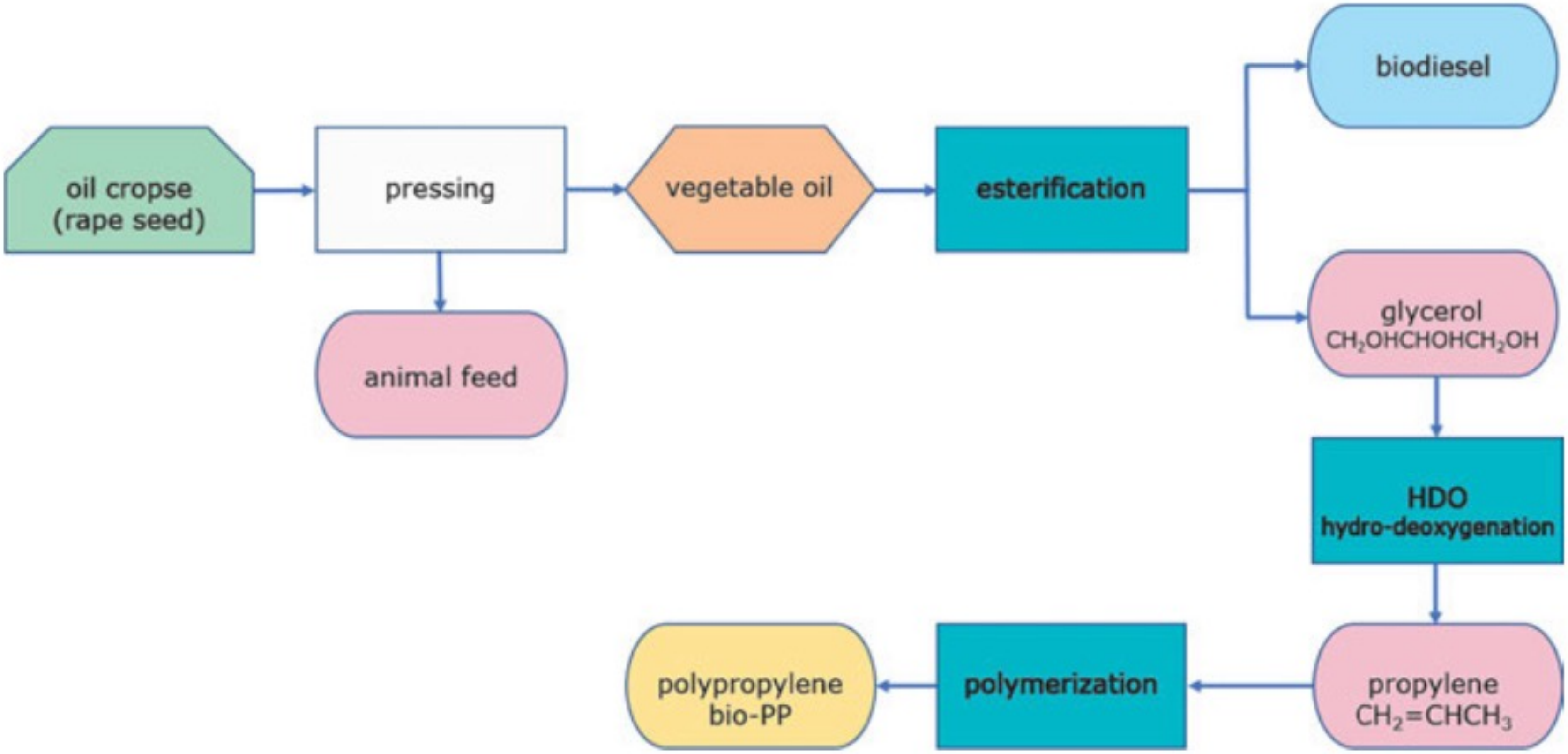


Figure 3.26: Process flow diagram for the production of bio-PP (route 2).

Bio-Based Polypropylene

Lyondell Basell and Neste bio-PP and bio-PE.
Food packaging marketed under the brand names CirculenTM and Circulen PlusTM, the new family of Lyondell Basell circular economy product brands.

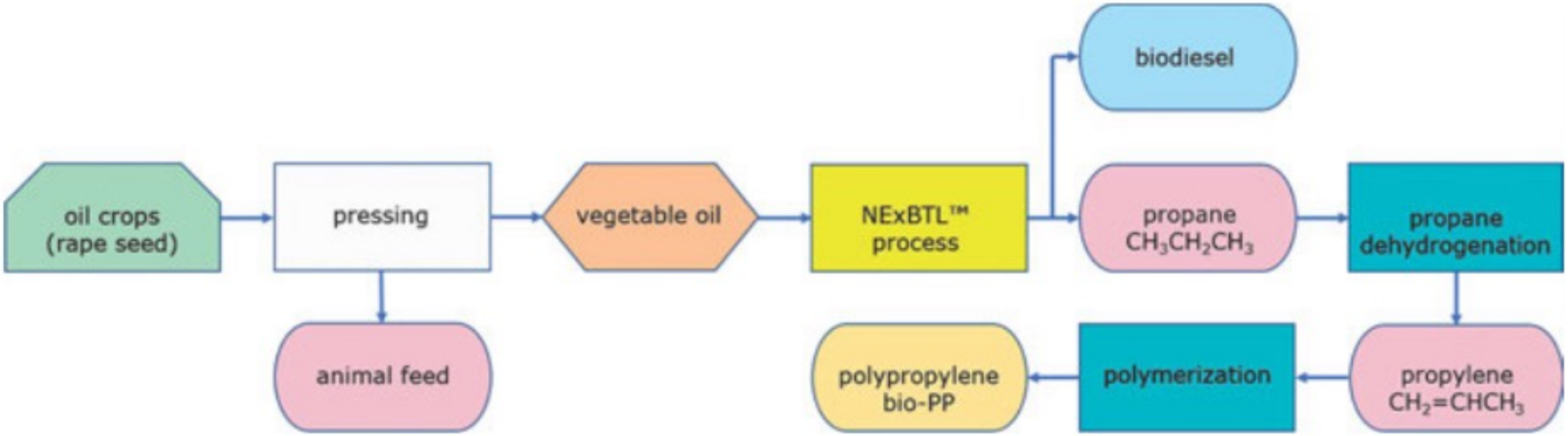


Figure 3.27: Process flow diagram for production of bio-PP (route 3).

Bio-Based Polypropylene

Cathay Industrial Biotech

Cobalt Technologies, Butamax Advanced Biofuels, Metabolic Explorer, Eastman Renewable Materials

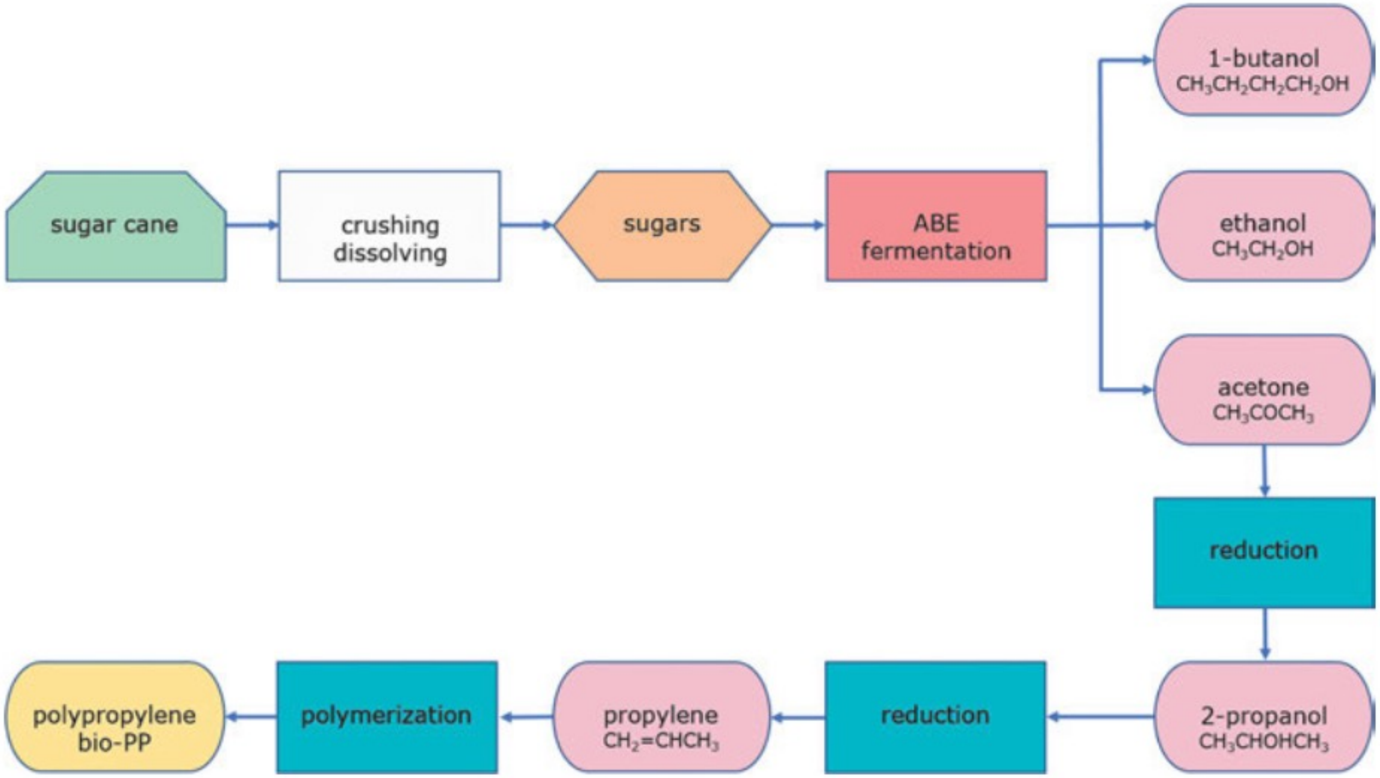


Figure 3.28: IEA process flow diagram for the production of bio-PP (route 4).

Bio-Based Polypropylene

Olefin metathesis can also be applied to produce bio-based propylene, starting from both bio-based ethylene ($CH_2{=}CH_2$) and 2-butylene ($CH_3CH{=}CHCH_3$).

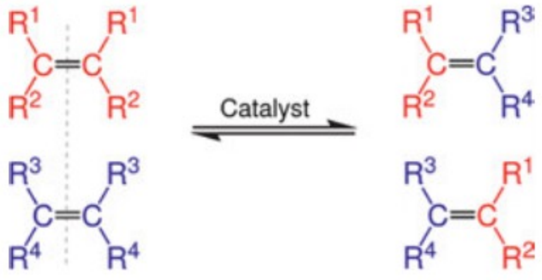


Figure 3.29: Olefin metathesis: Metathesis of ethylene and 2-butylene (R^1, R^2, and R^3 are -H, and R^4 is $-CH_3$) results in 2 molecules of propylene.

In the process, bio-based ethylene is obtained from sugar fermentation. Bio-based 2-butylene can be produced from bio-based ethylene, via dimerization into 1-butylene and subsequent isomerization into 2-butylene.

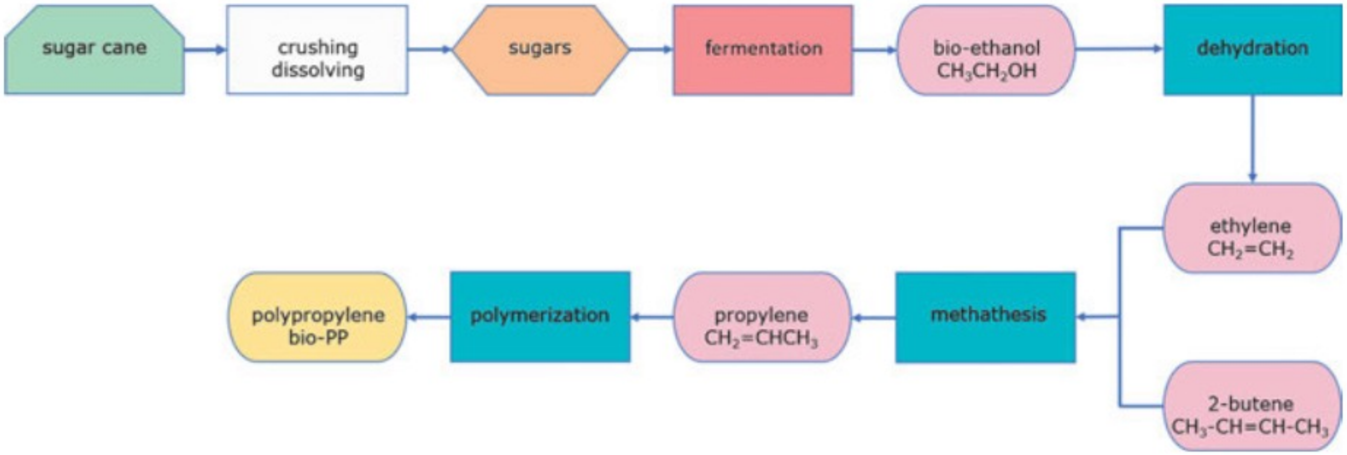


Figure 3.30: Process flow diagram for the production of bio-PP (route 5).

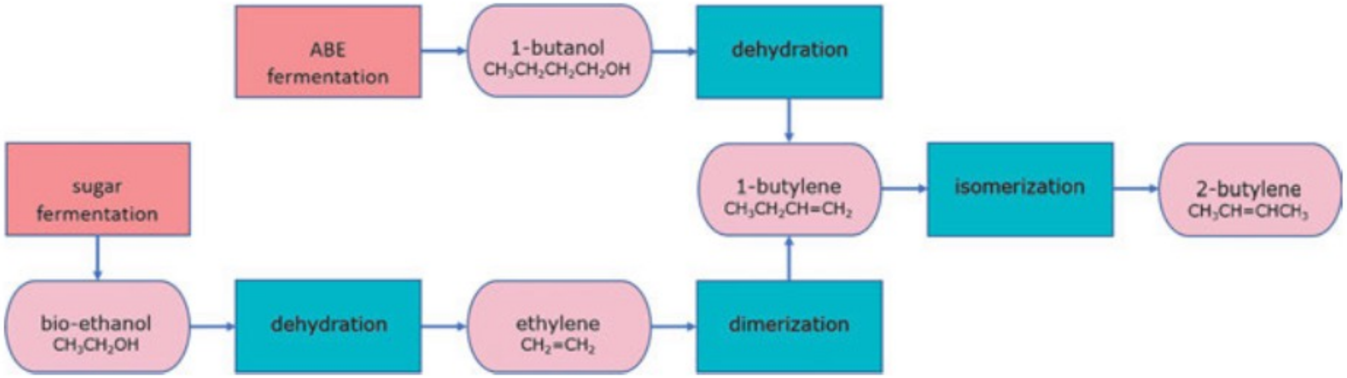


Figure 3.31: Process flow diagram for the production of 2-butylene.

Bio-Based Polypropylene

France-based Global Bioenergies (GBE) announced a process for the direct conversion of glucose to propylene using bioengineered bacteria.

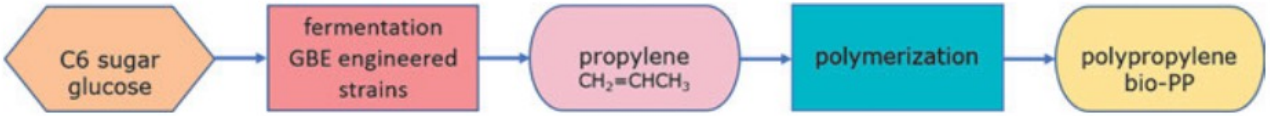


Figure 3.32: Process flow diagram for the production of bio-PP (route 6).

Bio-Based PVC

Inovyn “bio-attributed” PVC tradename BiovynTM.

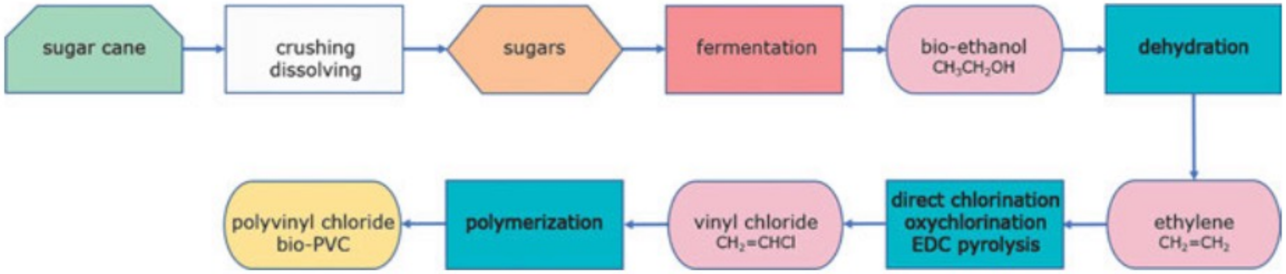


Figure 3.36: Process flow diagram for production of bio-PVC.

- Chlorine (Cl_2) and ethylene ($CH_2{=}CH_2$) are used to produce 1,2-dichloroethane (ClCH2CH2Cl)
- Oxychlorination process ethylene reacts with hydrogen chloride (HCl) and oxygen to form 1,2-dichloroethane.
- 1,2-Dichloroethane converted to vinyl chloride by thermal cracking (EDC *pyrolysis*)
- The hydrogen chloride (HCl) by-product can be recycled to the oxychlorination plant.

Bio-Based PVC

Inovyn bio-PVC is part of INEOS which has this statement on their webpage.

Several INEOS businesses continue to substitute fossil-based raw materials with recycled and bio-based feedstocks at commercial scale.

For example, at our olefins plant in Cologne (Germany), biomass co-produced by the wood pulping industry has been successfully converted into bio-olefins. Similarly, our Inovyn plant in Tavaux (France) is producing bio-attributed epichlorohydrin (REODRINTM) from renewable feedstocks that do not compete with the food chain, reducing GHG emissions by up to 70% compared to the fossil-based equivalent. INEOS has also started producing commodity chemicals, such as phenol, acetone, styrene, and PVC, with bio-based feedstocks. INEOS' bio-attributed products can be made with 100% substitution of bio-feedstock on a mass-balance basis and provide significant GHG savings in the value chains of our products. It results in products which have a proven positive impact on the environment without sacrificing product performance.

Using alternative feedstocks can also have a positive impact on INEOS' emissions from its operations by reducing non-biogenic emissions released from chemical reactions or when process steps can be avoided by using more refined or recycled feedstocks. This is why the use of alternative feedstocks is included in our 2030 roadmaps, even if the impact of this pathway on scope 1 and scope 2 emissions is modest.

Fossil-Based Polystyrene

Route 1

Ddehydrogenation of ethylbenzene produced on a large scale by combining benzene (C_6H_6) and ethylene ($CH_2=CH_2$) in an acid-catalyzed chemical reaction.

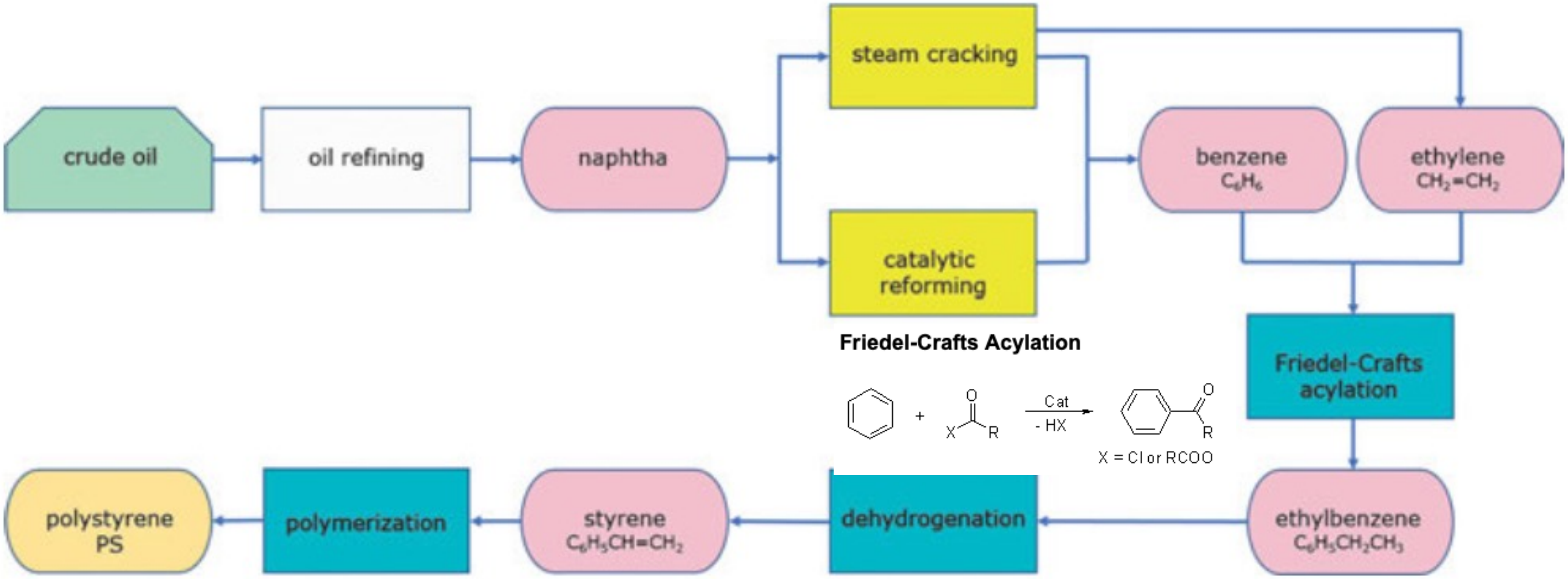


Figure 3.37: Process flow diagram for the production of PS (route 1).

Fossil-Based Polystyrene

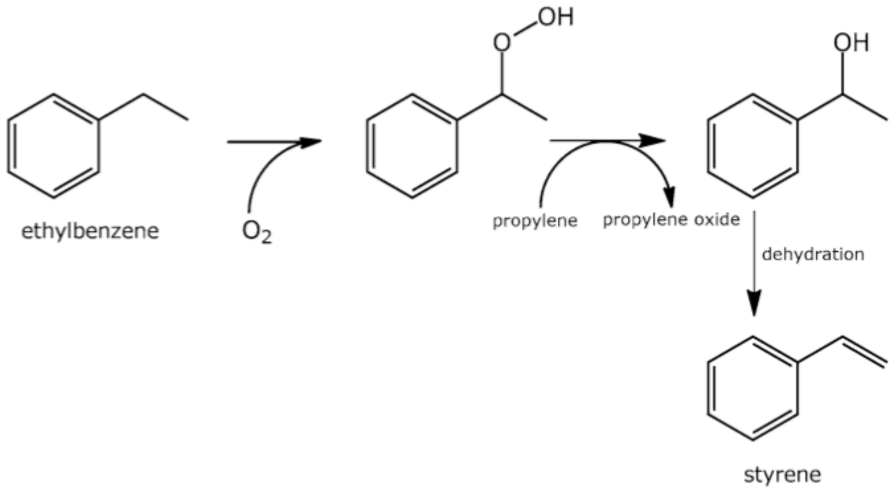


Figure 3.38: POSM and SM/PO processes.

Route 2
Propylene oxide— styrene monomer (POSM, Lyondell Chemical Company) or styrene monomer/propylene oxide (SM/PO) (Shell). Ethylbenzene ($C_6H_5CH_2CH_3$) is treated with oxygen (O2) to form the ethylbenzene hydroperoxide. This hydroperoxide is then used to oxidize propylene (CH2=CHCH3) to propylene oxide. The resulting 1-phenylethanol is dehydrated to give styrene

Fossil-Based Polystyrene

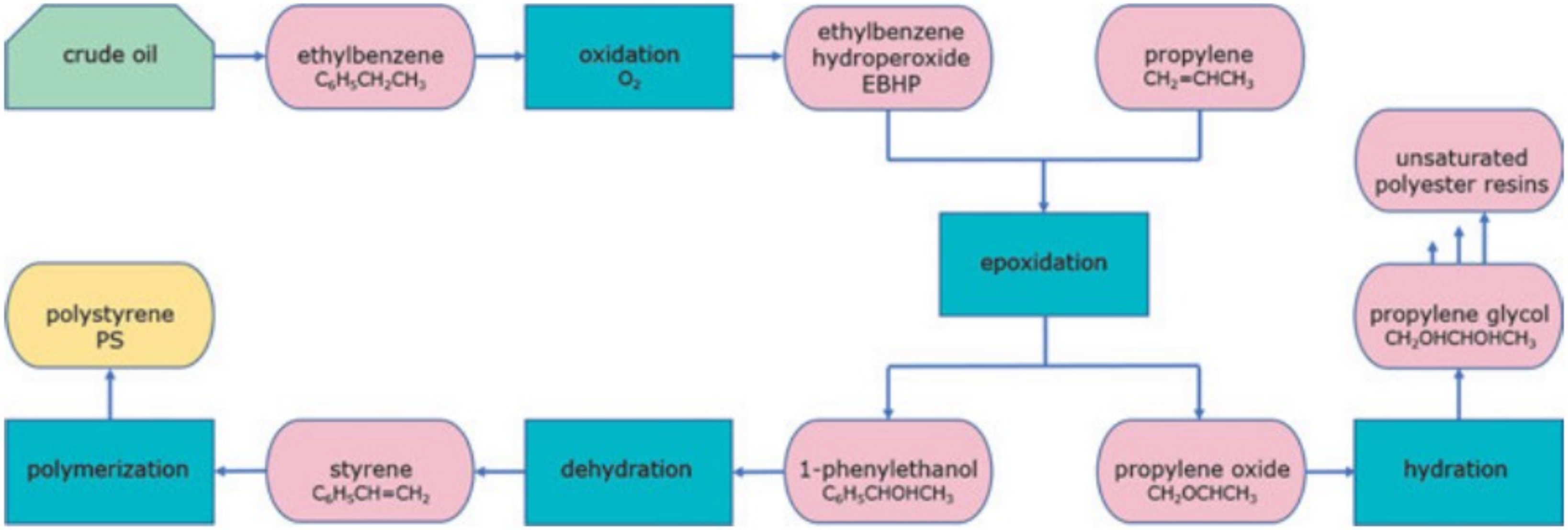


Figure 3.39: Process flow diagram for the production of PS (route 2).

Route 2

Propylene oxide— styrene monomer (POSM, Lyondell Chemical Company) or styrene monomer/propylene oxide (SM/PO) (Shell). Ethylbenzene ($C_6H_5CH_2CH_3$) is treated with oxygen (O2) to form the ethylbenzene hydroperoxide. This hydroperoxide is then used to oxidize propylene (CH2=CHCH3) to propylene oxide. The resulting 1-phenylethanol is dehydrated to give styrene

Bio-Based Polystyrene

Dow Chemical Proposed Route

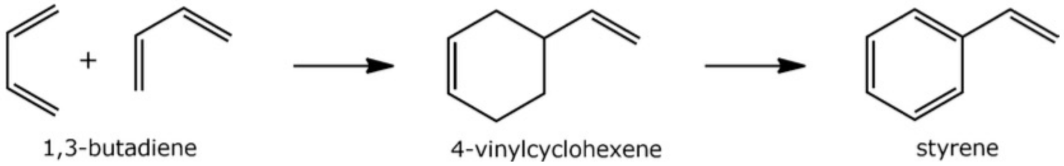


Figure 3.40: Diels–Alder cyclic dimerization of 1,3-butadiene.

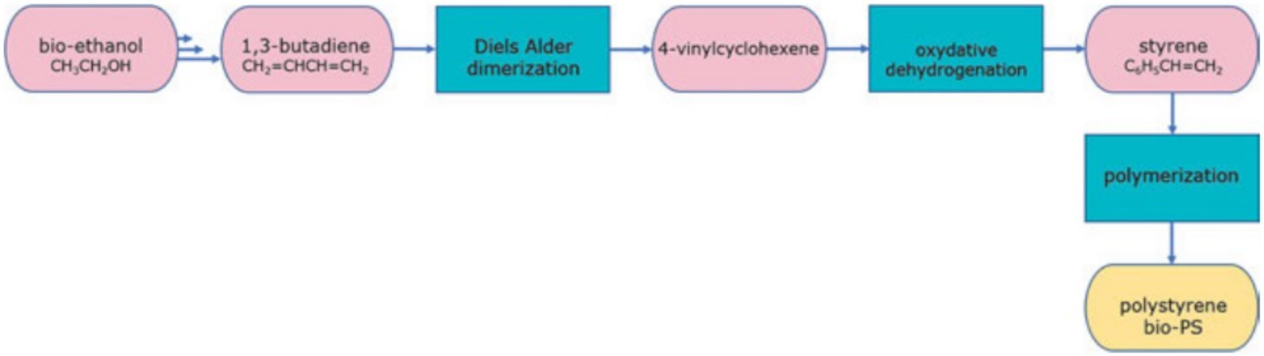


Figure 3.41: Process flow diagram for production of bio-PS (route 1).

Bio-Based Polystyrene

Dutch BioBTX Company

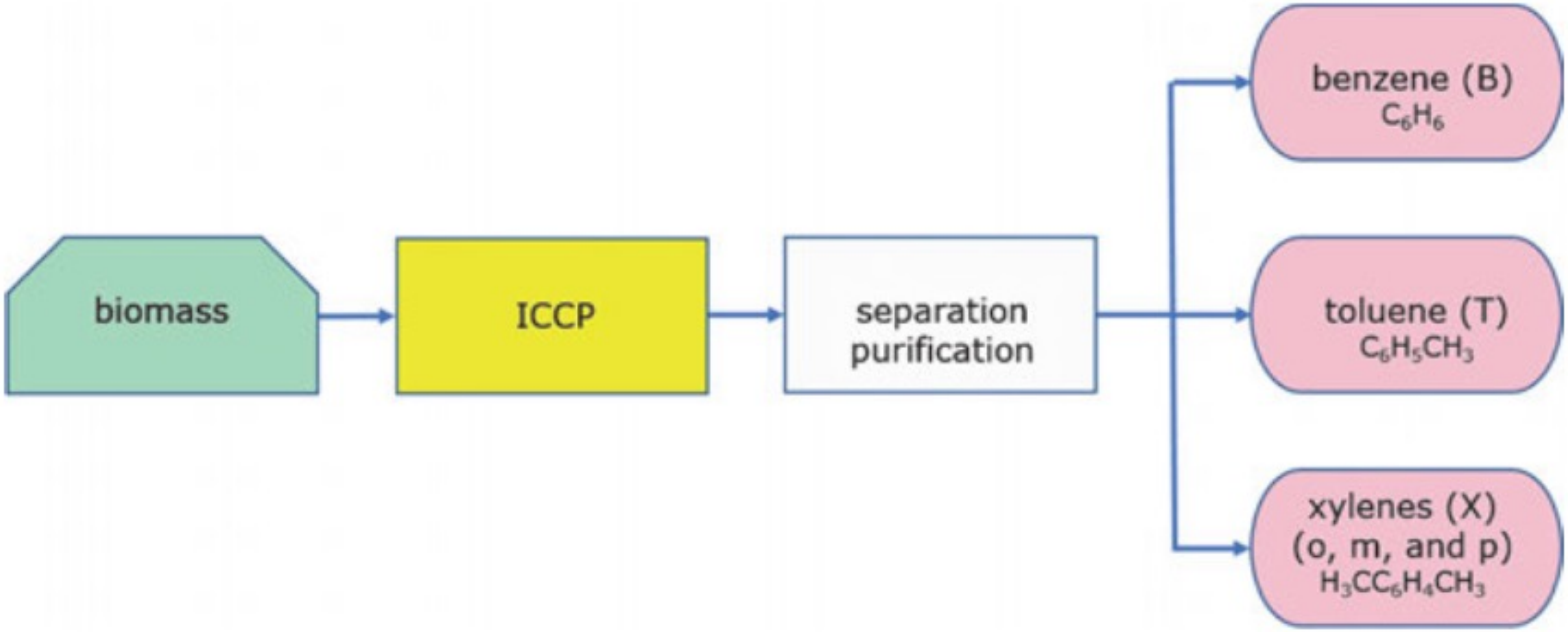


Figure 3.42: Process flow diagram for production of bio-BTX.

Bio-Based Polystyrene

Dutch BioBTX Company

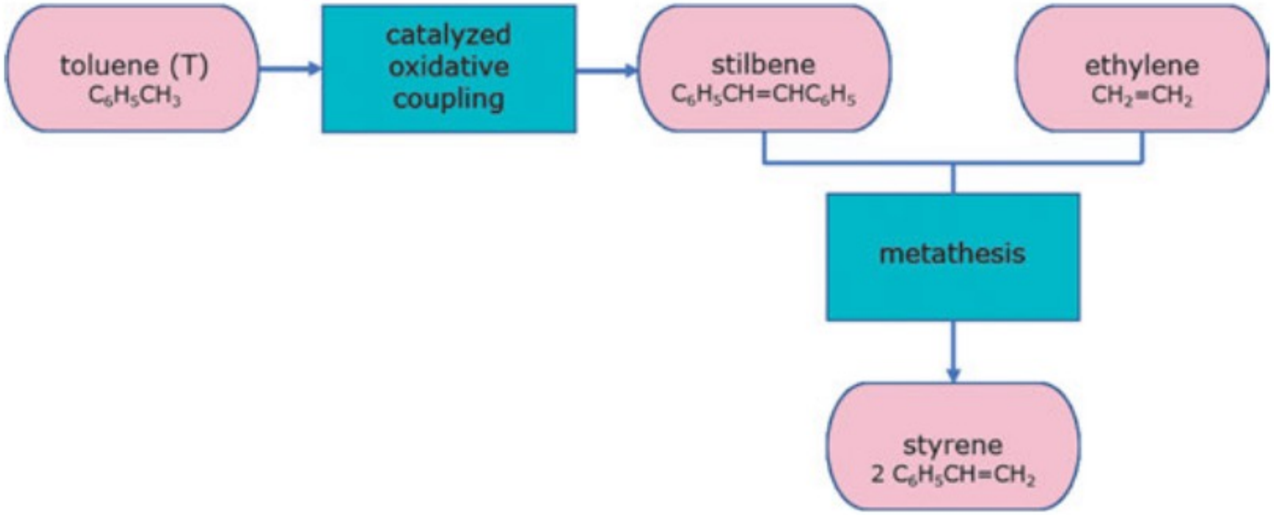


Figure 3.43: Process flow diagram for the production of bio-based styrene.

Bio-Based Polystyrene

Dutch BioBTX Company

Bio-based benzene can be used, together with bio-based ethylene (from bio- ethanol), to produce in a Friedel-Crafts acylation bio-based ethylbenzene. Ethylbenzene can be dehydrogenated to bio-based styrene. The resulting bio-based styrene could be the basis for bio-based polystyrene (bio-PS).

Xylene or dimethylbenzene is any one of three isomers of dimethylbenzene. Xylene exists in three isomeric forms. The isomers can be distinguished by the designations *ortho*- (o-), *meta*- (m-) and *para*- (p-), which specify to which carbon atoms (of

Aside: Bio-Based PET from BioBTX

Dutch BioBTX Company

Xylene or dimethylbenzene is any one of three isomers of dimethylbenzene. Xylene exists in three isomeric forms. The isomers can be distinguished by the designations *ortho*- (o-), *meta*- (m-) and *para*- (p-), which specify to which carbon atoms (of the benzene ring) the two methyl groups are attached. On industrial scale, xylenes are produced by methylation of toluene, and benzene. *p*-Xylene is the principal pre- cursor to terephthalic acid and dimethyl terephthalate, both monomers used in the production of polyethylene terephthalate (PET). *o*-Xylene is an important precursor to phthalic anhydride.

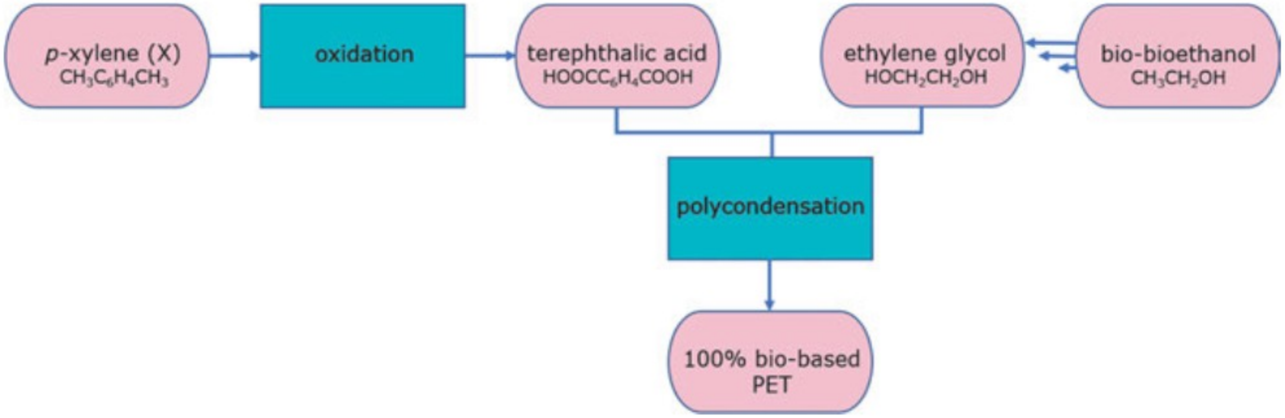


Figure 3.44: Process flow diagram for the production of bio-PET.

Bio-Based Polystyrene

Microorganisms are utilized for the production of styrene. Phenylalanine, an essential α-amino acid, is produced by a fermentation process that use glucose or sucrose as the carbon source using specially engineered micro-organisms for the biotransformation.

For example, L-phenylalanine can be produced from glucose via the glycolysis pathway and the subsequent shikimate pathway. In the *glycolysis* pathway, glucose is converted into pyruvate (CH_3COCOO^-).

The shikimate pathway (shikimic acid pathway) is a seven-step metabolic pathway for the biosynthesis of aromatic amino acids (such as L-phenylalanine). Subsequently, a co-culture system can be used consisting of L-phenylalanine ammonia lyase (PAL, wherein NH3 is released) and phenylacrylic acid decarboxylase (FDC1, wherein CO2 is released).

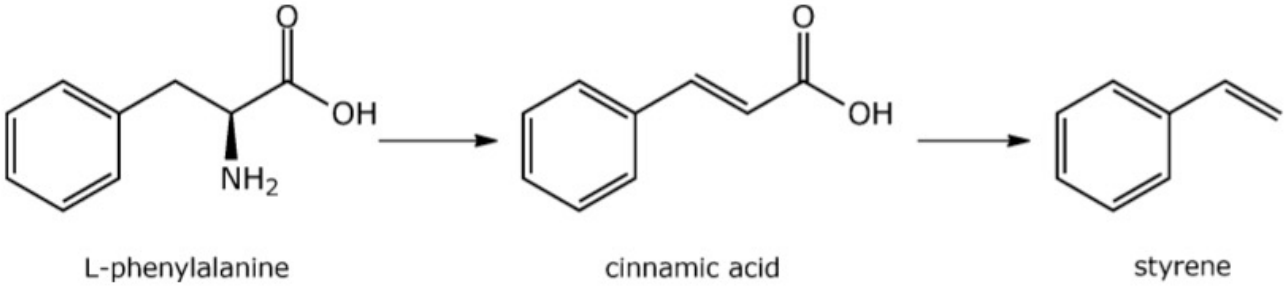


Figure 3.45: Synthesis of styrene from L-phenylalanine.

Bio-Based Polystyrene

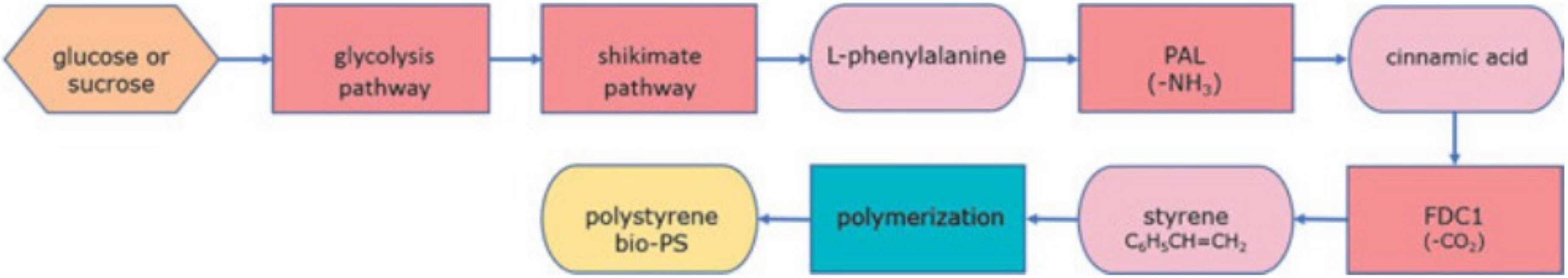


Figure 3.46: Process flow diagram for the production of bio-PS (route 3).

Fossil-Based Polyvinylacetate (PVAc)/Polyvinyl alcohol (PVA) /Polyethylenevinylacetate (EVAc)

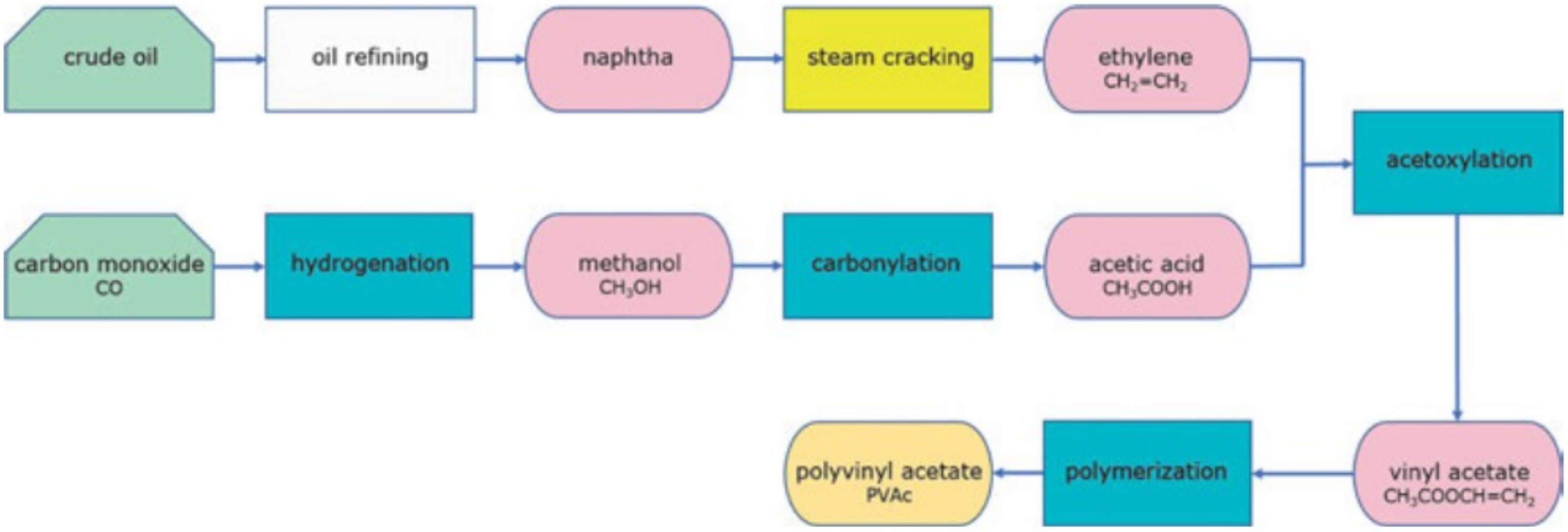


Figure 3.47: Process flow diagram for production of PVAc.

Fossil-Based Polyvinylacetate (PVAc)/Polyvinyl alcohol (PVA) /Polyethylenevinylacetate (EVAc)

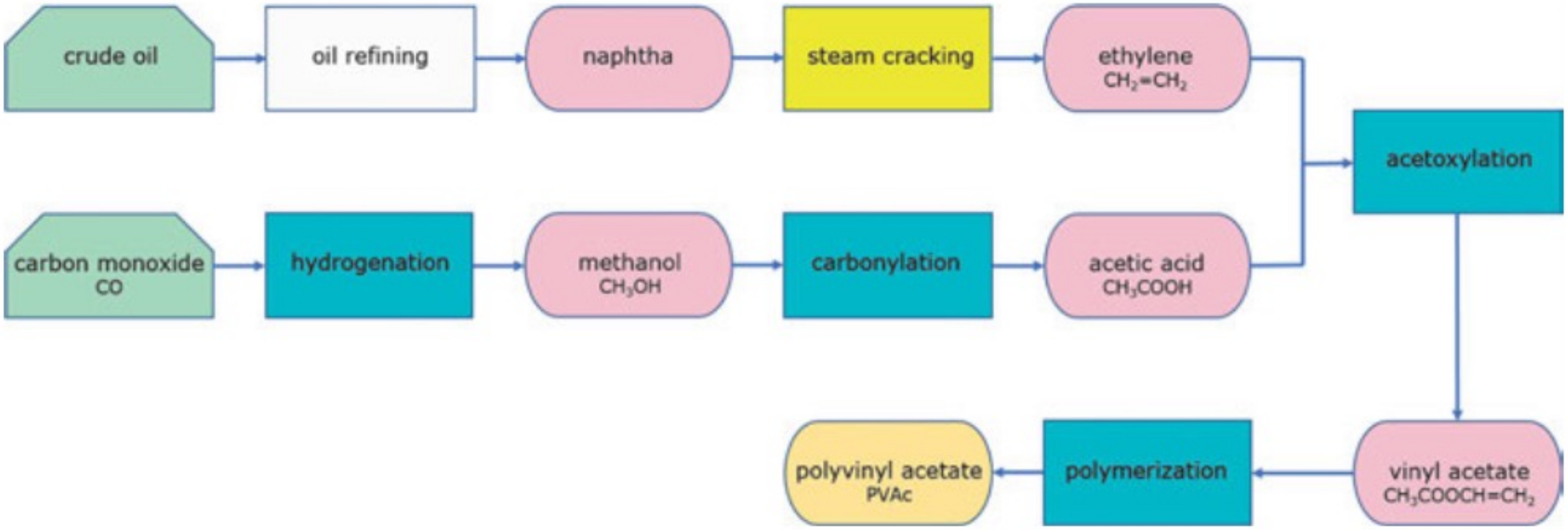


Figure 3.47: Process flow diagram for production of PVAc.

Polyvinylacetate can be hydrolyzed to polyvinyl alcohol (PVA)

Sometimes, a base-catalyzed transesterification with ethanol (CH_3CH_2OH) produces PVA and ethyl acetate ($CH_3COOCH_2CH_3$)

Fossil-Based Polyvinylacetate (PVAc)/Polyvinyl alcohol (PVA) /Polyethylenevinylacetate (EVAc)

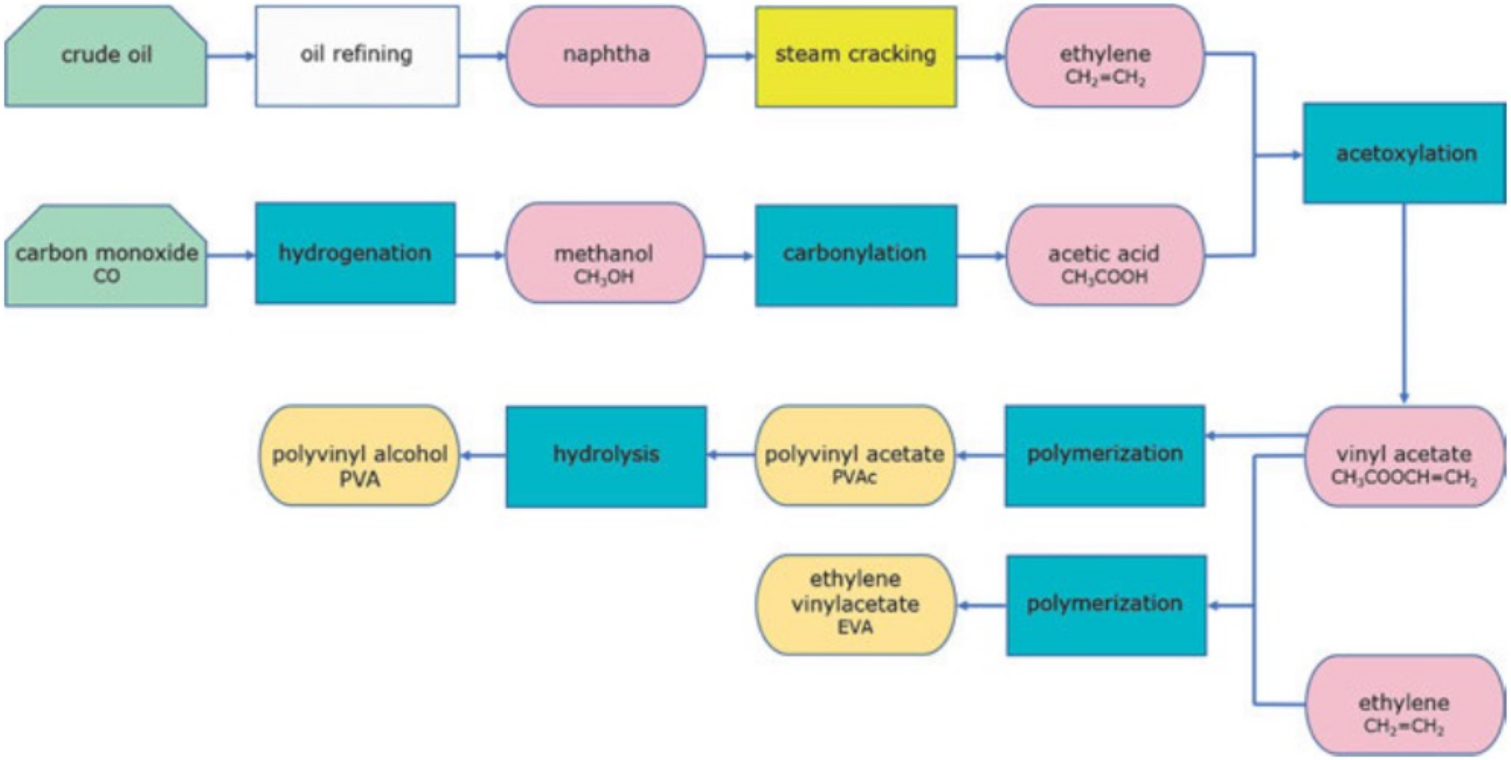


Figure 3.48: Process flow diagram for production of PVAc and PVA.

Bio-Based Polyvinylacetate (PVAc)/Polyvinyl alcohol (PVA) /Polyethylenevinylacetate (EVAc)

German chemical company Wacker Chemie

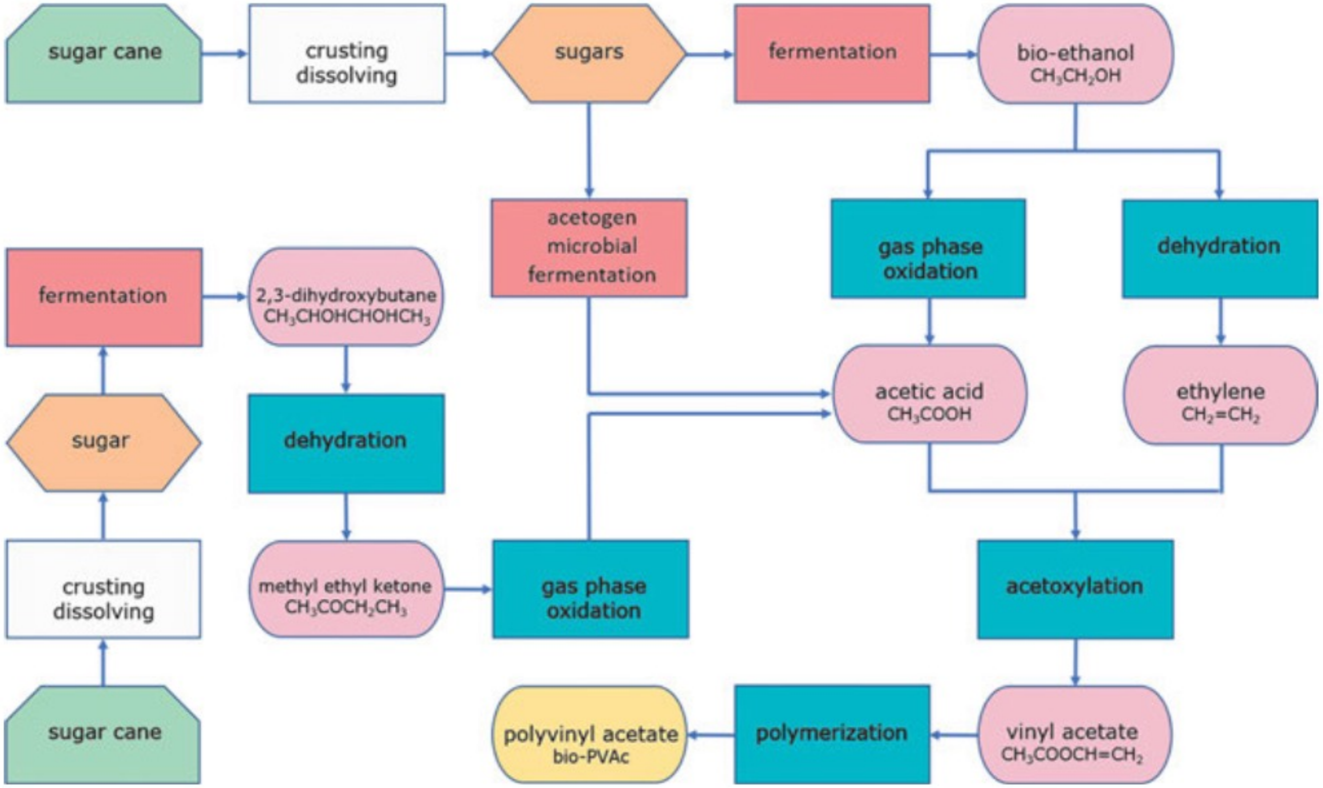


Figure 3.49: Process flow diagram for production of bio-PVAc.

Fossil-Based Polyacrylic Acid (sodium acrylate super absorbant)

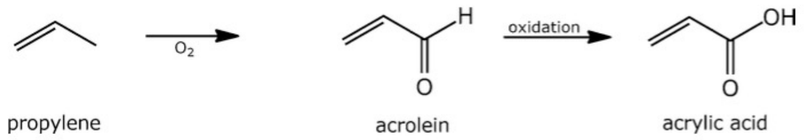


Figure 3.50: Oxidation of propylene to acrylic acid.

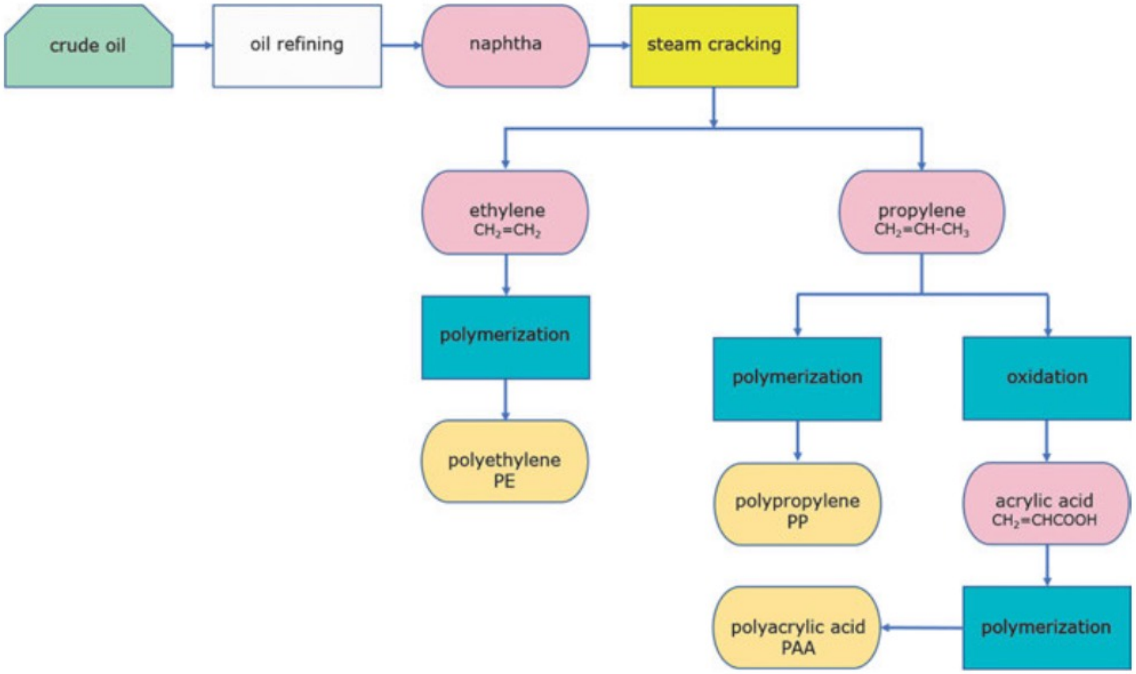


Figure 3.51: Process flow diagram for production of PAA (and PE).

BASF, Dow, Arkema, Evonik, Nippon Shokubai, LG Chemical, Mitsubishi, Jiansu Jurong Chemical, and Formosa Plastics

Proposed Bio-Based Polyacrylic Acid (sodium acrylate super absorbant)

Genomatica

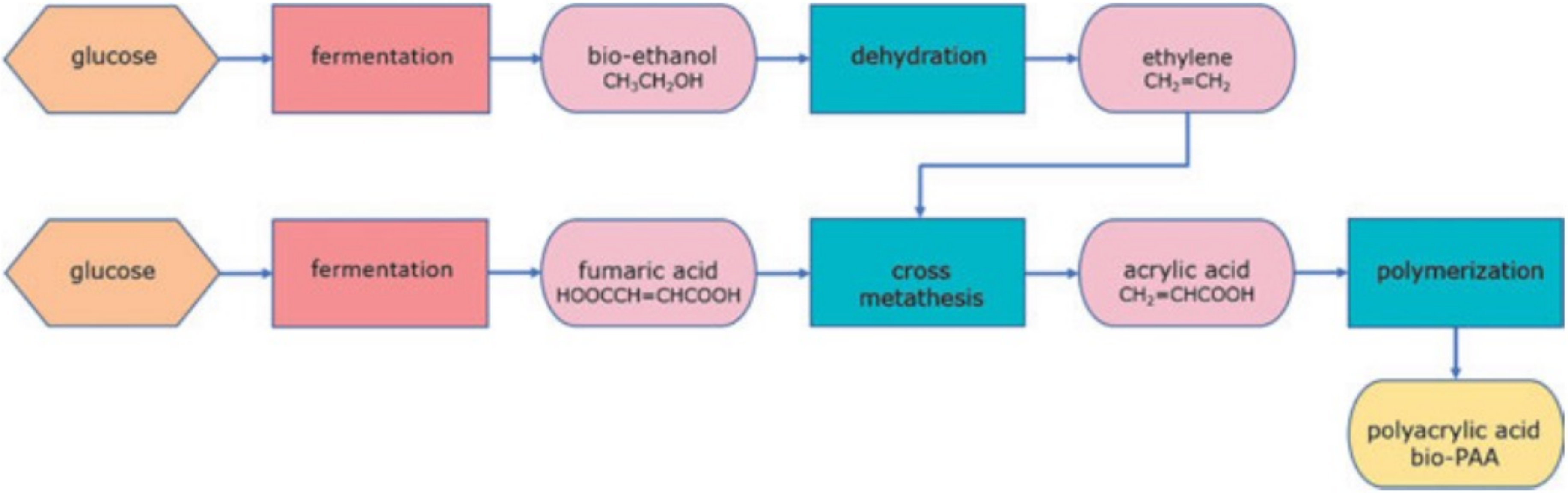
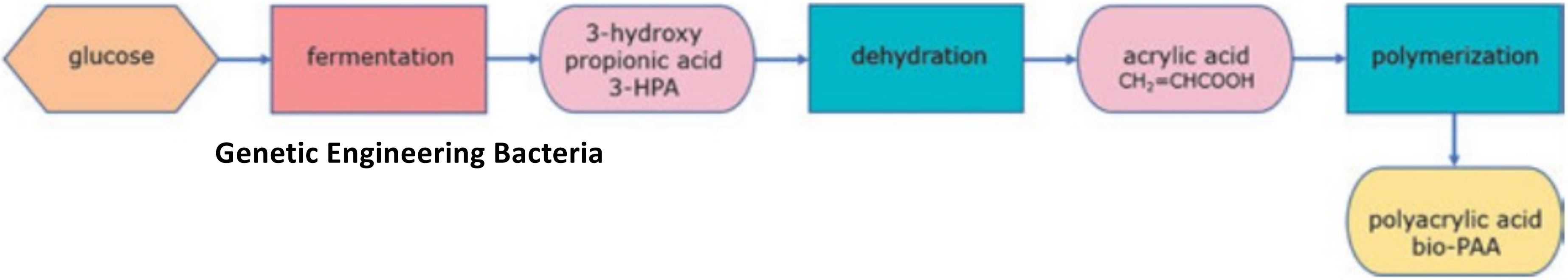


Figure 3.52: Process flow diagram for production of bio-PAA (route 1).

Proposed Bio-Based Polyacrylic Acid (sodium acrylate super absorbant)

BASF, Cargill, and Novozymes



Genetic Engineering Bacteria

Figure 3.53: Process flow diagram for production of bio-PAA (route 2).

Dow Chemical and OPX Biotechnologies (OPXBio) similar process

Proposed Bio-Based Polyacrylic Acid (sodium acrylate super absorbant)

Novomer

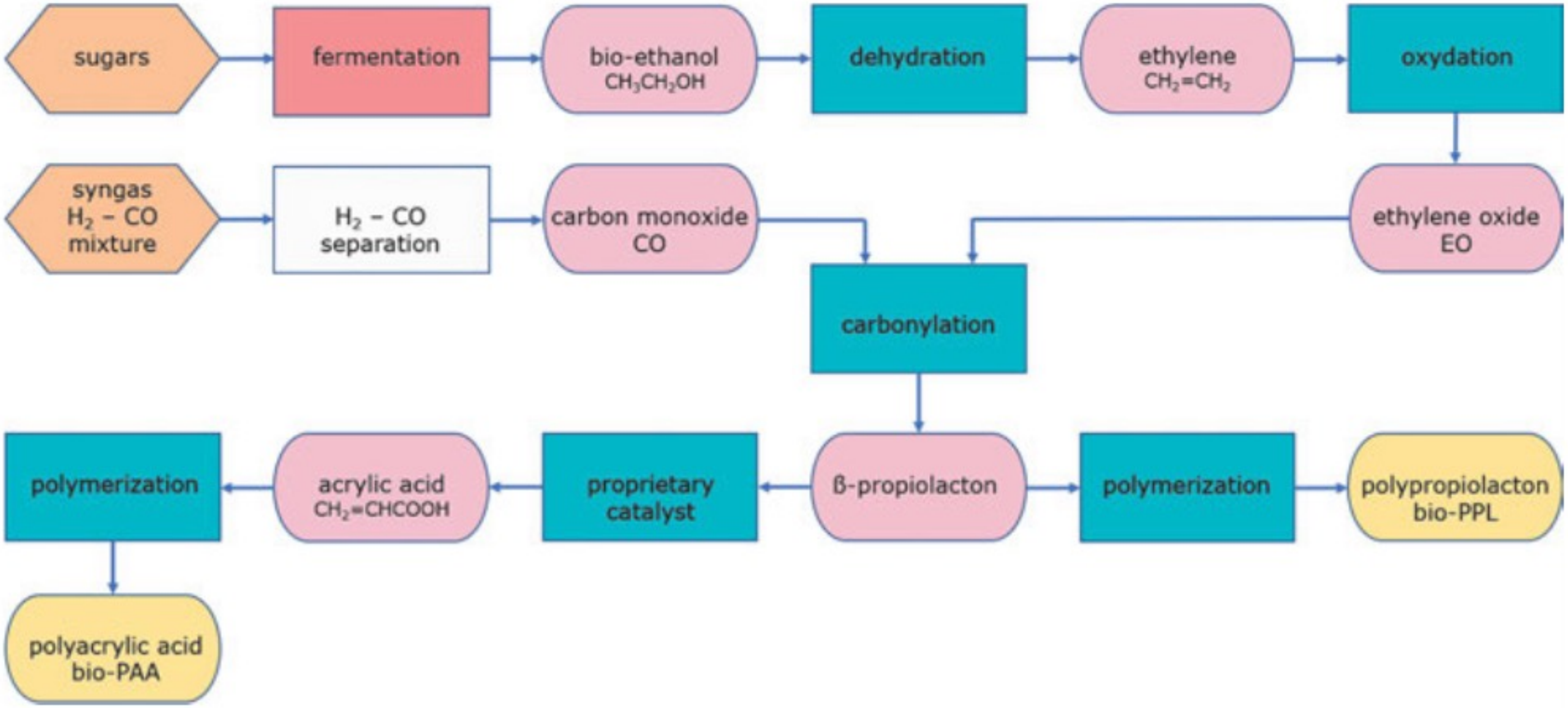


Figure 3.54: Process flow diagram for production of bio-PAA (route 3).

Proposed Bio-Based Polyacrylic Acid (sodium acrylate super absorbant)

Arkema Group

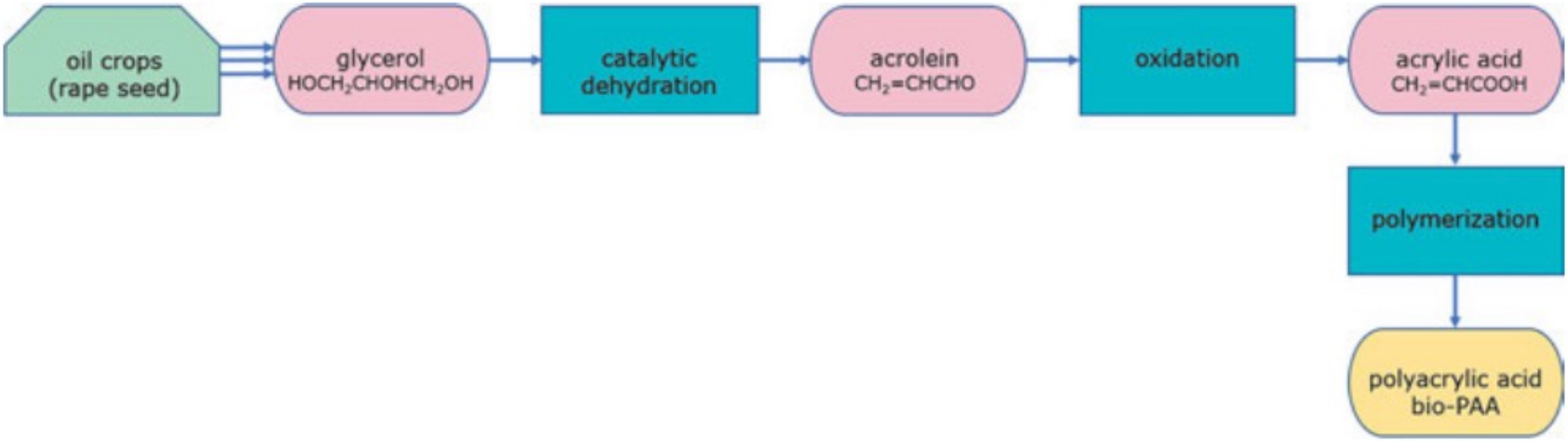
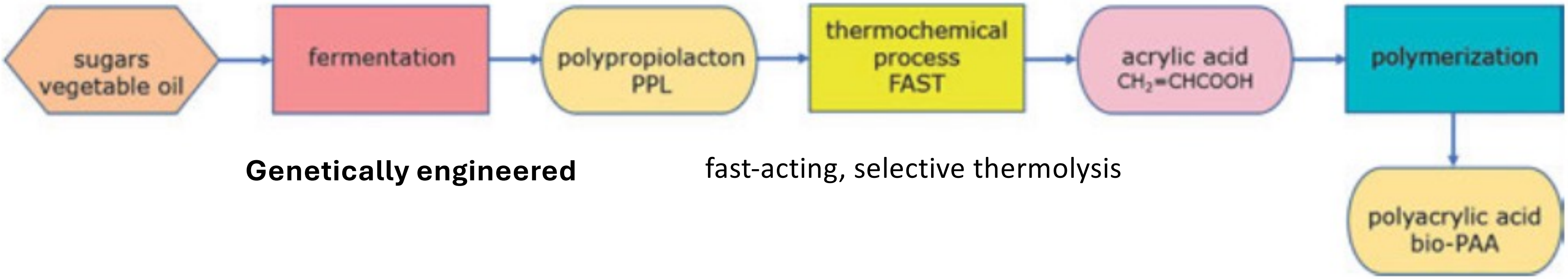


Figure 3.55: Process flow diagram for production of bio-PAA (route 4).

Proposed Bio-Based Polyacrylic Acid (sodium acrylate super absorbant)

Metabolix

Commercial to this stage



Genetically engineered

fast-acting, selective thermolysis

Figure 3.56: Process flow diagram for production of bio-PAA (route 5).

Proposed Bio-Based Polyacrylic Acid (sodium acrylate super absorbant)

Myriant (GC Innovation America)
and SGA Polymers

Commercial to this stage

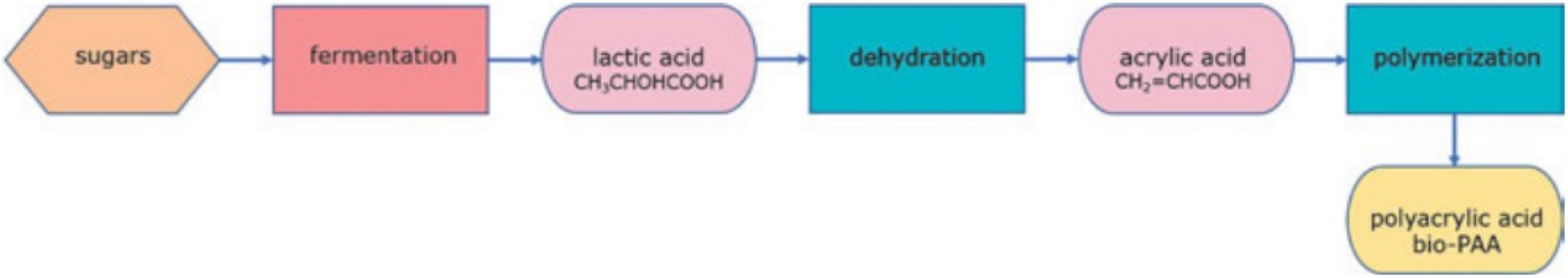
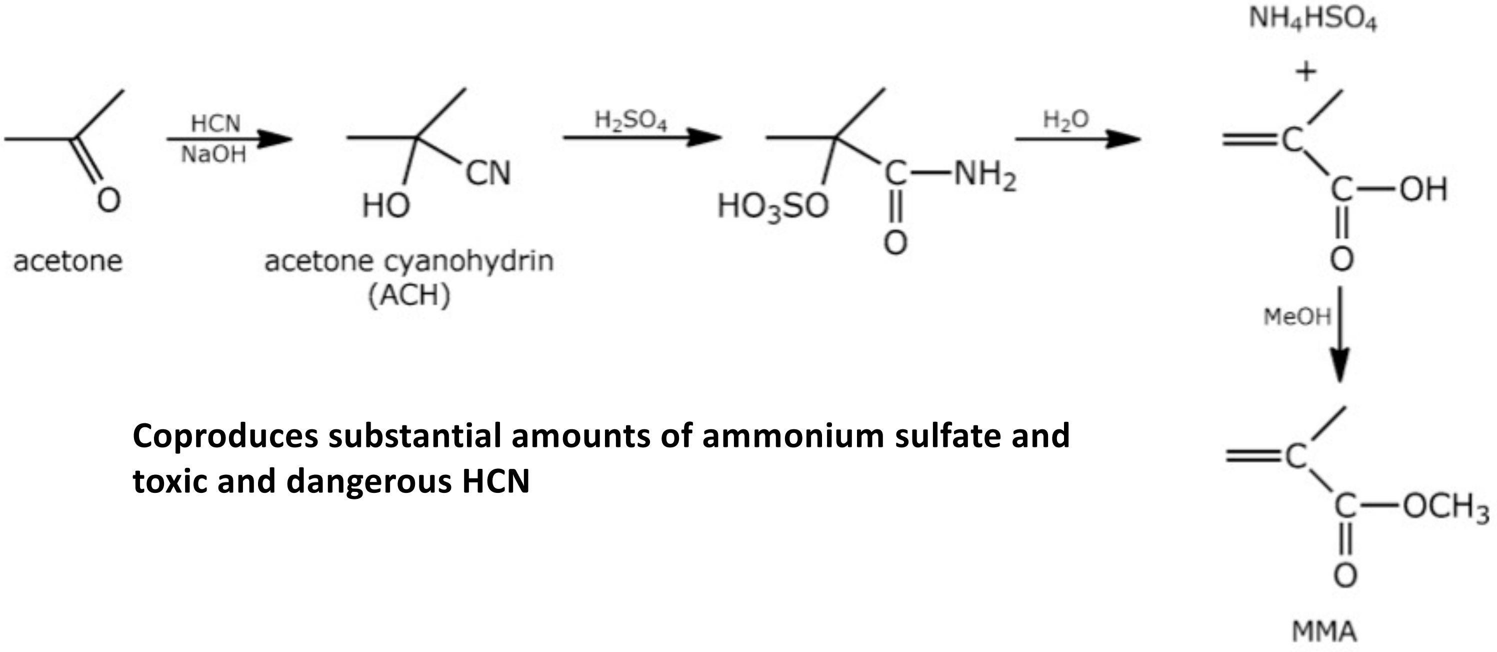


Figure 3.57: Process flow diagram for production of bio-PAA (route 6).

Fossil-Based Polymethylmethacrylate

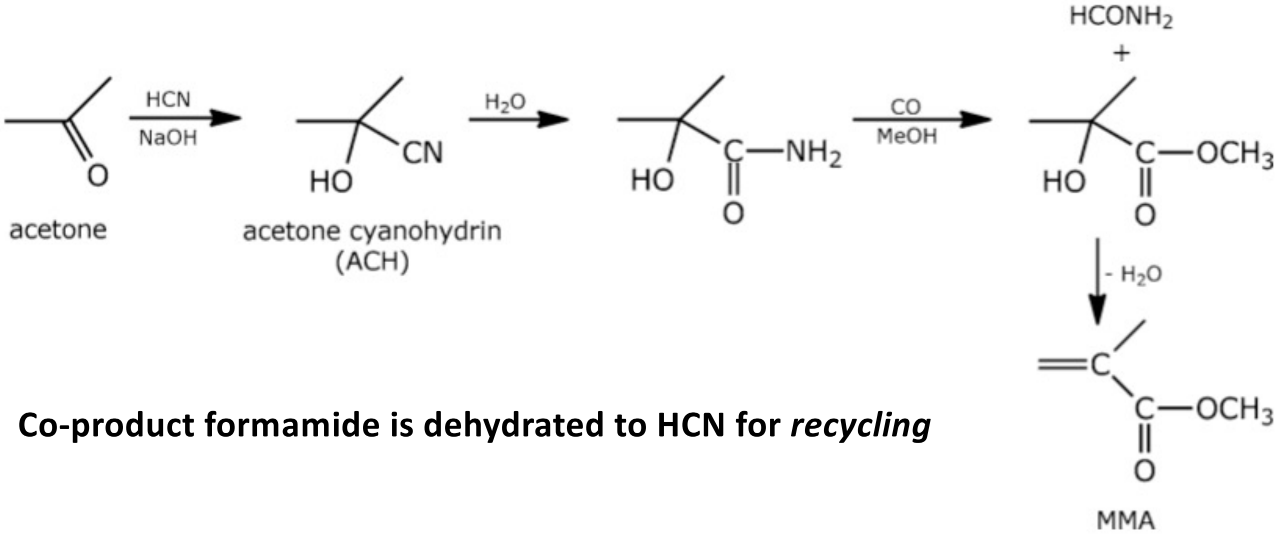


Coproduces substantial amounts of ammonium sulfate and toxic and dangerous HCN

Figure 3.58: Cyanohydrin route to methyl methacrylate (MMA).

Fossil-Based Polymethylmethacrylate

Mitsubishi Route



Co-product formamide is dehydrated to HCN for *recycling*

Figure 3.59: Mitsubishi Gas Chemical (MGC) route to methyl methacrylate (MMA).

Fossil-Based Polymethylmethacrylate

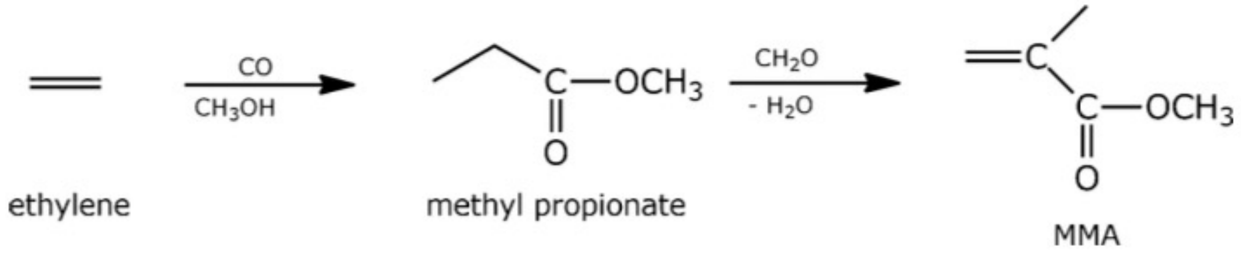
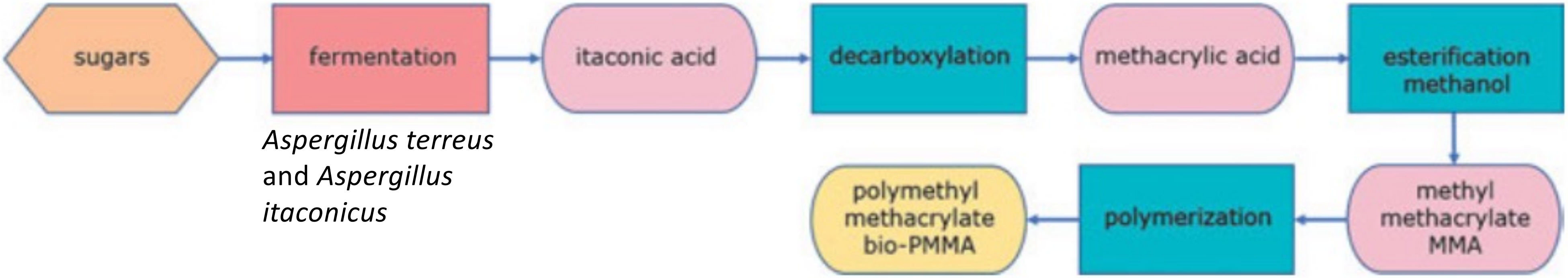


Figure 3.60: The methyl propionate route to methyl methacrylate (MMA).

Bio-Based Polymethylmethacrylate

BASF, Dow Chemicals, Arkema Group, Asahi-Kasei, Mitsubishi Rayon, and Evonik. Both bio-based methyl methacrylate (bio-MMA) and polymethyl methacrylate (bio-PMMA) are **not yet commercially available**.



Aspergillus terreus and *Aspergillus itaconicus*

Figure 3.61: Process flow diagram for the production of bio-PMMA (route 1).

Bio-Based Polymethylmethacrylate

Lucite International and Mitsubishi Rayon

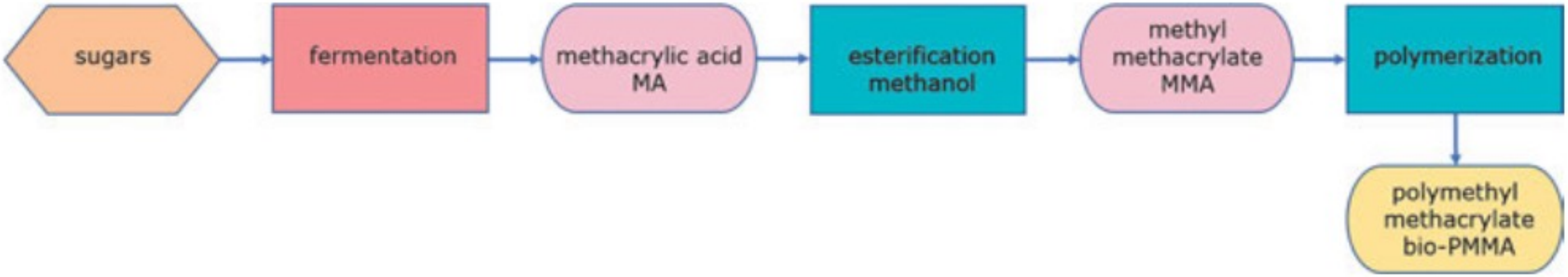


Figure 3.62: Process flow diagram for the production of bio-PMMA (route 2).

Bio-Based Plastics

Bio-Based Plastics

Bio-Based Plastics

Bio-Based Plastics

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Bio-Based Plastics

Bio-Based Plastics

Challenges: the ‘5Es’

We have identified five main challenges that hinder the implementation of bioplastics.

Economics

most bioplastics are currently more expensive to produce than fossil-based plastics, mostly owing to economies of scale and the price competitiveness of crude oil.

Efficiency

bioplastic manufacturing processes can be less energy efficient than fossil-based plastic processes and come with other environmental burdens associated with agricultural farming.

End of life

For most bioplastics, recycling streams have yet to be established to make them truly ‘circular’. Consumers remain uncertain of how to deal with bioplastics after use. Compostable bioplastics are often rejected by composters.

Ethics

using first-generation biomass, which is often edible, remains controversial owing to potential competition with food production. Processes to efficiently use second-generation biowastes need to be established.

Education

Consumers and plastic converters are confused about the usefulness of bioplastics, owing to inconsistent labelling, contradicting life cycle assessments and ‘greenwashing’. Improved information distribution and consistent global standards need to be established.