Upgrading Products from Thailand Sugarcane Industry via Bioplastic

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Agenda of the talk

01 Introduction to bioplastics
Bio-based plastic and Biodegradable

02 Bioplastic production
Process overview, Bio-based plastic, and Biodegradable

03 Limitations of bioplastics
Properties and process

04 Bioplastic compounding
Blends and Composites

Bioplastics are plastic materials produced from renewable biomass sources, such as vegetable fats and oils, corn starch, straw, woodchips, sawdust, recycled food waste, etc. Bioplastic can be made from agricultural by-products and also from used plastic bottles and other containers using microorganisms.

Start of life functionality

1st Renewable resource

2st Non-renewable resource

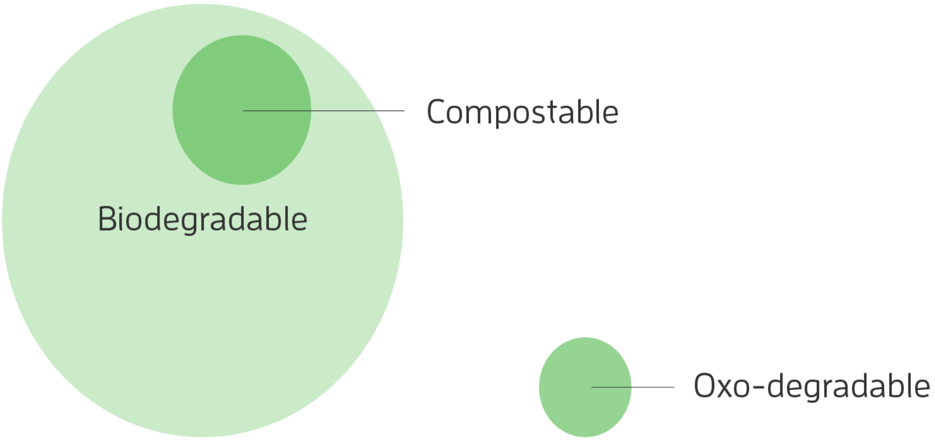
End of life functionality

3st Compostable

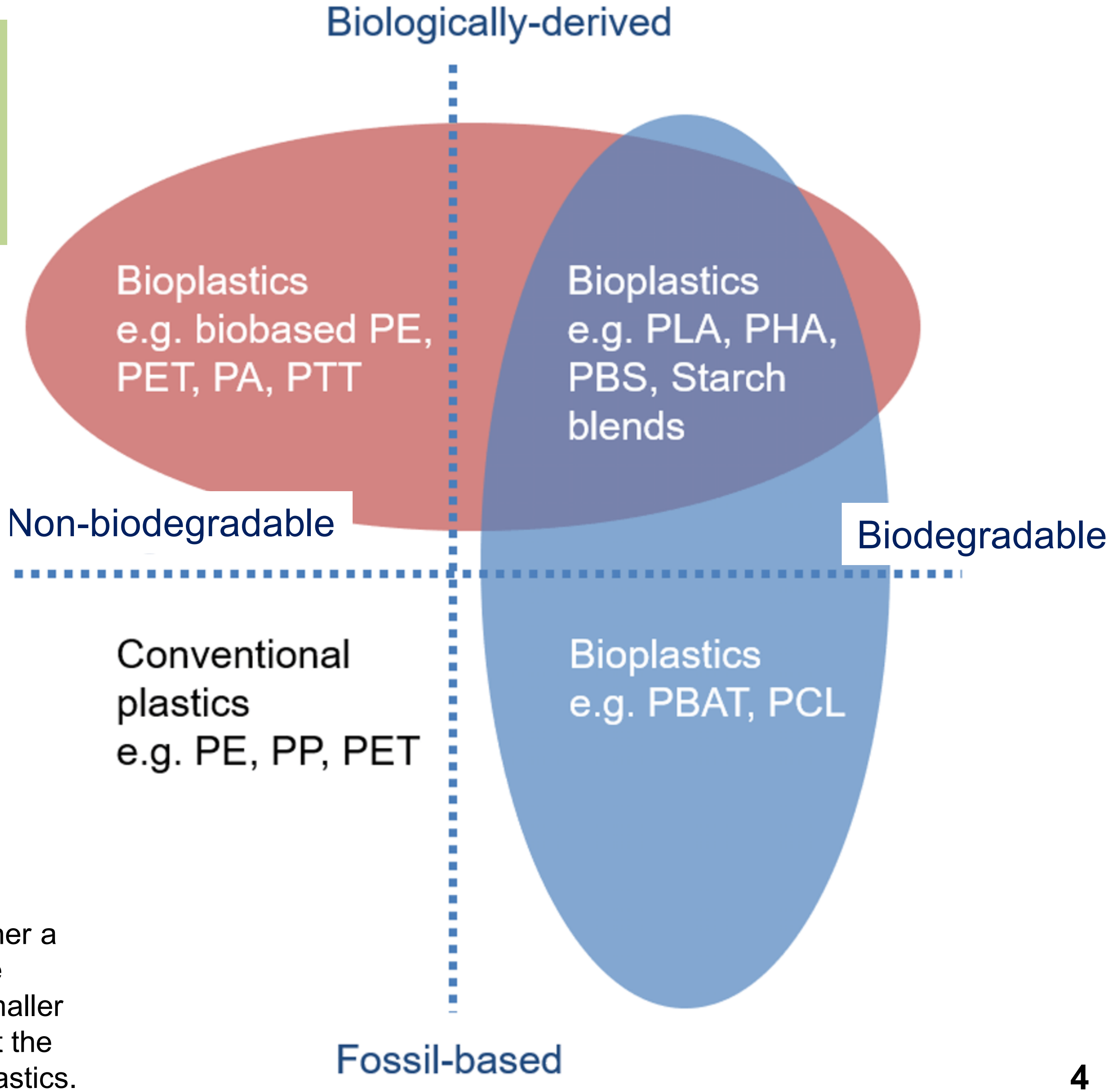
4st Biodegradable

Understanding Bioplastics

- Understanding bioplastics: Bio-based vs. biodegradable
- Biodegradable vs. compostable vs. oxo-degradable plastics

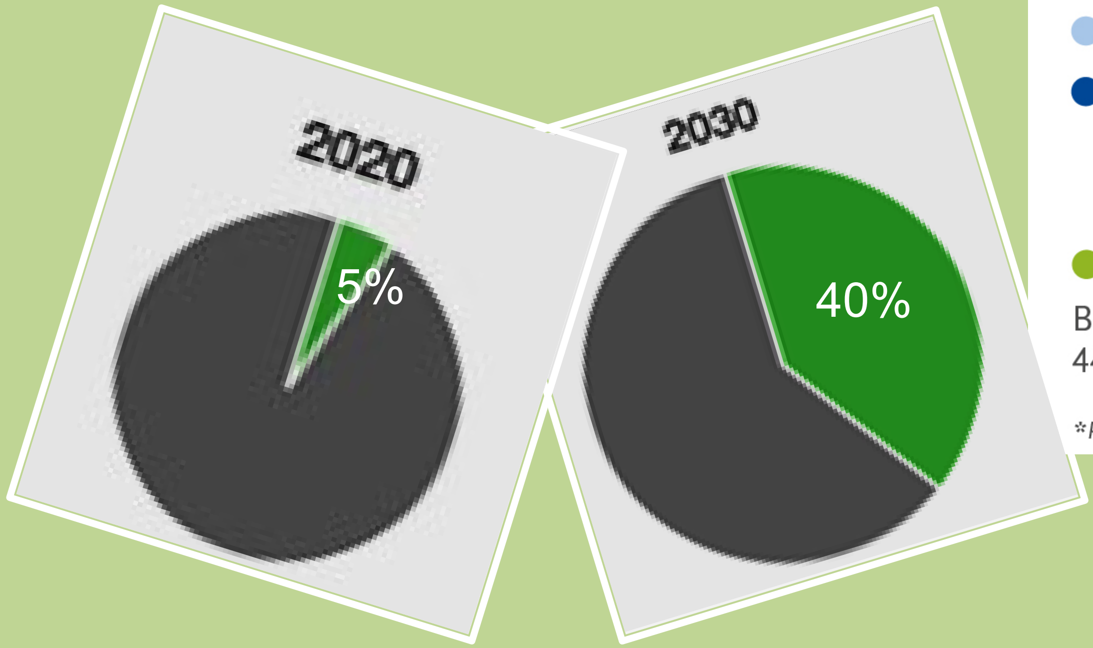


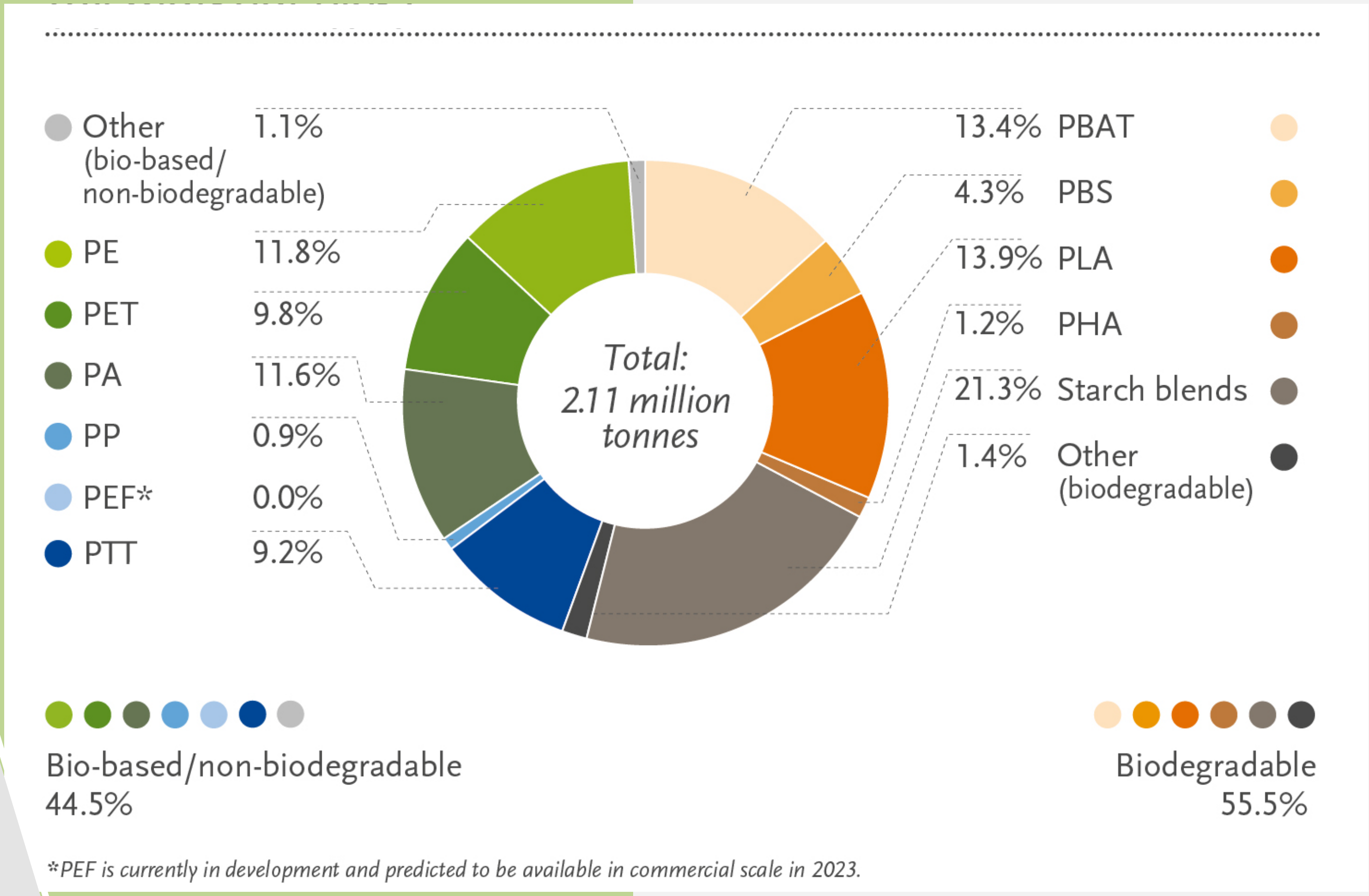
They are neither a bioplastic nor a biodegradable plastic, but rather a conventional plastic mixed with an additive in order to imitate biodegredation. Oxo-degradable plastics quickly fragment into smaller and smaller pieces, called microplastics, but don't break down at the molecular or polymer level like biodegradable and compostable plastics.



Global production capacities of bioplastics 2019

How will the market for bioplastics change in the coming years?





Grand View Research

European Bioplastics

Sources of BIOPLASTICs

Corn

Sugarcane

Casava

Feedstocks

Agricultural building blocks

Polysaccharides

- Starch /sugars
- Lignocellulosics
  - Woods
  - Straws
  - Stover, etc.
- Others
  - Pectins
  - Chitosan
  - Gums

Facts/Proteins

- Animals
  - Casein
  - Oils
  - Whey
  - Gelatin
- Vegetable
  - Casein
  - Oils
  - Whey
  - Gluten

Polymers

Direct Fermentation

Polyhydroxy alkanoates PHA's

- PHB
- PHBH
- PHBV

Polyhydroxybutyrate (PHB)

3-hydroxybutyrate-co-3-hydroxyhexanoate (PHBH)

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

Bio-technological origin

- PLA
- Nylon 11
- Polyethylene
- Polypropylene
- Aliphatic
- Polycarbonate

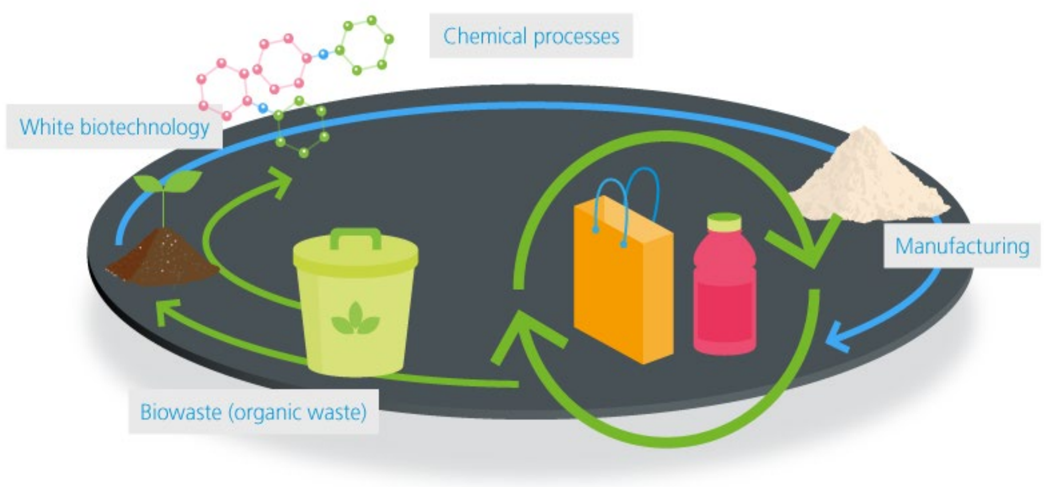
Petroleum/Natural Based

- Starch blends
- Nylon 6,10
- Nylon 6,12
- PET
- PTT
- PBS
- Polyurethane

Benefits of Bioplastics

GC Innovation America is part of Thailand-based chemicals company PTT Global Chemical Public Company Ltd, which is developing biobased chemicals, including biopolymers, using succinic acid derived from renewable sources.

Bioplastics closing the loop



Bioplastics everyday

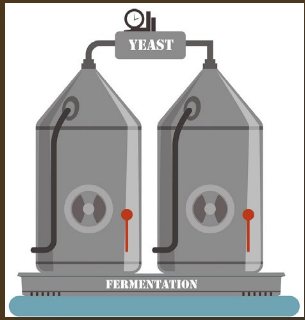
Here are just a few examples:

The EU-funded EUROPHA project is developing 100% natural, biodegradable polyhydroxyalkanoate (PHA-based bioplastics) for food packaging applications

New York-based Ecovative Design has developed technology that harnesses fungi to grow biobased plastic alternatives that can be made into a wide range of products, from insulated jackets, technical wear and footwear, to sponges for applying cosmetics.

A

BIOPLASTIC MANUFACTURING

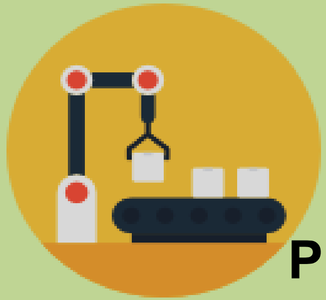


Up-stream Processing

Mid-stream Processing

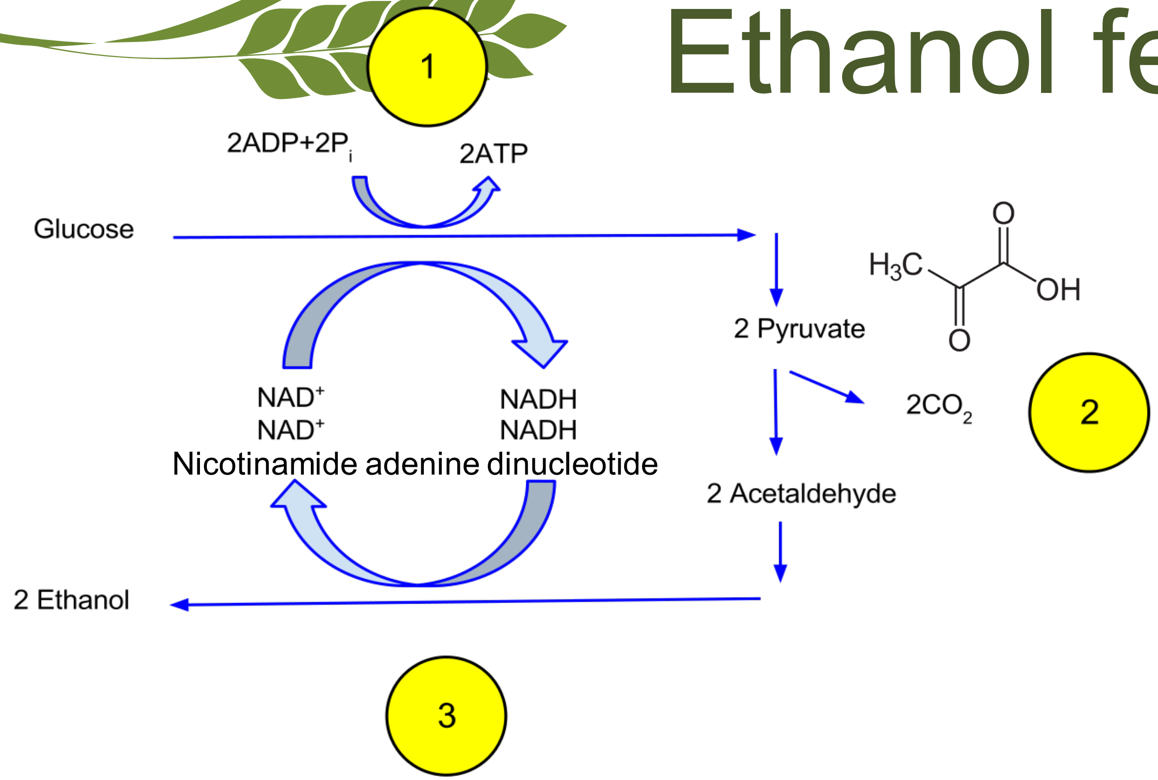
Down-stream Processing

Harvesting → Fermentation → Biorefinery → Polymerization → Compounding → Product manufacturing



Product manufacturing

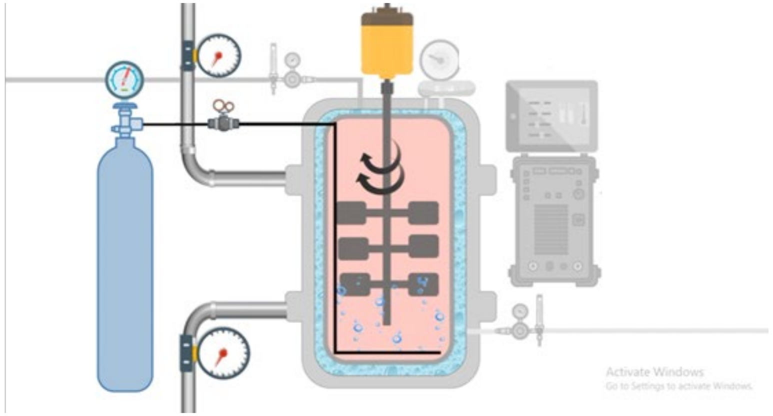
Ethanol fermentation



1. One glucose molecule breaks down into two pyruvates. The energy from this exothermic reaction is not used to bind the inorganic phosphates to ADP and convert NAD+ to NADH.
2. The two pyruvates are then broken down into two acetaldehydes and give off two CO_2 as a by-product.
3. The two acetaldehydes are then converted to two ethanol by using the H- ions from NADH, converting NAD back into NADH.

The overall chemical formula for alcoholic fermentation is:

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$$



In the first step of alcoholic fermentation, the enzyme invertase cleaves the glycosidic linkage between the glucose and fructose molecules.

$$C_{12}H_{22}O_{11} + H_2O + \text{invertase} \rightarrow 2\ C_6H_{12}O_6$$

Invertase is an enzyme that catalyzes the hydrolysis (breakdown) of sucrose (table sugar) into fructose and glucose.

https://polymerinnovationblog.com/from-sugar-to-bioplastics-fermentation-in-action/

Biorefinery

Fuels and energy

Petroleum

Chemicals

Fuels and energy

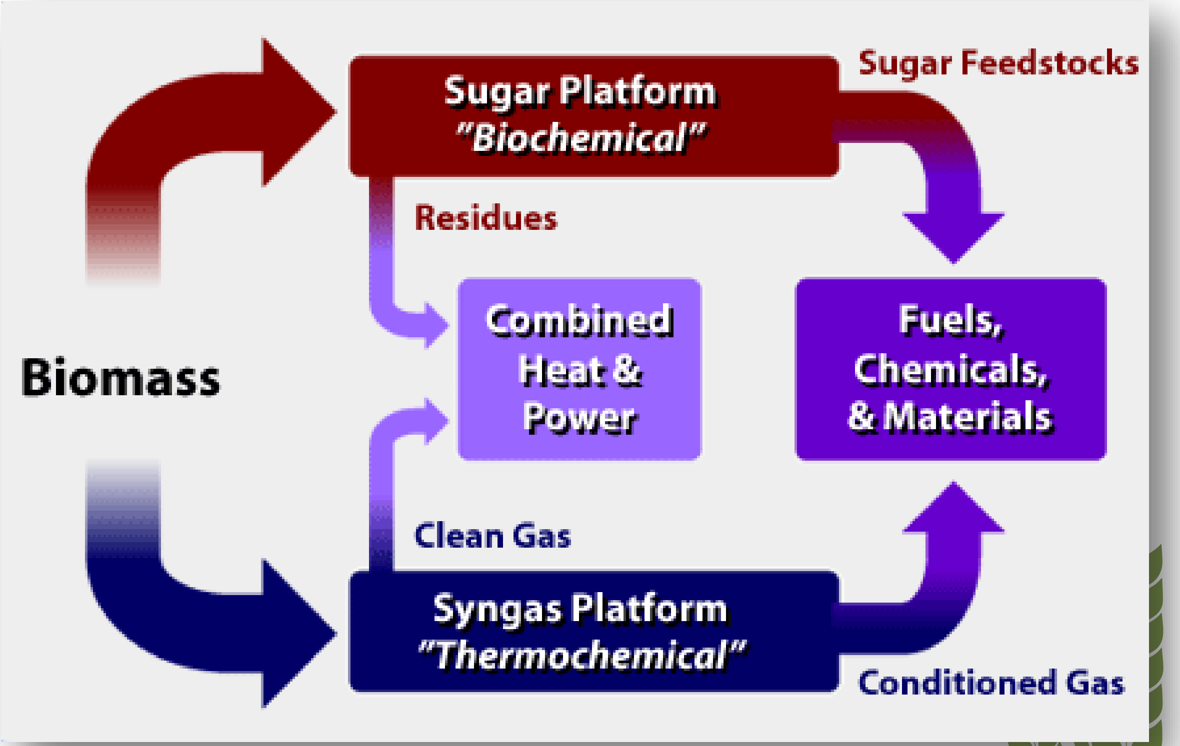
- Bioethanol
- Biodiesel
- Biogas
- Hydrogen

Biomass

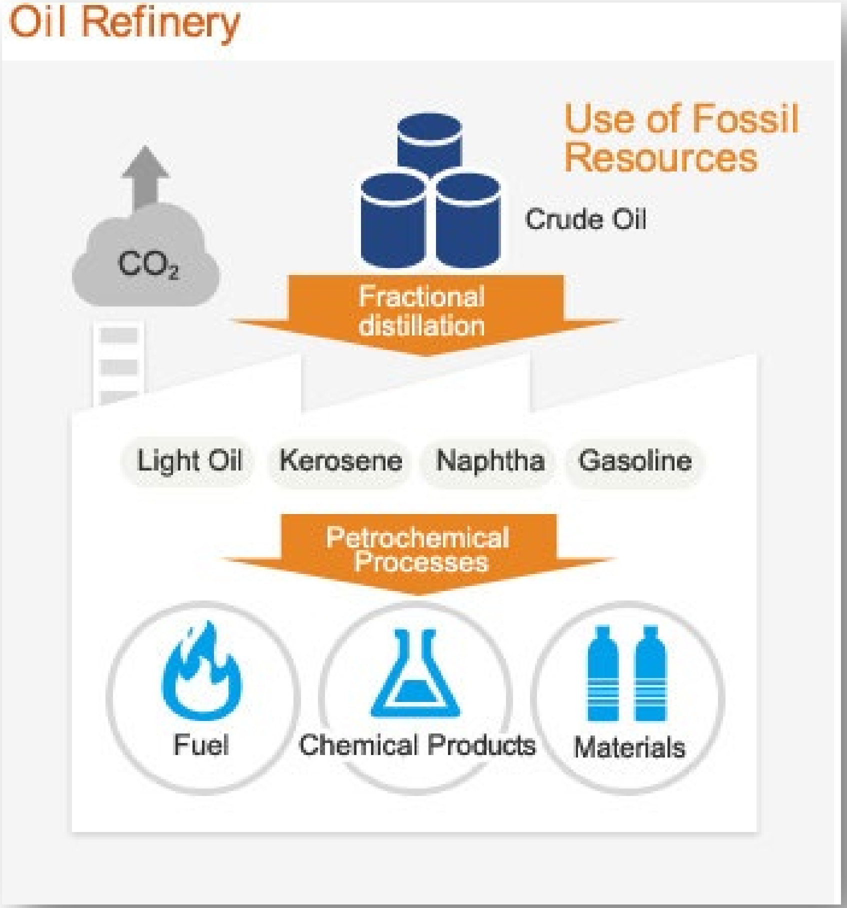
Biorefinery

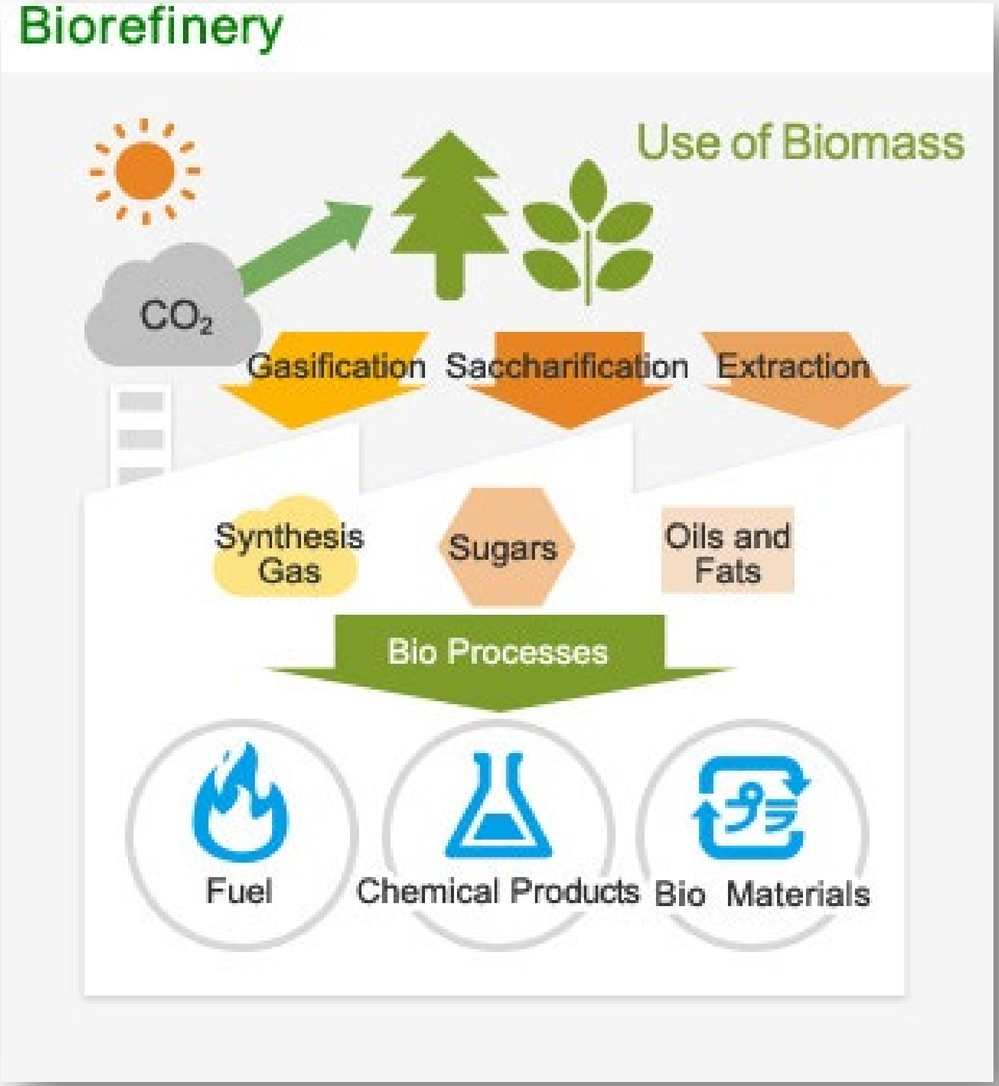
Material utilization

- Basic and fine chemicals
- Biopolymer and bioplastics



REFINERY
PROCESSES

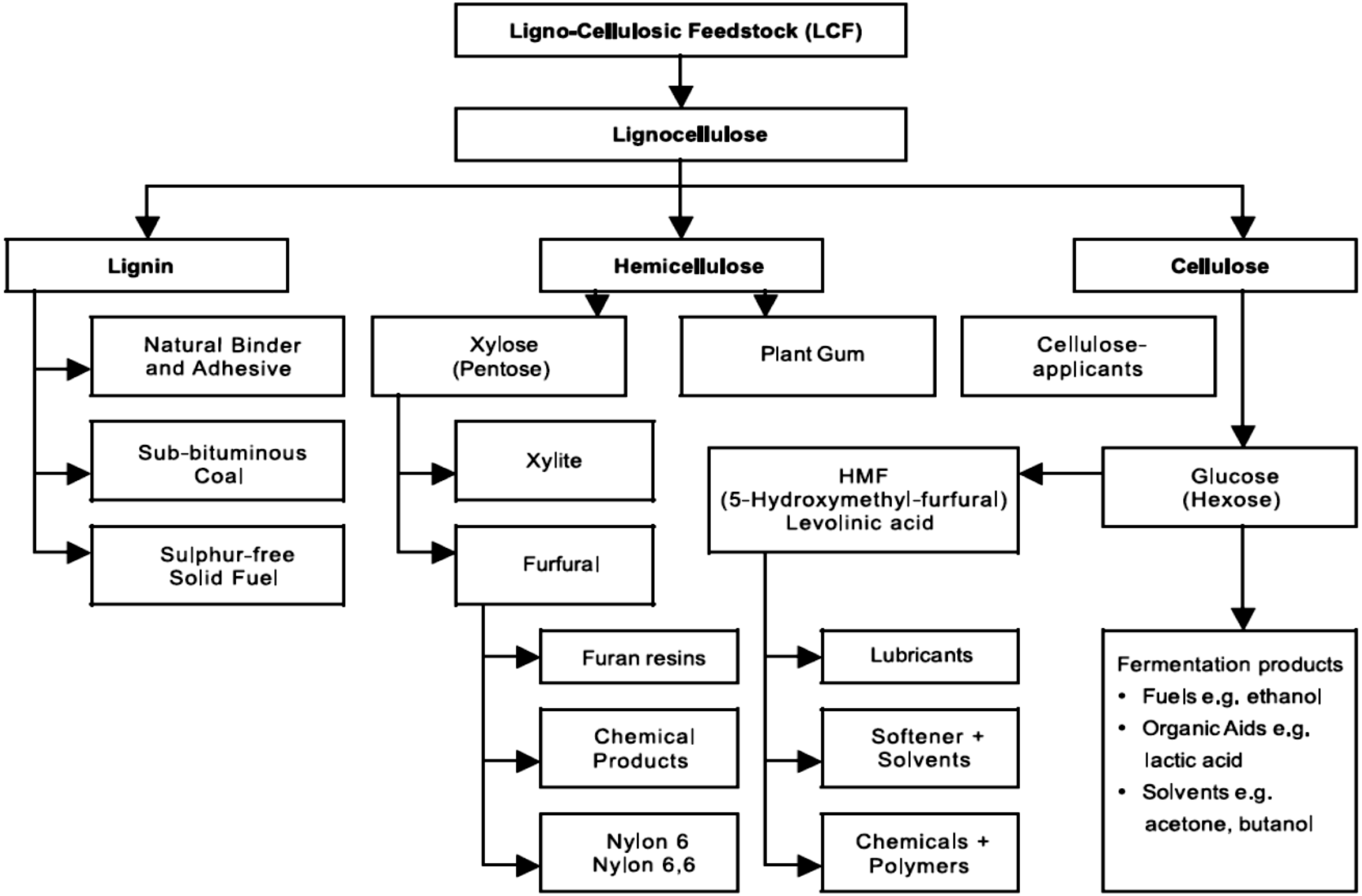




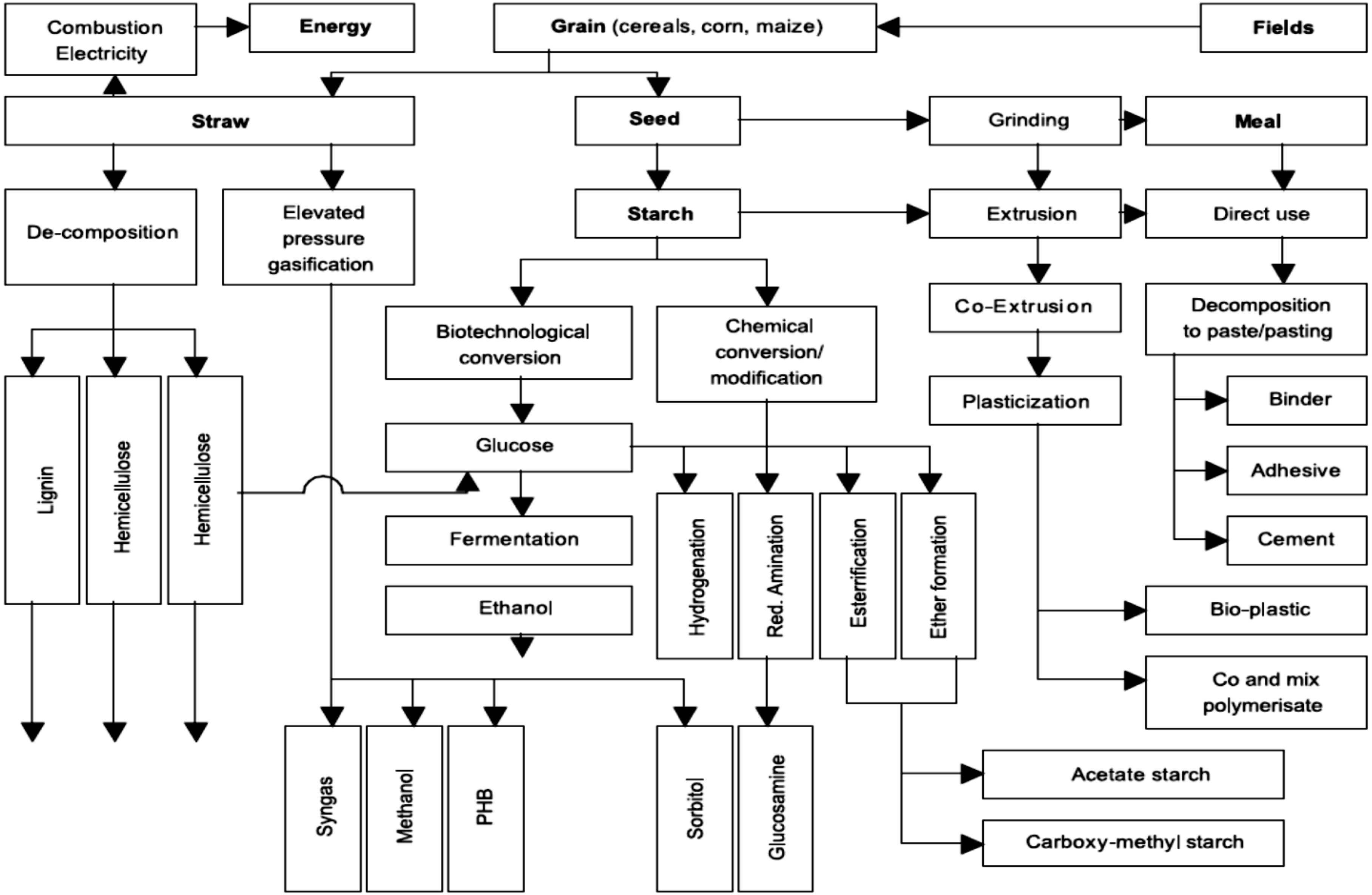
Biorefinery types

LCF

biorefinery

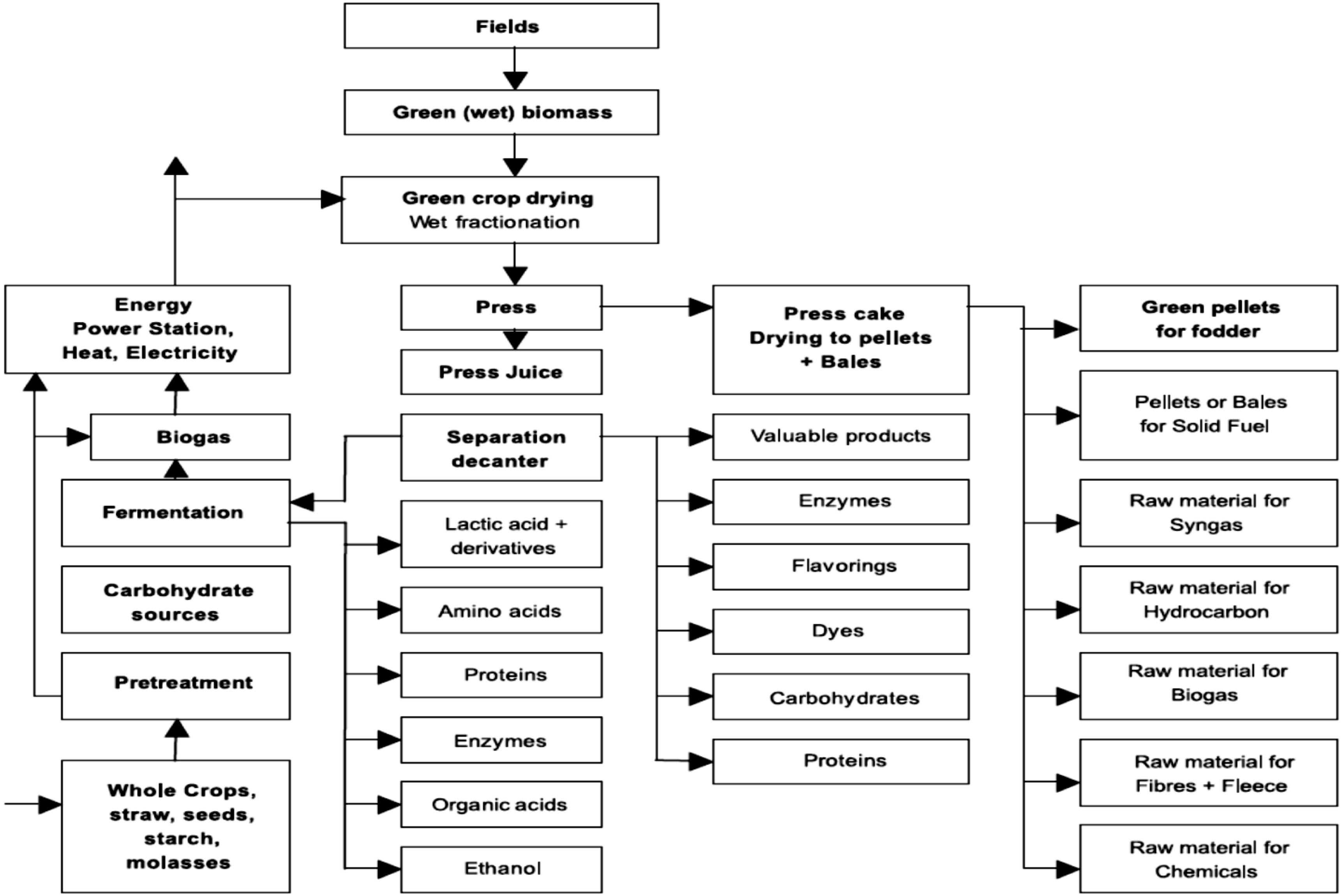


Biorefinery types



whole crop biorefinery

Biorefinery types



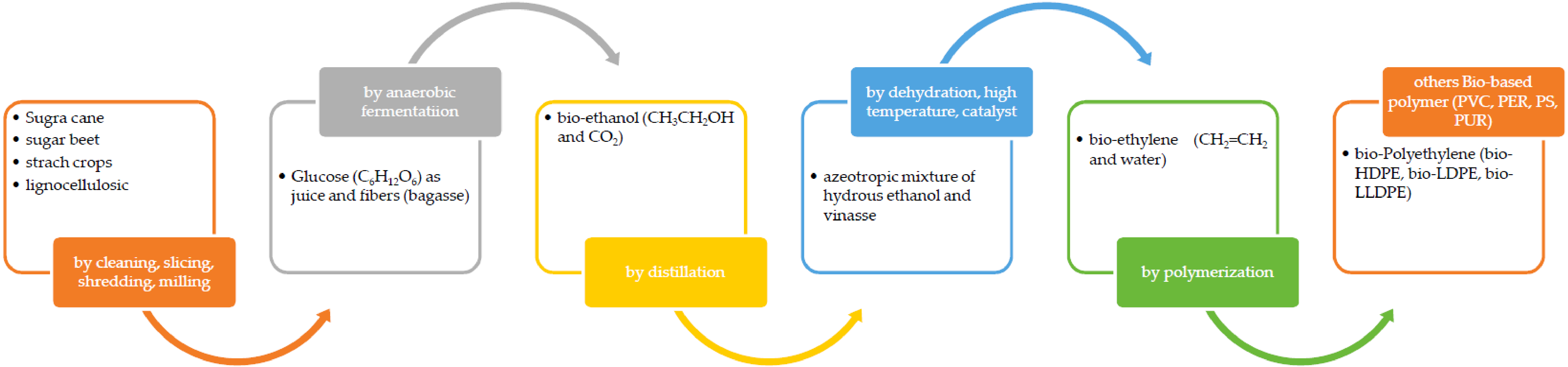
HOW Bio-PE IS PRODUCED

Braskem production

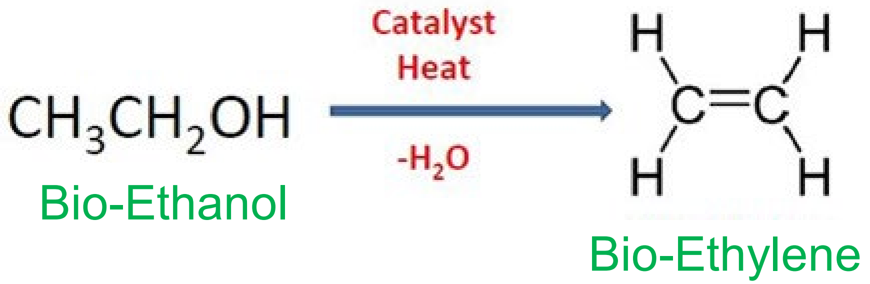
Braskem receives its ethanol from suppliers mainly through railways. The ethanol from sugarcane in Braskem's ethylenne plant goes through a dehydration process and is transformed into green ethylene. The green ethylene then goes to the polymerization plants where it is transformed into I'm greenTM Polyethylene, the plastic made from sugarcane. From this point, I'm greenTM Polyethylene follows to Customers. See below the production flow of Braskem's I'm greenTM Polyethylene, from the planting of sugarcane, a renewable raw material, to the transformation of biopolymer in day-to-day products and their disposal.

Bio-PE

General scheme for Bio-PE

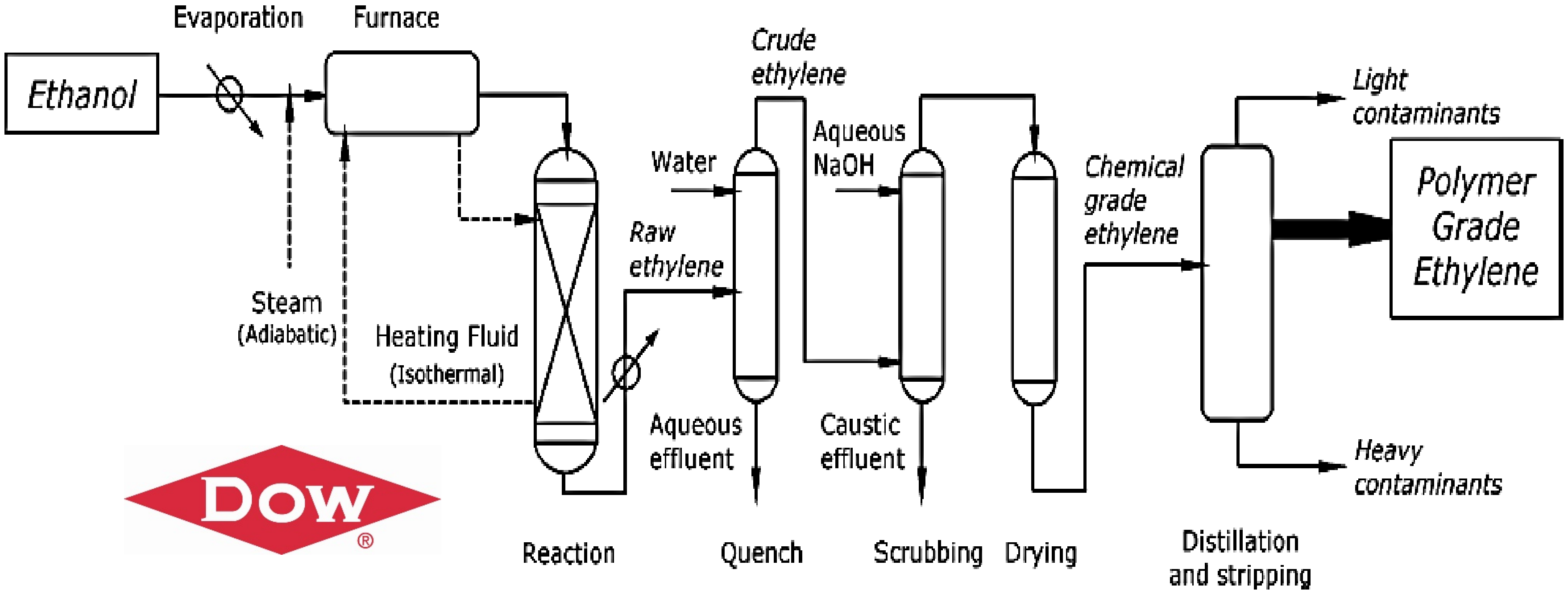


Dehydration of Bio-Ethanol to Bio-Ethylene



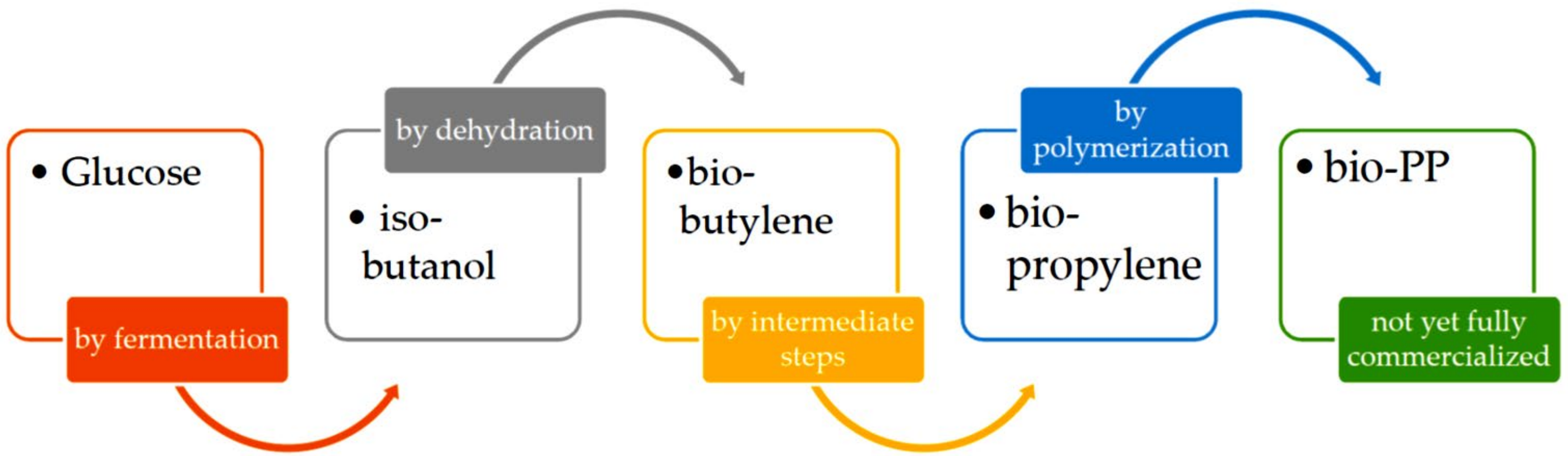
DOW scheme for Bio-PE

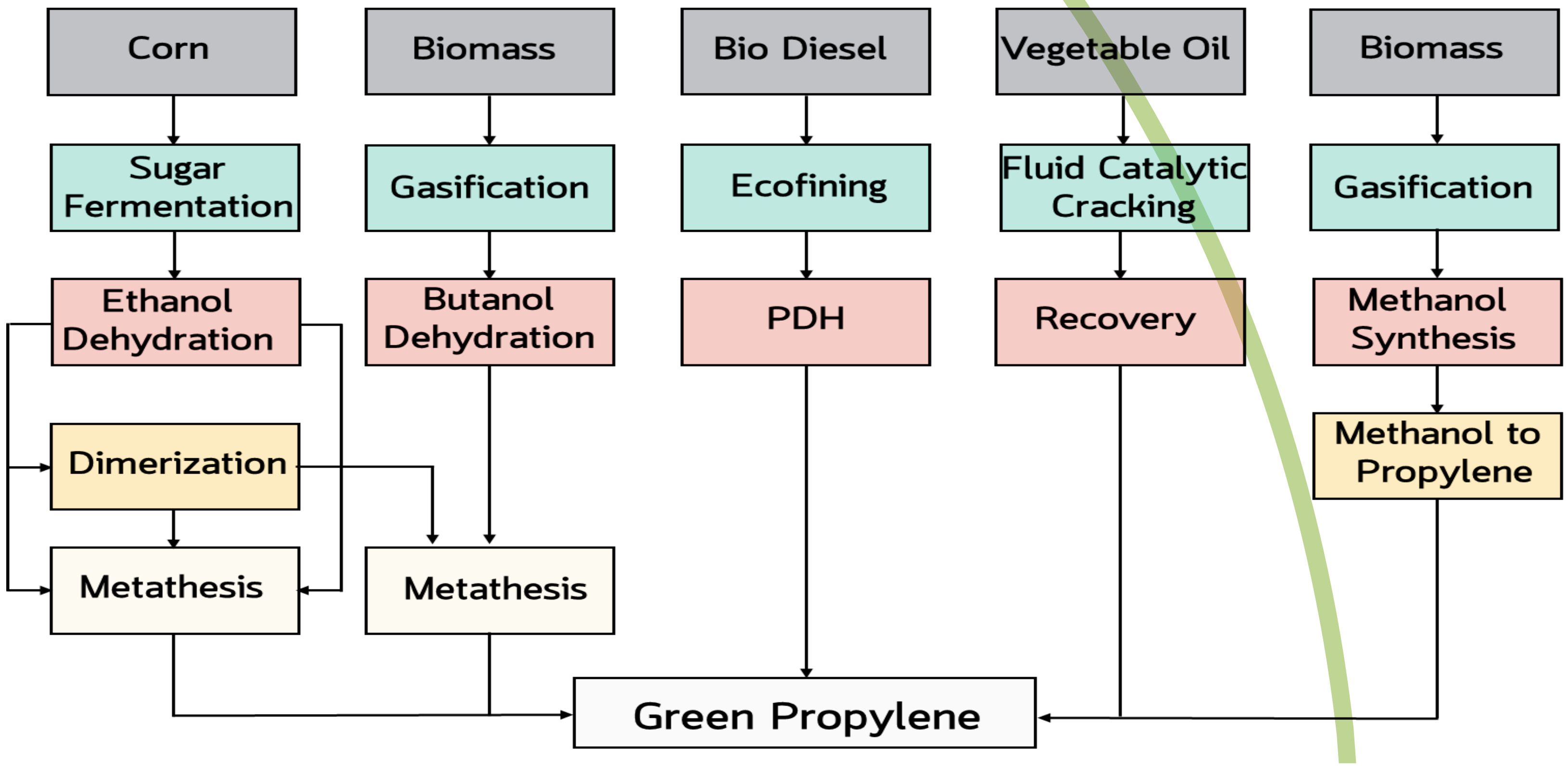
- Entire life cycle of petroleum based PE emits 4.55 kg-CO_2 eq./kg-PE
- Sugar cane plantation can captures 3.2 kg-CO_2 eq./kg-PE. Thus, the Bio-PE life cycle emits only 1.35 kg-CO_2 eq./kg-PE.



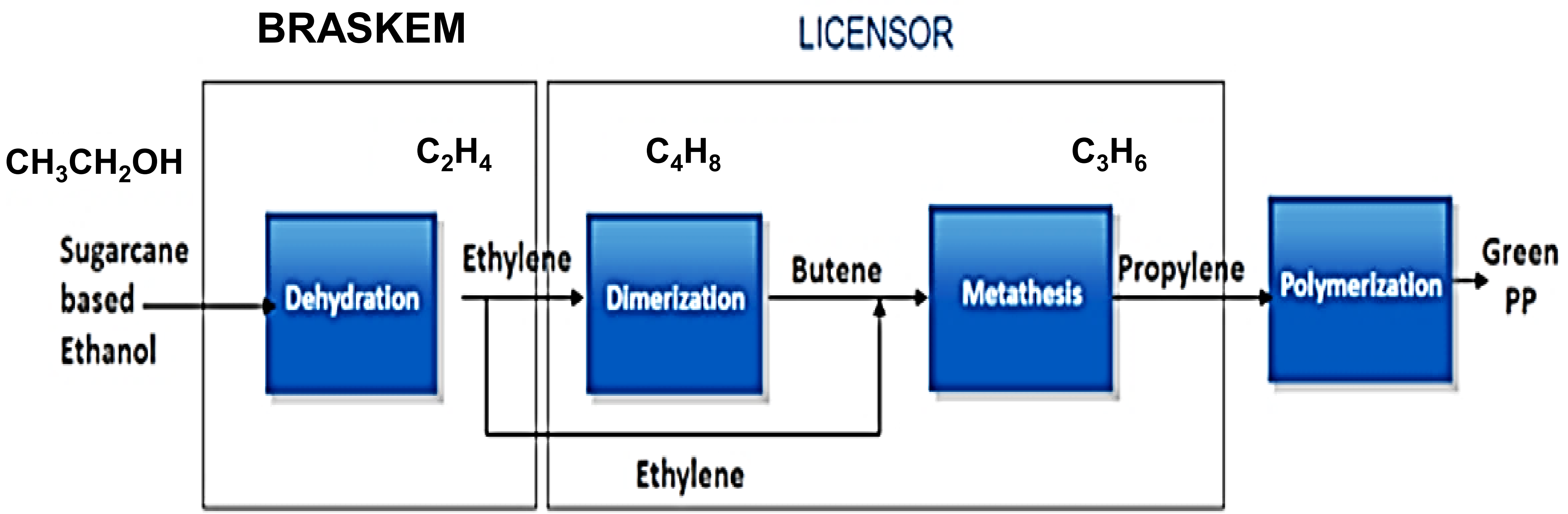
$$2\ CH_3CH_2OH \rightarrow CH_3CH_2OCH_2CH_3 \rightarrow H_2C{=}CH_2 + 2\ H_2O$$

General scheme for Bio-PP

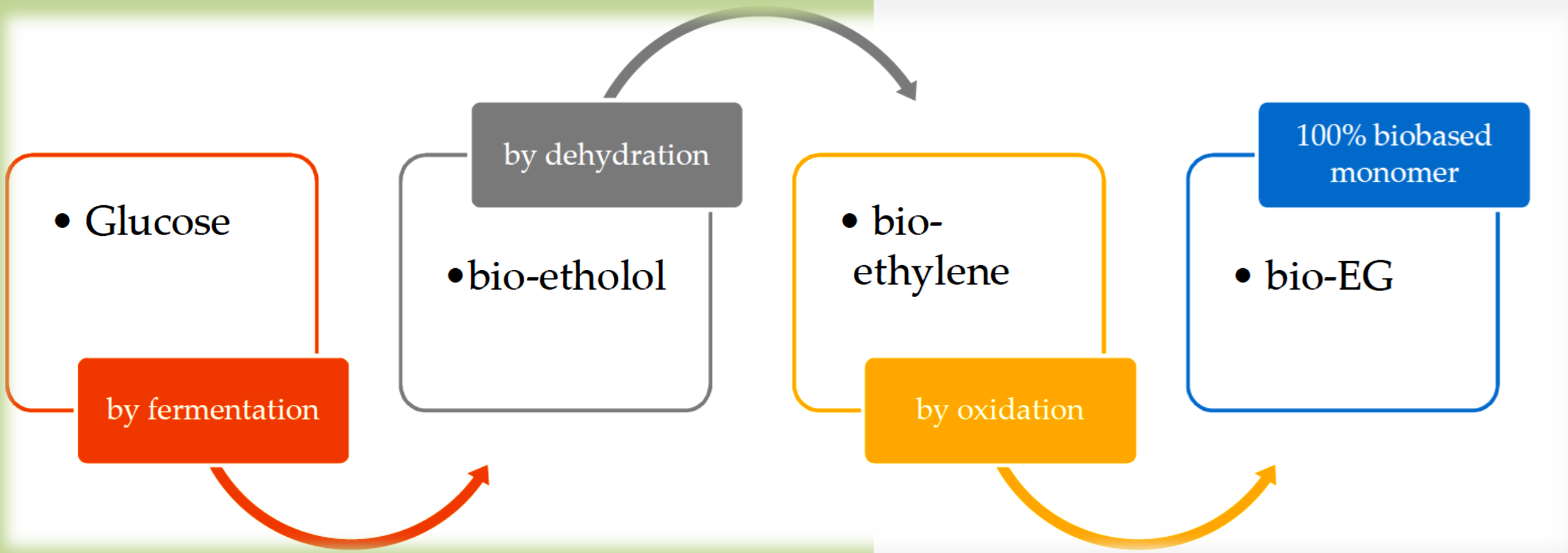


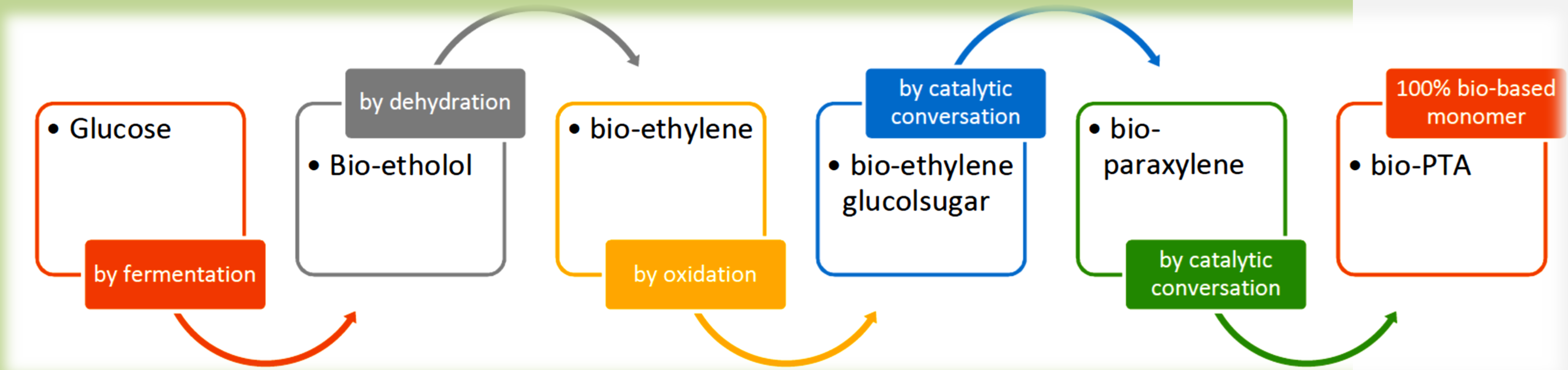


BRASKEM scheme for Bio-PP



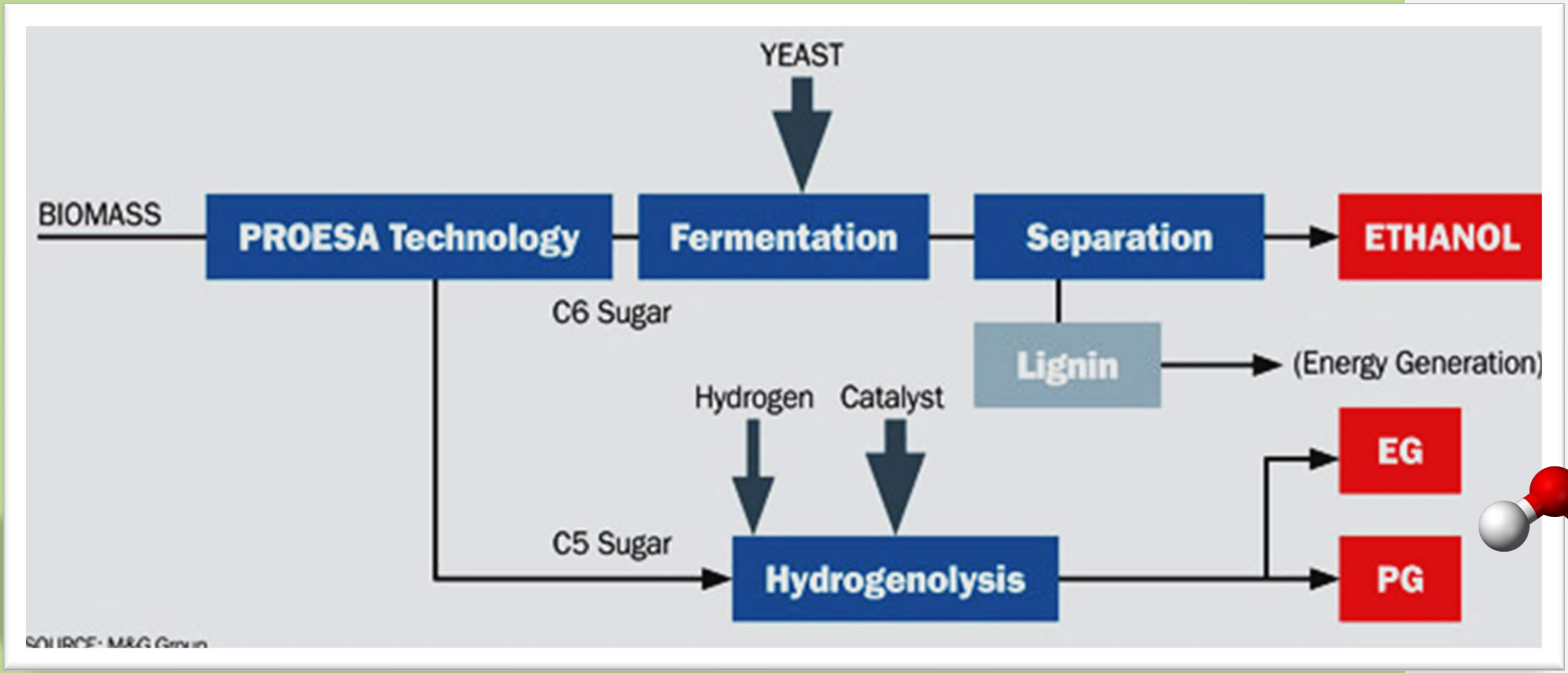
Scheme for Bio-monomer

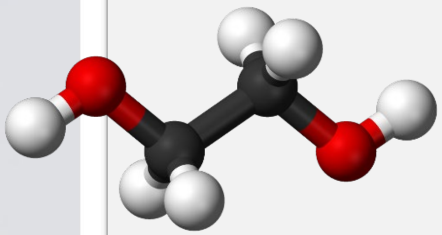


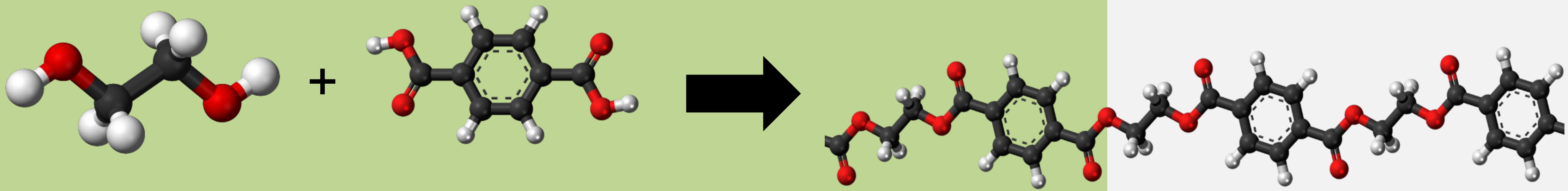


General scheme for Bio-EG and Bio-PTA monomers production

Scheme for Bio-PET



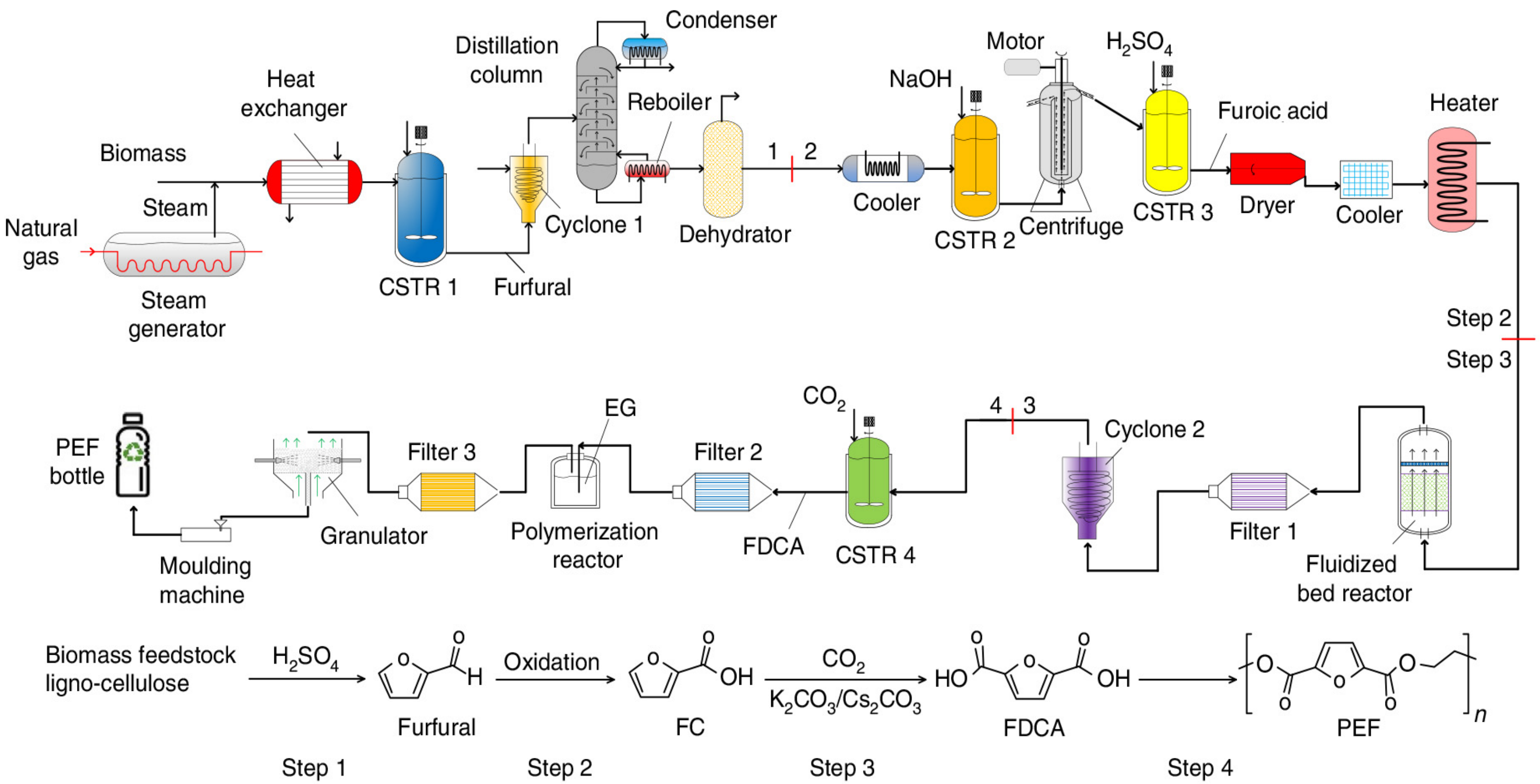




MEG
Mono Ethylene Glycol

PTA
Purified Terephthalic Acid

PET

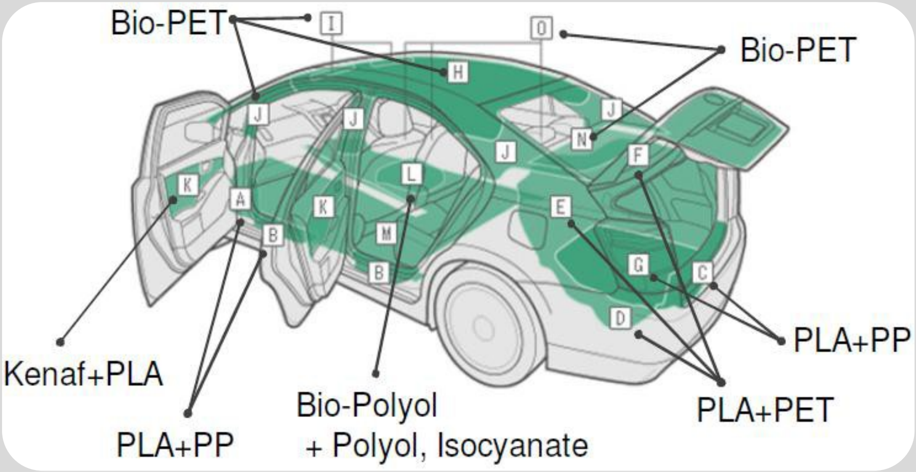


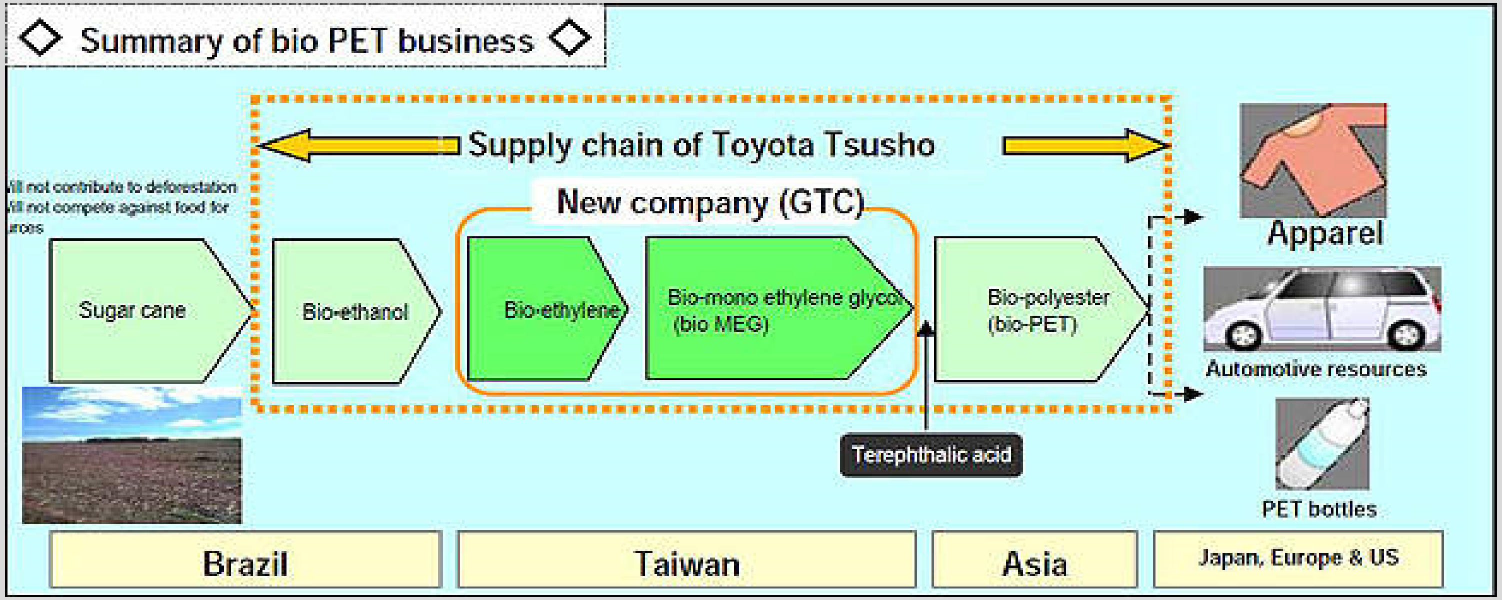
Polyethylene Furandicarboxylate

PEF

Durham University, UK

The process could start with something like the leftover plant material from sugarcane pressing. After a few reaction steps, which include the addition of some captured CO_2 and some ethylene glycol produced from corn plants, you'd end up with a plastic polymer called polyethylene furandicarboxylate - otherwise known as PEF. Functionally, it's similar to the PET plastic used for water and soda bottles



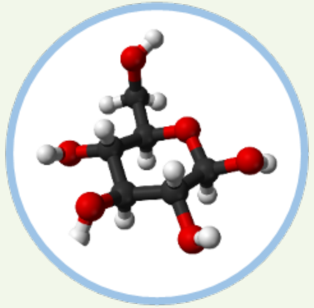


A Bio-PET business

Thailand
Bioplastics

Feedstock
cassava
sugarcane

Biomass
sugar
starch



Monosaccharide
glucose

Monomer
bio monomer

Polymer
bio polymer

Plastics
bio plastics

Number of company in Thailand

- **Sugar industry** 60 companies
- **Starch industry** 113 companies
- **Glucose industry** 19 companies
- **Bio monomer industry (lactic acid)** 1 company
- **Bio polymer industry (expected)** 1 company
- **Bio plastic industry (lactic acid)** > 3,000 company

Source: The National Innovation Agency (NIA)

Thailand
Bioplastics

PTTMCC:
Capacity 60,000 tpa
Investment THB 7.10 Billion

PTTMCC:
Capacity 34,000 tpa
Investment THB 3.17 Billion

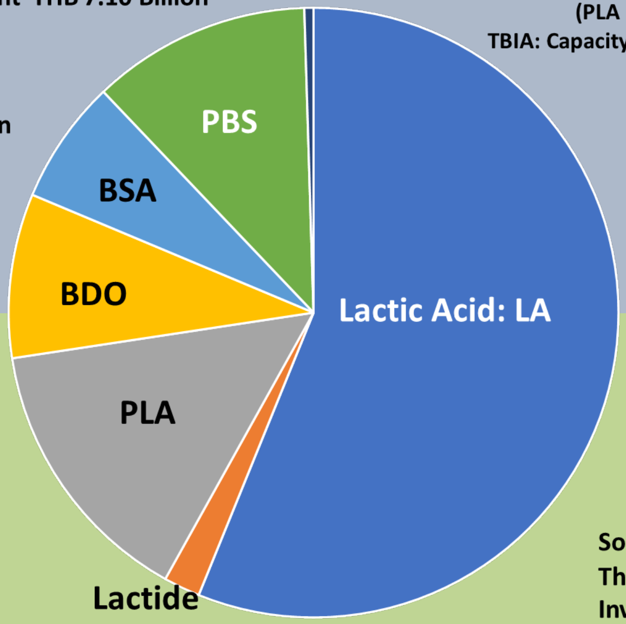
PTTMCC:
Capacity 45,000 tpa
Investment THB 3.24 Billion

PTTMCC/Nature Work:
Capacity 75,000 tpa (in USA)
Investment THB 5.28 Billion
(share 50%)

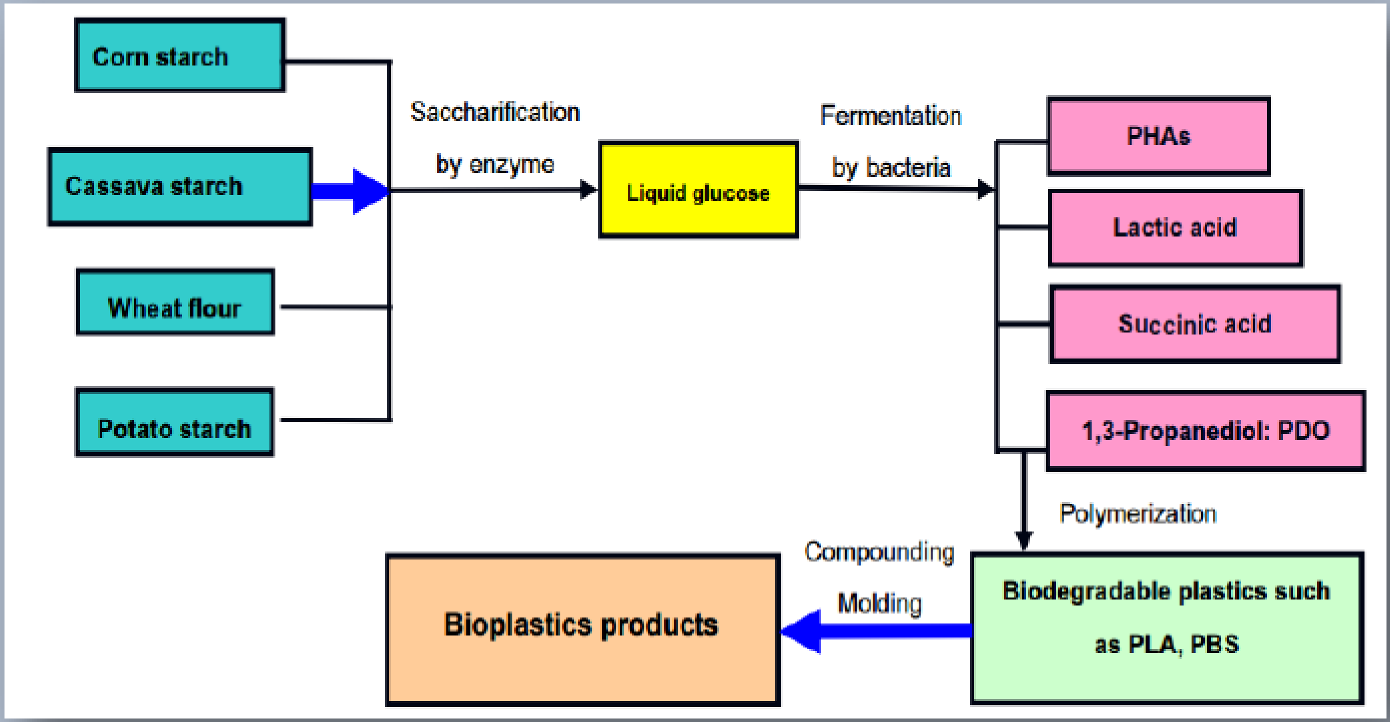
PURAC:
Capacity 10,000 tpa
Investment THB 3.15 Billion

Compound & Converter

TUSCO: Capacity 2,000 tpa (PLA Non-woven)
TBIA: Capacity 500 tpa



Source:
Thailand Board of Investment (BOI)



Thailand's Biopolymer Industry Ranking[1]

1st	The first PBS bioplastic plant in the world
2nd	PLA Producer in the world*

Total Corbion PLA, a 50/50 joint venture between Total and Corbion, announces its intention to build its second PLA plant with a capacity ramping up to 100,000 tons per annum. This expansion would make Total Corbion PLA the global market leader in PLA, firmly positioned to cater for the rapidly growing demand for Luminy® PLA resins. The new plant is planned to be located on a Total site in Grandpuits, France and to be operational in 2024.

Thailand
Bioplastics

Bio-BDO*
45,000
tons/year

BSA**
34,000
tons/year

Lactic Acid
330,000
tons/year

Source:
[1] Petroleum Institute of Thailand
*Note: * BDO = Bio-base 1,4-Butanediol;*
***BSA = Bio Succinic Acid*

CASSAVA

Export[1]

Quantity = 10 Million tons/Year
Value = $ 2.3 Million[1]
According to National Innovation Agency (NIA) research, using cassava starch as a feedstock for bioplastic products is 30% cheaper than using corn starch.

Cassava Pellets
Chip Native Starch
Sago Modified Starch

SUGARCANE

Export[2]

Quantity = 6 Million tons/Year
Value = $ 2.3 Million
Bioplastic production processes consumes only 54,000 tons of sugar per year which is less than 1% of the total export. Moreover, the processing of sugarcane to produce bioplastics creates almost 10-times value added benefits.[3]

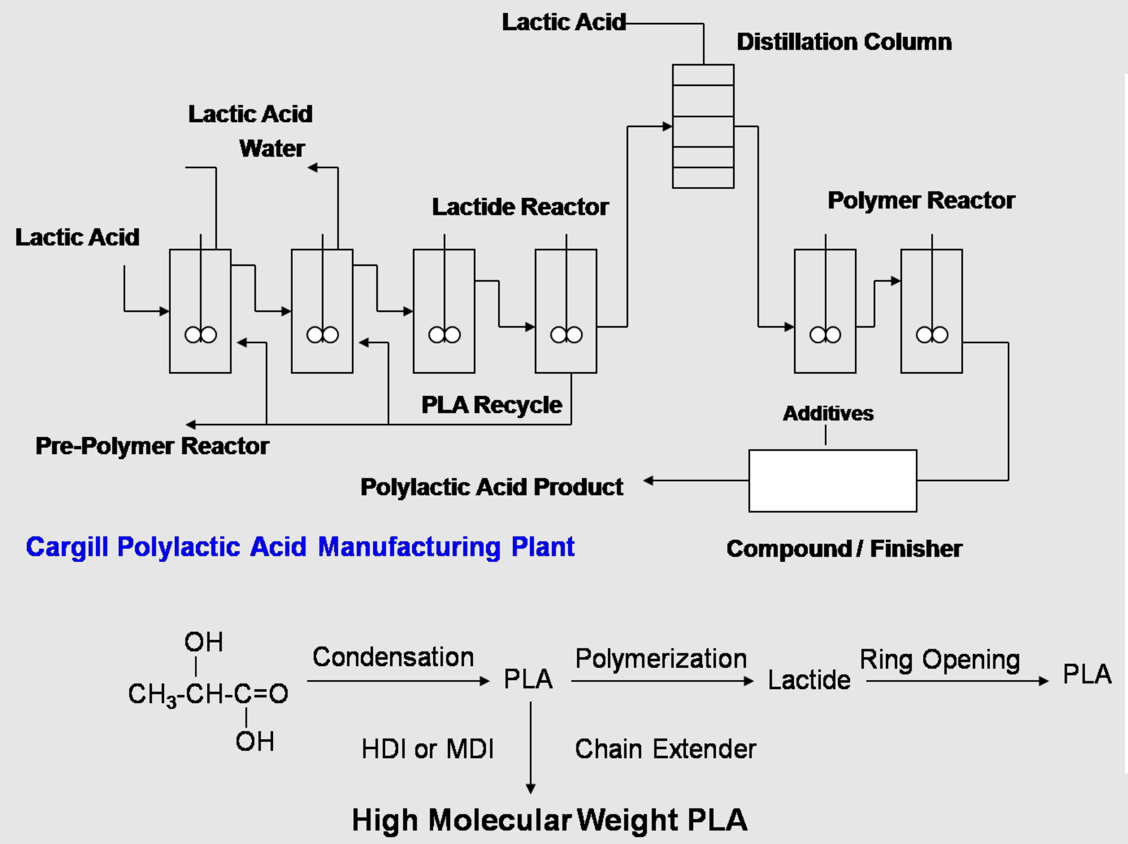
Raw Sugar
White Sugar

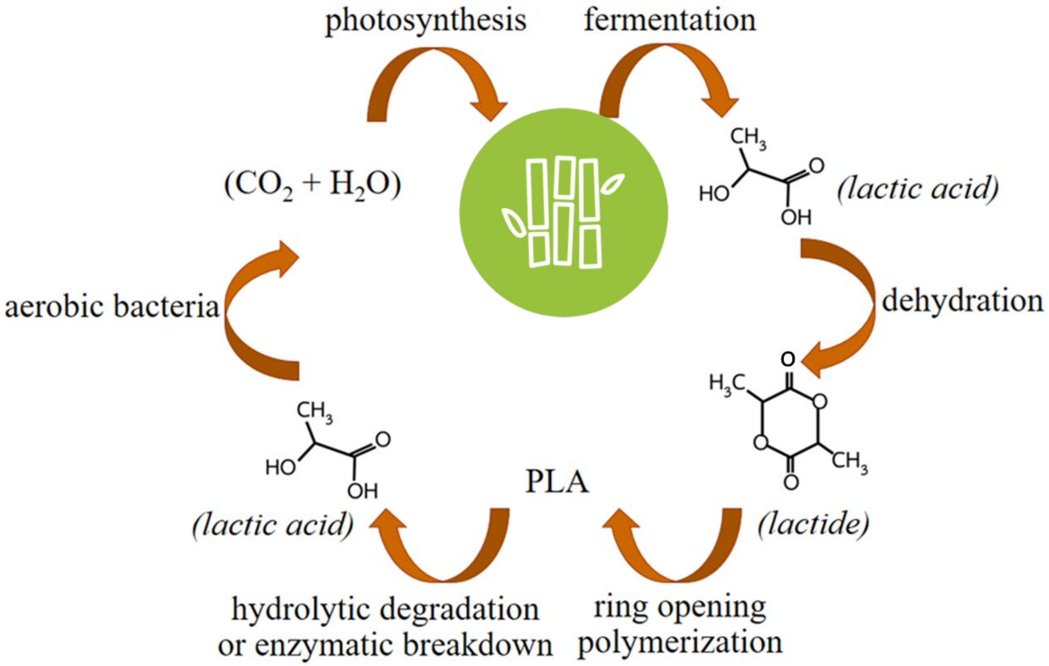
6x - 15x
Value Added

Ethanol	Biogas	Biomass	Lactic Acid
1,058 million liter/years[4]	1,523 million liter/years[4]	2,321 MW[4]	330,000 tons/year[4]
Citric Acid	**Sorbitol**	**Lysine**	**PBS***
15,000 tons/years[4]	43,000 tons/years[4]	47,000 tons/years[4]	20,000 tons/years[4]

Source:
[1, 2] Office of Agricultural Economics
[3] Thailand Bioplastics Industry Association (TBIA)
[4] Petroleum Institute of Thailand and BIOTEC
Note:
** PBS = Polybutylene Succinate*
Exchange rate (BOT, May 1, 2017):
USD 1 = THB 34.70

Polylactic acid: PLA



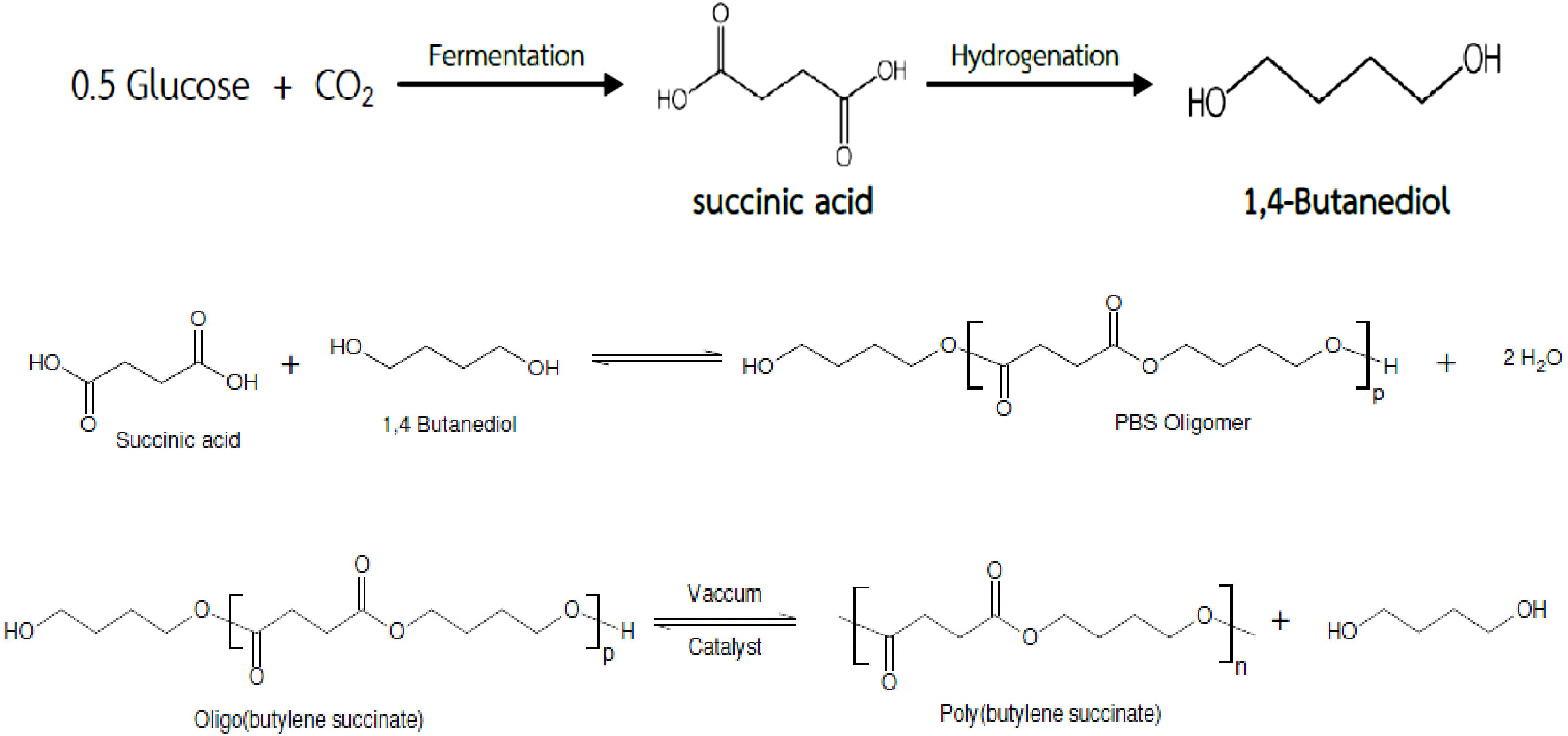


Sources of BIOPLASTICs

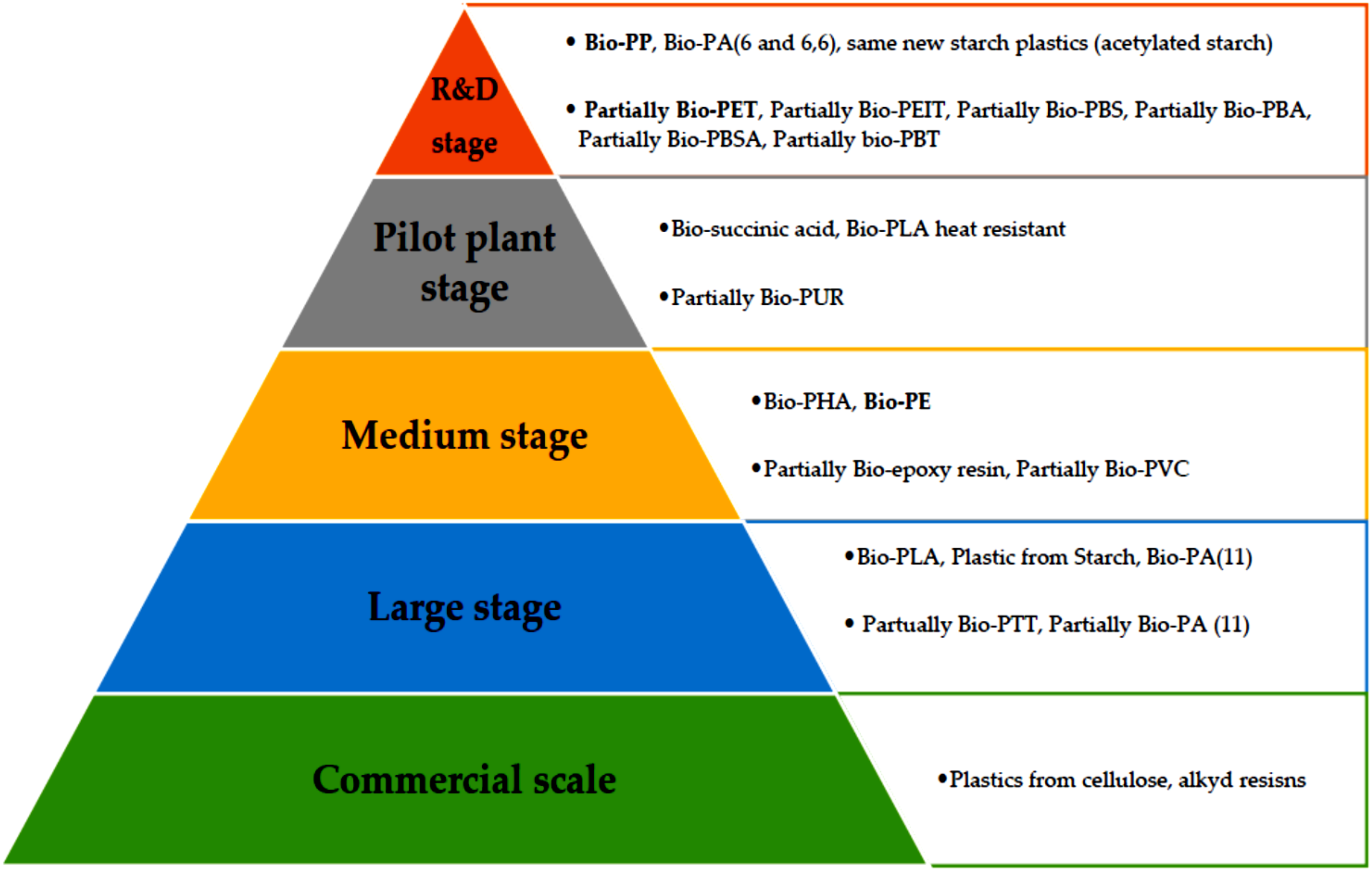
Corn

Sugarcane

Casava



Development stages for emerging bio-based polymers



Limitations of Bioplastic

CHALLENGES OF BIOPLASTICS

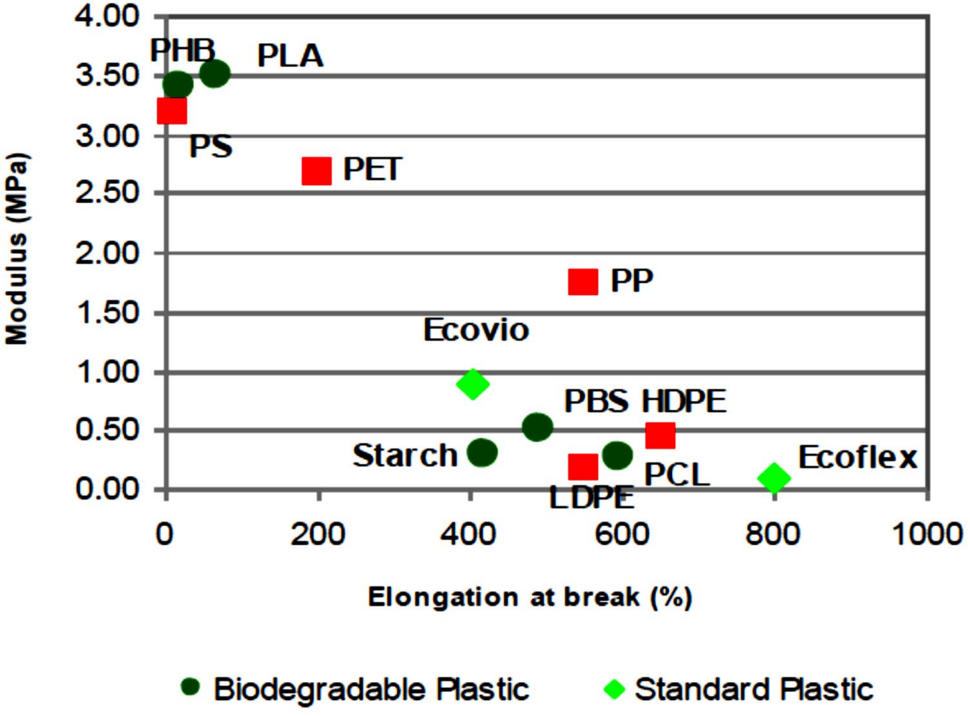
01 **Specific properties**

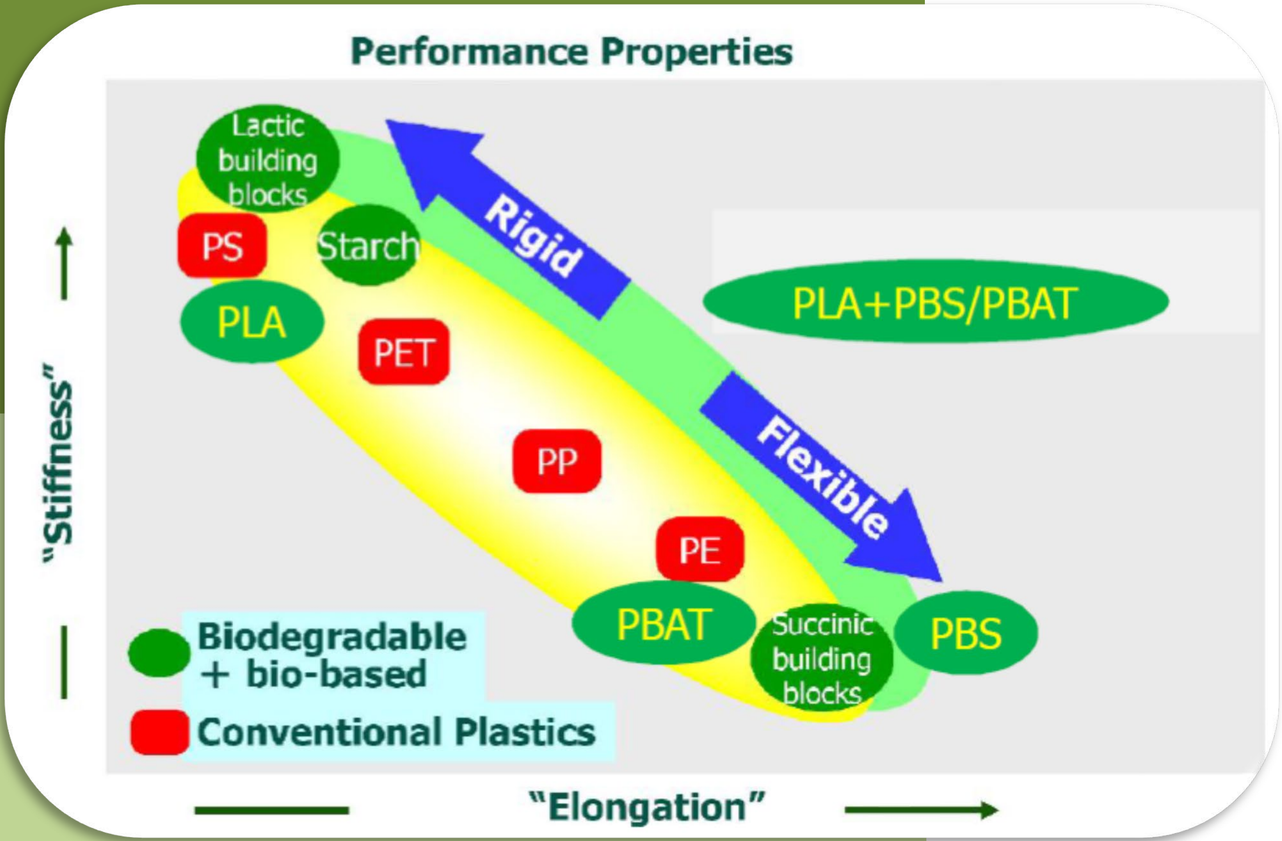
02 **Specific process**

03 **Food crisis**

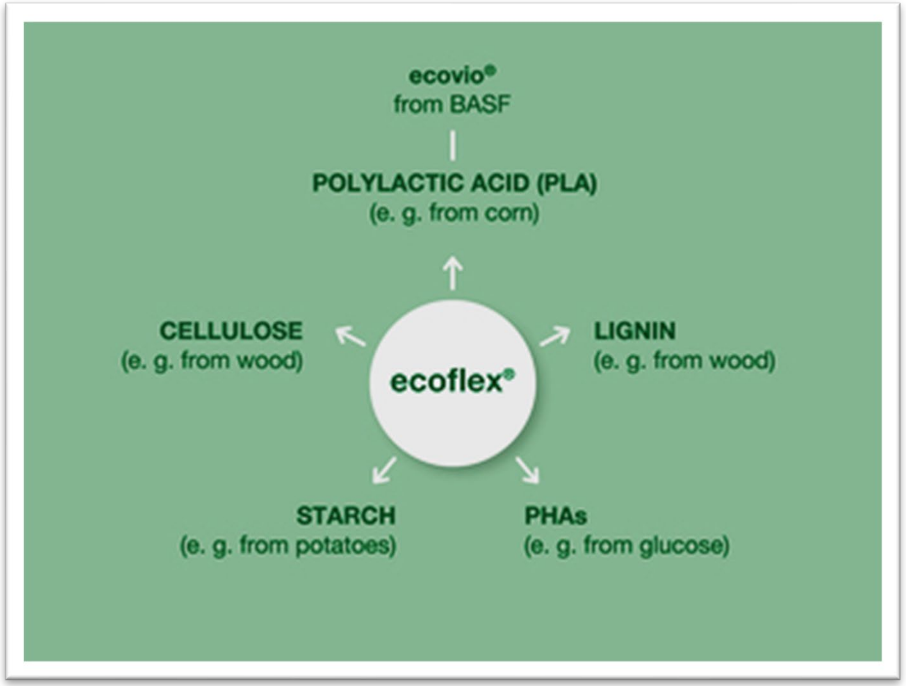
04 **Waste collection**

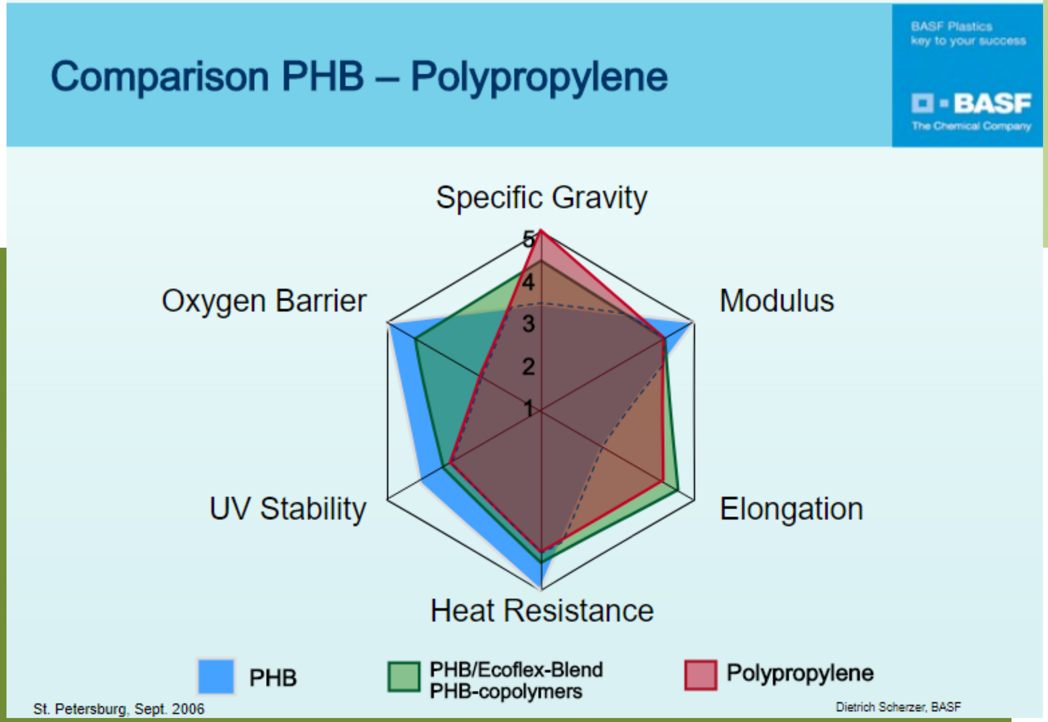
- The bioplastic making process is expensive to process compare to petroleum plastic.
- Bioplastic is not stable, durable compare to petroleum plastic.
- Bioplastic has a lot of competition between bioplastic industries or food manufacturing units.
- Bioplastic also produced pollution due to fertilizers and pesticide using during crop production.





MECHANICAL PROPERTIES





- Ecovio®

  45 % PLA + Ecoflex®, BASF (D)
- Ecovio® L-Foam

  75 % PLA + Ecoflex®, BASF (D)
- Bio-Flex®

  PLA + Copolyester, FKuR (D)

Similar to PET and/or PS (converting)

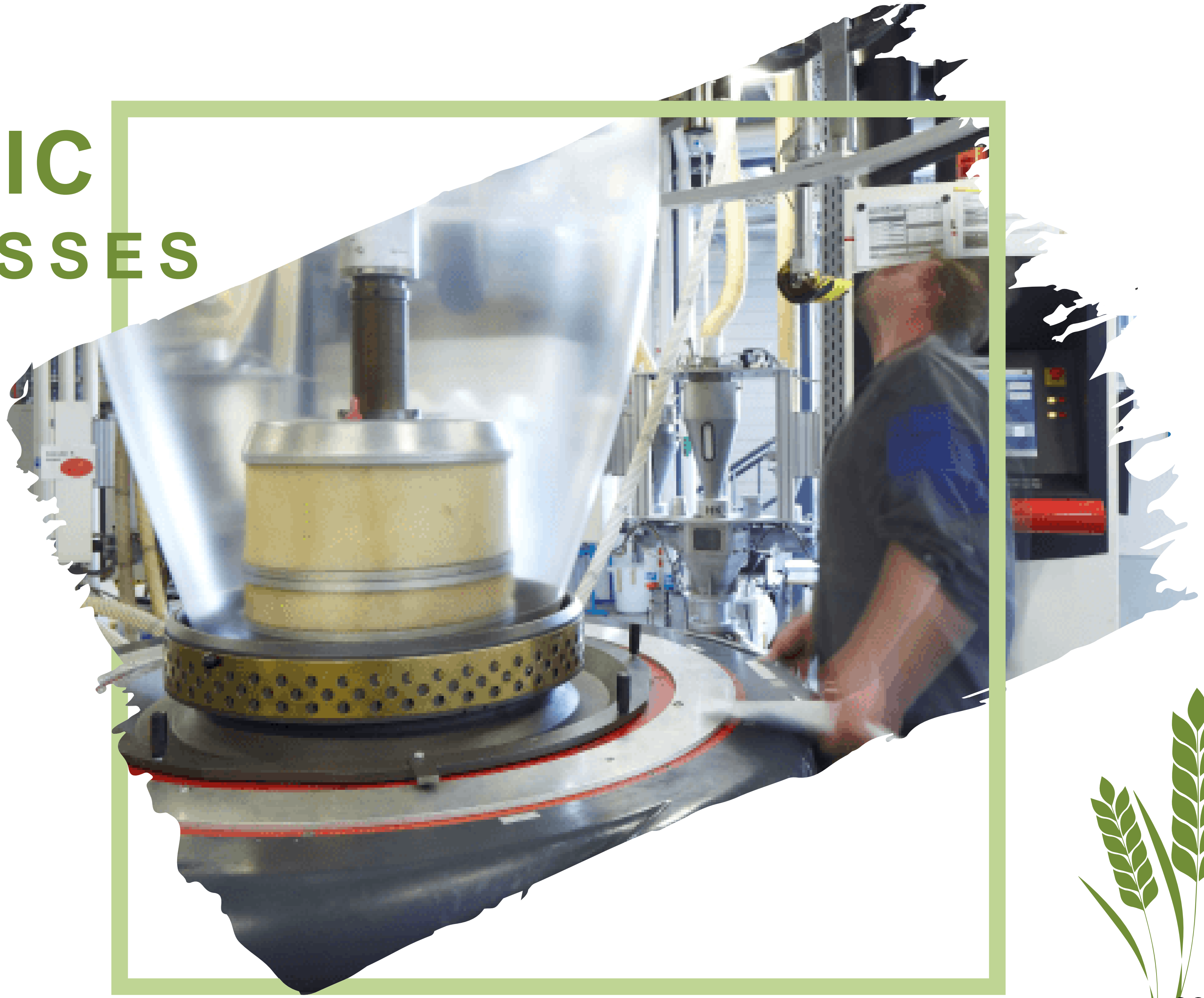
Sensitive to temperature!

Source: www.basf.com 2008-09-12
YU L. et al. 2006

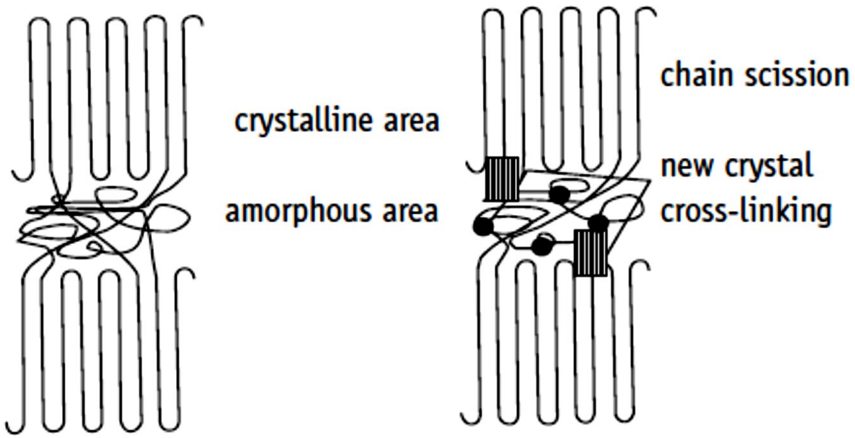
BIOPLASTIC
PROCESSES

Most biodegradable polymers can be processed using a variety of processing methods.

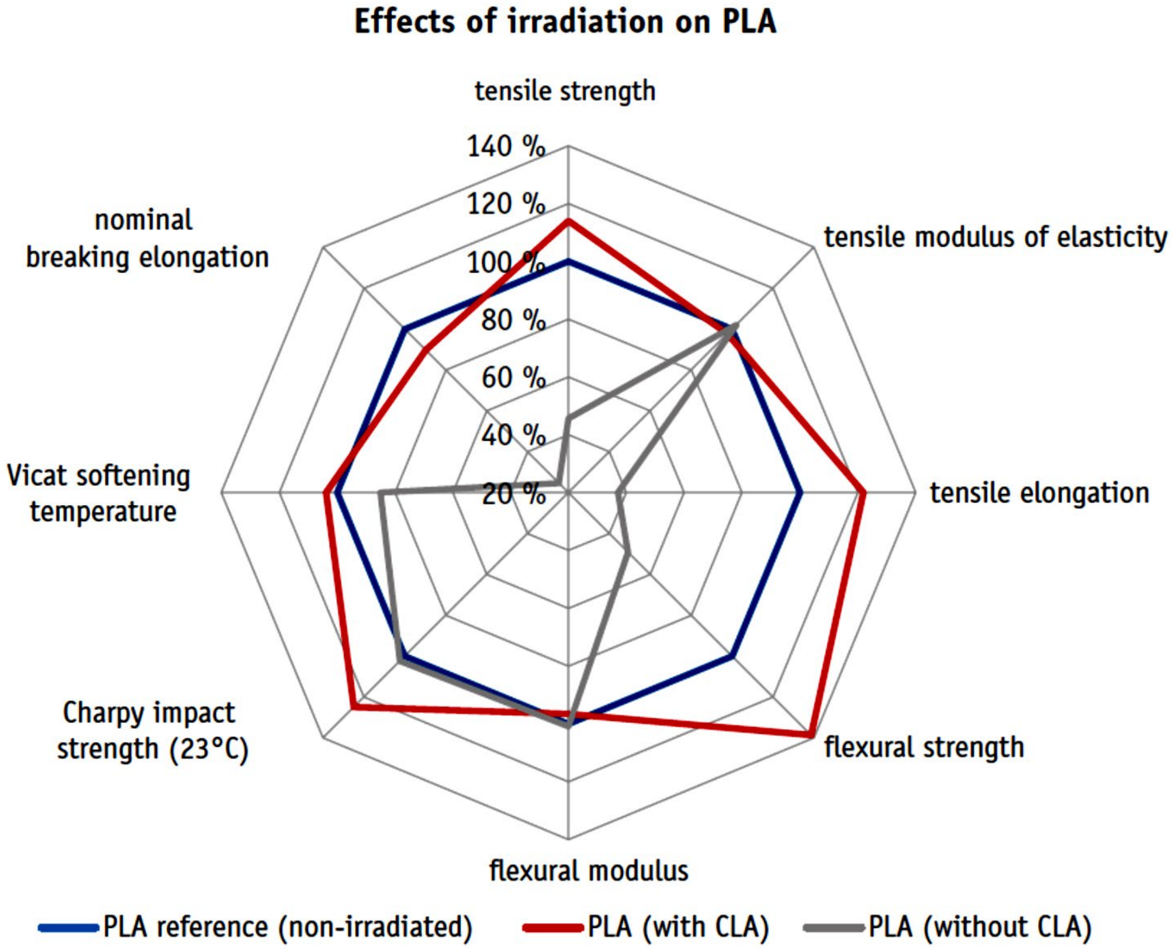
1. Injection molding
2. Compression molding
3. Film casting
4. Blow molding
5. Blown film extrusion
6. Thermoforming
7. Fiber spinning



PLA
Modification



Effect of irradiation cross-linking on the morphology of a non-irradiated and an irradiated semi-crystalline polymer



Effects of irradiation on the characteristics of PLA

Main issues

1. Interaction with water
    - Hydrolysis
    - Voids or bubbles
    - Unstable shaping
2. Narrow processing temperature window
3. Low crystallization rate
4. Require low shear stress
5. Well cleaning after process is required

- The processing window of biodegradable polymers is very narrow. Therefore, it is tough to process biodegradable polymers between the melting point and the point of decomposition.

Concerned factors:

- **melt temperature,**
- **screw speed,**
- **injection speed,**
- **and proper drying.**

Gels, black specs, and yellowing are created when the polymer is exposed to too much heat.

Suggestion solutions:

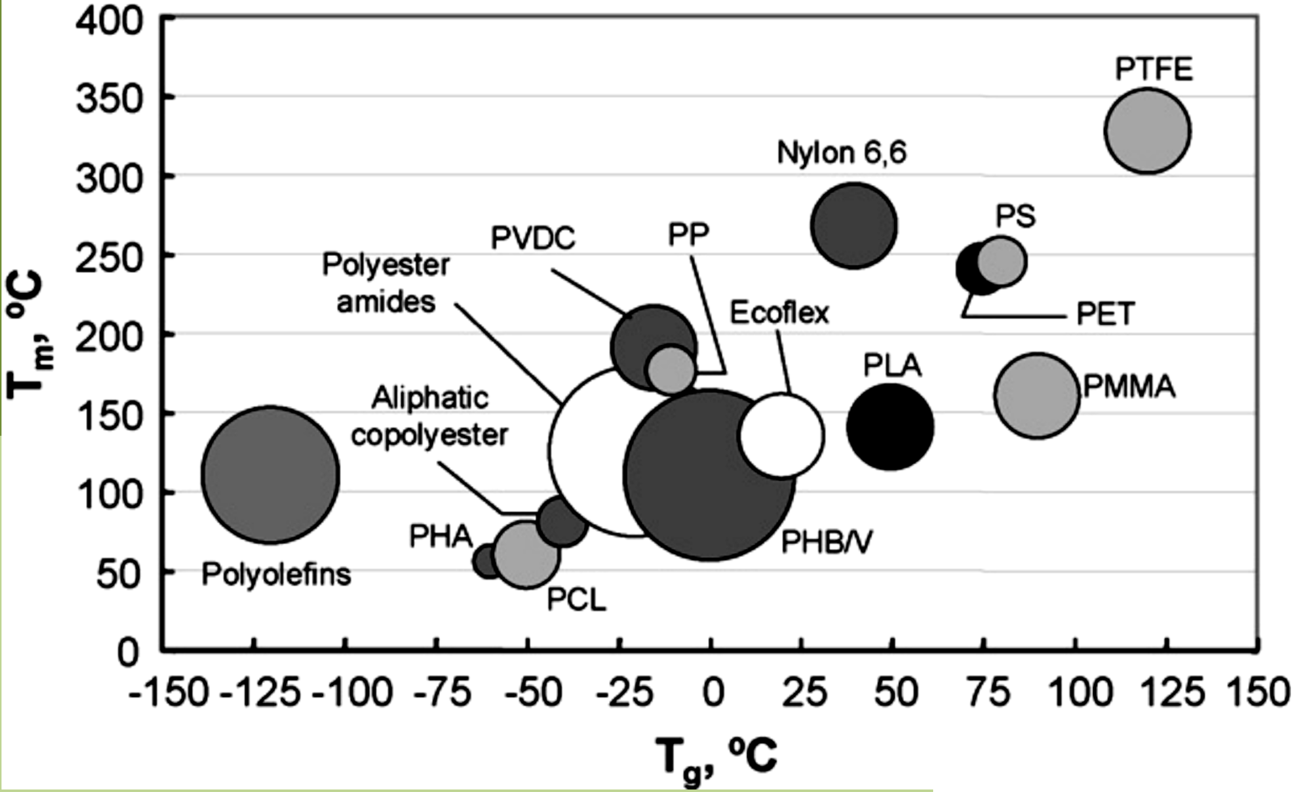
- **operating condition adjustment**
- **equipment design**
- **material selection and development**

Bio-PE
very suitable

PLA-blend
suitable

TPS-blend
less suitable

Key parameters are the **melt stiffness** (extensional viscosity) and the swelling and sagging behavior.

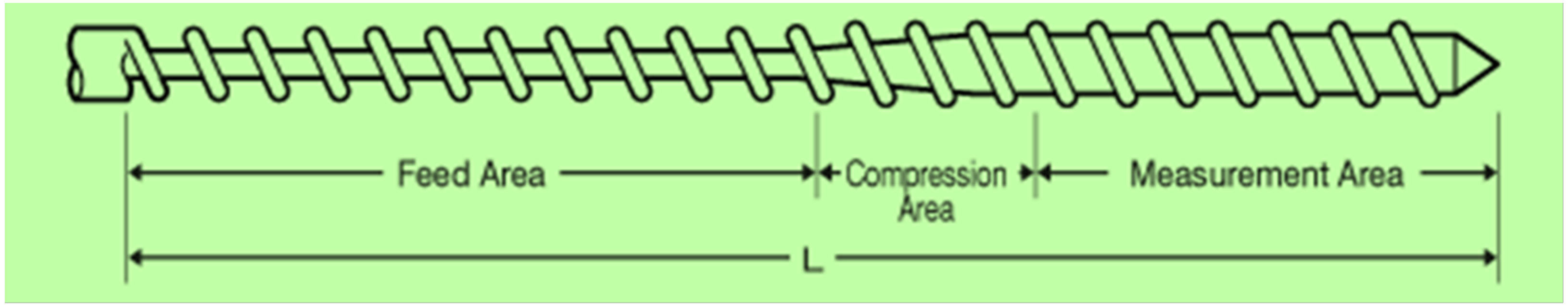


Comparison of glass transition and melting temperatures of PLA with other thermoplastics.

Progress in Polymer Science 33 (2008) 820–852

OPERATING conditions

PBAT/PLA co-polyester and also pure PBS offer high tensile strengths; these are, however, accompanied by high values for the breaking elongation and a low modulus of elasticity. These films exhibit a correspondingly soft behavior, which restricts the application range.



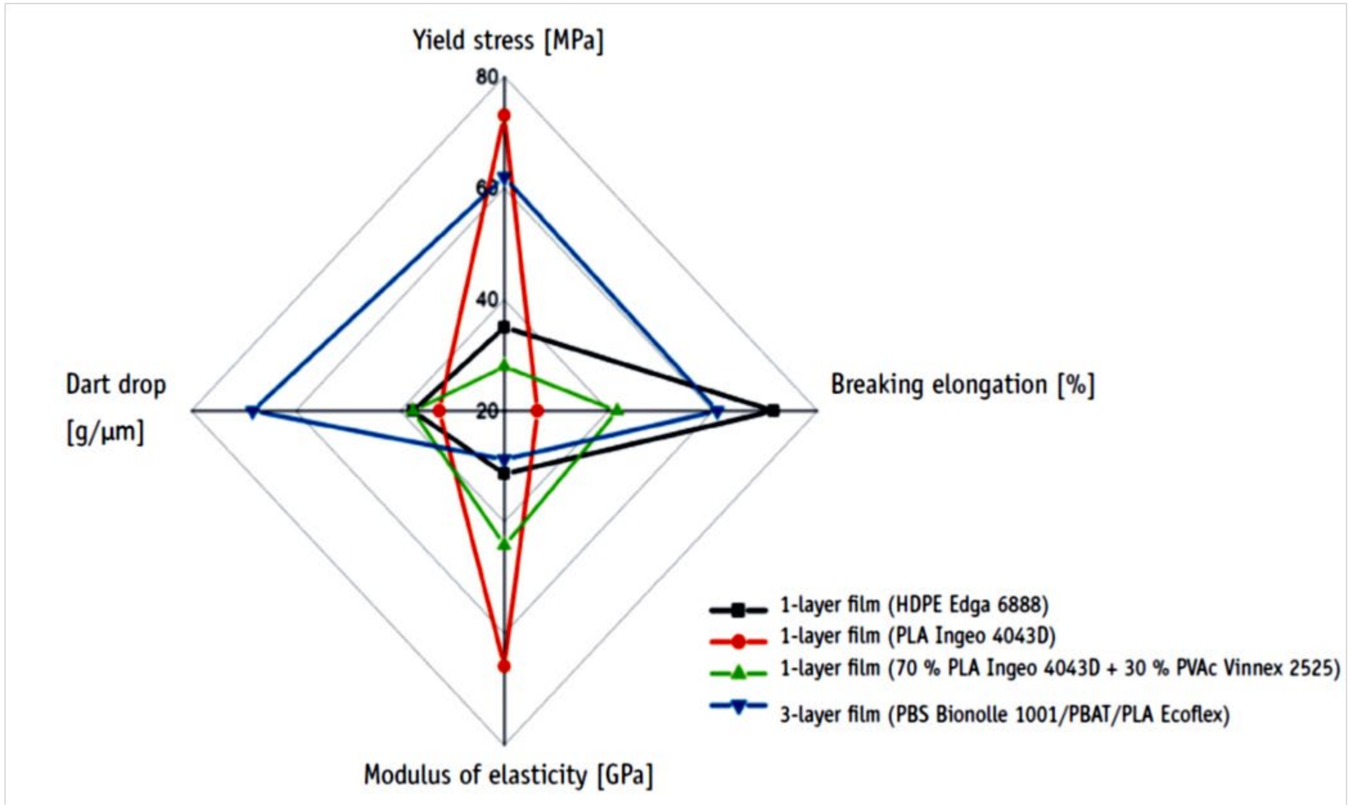
L/D ratio = 24
Compression ratio = 2.4

L/D ratio = 26
Compression ratio = 3.4

- Although biodegradable polymers are semicrystalline and have low melting temperatures, they are relatively slow to crystallize. Cycle time and heat resistance can be improved by using nucleation technology.

- Biodegradable polymers tend to stick to metal surfaces during processing and absorb moisture on exposure to ambient air.
- Biodegradable polymers are hygroscopic and must be dried to avoid a drop in molecular weight, melt viscosity, as well as increased potential for flashing and brittle parts.

In the case of PLA, roller temperatures are set relatively higher to 255 °C to prevent condensation of lactide monomers and slippage of web on the rollers.
- The die is positioned as close as possible to the entrance nip however keeping it slightly higher than the nip can help in accommodating drooping of the molten polymer avoiding any chance of trapping air and reducing film defects.



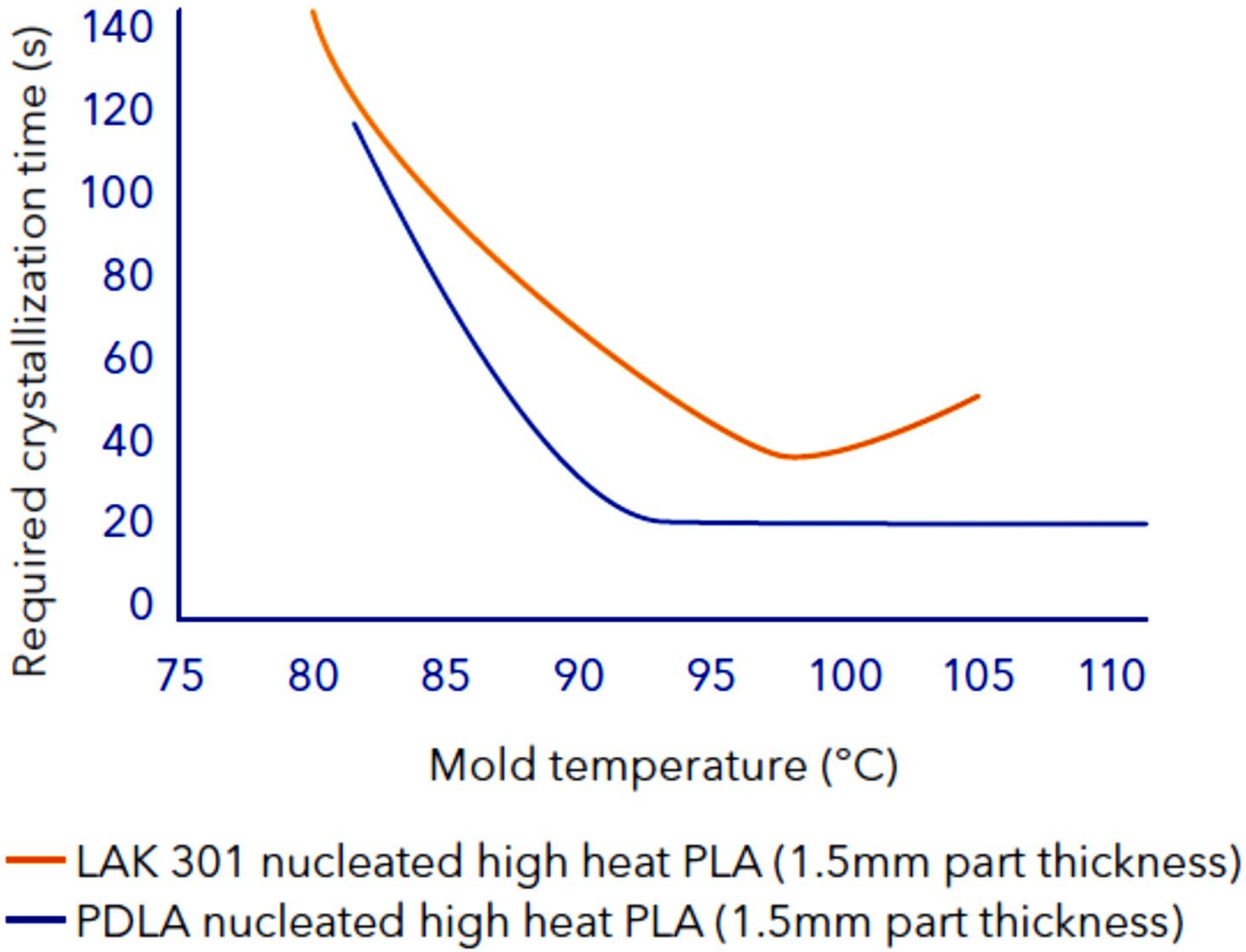
Molten PLA extrudate coming out from the die

- External deckles are used on the die to adjust the film width because
- of the thermal sensitivity of biodegradable polymers.
- Particularly effective with PLA is the polyvinyl acetate-based binder.
- The (PLA-PVAc)/(PLA-PBAT) combination gives high mechanical properties, particularly puncture resistance and breaking elongation.

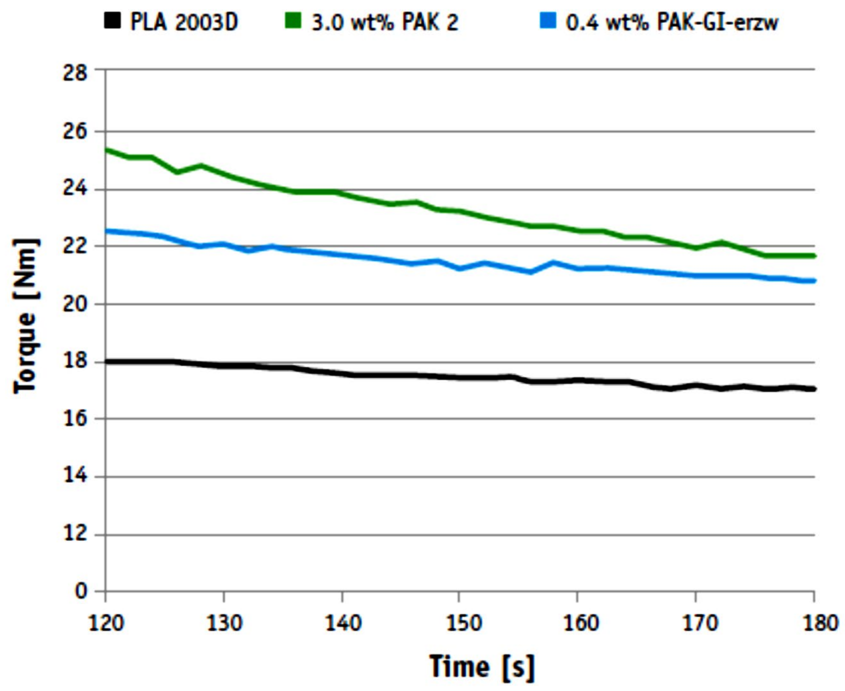
DEMOLDING BEHAVIOR

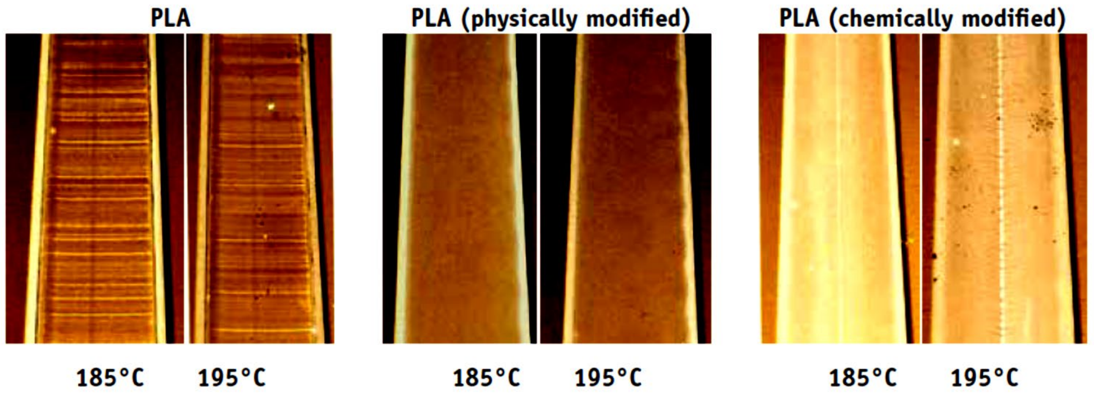
The forces which thereby act upon the ejector are dependent on

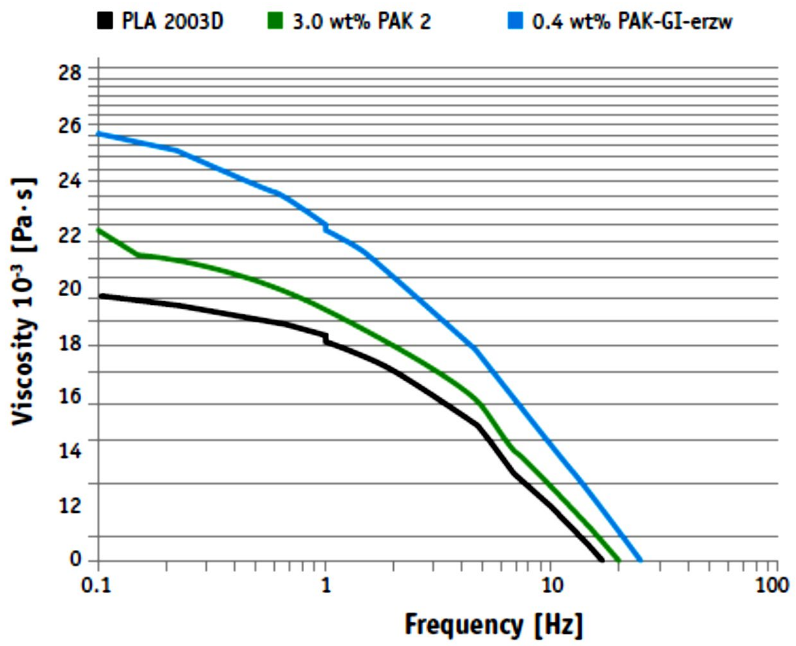
the shrinkage,
the coefficient of friction between the injection molding and the cavity,
the stiffness of the material.



Demoulding agents based on N,N'-ethylenbis (stearamid): PHB, Bio-PE, PLA and Bio-PA


PLA 2003D
3.0 wt% PAK 2
0.4 wt% PAK-GI-erzw
Torque [Nm]
Time [s]
28
26
24
22
20
18
16
14
12
0
120
130
140
150
160
170
180


PLA
PLA (physically modified)
PLA (chemically modified)
185°C
195°C
185°C
195°C
185°C
195°C


PLA 2003D
3.0 wt% PAK 2
0.4 wt% PAK-GI-erzw
Viscosity 10^{-3} [Pa·s]
Frequency [Hz]
28
26
24
22
20
18
16
14
12
0
0.1
1
10
100

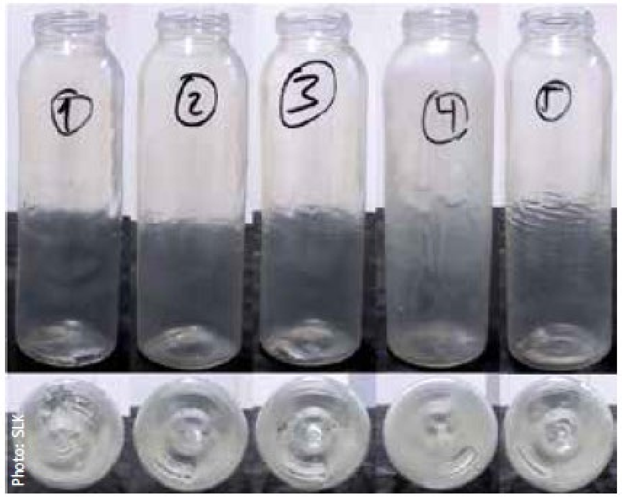


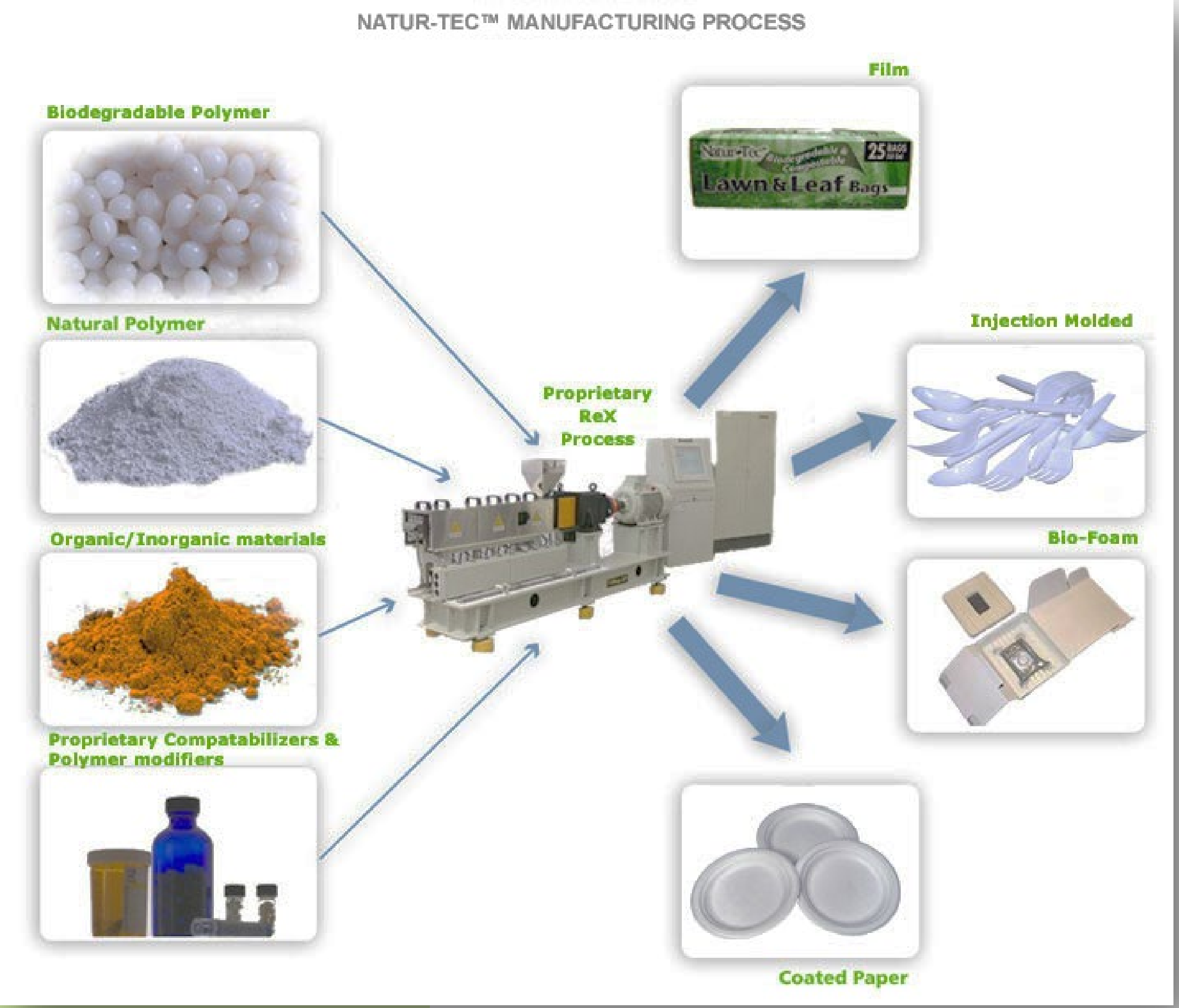
Photo: SLK

C O M P O U N D I N G

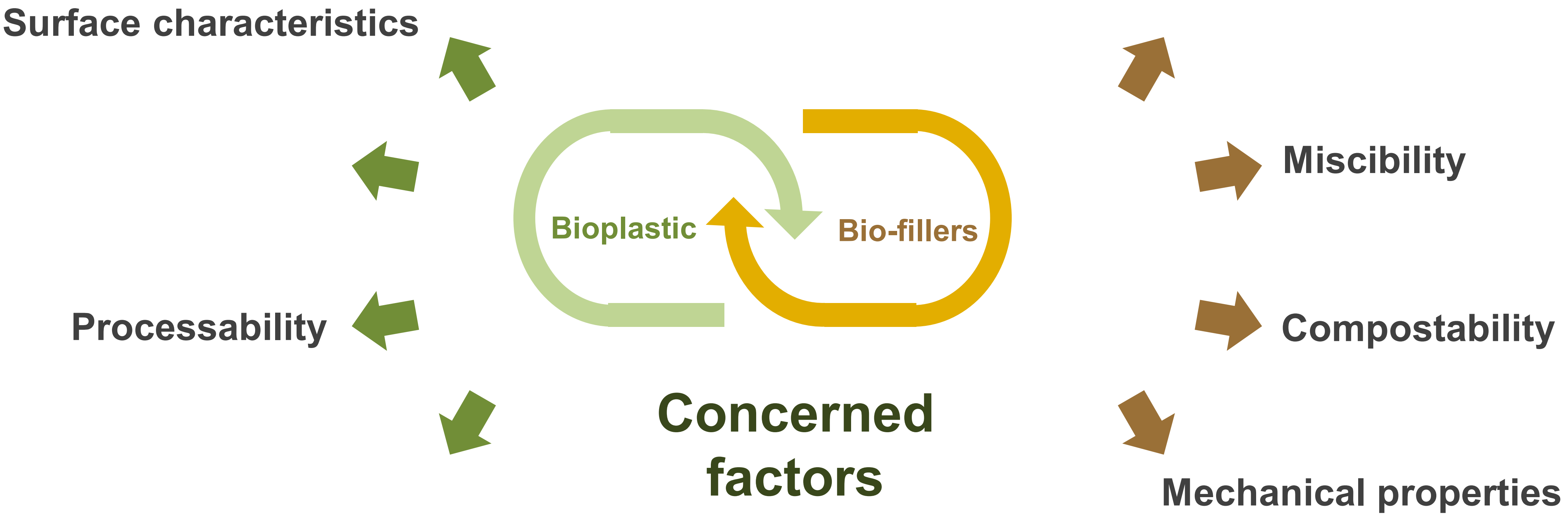
Additives for the improvement of:

- **Mechanical properties**
- **Processability**
- **Chemical modification**
- **Surface modification**
- **Decoration**

- Additives are specially designed for using in combination with biopolymers, mainly PLA (poly(lactic acid)) PHA, (poly(hydroxy alcanoates)), starch based polymers etc.
- They can be used as plasticizers, chain extender, nucleating agent and nanofiller compatibilizer; furthermore, showing low volatilities, low migration, good thermal stability and total biodegradability.



Blends and composites



Examples

SURFACE MODIFICATION OF SUGARCANE BAGASSE CELLULOSE AND ITS EFFECT ON MECHANICAL AND WATER ABSORPTION PROPERTIES OF SUGARCANE BAGASSE CELLULOSE/ HDPE COMPOSITES

BioResources Vol 5, No 2 (2010)

Cellulose fibres from sugarcane bagasse were bleached and modified by zirconium oxychloride in order to improve the mechanical properties of composites with high density polyethylene (HDPE).

Alkaline surface modification of sugar cane bagasse

Journal Advanced Composite Materials
Volume 9, 2000 - Issue 2

The treatment with calcium hydroxide [$Ca(OH)_2$] chemically modifies the surface of the bagasse fibre producing a calcium carbonate deposit on the surfaces, whereas sodium hydroxide [NaOH] has little or no effect. The main action of NaOH on the fibre is to remove the lignin binder of the cellulosic material.

Improved properties of keratin-based bioplastic film blended with microcrystalline cellulose: A comparative analysis

Journal of King Saud University - Science
Volume 32, Issue 1, January 2020, Pages 853-857

Bioplastic (K-60) was developed from the keratin, extracted from the chicken feathers using an alkaline agent (NaOH), and mixed with PVA/glycerol to synthesize protein-based bioplastic. Further, microcrystalline cellulose (2%) was used as an additive to K-60 bioplastic to develop an improved bioplastic (KC-60).

Bioplastics from Blends of Cassava and Rice Flours: The Effect of Blend Composition

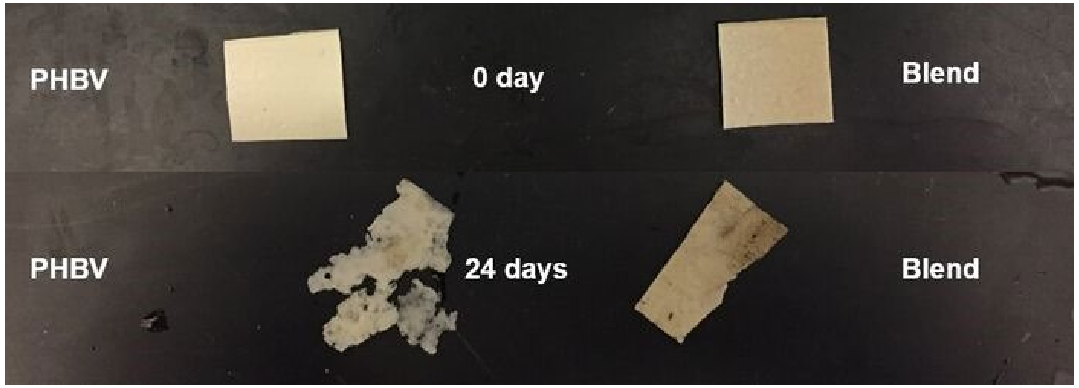
Examples

This Bioplastic and Rubber Blend is Biodegradable, Flexible, and Tough

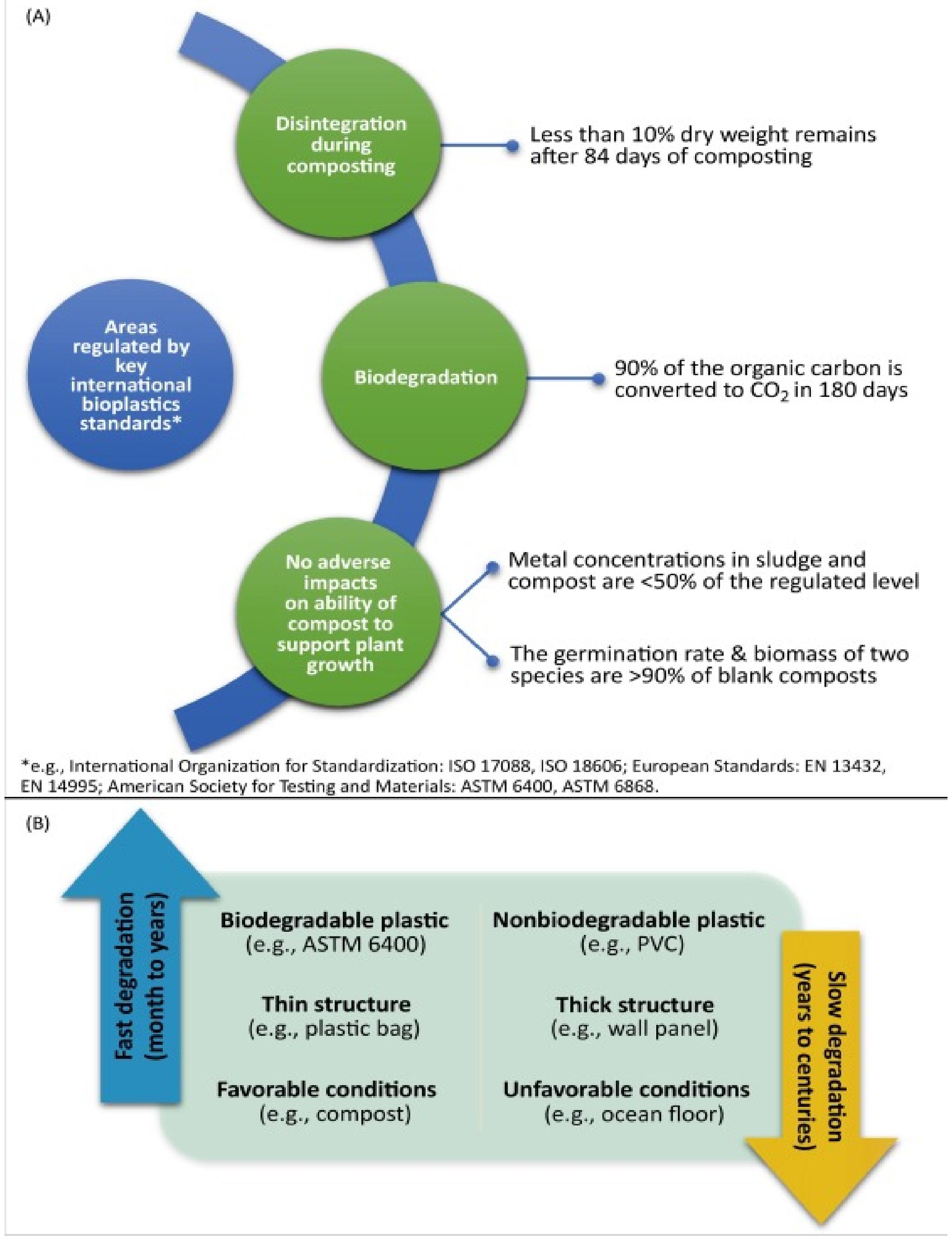
Natural rubber (NR), polymers of isoprene, is harvested in the form of latex from rubber trees. It is stretchable and highly resilient to physical stress, and yet susceptible to bacterial degradation. NR is commonly added during the productions of many polymer-based products, as a toughening agent. But the Ohio State team went to a couple of steps further.

The team of material chemists added an acrylic coagent (to perform cross-linking between PHBV and NR) and an organic peroxide (to catalyze the polymerization) in their process, which allow PHBV to be firmly grafted onto the rubber backbones. The two additives also decreased PHBV crystallinity and crystal size, making the final PHBV-NR blend much less brittle.

With 75% tougher and 100% more flexible than PHBV alone, the bioplastic and natural rubber mix holds great promise to replace the current food packaging material, which constitutes the largest source of single-use plastics at the moment.



Natural rubber-bioplastic blend showed better stability against degradation (Ohio State U)



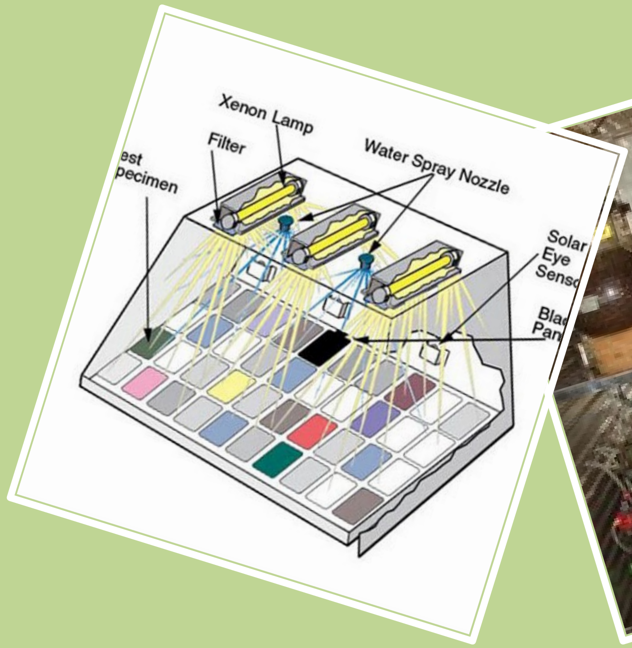
Trends in Plant Science

Standard	Description
AS 4736-2006	Biodegradable plastics—biodegradable plastic suitable for composting and other microbial treatment
ASTM D5209-92	Standard test method for determining the aerobic biodegradation of plastic materials in the presence of municipal sewage sludge
ASTM D5338-98	Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions
DIN V 54900-2	Testing of compostability of plastics—Part 2: testing of the complete biodegradability of plastics in laboratory tests
EN 13432:2000	Requirements for packaging recoverable through composting and biodegradation—test scheme and evaluation criteria for the final acceptance of packaging
ISO 14851:1999	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium—method by measuring the oxygen demand in a closed respirometer
ISO 15314:2004	Methods for marine exposure ISO 16221:2001 water quality—guidance for the determination of biodegradability in the marine environment
CEN/TR 15822	Plastics: biodegradable plastics in or on soil—recovery, disposal and (under approval) related environmental issues
AFNOR NF U52-001	Biodegradable materials for use in agriculture and horticulture-mulching products—requirements and test methods

STANDARD

Compostability test

- Mechanical test
- Thermal analysis
- Physical observation
- Test related to applications



"Learning is a never-ending process. Those who wish to advance in their work must constantly seek more knowledge, or they could lag behind and become incompetent."

His majesty late king bhumibol adulyadej

Thank You

for your attention

ryeetsor@hotmail.com