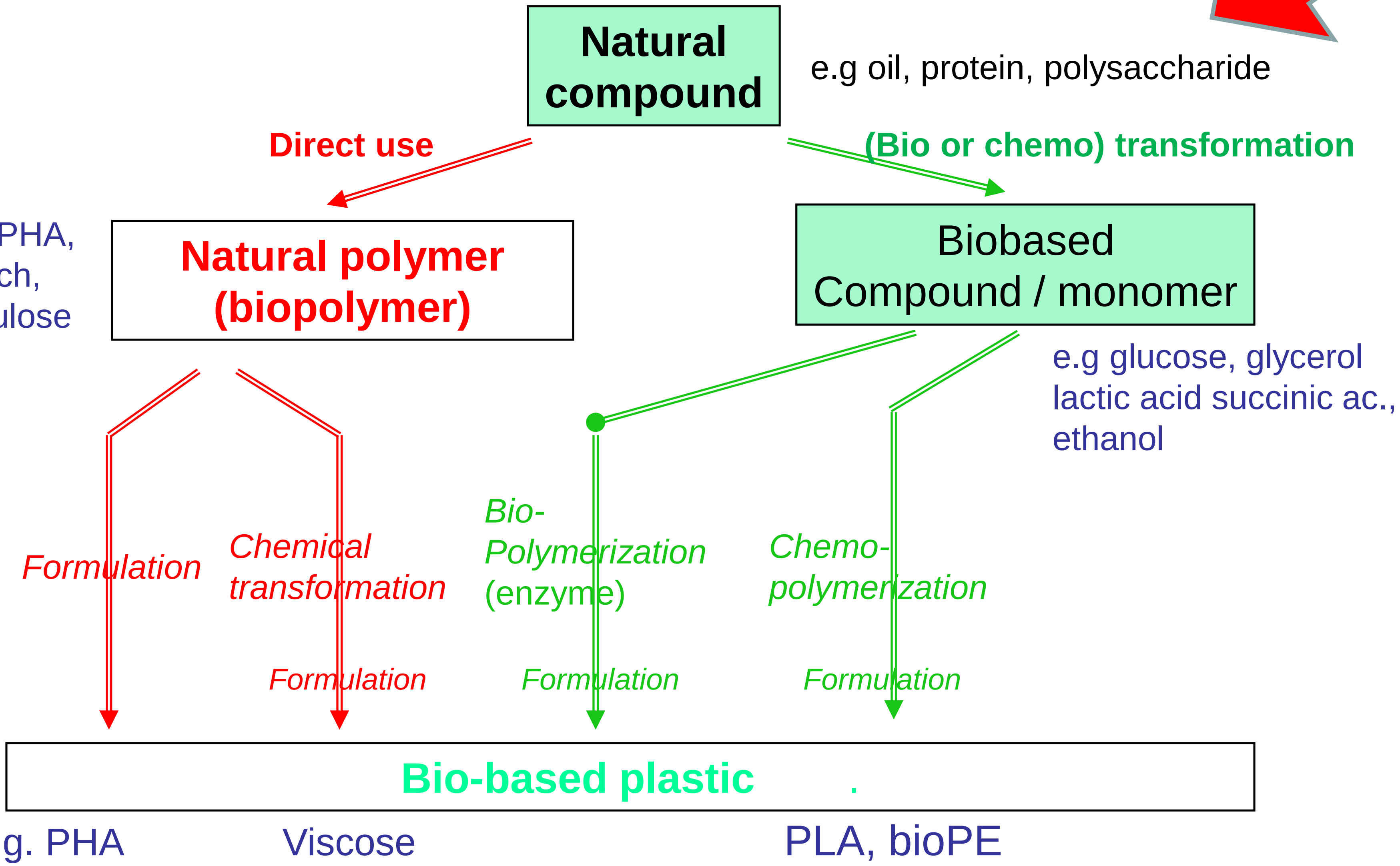
Producing bio-based plastics



Natural compound

e.g oil, protein, polysaccharide

Direct use

(Bio or chemo) transformation

e.g PHA, starch, cellulose

Natural polymer (biopolymer)

Biobased Compound / monomer

e.g glucose, glycerol lactic acid succinic ac., ethanol

Formulation

Chemical transformation

Bio-Polymerization (enzyme)

Chemo-polymerization

Formulation

Formulation

Formulation

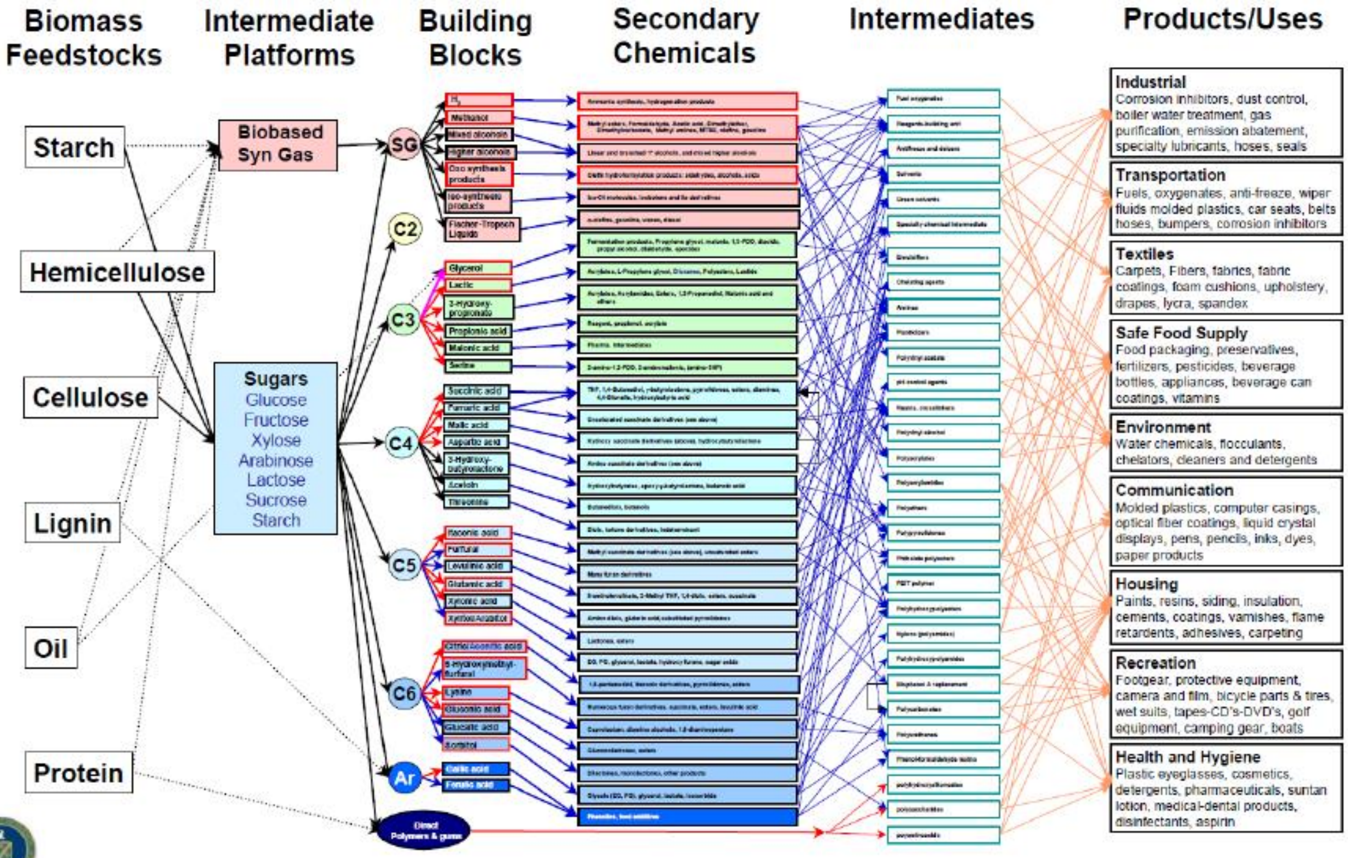
Bio-based plastic .

e.g. PHA

Viscose

PLA, bioPE

Most promising platform molecules (2) - U.S. DoE



Industrial
Corrosion inhibitors, dust control, boiler water treatment, gas purification, emission abatement, specialty lubricants, hoses, seals

Transportation
Fuels, oxygenates, anti-freeze, wiper fluids molded plastics, car seats, belts hoses, bumpers, corrosion inhibitors

Textiles
Carpets, Fibers, fabrics, fabric coatings, foam cushions, upholstery, drapes, lycra, spandex

Safe Food Supply
Food packaging, preservatives, fertilizers, pesticides, beverage bottles, appliances, beverage can coatings, vitamins

Environment
Water chemicals, flocculants, chelators, cleaners and detergents

Communication
Molded plastics, computer casings, optical fiber coatings, liquid crystal displays, pens, pencils, inks, dyes, paper products

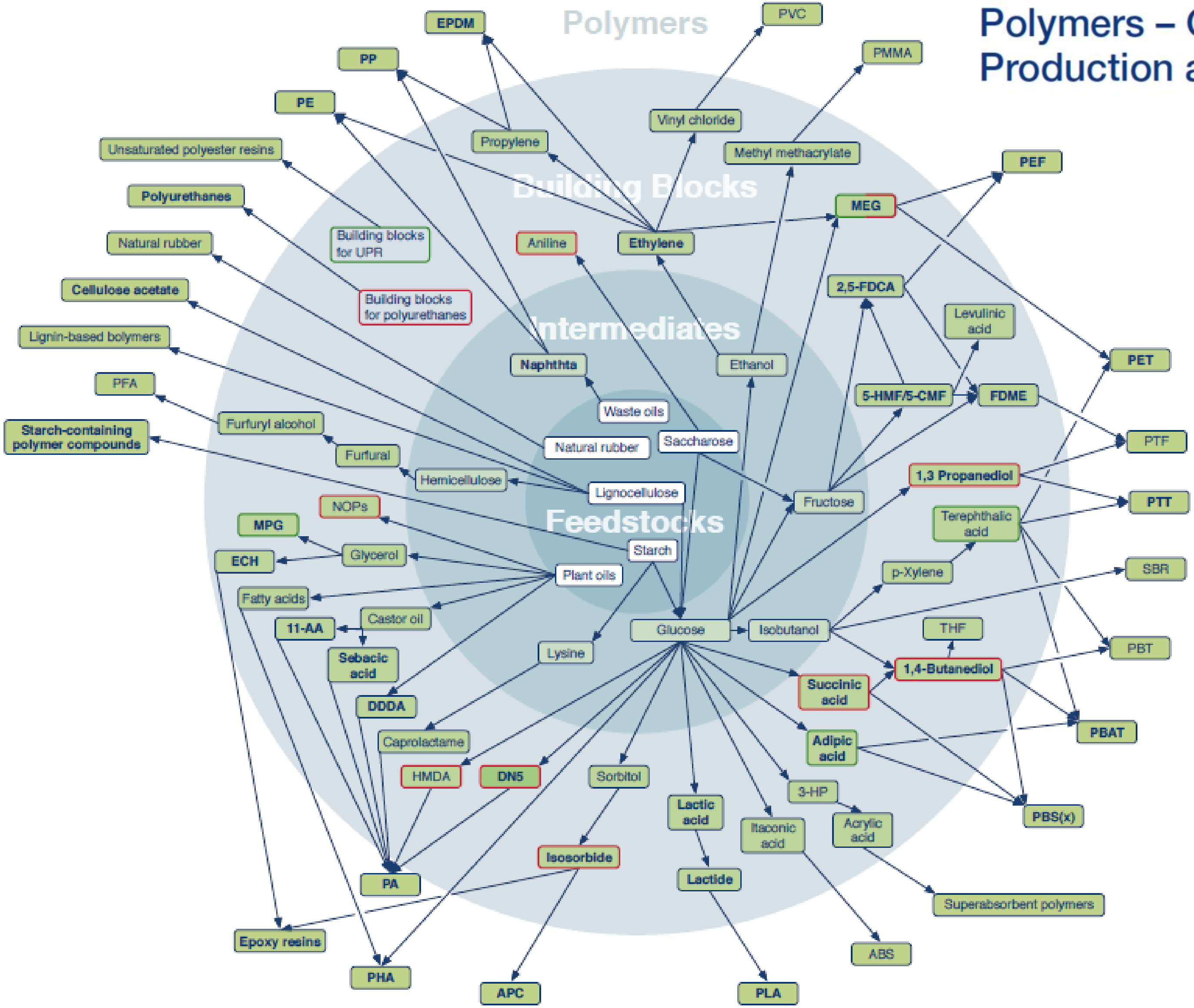
Housing
Paints, resins, siding, insulation, cements, coatings, varnishes, flame retardents, adhesives, carpeting

Recreation
Footgear, protective equipment, camera and film, bicycle parts & tires, wet suits, tapes-CD's-DVD's, golf equipment, camping gear, boats

Health and Hygiene
Plastic eyeglasses, cosmetics, detergents, pharmaceuticals, suntan lotion, medical-dental products, disinfectants, aspirin

Figure 1 – Analogous Model of a Biobased Product Flow-chart for Biomass Feedstocks

Bio-based Building Blocks and Polymers – Global Capacities, Production and Trends 2019–2024



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January 2020

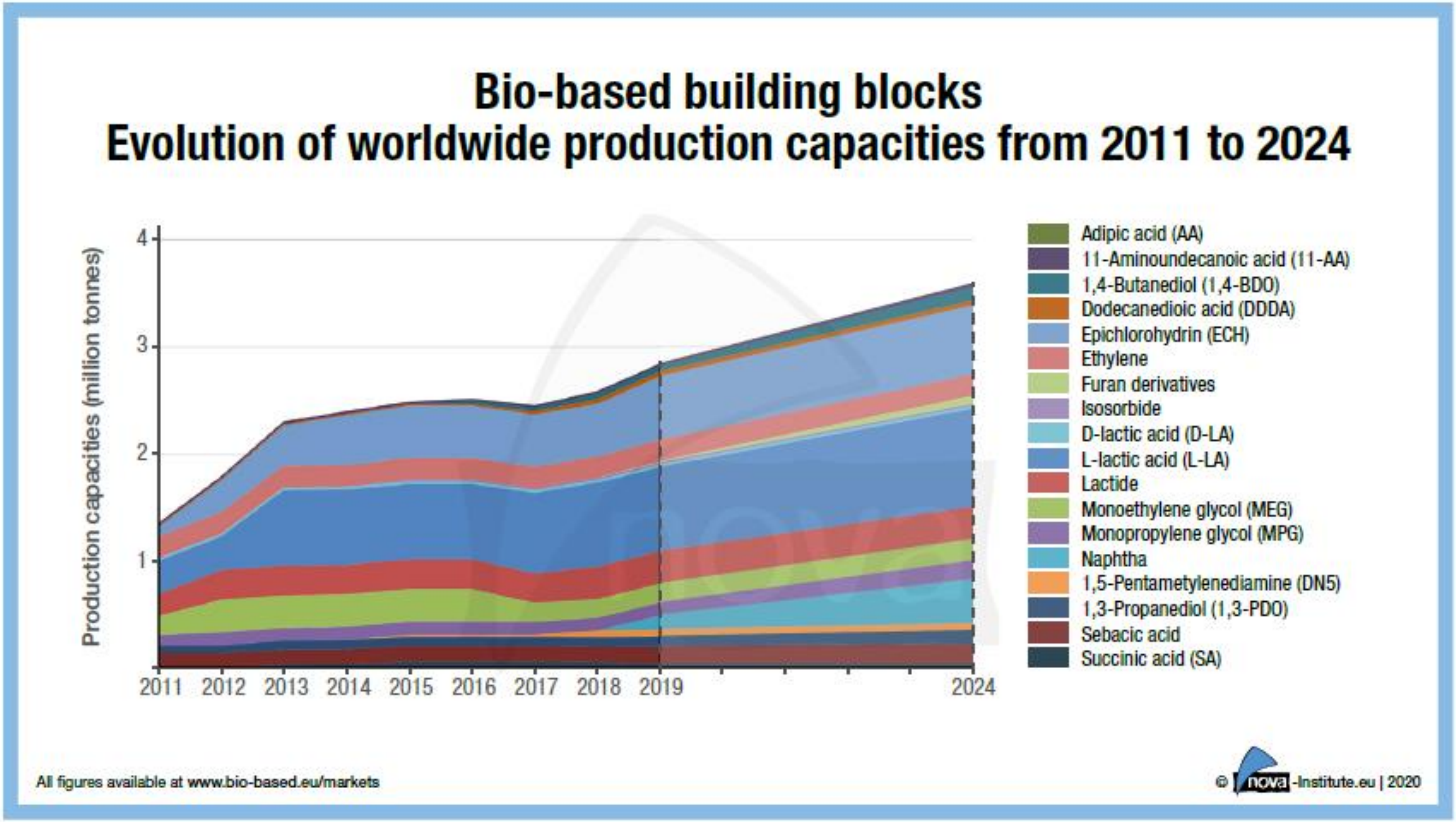
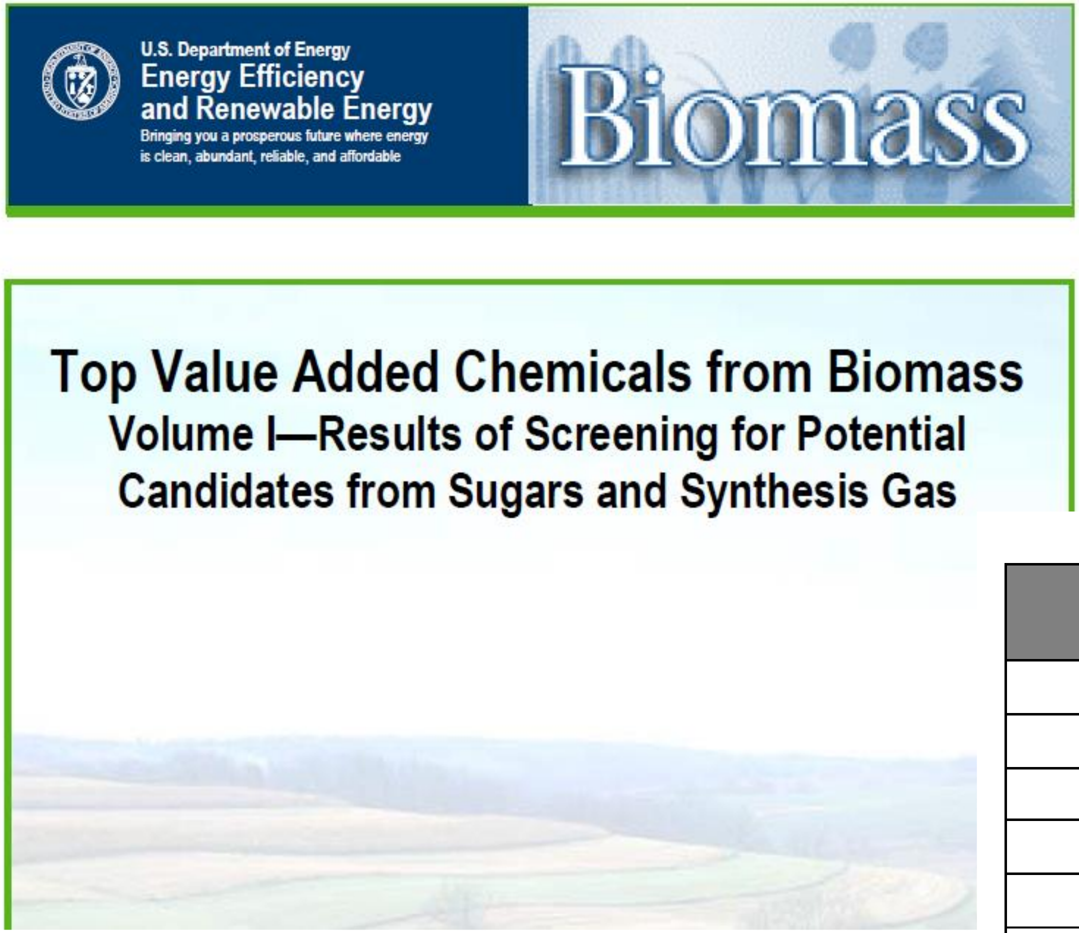


Figure 7: Bio-based building blocks – Evolution of worldwide production capacities from 2011 to 2024



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Energy Efficiency
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is clean, abundant, reliable, and affordable

Biomass

Top Value Added Chemicals from Biomass
Volume I—Results of Screening for Potential
Candidates from Sugars and Synthesis Gas

Building Blocks
1,4 succinic, fumaric and malic acids
2,5 furan dicarboxylic acid
3 hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol/arabinitol

building blocks produced from renewable carbon through green chemical conversion routes or via microbial conversions.

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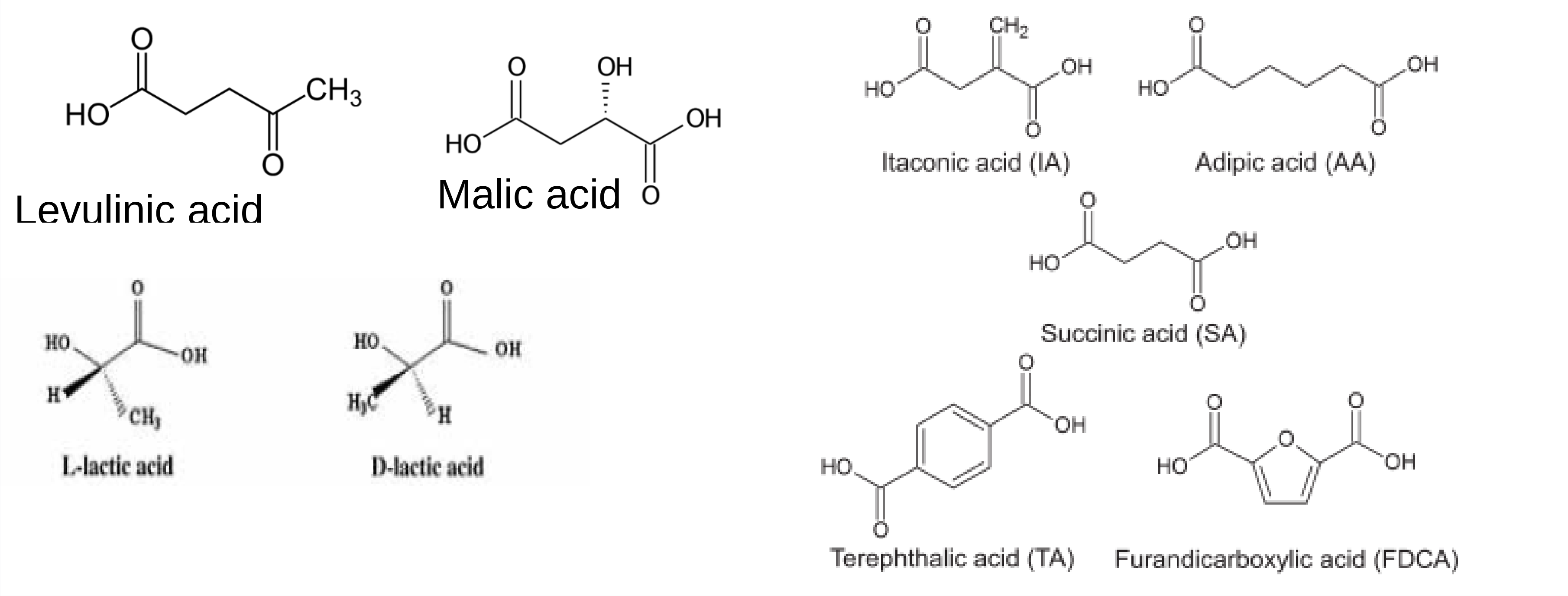
http://www.industrialbiotech-europe.eu/new/wp-content/uploads/2015/06/BIO-TIC-roadmap.pdf

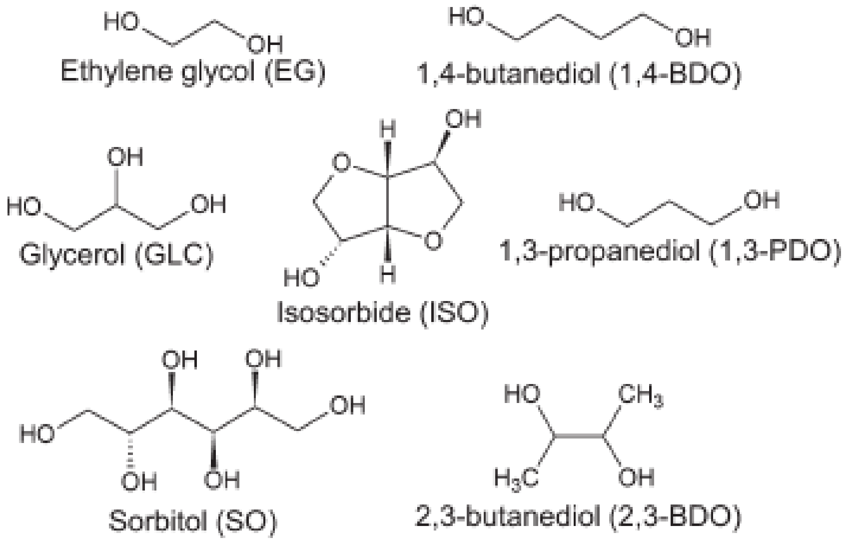
● Not biodegradable

Table 4. Bio-based synthetic polymers obtained from bio-based monomers or a combination of bio- and fossil-based monomers.

Polymer		Properties and applications	
Poly(trimethylene terephthalate) - PTT*	●	Polyester. Same properties as fossil-based PTT. Scarcely biodegradable. Semi crystalline thermoplastic, easily molded or thermoformed and spun into fibres. Good tensile and flexural strength, excellent flow and surface finish. Used in textiles and engineering applications (automotive parts, mobile phone housings.	
Poly(ethylene terephthalate)-PET*	●	Polyester. Same properties as the fossil-based PET. High-performance plastic used for engineering applications, fibres, films, bottles.	
Poly(1,4-butylene succinate) - PBS		Polyester. Biodegradable in soil and biocompostable. Its T_m of 115 °C and tensile strength of 30–35 MPa make PBS suitable for applications in packaging as an alternative to polyolefins.	[5
Poly(ethylene succinate) - PES		Moderately biodegradable. Good oxygen barrier and elongation properties. Used for film applications.	
Poly(ethylene furanoate) - PEF	●	Polyester. Durable, good oxygen barrier. T_m of 211 °C and T_g of 86 °C. Suitable for packaging, in the food and beverage industry.	[
Poly(trimethylene furanoate) - PTF	●	Polyester. Not biodegradable. T_m of 172 °C, T_g of 57 °C, good oxygen barrier properties. Employed in light weighting packaging.	
Poly(butylene furanoate) - PBF		Polyester. T_m of 172 °C, T_g of 44 °C. Potential replacer of PET and PBT.	[
Poly(1,4-butylene adipate-*co*-1,4-butylene terephthalate) - PBAT		Polyester. Biodegradable. Used in blends with PLA and fibers due to low thermo-mechanical properties. Obtained from fossil feedstock or bio-tereftalic acid	
Unsaturated polyester resins - UPR	●	Properties varies according the percentage of unsaturated diacid (e.g. itaconic acid) and the curing procedure. Applied in waterborne UV-curable coatings for wood and flooring industry.	
Poly(L-lactide) -PLLA		Polyester. Thermoplastic. Processable by extrusion, injection molding, blow molding. Degradable by hydrolysis rather than microbial attack. Industrially compostable. Crystallinity can be controlled by co-polymerization of selected ratios of L- to D-stereoisomers of lactic acid or lactide. Mechanical, thermal and barrier properties justify applications in food packaging. Used for medical applications and drug delivery because of its biocompatibility.	[
Polyamides containing four carbons - 4C PAs: 4; 4.6 and 4.10	●	Not biodegradable. 4C PAs match properties of fossil-based PAs 6 and 6.6, such as thermal durability and mechanical strength, with a Tm above 250°C. All 4C PAs have higher dielectric strength and higher retention of tensile properties as compared to PA 6.6. PA 4.10 has low moisture uptake. Applications range from water management to cable coating, food contact products and automotive.	[
Polyamides with longer chains. PAs: 6.10; 10.10; 11 and 12	●	Long chain carbon monomers confer flexibility to these polymers, which find application in fuel lines in cars, offshore pipelines, gas distribution piping systems, electronics, sports equipment, furniture and automobile components.	
Polyvinyl chloride – PVC*	●	Not biodegradable and poorly chemically degradable. Same properties as fossil-based PVC. Used in construction profile applications, bottles and non-food packaging. When made more flexible by the addition of plasticizers, it is used in electrical cable insulation, imitation leather, flooring and as rubber replacer.	[
Polyethylene – PE* (from bio-ethanol)	●	Polyolefin. Same properties of fossil-based PE. Not biodegradable, recyclable through dedicated infrastructures. Thermoplastic. High Density PE (more crystalline) finds applications in construction sector. Low Density Polyethylene is used in packaging. Ultrahigh Molecular Weight Polyethylene has applications in medical devices and bulletproof vests.	
Polypropylene - PP*	●	Polyolefin. Same properties as the fossil PP. Not biodegradable, non-polar. Partially crystalline thermoplastic with low density. Used in a large variety of applications and in packaging.	
Poly(methyl methacrylate)–PMMA*	●	Not biodegradable. Lightweight material used as glass replacement in automotive for shatterproof and UV resistant properties.	[
Ethylene propylene diene monomer – EPDM (synthetic rubber)	●	Not biodegradable. Good resistance to hot water and polar solvents but poorly resistant to aromatic and aliphatic hydrocarbons. Chlorine-free synthetic rubber used for technical clothing, elastomers with shock absorption. Ozone and thermal resistant. Electrical insulation properties. Used also for automotive applications.	
Polyurethanes -PURs		Produced through the reaction of a diisocyanate with a polyol. Microbial degradation depends on the chemical structure. Often blended with polyethers to increase flexibility or extensibility. Used as de-halogenated flame retardant foams, paints, powder coatings, medical devices (blood contacting applications). Biodegradable polyurethane scaffolds have been used in tissue regeneration.	[
Poly(furfuryl alcohol) - PFA	●	Not biodegradable. Synthesized from bio-based furfuryl alcohol (FA) deriving from sugars. Used in the fabrication of nanoporous carbons structures for molecular sieve adsorbents, membranes and as a component for electrochemical and electronic devices.	
Acrylonitrile butadiene styrene - ABS	●	Obtained from butadiene rubber dispersed in a matrix of styrene-acrylonitrile copolymer. Not biodegradable. Thermoplastic, used to make light, rigid, moulded products such as pipes, automotive parts. Used also for its flame retardant properties.	[5
Polyacrylic superabsorbent polymers - PA-SA		Its high swelling capacity is tuneable by controlling the degree of crosslinking. Its biodegradation in soil can be improved under conditions that maximize solubilisation. Find applications in personal disposable hygiene products, such diapers and sanitary napkins.	[
Poly(itaconic acid) - PIA	●	Due to the presence of a vinyl moiety, itaconic acid is structurally similar to acrylic and methacrylic acid, providing a suitable bio-based alternative to poly(meth)acrylates via radical polymerization to yield poly(itaconic acid) (PIA). Applications include fibers, coatings, adhesives, thickeners, binders. As co-monomer itaconic acid gives glass-ionomer dental cement.	



Some bio-based monomers for polymer production



Scheme 1. Most important bio-based dicarboxylic acids and polyols currently available for the enzymatic synthesis of polyesters.

Some bio-based monomers for polymer production

Monomer	Biotechnological route		Company	Status	Application of the corresponding bio-based polyesters	.
Sorbitol	Fermentation + hydrogenation		Roquette, ADM	Market	Functional polyesters; coatings	
Isosorbide	Sorbitol dehydration		Roquette	Market	Thermosetting resins	
Ethylene glycol	Ethanol dehydration		India Glycols Ltd, Greencol Taiwan	Market	PET; PEF	
1,3-propanediol	Fermentation		Du Pont, Tate & Lyle, Metabolic Explorer	Market	PTT; fibers; elastomers; polyester-urethanes	
1,4-butanediol	Fermentation, succinic acid hydrogenation		Novamont, BioAmber, Genomatica, Mitsubishi	Market	PBAT; PBS; PBT	
Adipic acid	Fermentation + hydrogenation		Celexion LLC, BioAmber, Rennovia, Verdezyme	Market	Resins; polyester-amines; polyester-urethanes	
Itaconic acid	Fermentation		Qingdao Kehai Biochemistry, Itaconix	Market	Photocurable precursors; plasticizers	
Lactic acid	Fermentation		Nature Works, BASF, Purac, Cargill, BBCA, Galactic	Market	PLA	
Succinic acid	Fermentation		BioAmber, Myriant, Reverdia, BASF, Purac, Succinity	Market	Textiles; coatings; PBS; PBT	
Terephthalic acid	Isobutylene oxidation, fermentation		Virient, Annellotech, Genomatica	Pilot plant	PET; coatings	
Levulinic acid	Fermentation, acid treatment of C6 sugars		GFBiochemicals, Bio-on, Biofine Renewables	Market	Coatings, hyperbranched dendrimeric polyesters	
Malic acid	Fermentation		Novozymes	Pilot plant	Functionalized chiral polyesters	
2,5-furandicarboxylic acid	Fermentation + dehydration + oxidation		Avantium	Pilot plant	PEF; polyester-urethanes	

Not only Bio-Ethanol:
Bio-Based building blocks and monomers from fermentations

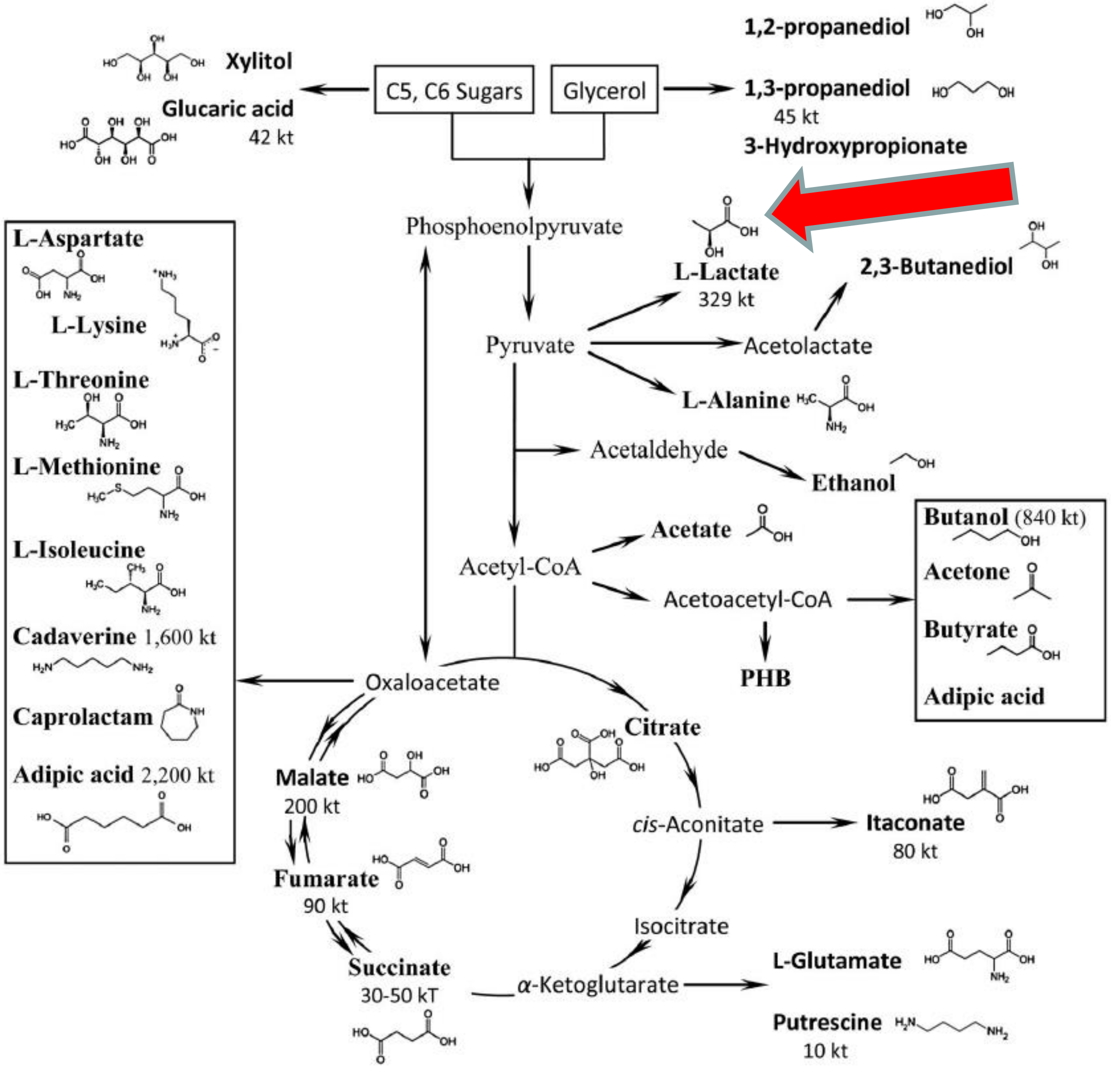
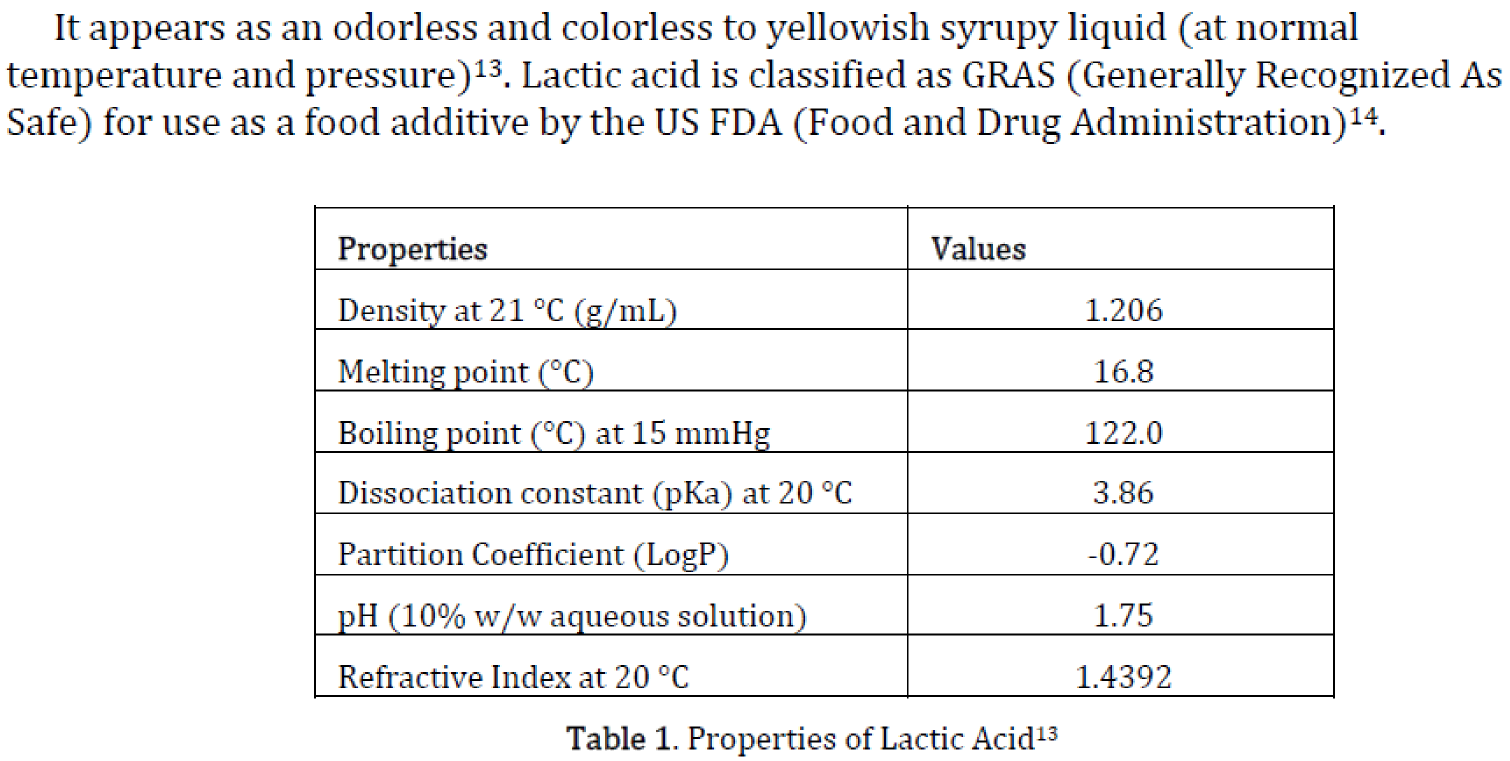


Fig. 2 Building blocks that could be produced *via* fermentation. Numbers next to biochemicals designate the total annual production in thousands of t.

Lactic acid was first discovered in sour milk by Scheele in 1780, who initially considered it a milk component. In 1789, Lavoisier named this milk component lactic acid. In 1857, however, Pasteur discovered that it was not a milk component, but a fermentation metabolite generated by certain microorganisms[11].



It appears as an odorless and colorless to yellowish syrupy liquid (at normal temperature and pressure)[13]. Lactic acid is classified as GRAS (Generally Recognized As Safe) for use as a food additive by the US FDA (Food and Drug Administration)[14].

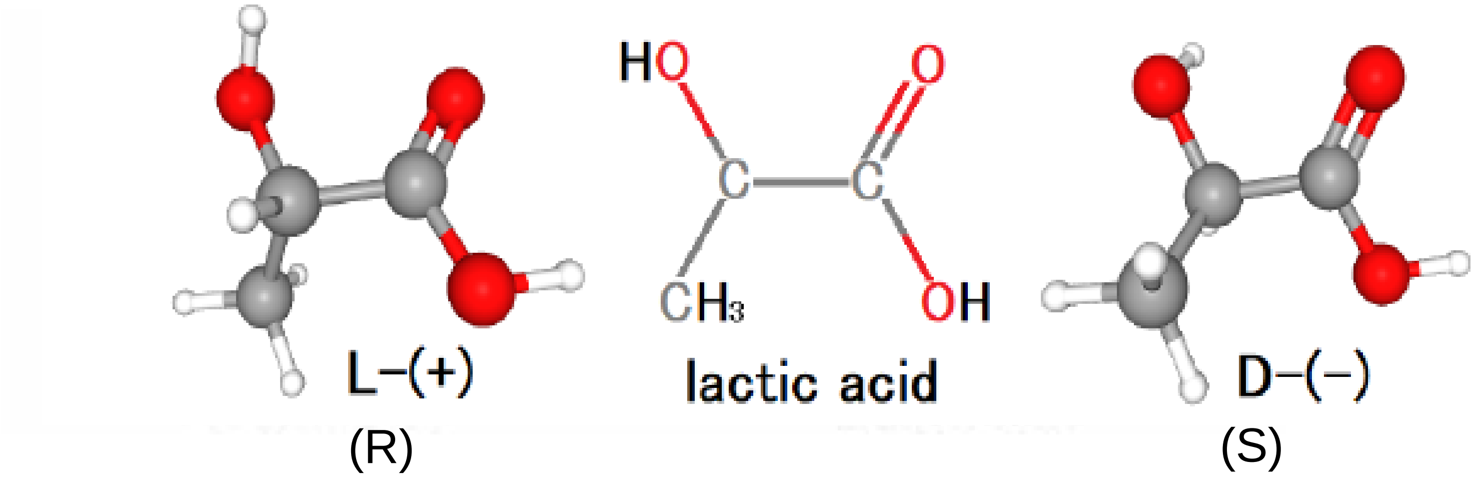
Properties	**Values**
Density at 21 °C (g/mL)	1.206
Melting point (°C)	16.8
Boiling point (°C) at 15 mmHg	122.0
Dissociation constant (pKa) at 20 °C	3.86
Partition Coefficient (LogP)	-0.72
pH (10% w/w aqueous solution)	1.75
Refractive Index at 20 °C	1.4392

Table 1. Properties of Lactic Acid[13]

Lactic acid is a useful chemical, used in the food industry (as a flavoring, acidulant, and preservative), in the pharmaceutical, cosmetic and textile industries. It can be used in the chemical industry as a raw material for the production of lactate ester, propylene glycol, 2,3-pentanedione, propanoic acid, acrylic acid, acetaldehyde.

Lactic acid

Lactic acid (2-hydroxypropionic acid), CH3–CHOHCOOH, is a simple chiral molecule which exists as two enantiomers.



Chemical synthesis of lactic acid is mainly based on the hydrolysis of lactonitrile by strong acids, which provide only the racemic mixture of D- and L-lactic acid.

PLA was discovered in 1932 by Carothers (DuPont) who produced a low molecular weight product by heating lactic acid under vacuum. In 1954 Du Pont produced the polymer with a molecular weight greater and patented.

Lactic acid: chemical synthesis

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

$$CH_3CH(OH)CN + 2H_2O + \tfrac{1}{2}H_2SO_4 \rightarrow CH_3CH(OH)COOH + \tfrac{1}{2}(NH_4)2SO_4$$

$$CH_3CH(OH)COOH + CH_3OH \leftrightarrow CH_3CH(OH)COOCH_3 + H_2O$$

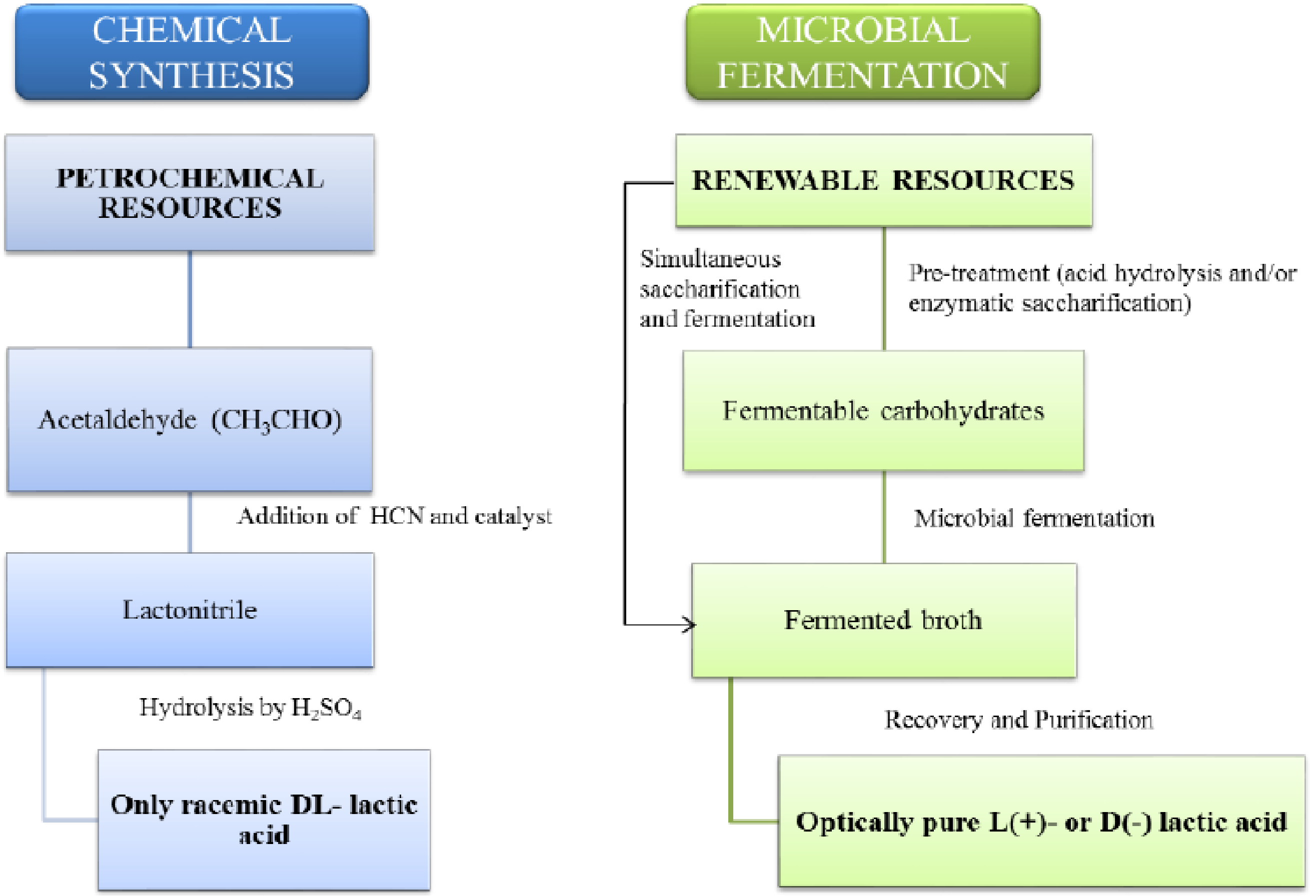


Figure 4. Overview of the two manufacturing methods of lactic acid, chemical synthesis and microbial fermentation[11].

During the production of lactic acid by chemical synthesis, the racemic form, which is an equal mixture of L(+)-lactic acid and D(-)-lactic acid, is obtained. An optically pure L(+)-lactic acid (or D(–)-lactic acid) can be obtained by microbial fermentation of renewable resources.

Approximately 90% of the total lactic acid produced worldwide is made by bacterial fermentation and the remaining portion is produced synthetically by the hydrolysis of lactonitrile.

The fermentation processes to obtain lactic acid can be classified according to the type of bacteria used. The carbon source for microbial production of lactic acid can be either sugar in pure form such as glucose, sucrose, lactose or sugar containing materials such as molasses, whey, sugarcane bagasse, cassava bagasse, and starchy materials from potato, tapioca, wheat and barley.

Sucrose-containing materials such as molasses are commonly exploited raw materials for lactic acid production because they represent cheaper alternatives.

Sugarcane bagasse is reported to be used as support for lactic acid production by ***Rhizopus oryzae*** and ***Lactobacillus*** in solid-state fermentation by supplementing sugars or starch hydrolysates as carbon source.

The selection of microorganism is based on which raw material it has to ferment, as each microorganism has a different metabolism with different substrates. Microorganisms used in fermentation can be divided into two groups: **bacteria** and **fungi**.

Lactic acid bacteria (LAB) can be classified, according to fermentation end-product, into:

a) **obligatory homofermentative** LAB, such as Lactobacillus amylophilus, Lactobacillus acidophilus and Lactobacillus salivarius. They normally metabolize glucose by glycolysis pathway, which results in the production of lactic acid as the sole end product.

b) **obligatory heterofermentative** LAB, such as L. brevis, L. reuteri and L. fermentum. They ferment sugar into ethanol, CO2, and lactic acid by the pentose phosphate pathway.

c) facultative heterofermentative LAB, such as Lactococcus lactis, L. alimentarius and L. casei use both pathways for fermentation.

Most of LAB produce only one isomer of lactic acid, that depends on the stereospecificity of their lactate dehydrogenase enzyme (LDH).

Besides LAB, which are commonly employed, there are filamentous fungi, such as Rhizopus, that can produce lactic acid from the aerobic metabolism of glucose. R. oryzae fermentation requires a simple medium but vigorous aeration for small production of L(+)-lactic acid.

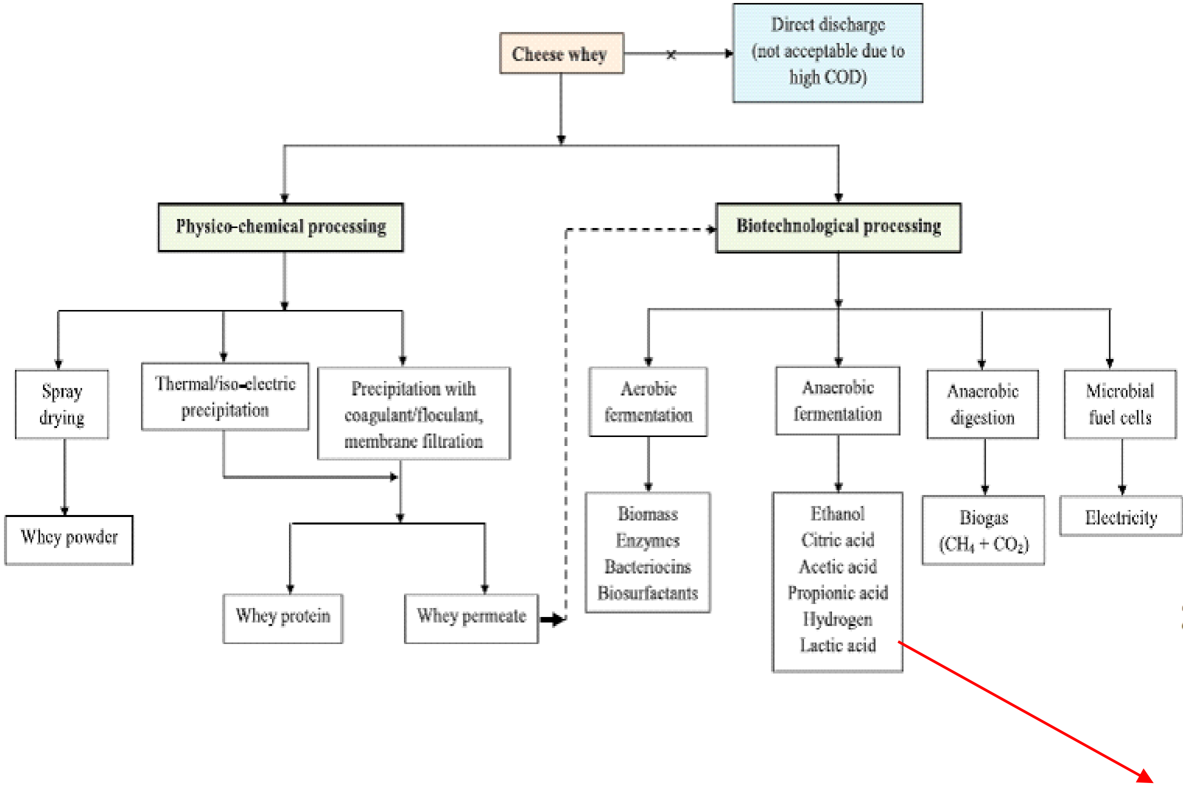
The low production is partially attributed to the formation of byproducts (e.g. fumaric acid and ethanol)

Other feedstock for production of lactic acid are: glycerol, which is a by-product of biodiesel production; microalgae, that have high fermentable sugar contents and they grow almost anywhere with an harvesting cycle of few days.

Whey can be a potent and suitable raw material for lactic acid production because it consists of lactose, fats, protein, mineral salts, vitamins, and other essential nutrients for microbial growth.

This process may be environmentally sustainable, because large volumes of whey are produced by the manufacturing of cheese as a byproduct.

Milk whey: 180-190 M t/year



Cheese whey

Direct discharge (not acceptable due to high COD)

Physico-chemical processing

Biotechnological processing

Spray drying

Thermal/iso-electric precipitation

Precipitation with coagulant/floculant, membrane filtration

Whey powder

Whey protein

Whey permeate

Aerobic fermentation

Anaerobic fermentation

Anaerobic digestion

Microbial fuel cells

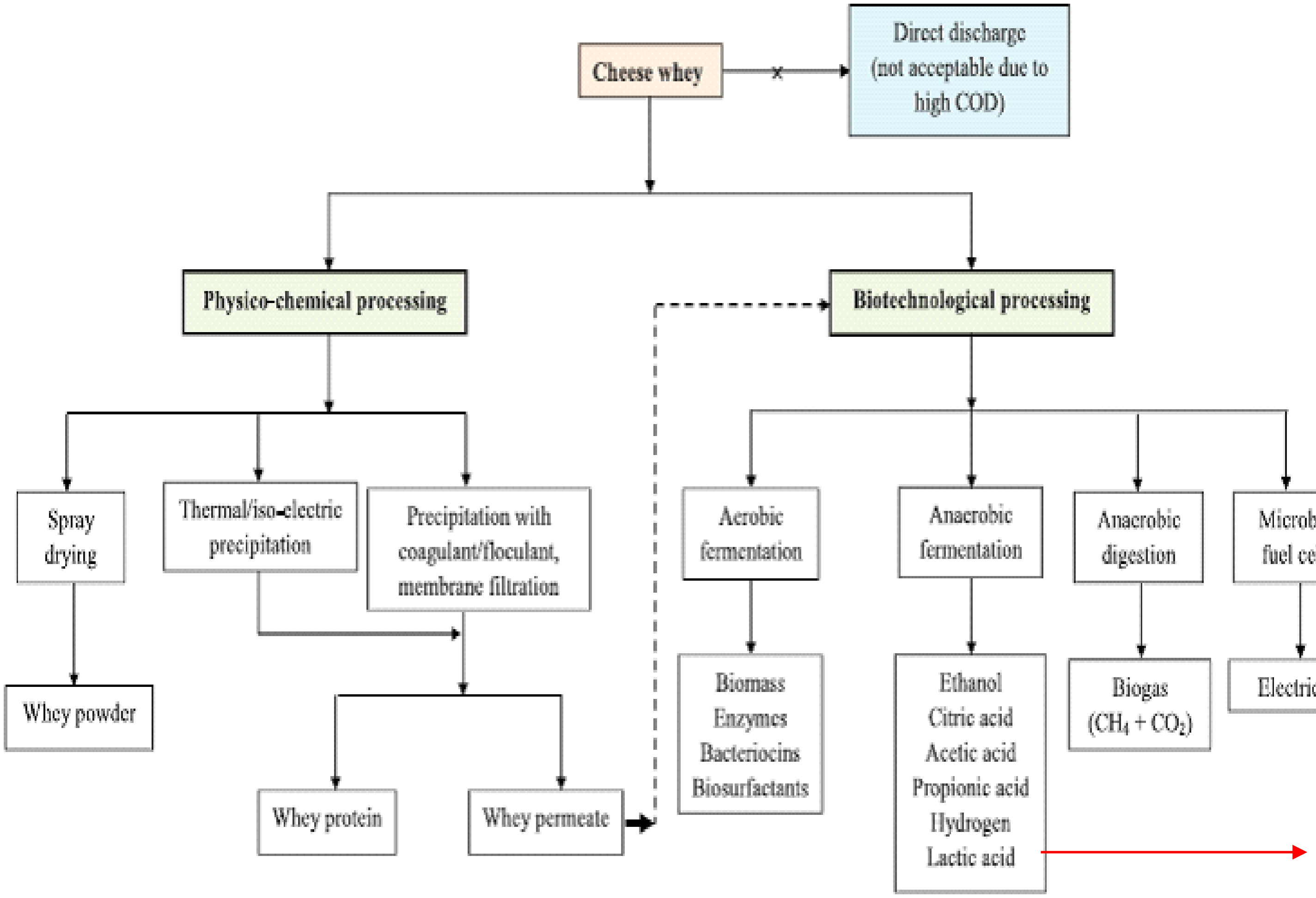
Biomass
Enzymes
Bacteriocins
Biosurfactants

Ethanol
Citric acid
Acetic acid
Propionic acid
Hydrogen
Lactic acid

Biogas ($CH_4 + CO_2$)

Electricity

cellulac U.K.



Cheese whey

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Spray drying

Whey powder

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Precipitation with coagulant/floculant, membrane filtration

Whey protein

Whey permeate

Biotechnological processing

Aerobic fermentation

Biomass
Enzymes
Bacteriocins
Biosurfactants

Anaerobic fermentation

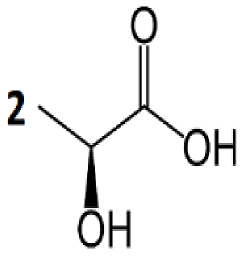
Ethanol
Citric acid
Acetic acid
Propionic acid
Hydrogen
Lactic acid

Anaerobic digestion

Biogas ($CH_4 + CO_2$)

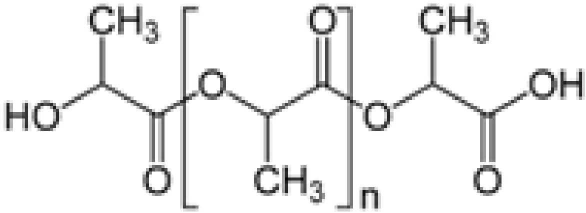
Microbial fuel cells

Electricity



Acido lattico

Bio-based lactic acid for bio-based polylactic acid (PLA): bio-based polyester



Among polymers, polyesters are a widely used class with applications ranging from clothing to food packaging and from the car industry to biomedical applications.

PLA currently is the most important bio-based polyester in terms of volume, with a **capacity of approximately 800 000 tons/y.**

Besides high product specificity, as it produces a desired optically pure L-(+)- or D-(-)-lactic acid, the biotechnological production of lactic acid offers several advantages compared to chemical synthesis like low cost of substrates, low production temperature, and low energy consumption

PLA-based products had already been developed by the 1940s and 1950s, but their production became economically viable only 70 years later. This demonstrates the importance of optimizing the productivity and robustness of bioconversions to achieve cost-effective production.

The success of bio-based polyesters does not rely solely on their capacity to replace fossil-based polymers while being economically competitive. Rather, the next generation of bio-based polyesters should bring entirely new advanced chemical and functional properties to the polymer scenario.

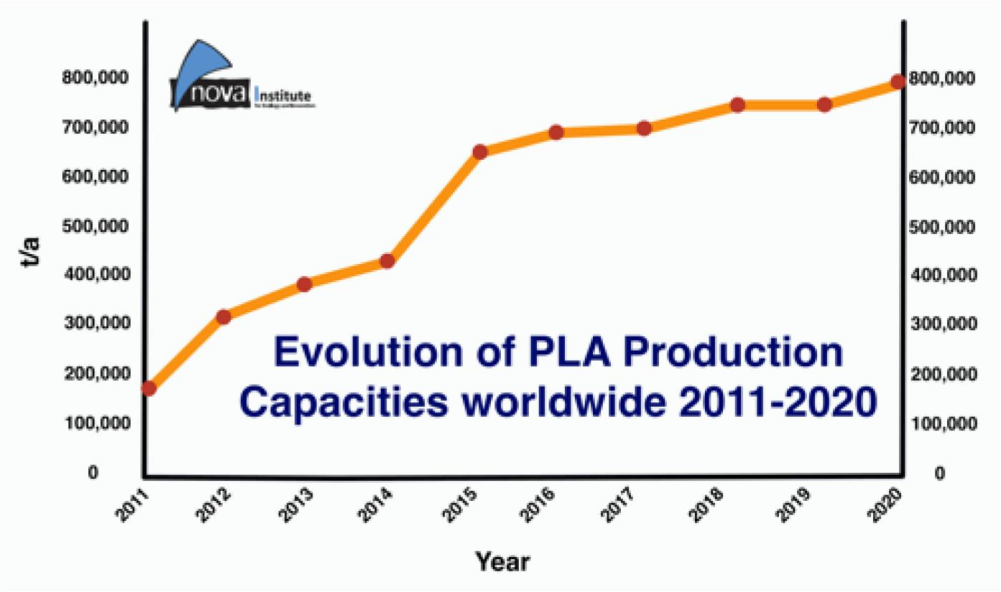


Fig.3–Evolution of PLA production capacities (t/a) from 2011 to 2020

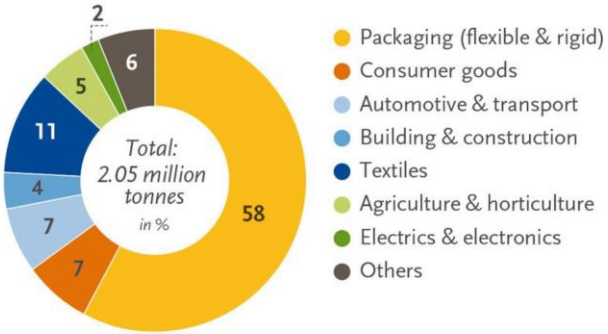
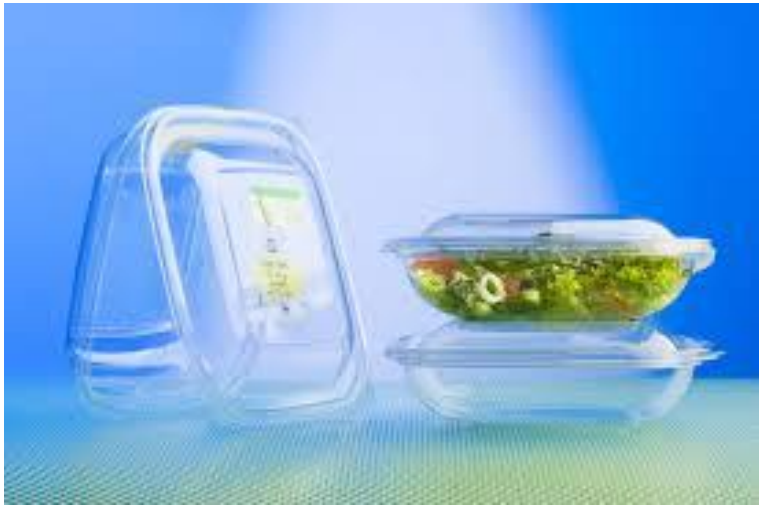
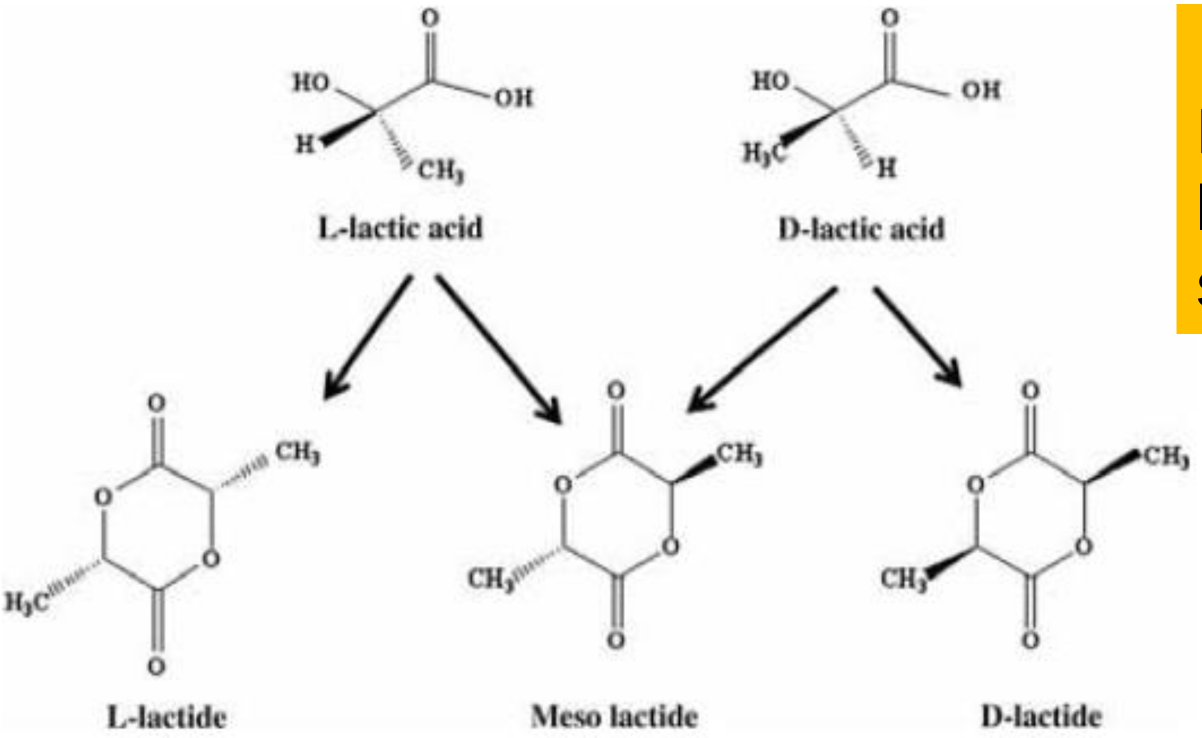


Fig.7–Global production capacities of bioplastics in 2017 (by market segment)
Source: European Bioplastics, nova-Institute (2017)



Lactic acid and lactide have stereoisomers



LL-Lactide

(mp 97 C)

LD-Lactide

(mp 52 C)

DD-Lactide

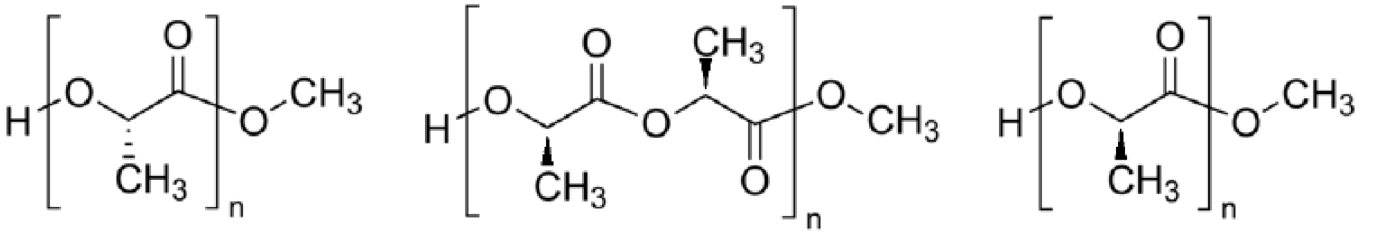
(mp 97C)

Depending on methods used for synthesis, PLA can have different stereoisomers:

- Poly(L-lactide) (PLLA) and Poly(D-lactide) (PDLA) are isotactic forms, in which the configurational repeating unit is essentially an isomer of lactic acid (L-lactic and D-lactic respectively). These are optically pure forms of PLA and have crystalline form.
- Poly(DL-lactide) (PDLLA) is the syndiotactic polymer, in which configurational repeating unit consists of two monomers that are enantiomeric.

- If enantiomeric forms of lactic acid are bonded in a random sequence distribution, the polylactide is atactic.

Stereoisomers of PLA:



Poly-L-Lactic Acid
(PLLA)

Poly-D-L-Lactic Acid
(PDLLA)

Poly-D-Lactic Acid
(PDLA)

Figure 5. Structure of polylactide stereoisomers.

isotactic

syndiotactic

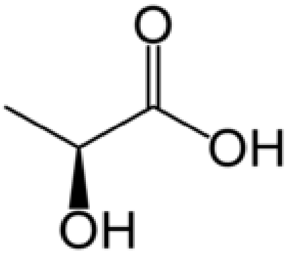
isotactic

A very important property is the rate of crystallinity, which is the degree of structural order respect to amorphous content.

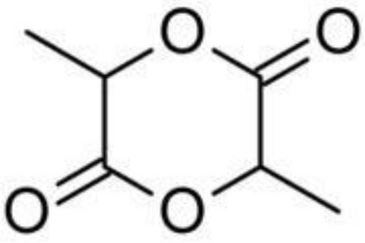
PLA with a high rate of crystallinity can be obtained with an optically pure PLA, while the lower optically pure is amorphous.

The crystallinity influences many properties, such as the melting temperature (Tm), and the glass transition temperature (Tg) of PLA.

From lactic acid to lactide

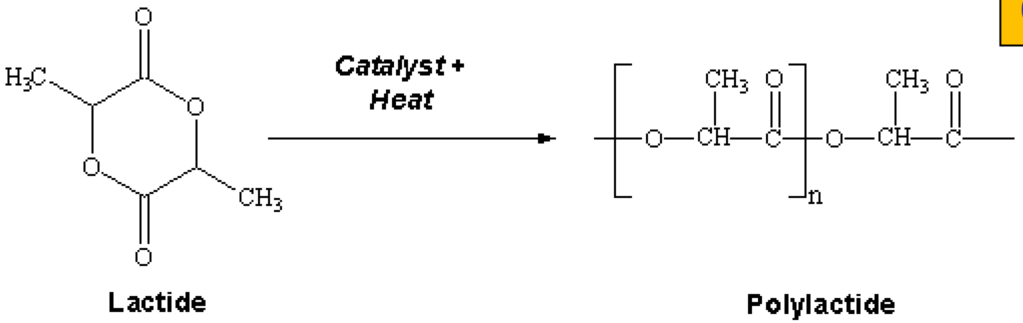


(S)-lactic acid



Lactide

Lactide is the cyclic di-ester of lactic acid, i.e., 2-hydroxypropionic acid.
Lactic acid can not form a lactone but first forms a dimer, which contains an hydroxy group at a convenient distance from the carboxylic group for the formation of a lactone. The dimer readily forms a six-membered cyclic diester known as lactide



Ring opening polymerization of lactide to polylactide

- **Monomer produced in fermentation**

- **Chemical polymerization**

Ring Opening Polymerization

Ring opening polymerization (ROP) is the most common route to achieve high molecular weight polylactide. This process involves the ring opening of the lactide, that is the cyclic intermediate dimer of lactic acid, in the presence of a transition metal catalyst, such as aluminum, bismuth, lead, tin or zinc.

ROP of lactide can produce a polymer with wider range of molecular weight and specific properties by controlling synthesis conditions, like temperatures in combination with catalyst type and concentration, without chain coupling agent or azeotropic system[5,25].
Therefore, ROP has become very significant in PLA synthesis and is applied by some PLA leading producers, such as NatureWorks LLC.
However, the trace residues of the heavy metal catalyst need to be completely removed for medical and food applications. Additional purification steps are drawbacks in this route, because they are relatively complicated and expensive

Polylactic acid synthesis: Other methods

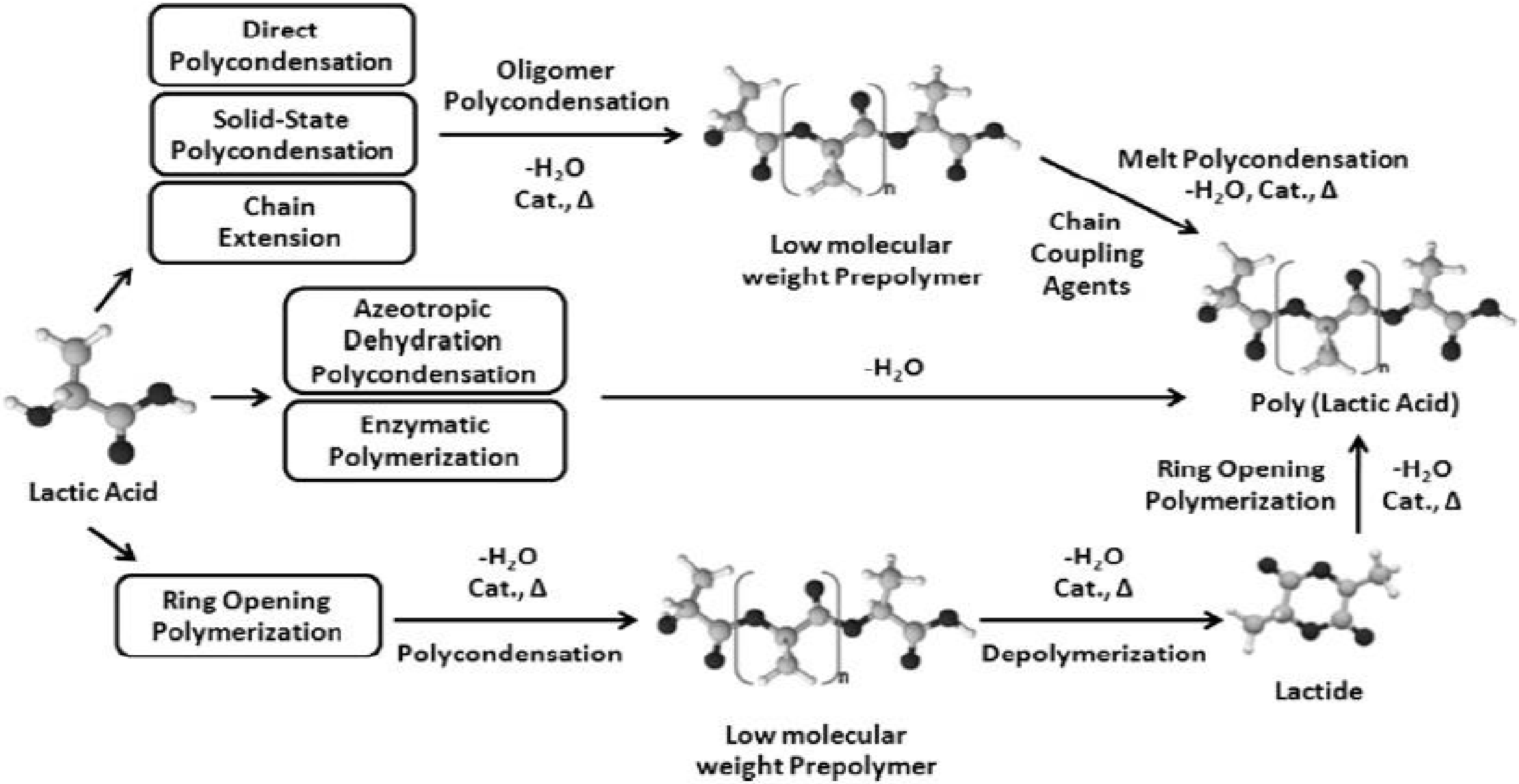


Figure 6. Main methods for PLA synthesis[24].

Enantiomerically pure poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA) are semicrystalline polymers, with the Tg in the range of **55-65 °C** and the **Tm** of about **180 °C.**

The glass transition temperature (Tg) is the temperature where an amorphous polymer changes from a rigid glassy material to a flexible, but not melted, material. The Tg could express a limit above which mechanical properties may change drastically.

Increasing the temperature over the Tg, PLA transitions from glassy to rubbery and behaves as a viscous fluid upon additional heating.

Below the Tg, PLA behaves as a glass with the ability to creep until cooled to approximately -45 °C, below which PLA will only behave as a brittle polymer.

The melting temperature is directly involved in the **processability and stability**. In fact, in order to reduce viscosity and consequently improve processability, the process temperatures are significantly higher than the Tm (from 190 to 250 °C)

The **thermal stability** of polylactides is poor at temperatures above the Tm. Reactions involved in the thermal degradation of lactide polymers include transesterification, thermooxidative degradation, and thermohydrolysis.

The thermal degradation of PLA is accelerated when polymer has high moisture content, catalyst and other impurities.
During extrusion, optimal drying conditions can reduce degradation. PLA can be purified in order to enhance thermal stability[21].

Radiation stability is important in medical devices because they need to be sterilized, and common sterilization methods use γ-or β-radiation. Radiations can cause crosslinking or chain scission reactions. These reactions might happen in the amorphous regions of the polymer.
The **hydrolytic degradation** of lactide polymers is undesirable during processing but is essential for most applications, such as temporary medical implants and packaging.
The temperature strongly influences the rate of hydrolysis because permeability increases at temperatures above the Tg. Hydrolytic stability can be also influenced by molar mass and purity of the polymer

Companies, e.g. Cargill Dow Polymer LLC, Shimadzu Corp, Mitsui Chemicals, Musashino Co. Are now producing PLA-targeting markets for **packaging materials**, **films, textile fibers**, along with **pharmaceutical** products. The US Food and Drug Administration (FDA) and European regulatory authorities have approved the PLA resins for all food type applications and some **chirurgical** applications such as **drug releasing systems**

PLLA has gained great attention because of its excellent biocompatibility and mechanical properties. It has extensive applications in **biomedical** fields, including suture, bone fixation material, drug delivery microsphere, and tissue engineering.

However, its long degradation times coupled with the high crystallinity of its fragments can cause inflammatory reactions in the body. In order to overcome this, PLLA can be used as a material combination of L-lactic and D, L-lactic acid monomers, being the latter rapidly degraded without formation of crystalline fragments during this process.

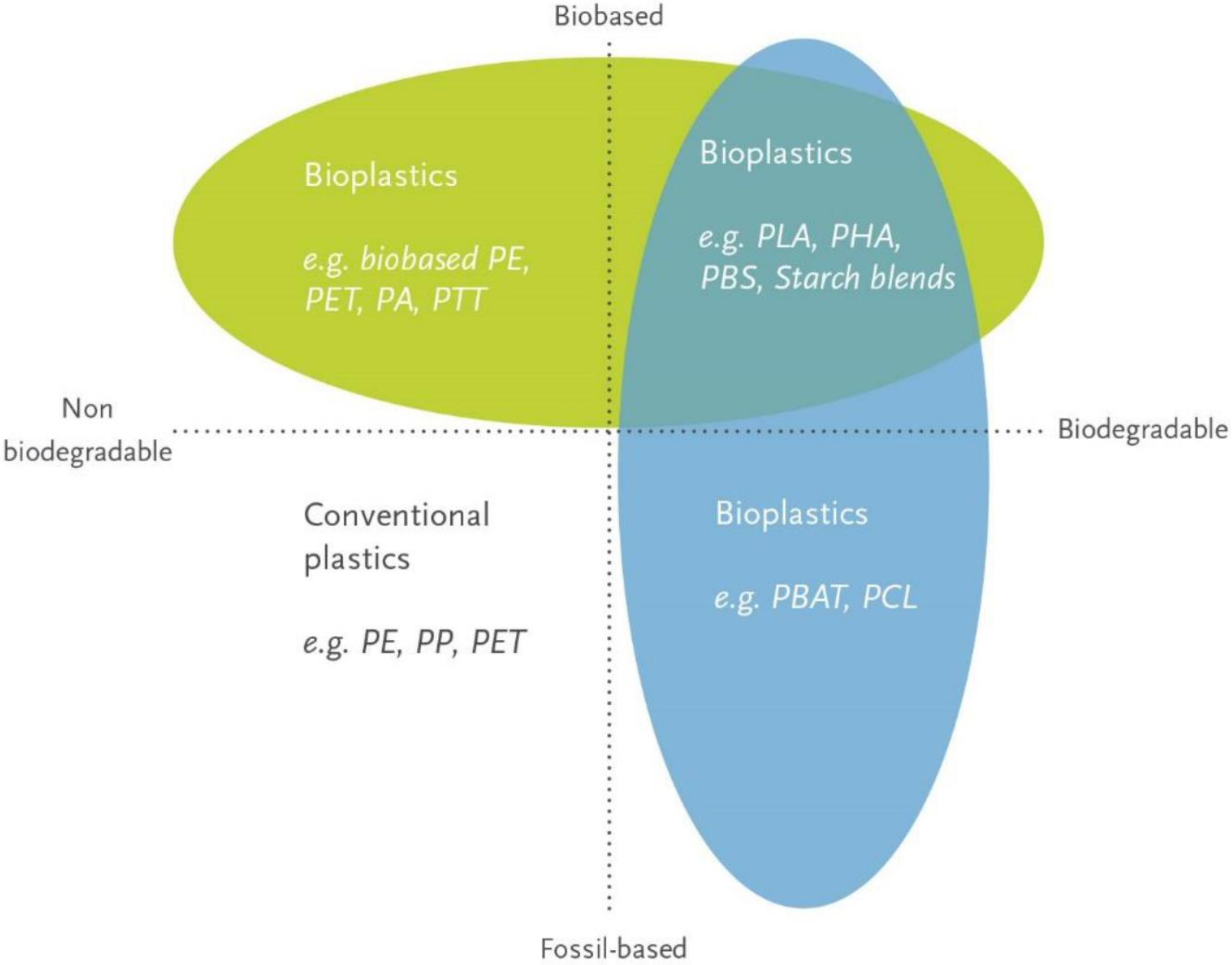
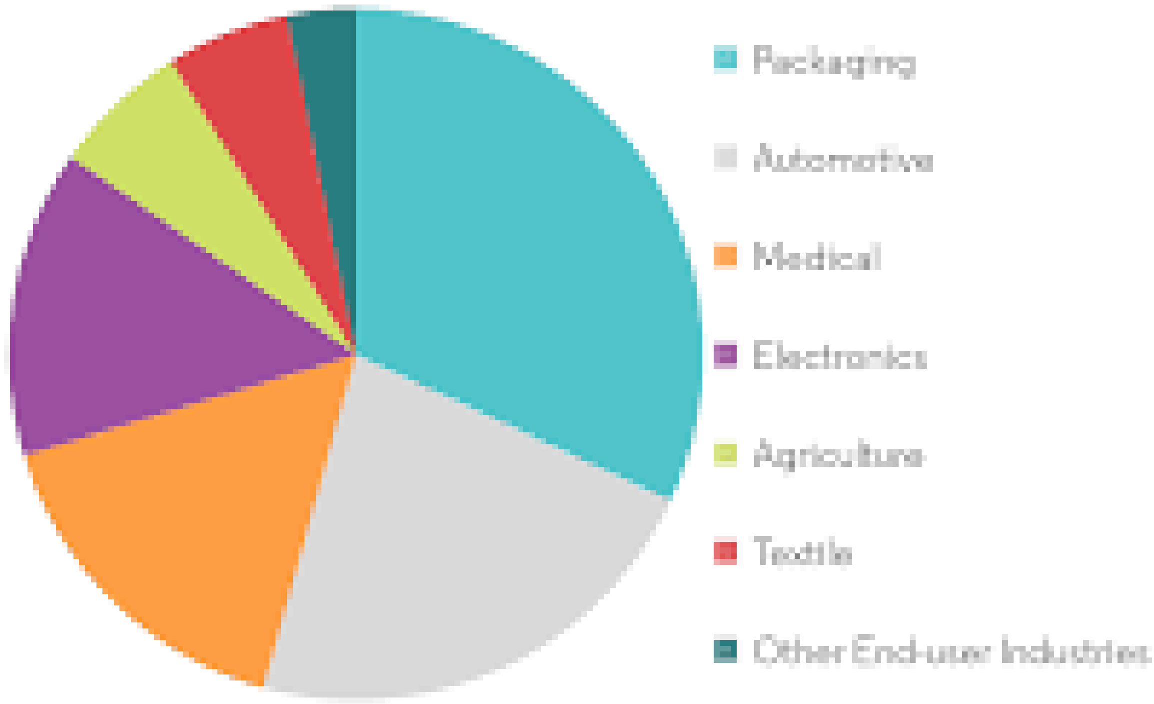


Figure 1. Some examples of bioplastics (biodegradable, biobased or both)[2]

Bio-polylactic Acid (PLA) Market, Volume (%), by End-user Industry, Global, 2018



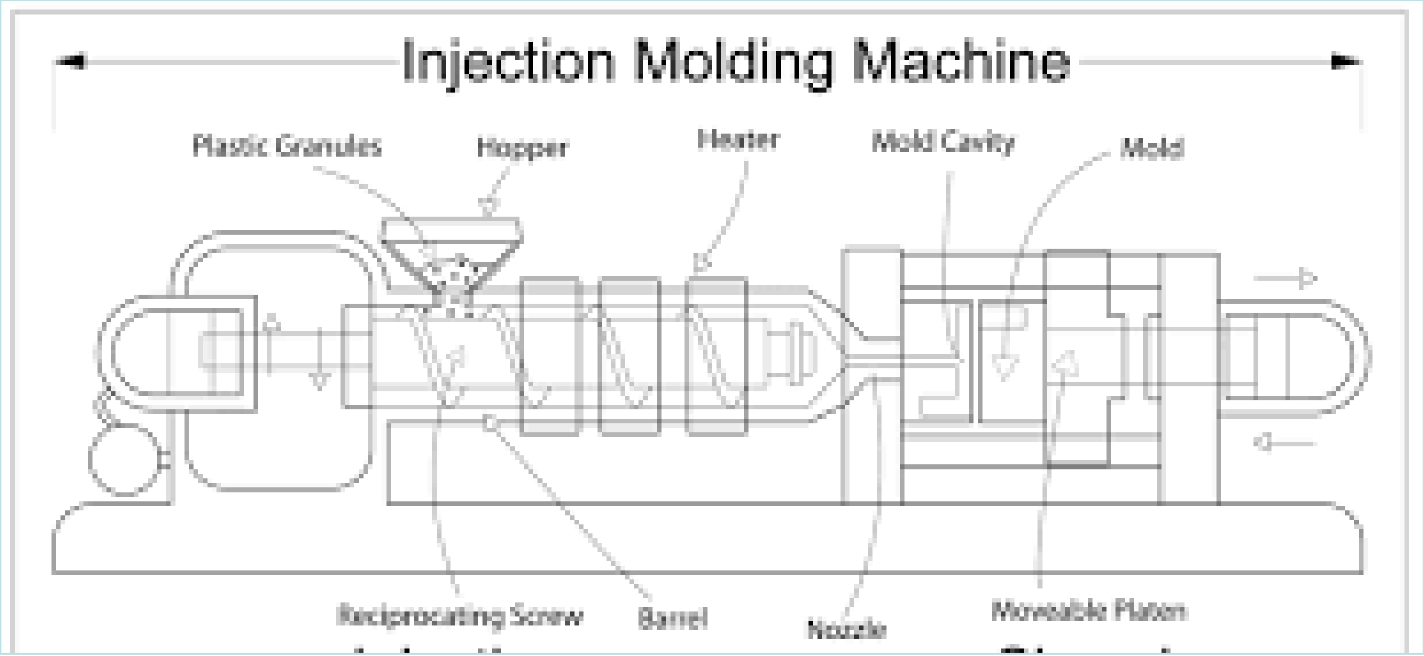
Source : Mordor Intelligence

https://www.youtube.com/watch?v=b1U9W4iNDiQ

Processing

Injection molding (stampaggio ad iniezione)

Injection molding is the most widely used converting process for thermoplastic articles, especially for those that are complex in shape and require high dimensional precision. All injection molding machines have an extruder designed so that the screw can provide enough injection pressure to deliver the polymer melt into the mold cavities.



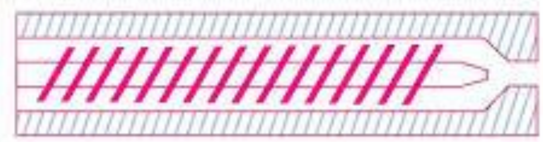
https://www.youtube.com/watch?v=3joRkM8yJMQ

Processing

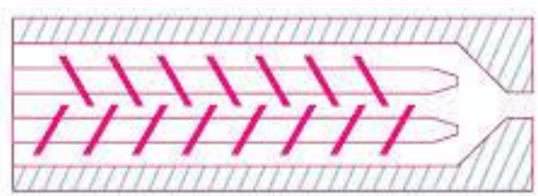
Drying and extrusion

Prior to processing of PLA, the first step is to dry polylactide to avoid hydrolysis and, consequently, Mw reduction. During industrial production, PLA is mostly dried to values below 0.025% w/w.

The extruder melts the resins fractioning them between the screw and the barrel, and also by an heater around the barrel.
In order to achieve an optimal melt viscosity for processing, temperature is set at **40-50 °C above the melting temperature.** However, extruding PLA at high temperatures can cause thermal degradation, so the process should be tightly controlled[32].



Vite singola



Bivite

Processing

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

Cast film and sheet

Cast is the main method to produce films with thickness ≤0.076mm and sheets with thickness typically ≥0.25mm. During the process, molten PLA is extruded through a lip die and quenched on polished chrome rollers refrigerated with cooled water.

Cast films usually have transparent appearance and low crystallinity due to the rapid cooling provided by the chilled rolls. Cast film extrusion has the advantages of providing good control of film thickness and good optical properties.

Roller temperature between 25 and 50 °C is recommended to avoid lactide condensation.

Thermoforming

Thermoforming is a process in which a flexible plastic is pressed into a final shape by vacuum or air pressure. It is a standard method to produce PLA containers used for short shelf-life product packaging applications.

https://www.youtube.com/watch?v=alq3RDZN4jo https://www.youtube.com/watch?v=1huDKqVY5nc

Foaming

PLA foam parts are lightweight materials with improved structural performance. They were extensively used for medical applications (sutures, implants, and screws), but also for packaging (cushioning and insulation).

During the process, a foaming agent (e.g. CO2, N2) is saturated into the PLA matrix at a pressure below 800 MPa at room temperature in a chamber. Then, the solubility of the blowing agents is reduced so bubbles can nucleate and create the foam structure. Finally, PLA matrix is cooled below Tg in order to vitrify https://www.youtube.com/watch?v=22VC_8xcyrs

Spinning

Spinning of polylactide has been used to produce PLA fibers for medical (e.g. surgical suture) and textiles application (e.g. breathable garments).

Conventional technologies can be used for processing PLA fabrics, but they require modified dyeing and finishing techniques due to its low affinity to water-soluble dyes.

In spinning of PLA fibers, a molten polymer or solution is extruded through a spinneret and is elongated by applying an external force. Then, the polymer filament is cooled until the temperature is below the Tg. During polylactide fibers production, it is important to control moisture content in order to avoid any possible hydrolytic degradation, and to achieve optimal parameters to obtain strong PLA fibers

Drug Delivery System

With its excellent properties, PLA can be used to produce different dosage forms such as nanoparticles, microparticles, microcapsules and pellets. The microparticles and nanoparticles of polylactide and derivatives may be used for sustained release and targeted delivery applications because of their small size, that allows permeation through biological barriers.

Microspheres and microcapsules have been widely applied in drug delivery systems (DDS) for the prolonged administration of numerous drugs such as contraceptives, local anesthetics, narcotic antagonists, and vaccines. They can also effectively deliver peptides and proteins effective with comparatively low doses.

Injectable microspheres of PLLA have been used as an embolic material in transcatheter arterial embolization, which is an effective method to manage arteriovenous fistula and massive hemorrhage. They can also be applied in temporary fillings in facial reconstructive surgery.

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eXPRESS Polymer Letters Vol.9, No.5 (2015) 435–455
Available online at www.expresspolymlett.com
DOI: 10.3144/expresspolymlett.2015.42

Properties and medical applications of polylactic acid: A review

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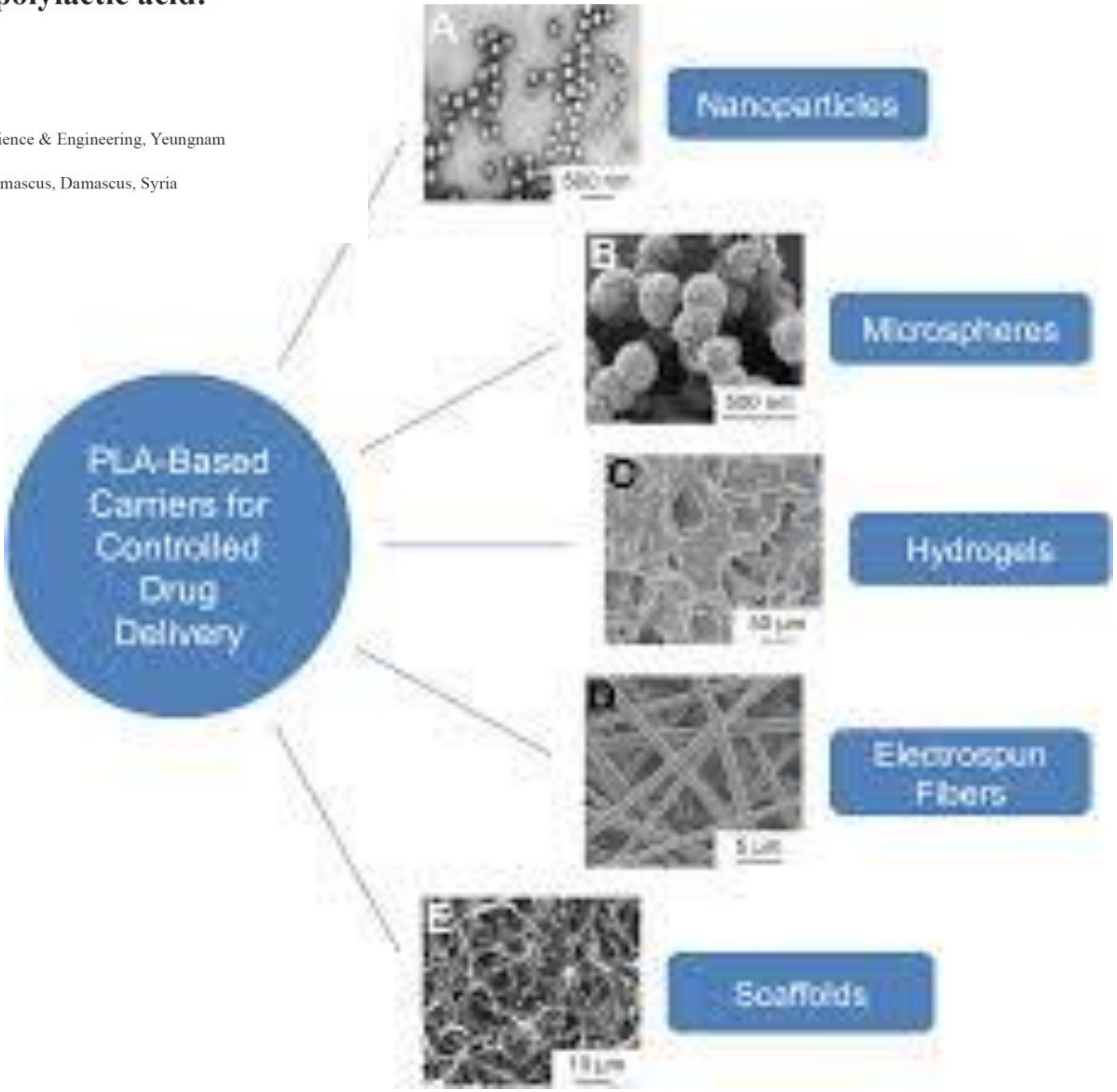
[2]Laboratory of Materials Rheology, Department of Chemistry, University of Damascus, Damascus, Syria

Received 30 September 2014; accepted in revised form 30 November 2014



Biomedical Applications

The successful implementation of PLA in biomedical applications relies on better mechanical and surface properties than conventional plastics (e.g., hydrophilicity, roughness, and reactive functionalities). Moreover, thanks to its bioresorption and biocompatible properties, PLA resins are approved by FDA and EFSA for food and medical applications.

Implants

PLA is widely used for medical implants because it degrades over time; therefore, the removal step of an implant is not required[32]. PLA implants are able to maintain mechanical properties for a period of time usually required for bone fracture healing.

PLA is commonly used in combination with other macromolecules, such as polyglycolic acid (PGA), collagen, and hydroxyapatite (HA) ceramic, to improve its functionality and mechanical properties. In addition, PLA composite devices may stimulate the natural cells growth around the implant.

PLA can replace metal in device implants, and avoid problems such as corrosion and distortion of MRI. Various applications include tissue growth, bone grafting, and fracture fixation devices (miniplates, screws, rods, and suture anchors).

Blends of biodegradable PLA with surfactants (ethylene oxide and propylene oxide) can have a potential use in dental or orthopedic implants, thanks to enhanced toughness. Drug-eluting stents made of PLA and PLA blends, in which the drug is either incorporated into the matrix or is adsorbed on the composite, are already present on the market.

Tissue engineering

Polylactic acid is found to be one of the most favorable matrix materials for tissue engineering, because of its excellent biocompatibility and mechanical properties.
PLLA fibers are the preferred material in applications that require **long retention** of the strength, such as in ligament and tendon reconstruction, and for the production of stents for vascular and urological surgery.

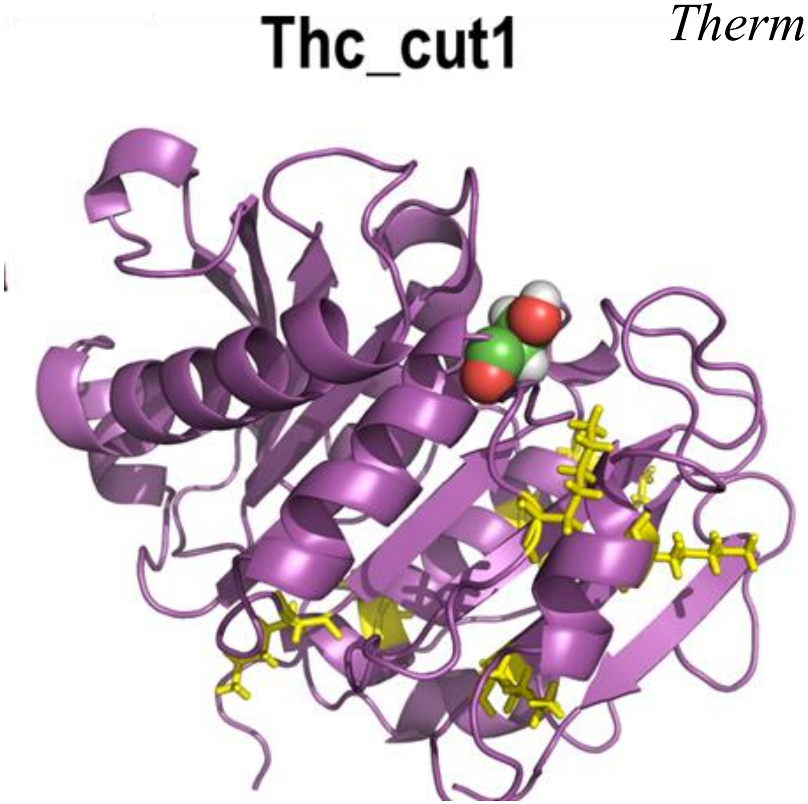
Three-dimensional porous scaffolds of polylactide have been created for culturing different cell types. These scaffolds are used in cell-based gene therapy for cardiovascular diseases, in muscle tissues, bone and cartilage regeneration, and other treatments.
PLA structures may take from 10 months to 4 years to degrade depending on the composition, porosity and crystallinity. Blending of PLA with other polymers with better wettability and faster degradation provides to tune its biodegradability to be compatible with the time taken for tissue growth and/or recovery.
3D printed PLA, PLA/hydroxyapatite and PLA/hydroxyapatite/silk composites have been developed as bone clip materials. Compared to other types of bone clips, these showed similar mechanical properties and superior biocompatibility19.

Future developments

An engineered polyhydroxyalkanoate (PHA) synthase was used as a base for the developing of one-step process PLA-producing bacteria. PHA synthase was chosen because the 3-hydroxybutyrate (3HB) monomer is structurally similar to LA. The polymerizing activity occur through continuous transesterification of lactate-coenzymeA (LA-CoA).

Adding the engineered PHA synthase to a LA-CoA producing Escherichia coli, it was able to convert LA into PLA without extraction and purification.

Enzymes for the modification/degradation of polyesters



Thermobifida cellulosilytica Cutinase 1

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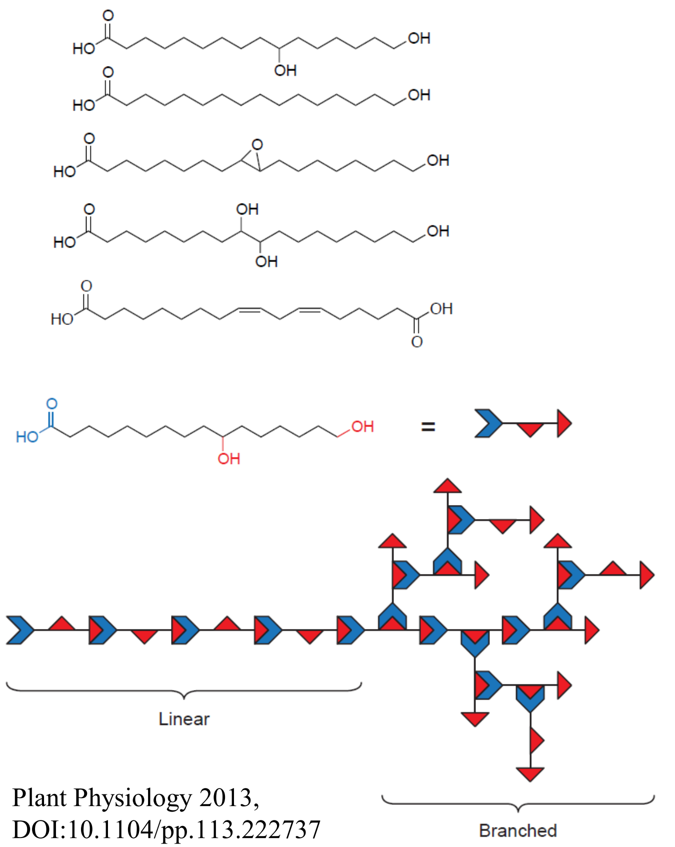
Scienze Chimiche e Farmaceutiche

BOKU

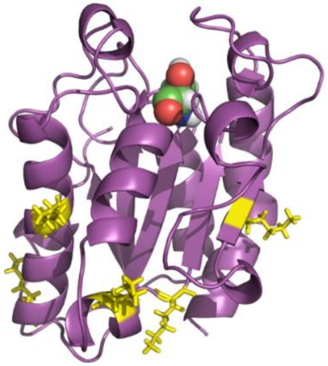
Pellis, A. et; *Catal. Sci. Technol.*, 2016, *6*, 3430.

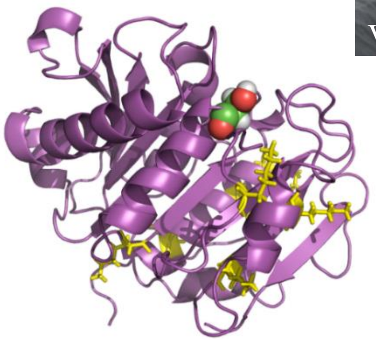
Cutinases are biosynthesized by pathogenic fungi to hydrolyze plant cutin

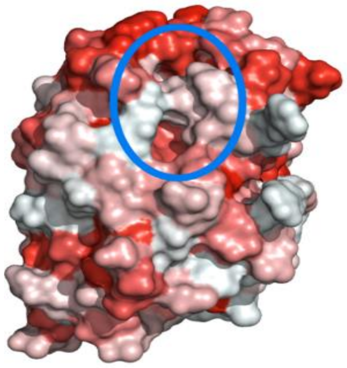

Valerio Ferrario

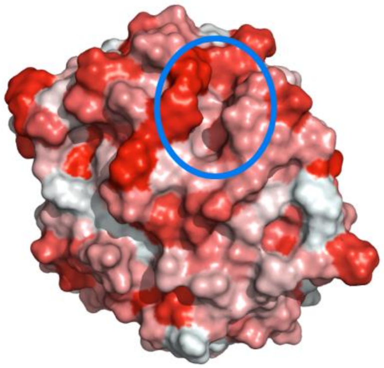


Plant Physiology 2013,
DOI:10.1104/pp.113.222737


Cutinase
Humicola insolence


Cutinase
Thermob. cellulosilytica



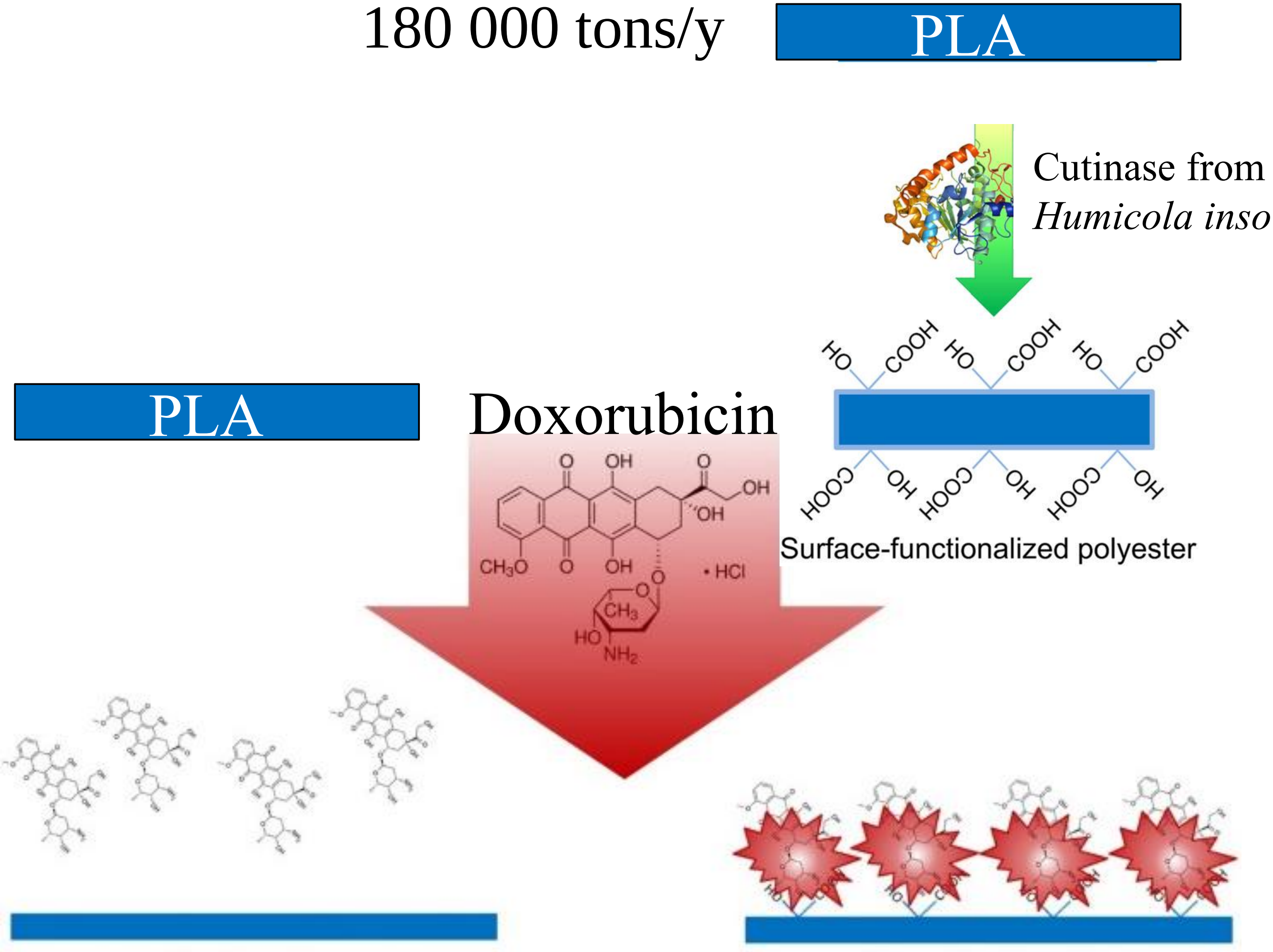


🔴 **Hydrophobicity**

Pellis A. et al. *Catalysts* 2016, *6*, 205.
Pellis, A. et al. *Catal. Sci. Technol.*, 2016, *6*, 3430.

Enzyme-catalyzed functionalization of poly(L-lactic acid)

180 000 tons/y



Cutinase from
Humicola insolens

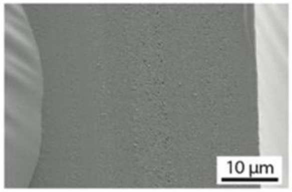
Surface-functionalized polyester

No adsorption

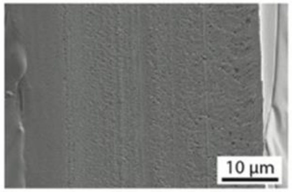
Adsorption

Pellis A. et al., *Process Biochem*., 59, 77-83, 2017.

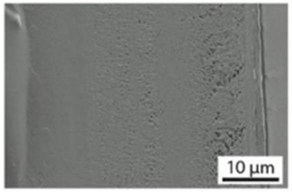
Cutinase hydrolysis of PLA preserves bulk properties



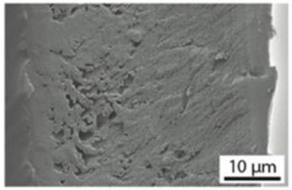
Start PLA



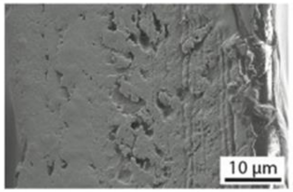
CTRL 48h



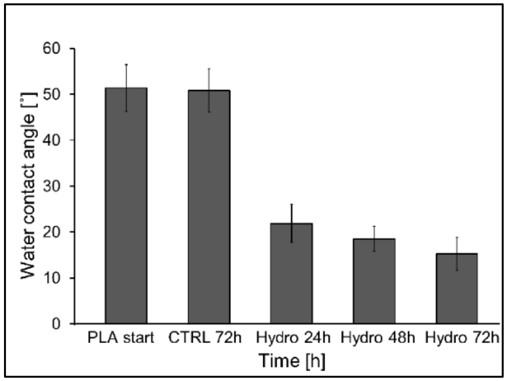
Hydro 24h



Hydro 48h



Hydro 72h



GPC

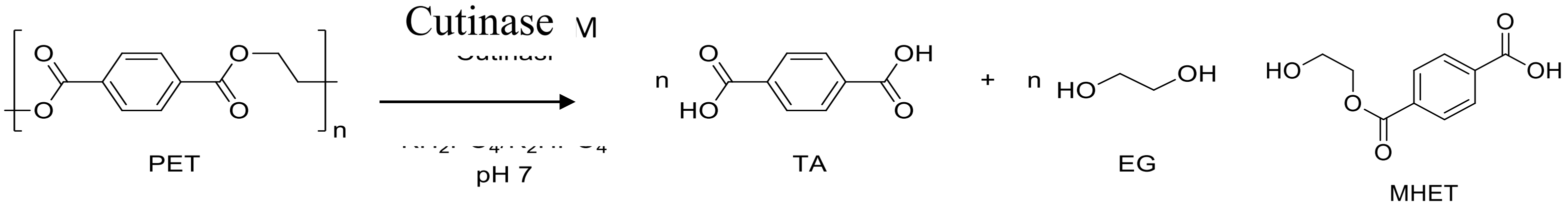
Treatment	**M_n**	**M_w**
Starting PLA	26493	188104
72h Enzymatic Hydrolysis	25874	181826
10min	18662	128248
20min	9466	51007
30min	6738	37827
60min	3984	18178

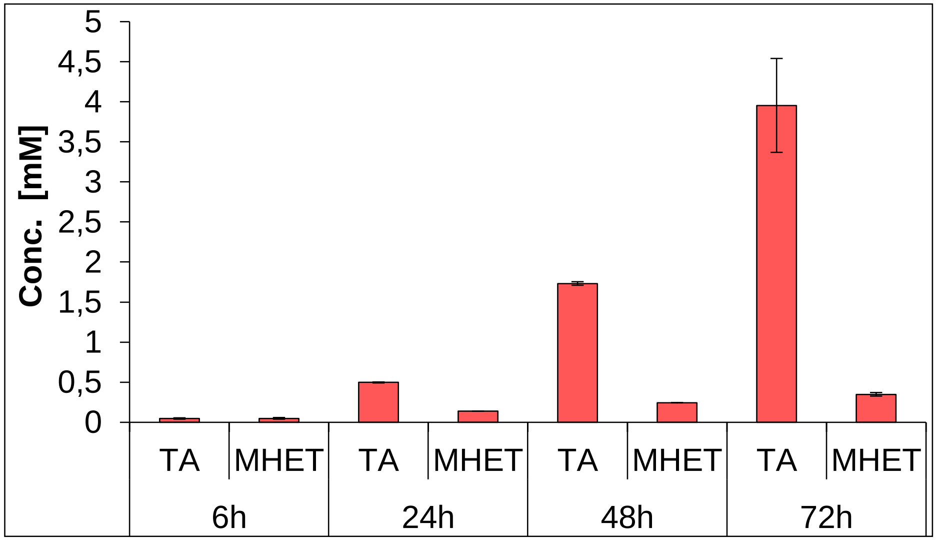
5 µM *Humicola insolens* cutinase

0.1 M NaOH

Pellis A. et al., *Process Biochem.*, 59, 77-83, 2017.

Hydrolysis of PET catalyzed by Cutinase 1 from *Thermobifida cellulosilytica*





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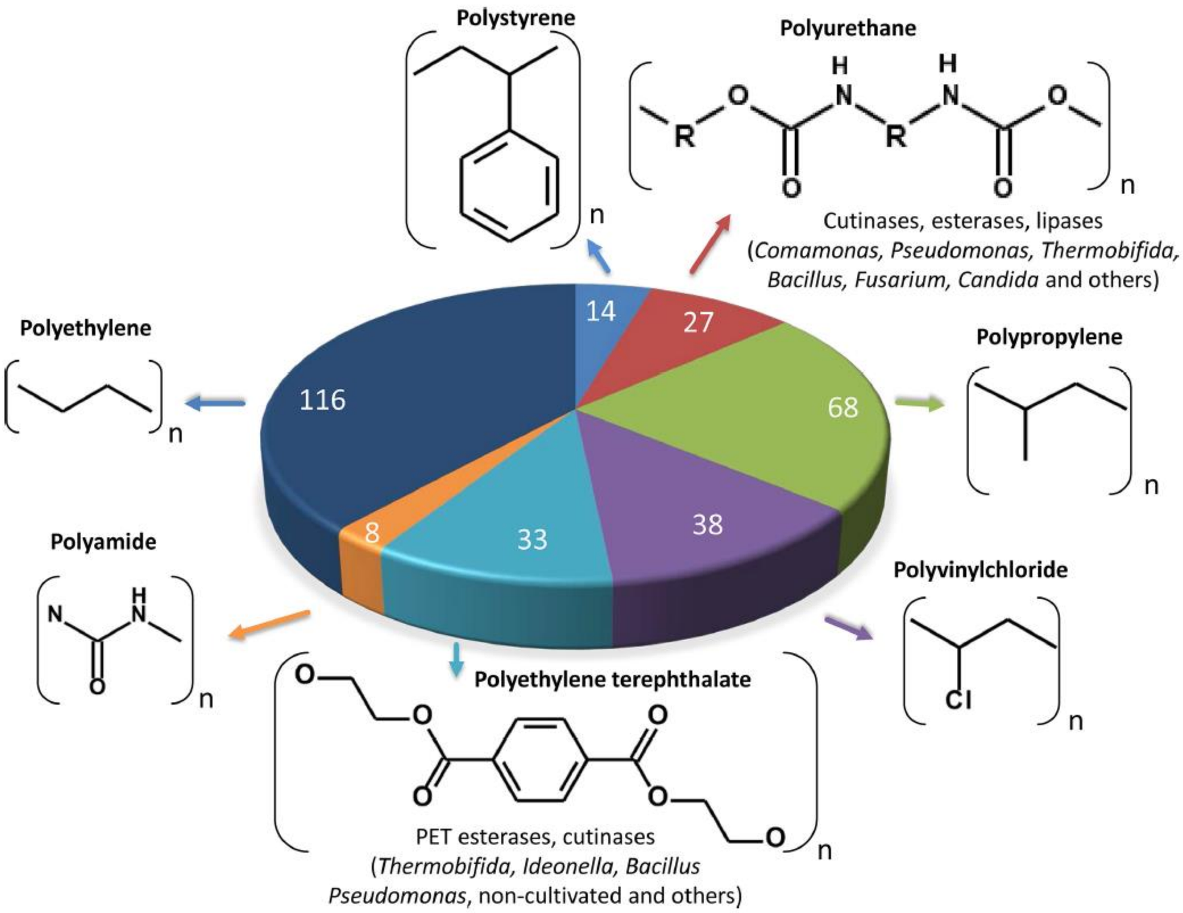
Nicola Piovesan, 2016, Thesis, Master in Chemistry, Univ. Trieste

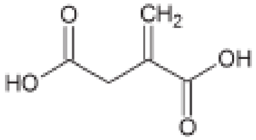


Cutinases, esterases, lipases (*Comamonas, Pseudomonas, Thermobifida, Bacillus, Fusarium, Candida* and others)

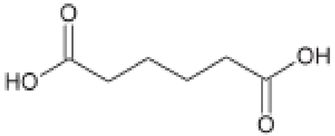
PET esterases, cutinases (*Thermobifida, Ideonella, Bacillus Pseudomonas*, non-cultivated and others)

FIG 1 Main synthetic polymers globally produced in 2016. Numbers in the chart indicate the global annual production (millions of tons) of the specified synthetic polymer. Global annual plastic production was extracted from references 1–4, and https://www.plasticsinsight.com/global-pet-resin-production-capacity, https://www.plasticsinsight.com/resin-intelligence/resin-prices/polyamide/, and https://www.plasticsinsight.com/world-plastics-production/. Monomers are depicted above the chart. Indicated are the names of bacterial genera producing verified enzymes with available protein sequences that are known to be involved in the breakdown of the high-molecular-weight polymers (not the additives, plasticizers, etc.). For detailed references on the individual enzymes, refer to the main text. For PA, PE, PS, PVC, and PP, no defined enzymes that act on the polymer have been identified at the level of amino acid or DNA sequences. For enzymes acting on dimers or oligomers and feeding them into the different metabolic pathways, see the main text. For additional structural information on the polymers we refer to ChEBI (https://www.ebi.ac.uk/chebi/init.do).

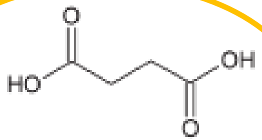
Biotecnological production of other di-carboxylic acids for polyesters



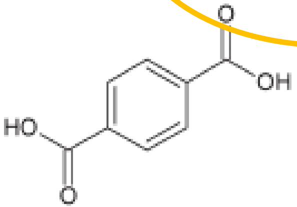
Itaconic acid (IA)



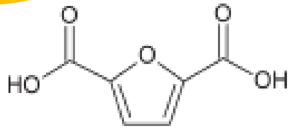
Adipic acid (AA)



Succinic acid (SA)

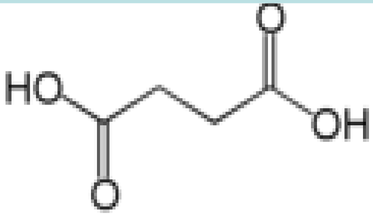


Terephthalic acid (TA)



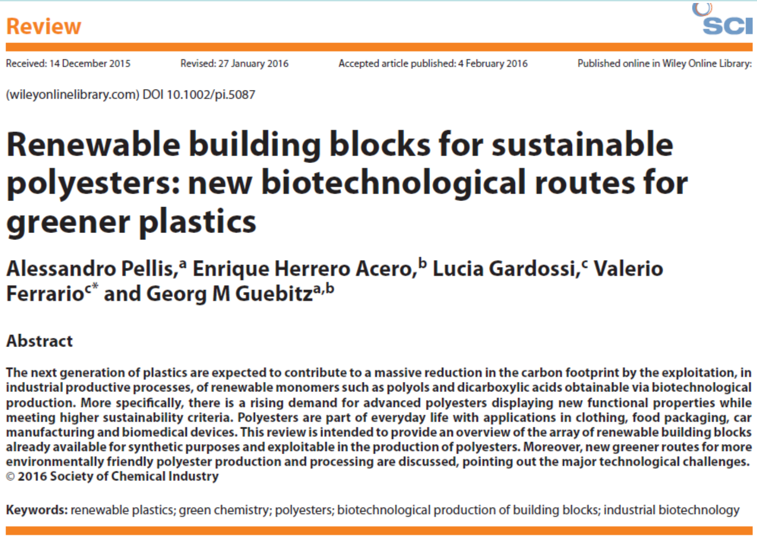
Furandicarboxylic acid (FDCA)

The high interest in SA is because of the fact that this dicarboxylic acid is a key component/intermediate in the production of several solvents, adhesives, printing inks, magnetic tapes, coating resins, plasticizers, emulsifiers, deicing compounds and chemical and pharmaceutical intermediates.



Succinic acid

Microbial strain able to convert raw hydrolysates from biomass to succinate (US Patent 6,743,610).


Review

Received: 14 December 2015 Revised: 27 January 2016 Accepted article published: 4 February 2016 Published online in Wiley Online Library:

(wileyonlinelibrary.com) DOI 10.1002/pi.5087

Renewable building blocks for sustainable polyesters: new biotechnological routes for greener plastics

Alessandro Pellis,[a] Enrique Herrero Acero,[b] Lucia Gardossi,[c] Valerio Ferrario[c*] and Georg M Guebitz[a,b]

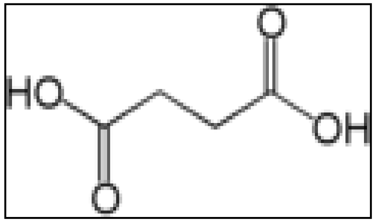
Abstract

The next generation of plastics are expected to contribute to a massive reduction in the carbon footprint by the exploitation, in industrial productive processes, of renewable monomers such as polyols and dicarboxylic acids obtainable via biotechnological production. More specifically, there is a rising demand for advanced polyesters displaying new functional properties while meeting higher sustainability criteria. Polyesters are part of everyday life with applications in clothing, food packaging, car manufacturing and biomedical devices. This review is intended to provide an overview of the array of renewable building blocks already available for synthetic purposes and exploitable in the production of polyesters. Moreover, new greener routes for more environmentally friendly polyester production and processing are discussed, pointing out the major technological challenges.

Keywords: renewable plastics; green chemistry; polyesters; biotechnological production of building blocks; industrial biotechnology

Succinic acid (SA)

Since 2008, various companies (such as DSM, BASF and Purac)
have shown an interest in the production of bio-based SA at
an industrial scale.
For SA the most important production process from renewable feedstock is microbial fermentation of various glucose sources by a variety of microorganisms such as genetically engineered microorganisms:



Escherichia coli,
Actinobacillus succiniproducens and
Anaerobiospirillum succiniproducens

The processes are in use by two companies: the Myriant SA biorefinery in Lake Providence (Louisiana, USA) that employs grain sorghum grits as its saccharificable starting material32 and the Reverdia process (used by DSM+Roquette) where ethanol and SA are co-produced through glucose fermentation.

Both processes run with genetically modified anaerobic bacteria, in such a way that alcoholic fermentation sustains the SA production.Theoretical calculations performed by Pinazo *et al.* concluded that, despite having a lower material efficiency, fermentative SA production is attracting attention due to its very competitive cost and market position close to competitiveness with an important petrochemical feedstock such as maleic anhydride.

From succinic acid (SA) to 1,4-butandiol and to adipic acid (AA)

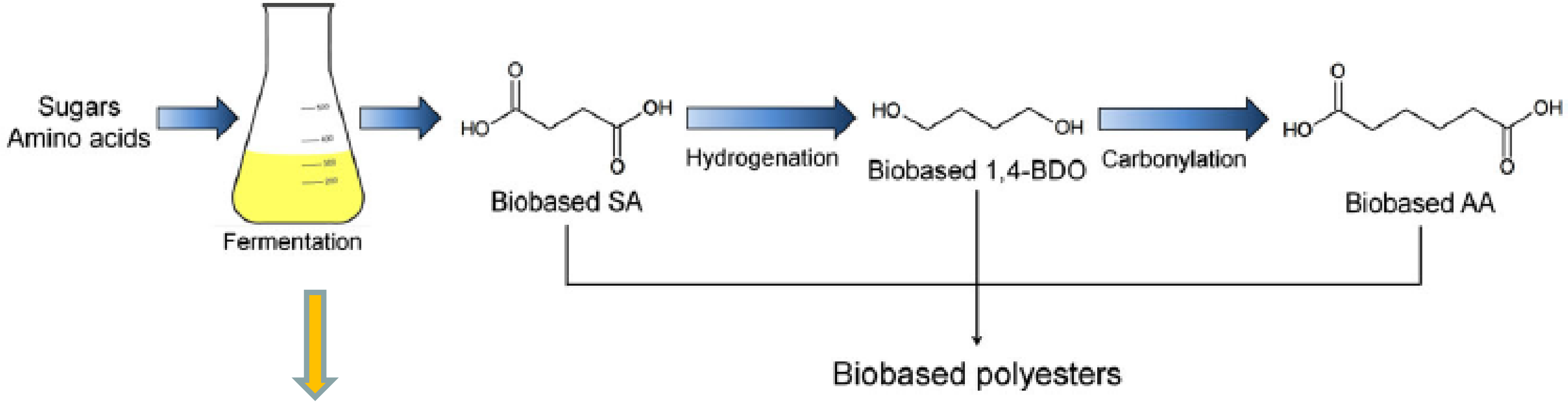
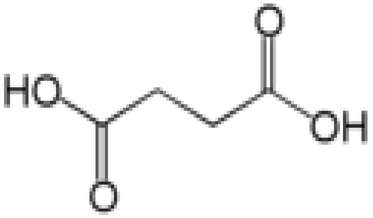
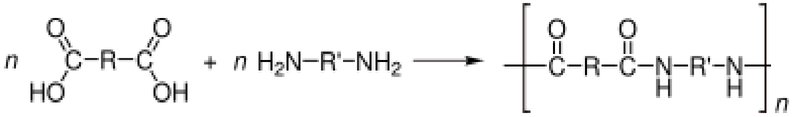


Figure 3. Biotechnological process for the production of bio-based succinic acid (SA) and its derivatives 1,4-butanediol (1,4-BDO) and adipic acid (AA).



Succinic acid

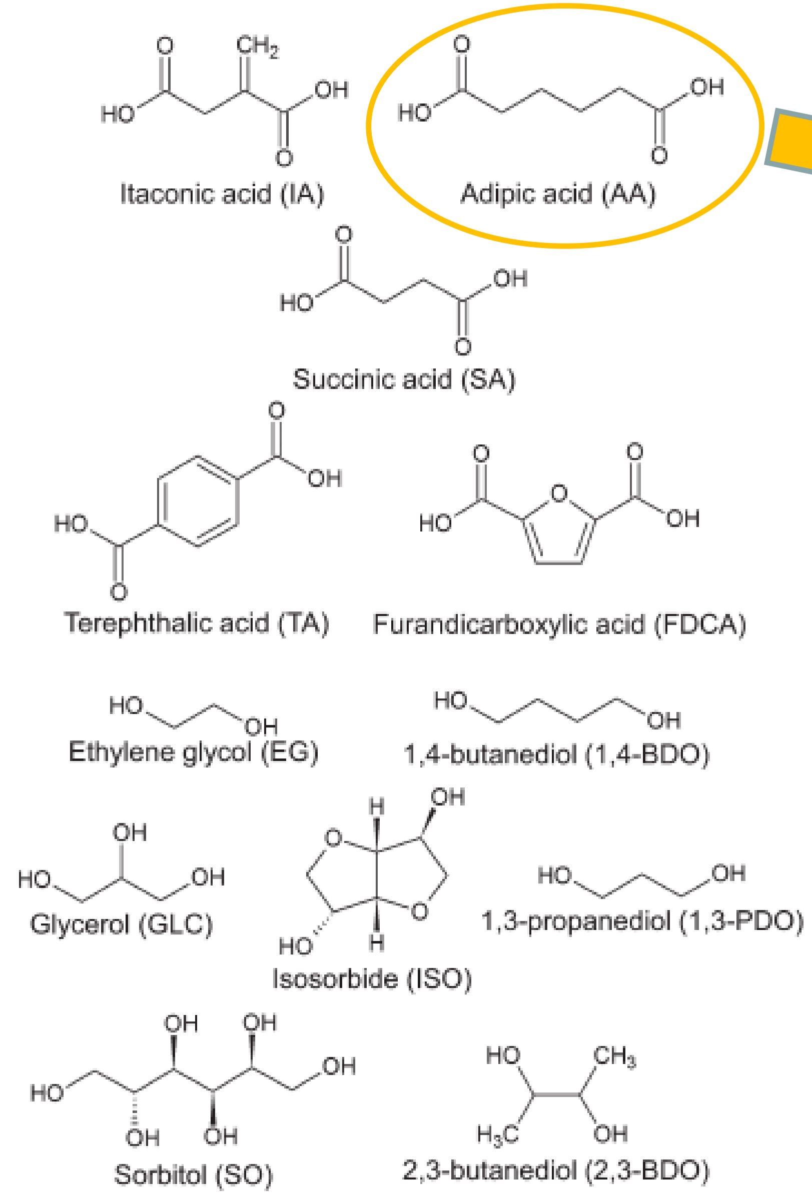


Adipic acid

nylon

Microbial strain able to convert raw hydrolysates from biomass to succinate (US Patent 6,743,610).

Biotecnological production of monomers:



Scheme 1. Most important bio-based dicarboxylic acids and polyols currently available for the enzymatic synthesis of polyesters.

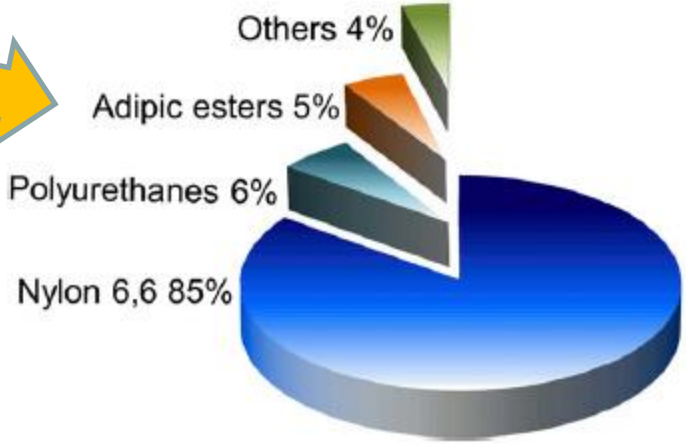
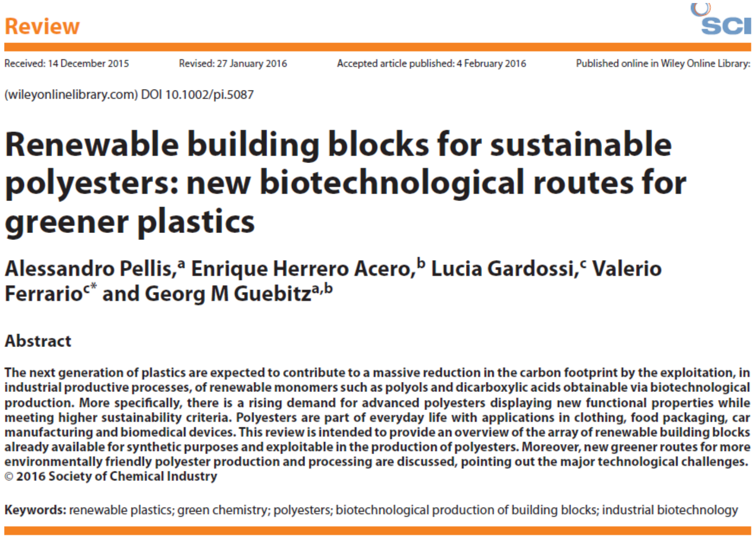


Figure 2. Most common commercial polymeric products derived from the bio-based monomer adipic acid.



Review

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Renewable building blocks for sustainable polyesters: new biotechnological routes for greener plastics

Alessandro Pellis,[a] Enrique Herrero Acero,[b] Lucia Gardossi,[c] Valerio Ferrario[c*] and Georg M Guebitz[a,b]

Abstract

The next generation of plastics are expected to contribute to a massive reduction in the carbon footprint by the exploitation, in industrial productive processes, of renewable monomers such as polyols and dicarboxylic acids obtainable via biotechnological production. More specifically, there is a rising demand for advanced polyesters displaying new functional properties while meeting higher sustainability criteria. Polyesters are part of everyday life with applications in clothing, food packaging, car manufacturing and biomedical devices. This review is intended to provide an overview of the array of renewable building blocks already available for synthetic purposes and exploitable in the production of polyesters. Moreover, new greener routes for more environmentally friendly polyester production and processing are discussed, pointing out the major technological challenges.

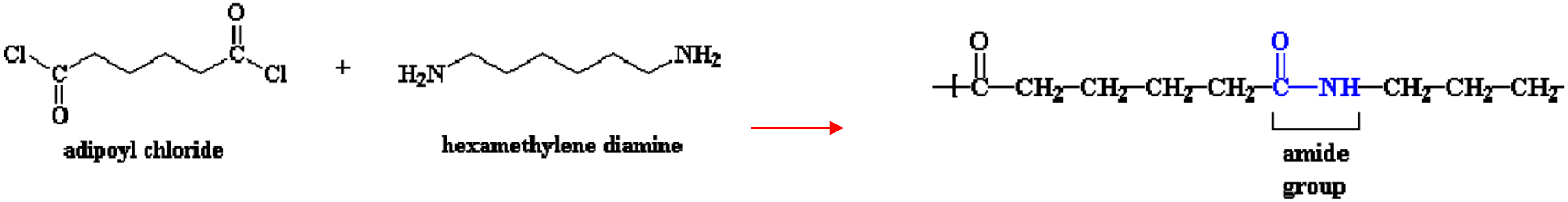
Keywords: renewable plastics; green chemistry; polyesters; biotechnological production of building blocks; industrial biotechnology

✹ Not biodegradable

Table 4. Bio-based synthetic polymers obtained from bio-based monomers or a combination of bio- and fossil-based monomers.

Polymer	Properties and applications	
Poly(trimethylene terephthalate) - PTT* ✹	Polyester. Same properties as fossil-based PTT. Scarcely biodegradable. Semi crystalline thermoplastic, easily molded or thermoformed and spun into fibres. Good tensile and flexural strength, excellent flow and surface finish. Used in textiles and engineering applications (automotive parts, mobile phone housings.	
Poly(ethylene terephthalate)-PET* ✹	Polyester. Same properties as the fossil-based PET. High-performance plastic used for engineering applications, fibres, films, bottles.	
Poly(1,4-butylene succinate) - PBS	Polyester. Biodegradable in soil and biocompostable. Its T_m of 115 °C and tensile strength of 30–35 MPa make PBS suitable for applications in packaging as an alternative to polyolefins.	[5
Poly(ethylene succinate) - PES	Moderately biodegradable. Good oxygen barrier and elongation properties. Used for film applications.	
Poly(ethylene furanoate) - PEF ✹	Polyester. Durable, good oxygen barrier. T_m of 211 °C and T_g of 86 °C. Suitable for packaging, in the food and beverage industry.	[
Poly(trimethylene furanoate) - PTF ✹	Polyester. Not biodegradable. T_m of 172 °C, T_g of 57 °C, good oxygen barrier properties. Employed in light weighting packaging.	
Poly(butylene furanoate) - PBF	Polyester. T_m of 172 °C, T_g of 44 °C. Potential replacer of PET and PBT.	[1
Poly(1,4-butylene adipate-*co*-1,4-butylene terephthalate) - PBAT	Polyester. Biodegradable. Used in blends with PLA and fibers due to low thermo-mechanical properties. Obtained from fossil feedstock or bio-tereftalic acid	
Unsaturated polyester resins - [illegible]PR ✹	Properties varies according the percentage of unsaturated diacid (e.g. itaconic acid) and the curing procedure. Applied in waterborne UV-curable coatings for wood and flooring industry.	
Poly(L-la[illegible]PLLA	Polyester. Thermoplastic. Processable by extrusion, injection molding, blow molding. Degradable by hydrolysis rather than microbial attack. Industrially compostable. Crystallinity can be controlled by co-polymerization of selected ratios of L- to D-stereoisomers of lactic acid or lactide. Mechanical, thermal and barrier properties justify applications in food packaging. Used for medical applications and drug delivery because of its biocompatibility.	[1
Polyamides containing four carbons - 4C PAs: 4; 4.6 and 4.10 ✹	Not biodegradable. 4C PAs match properties of fossil-based PAs 6 and 6.6, such as thermal durability and mechanical strength, with a Tm above 250°C. All 4C PAs have higher dielectric strength and higher retention of tensile properties as compared to PA 6.6. PA 4.10 has low moisture uptake. Applications range from water management to cable coating, food contact products and automotive.	[1
Polyamides with longer chains. PAs: 6.10; 10.10; 11 and 12 ✹	Long chain carbon monomers confer flexibility to these polymers, which find application in fuel lines in cars, offshore pipelines, gas distribution piping systems, electronics, sports equipment, furniture and automobile components.	
Polyvinyl chloride – PVC* ✹	Not biodegradable and poorly chemically degradable. Same properties as fossil-based PVC. Used in construction profile applications, bottles and non-food packaging. When made more flexible by the addition of plasticizers, it is used in electrical cable insulation, imitation leather, flooring and as rubber replacer.	[2
Polyethylene – PE* (from bio-ethanol) ✹	Polyolefin. Same properties of fossil-based PE. Not biodegradable, recyclable through dedicated infrastructures. Thermoplastic. High Density PE (more crystalline) finds applications in construction sector. Low Density Polyethylene is used in packaging. Ultrahigh Molecular Weight Polyethylene has applications in medical devices and bulletproof vests.	
Polypropylene - PP* ✹	Polyolefin. Same properties as the fossil PP. Not biodegradable, non-polar. Partially crystalline thermoplastic with low density. Used in a large variety of applications and in packaging.	
Poly(methyl methacrylate)–PMMA* ✹	Not biodegradable. Lightweight material used as glass replacement in automotive for shatterproof and UV resistant properties.	[2
Ethylene propylene diene monomer – EPDM (synthetic rubber) ✹	Not biodegradable. Good resistance to hot water and polar solvents but poorly resistant to aromatic and aliphatic hydrocarbons. Chlorine-free synthetic rubber used for technical clothing, elastomers with shock absorption. Ozone and thermal resistant. Electrical insulation properties. Used also for automotive applications.	
Polyurethanes -PURs	Produced through the reaction of a diisocyanate with a polyol. Microbial degradation depends on the chemical structure. Often blended with polyethers to increase flexibility or extensibility. Used as de-halogenated flame retardant foams, paints, powder coatings, medical devices (blood contacting applications). Biodegradable polyurethane scaffolds have been used in tissue regeneration.	[2
Poly(furfuryl alcohol) - PFA ✹	Not biodegradable. Synthesized from bio-based furfuryl alcohol (FA) deriving from sugars. Used in the fabrication of nanoporous carbons structures for molecular sieve adsorbents, membranes and as a component for electrochemical and electronic devices.	
Acrylonitrile butadiene styrene - ABS ✹	Obtained from butadiene rubber dispersed in a matrix of styrene-acrylonitrile copolymer. Not biodegradable. Thermoplastic, used to make light, rigid, moulded products such as pipes, automotive parts. Used also for its flame retardant properties.	[5
Polyacrylic superabsorbent polymers - PA-SA	Its high swelling capacity is tuneable by controlling the degree of crosslinking. Its biodegradation in soil can be improved under conditions that maximize solubilisation. Find applications in personal disposable hygiene products, such diapers and sanitary napkins.	[3
Poly(itaconic acid) - PIA ✹	Due to the presence of a vinyl moiety, itaconic acid is structurally similar to acrylic and methacrylic acid, providing a suitable bio-based alternative to poly(meth)acrylates via radical polymerization to yield poly(itaconic acid) (PIA). Applications include fibers, coatings, adhesives, thickeners, binders. As co-monomer itaconic acid gives glass-ionomer dental cement.	

Dal punto di vista chimico i nylon sono poliammidi, poiché contengono il caratteristico gruppo ammidico (che congiunge i monomeri da cui vengono sintetizzati), analogo a quello che lega gli amminoacidi nelle proteine.



Poiché i gruppi ammidici sono molto polari, le poliammidi sono caratterizzate da numerosi legami a idrogeno intra- e inter-molecolari che danno origine ad intense forze di coesione le quali, insieme alla regolarità delle catene, fanno sì che i nylon siano spesso cristallini e formino delle fibre caratterizzate da:

- ottima resistenza all'usura;
- elevato recupero elastico;
- facilità di tintura;
- buona solidità al colore;
- facilità di manutenzione.

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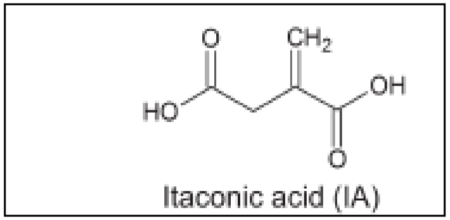


Itaconic acid (IA)

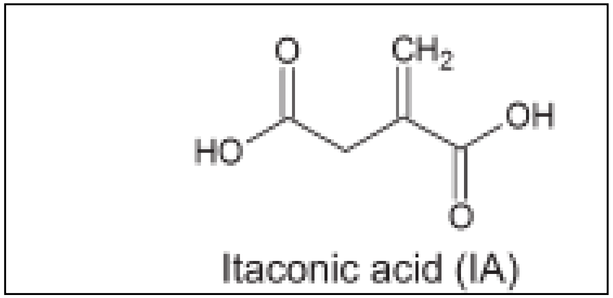
Itaconic acid (IA)

IA has been known since 1837 when Baup first described the thermal decomposition of citric acid, leading to IA.

Neither thermal decomposition nor alternative chemical methods are used for commercial production since fermentation by fungi is economically more profitable.

Biosynthesis of IA was first described by Kinoshita in 1932 who isolated the product from cultivation media of the osmophile eukaryotic *Aspergillus itaconicus*.

Various *Aspergillus terreus* strains were found more suitable for the fermentation process.



Itaconic acid (IA)

IA is currently used in paper-coating and carpet-backing, which are the primary consumers at the industrial scale. Some IA derivatives are used in medicines, cosmetics, lubricants and herbicides.

Polyols obtained by fermentations

Some bio-based monomers for polymer production

Monomer	Biotechnological route		Company	Status	Application of the corresponding bio-based polyesters	.
Sorbitol	Fermentation + hydrogenation		Roquette, ADM	Market	Functional polyesters; coatings	
Isosorbide	Sorbitol dehydration		Roquette	Market	Thermosetting resins	
Ethylene glycol	Ethanol dehydration		India Glycols Ltd, Greencol Taiwan	Market	PET; PEF	
1,3-propanediol	Fermentation		Du Pont, Tate & Lyle, Metabolic Explorer	Market	PTT; fibers; elastomers; polyester-urethanes	
1,4-butanediol	Fermentation, succinic acid hydrogenation		Novamont, BioAmber, Genomatica, Mitsubishi	Market	PBAT; PBS; PBT	
Adipic acid	Fermentation + hydrogenation		Celexion LLC, BioAmber, Rennovia, Verdezyme	Market	Resins; polyester-amines; polyester-urethanes	
Itaconic acid	Fermentation		Qingdao Kehai Biochemistry, Itaconix	Market	Photocurable precursors; plasticizers	
Lactic acid	Fermentation		Nature Works, BASF, Purac, Cargill, BBCA, Galactic	Market	PLA	
Succinic acid	Fermentation		BioAmber, Myriant, Reverdia, BASF, Purac, Succinity	Market	Textiles; coatings; PBS; PBT	
Terephthalic acid	Isobutylene oxidation, fermentation		Virient, Annellotech, Genomatica	Pilot plant	PET; coatings	
Levulinic acid	Fermentation, acid treatment of C6 sugars		GFBiochemicals, Bio-on, Biofine Renewables	Market	Coatings, hyperbranched dendrimeric polyesters	
Malic acid	Fermentation		Novozymes	Pilot plant	Functionalized chiral polyesters	
2,5-furandicarboxylic acid	Fermentation + dehydration + oxidation		Avantium	Pilot plant	PEF; polyester-urethanes	

1,4-Butanediol (1,4-BDO)

1,4-BDO is an important chemical that is used for the manufacture of over 2.5 million tons of polymers annually. Nowadays its production is almost entirely based on fossil carbon resources (production via the Reppe process in which acetylene is reacted with formaldehyde) with the exception of BASF and Bioamber that started production via hydrogenation of SA which is accessible from biogenic sources as described below.

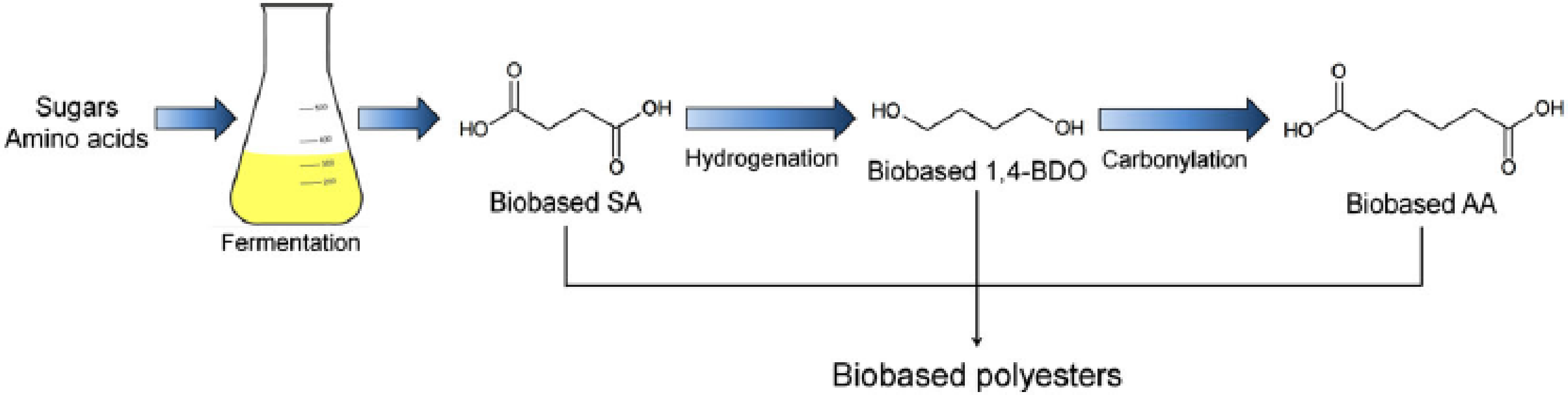
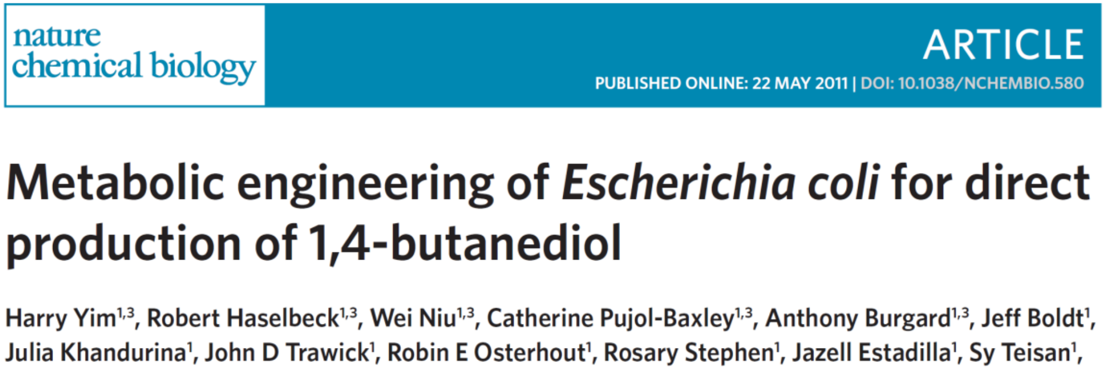


Figure 3. Biotechnological process for the production of bio-based succinic acid (SA) and its derivatives 1,4-butanediol (1,4-BDO) and adipic acid (AA).

In September 2016 Novamont opened the first plant at commercial scale in the world for the direct fermentation of sugar to produce 1,4-butandiol.



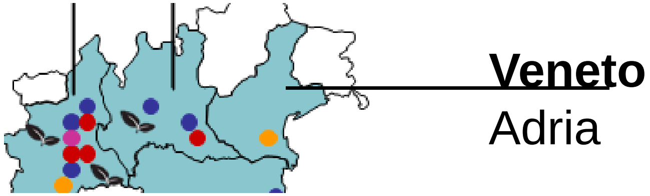
nature chemical biology

ARTICLE

PUBLISHED ONLINE: 22 MAY 2011 | DOI: 10.1038/NCHEMBIO.580

Metabolic engineering of *Escherichia coli* for direct production of 1,4-butanediol

Harry Yim[1,3], Robert Haselbeck[1,3], Wei Niu[1,3], Catherine Pujol-Baxley[1,3], Anthony Burgard[1,3], Jeff Boldt[1], Julia Khandurina[1], John D Trawick[1], Robin E Osterhout[1], Rosary Stephen[1], Jazell Estadilla[1], Sy Teisan[1],



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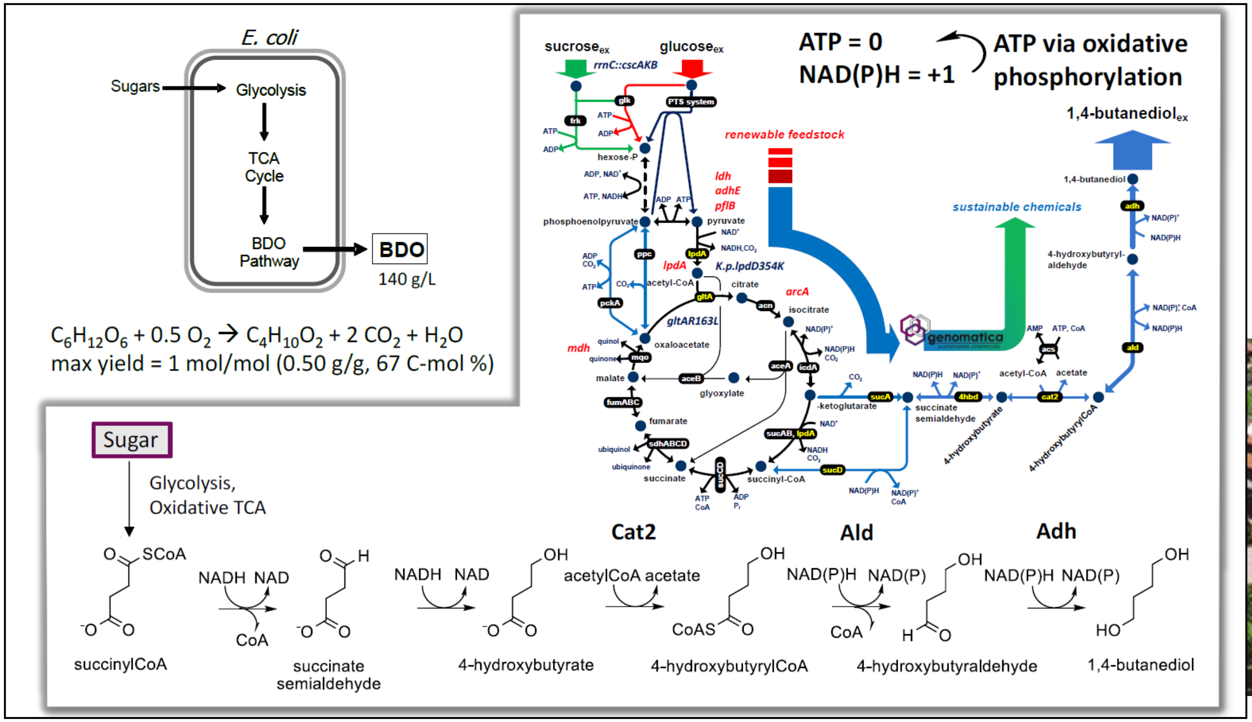
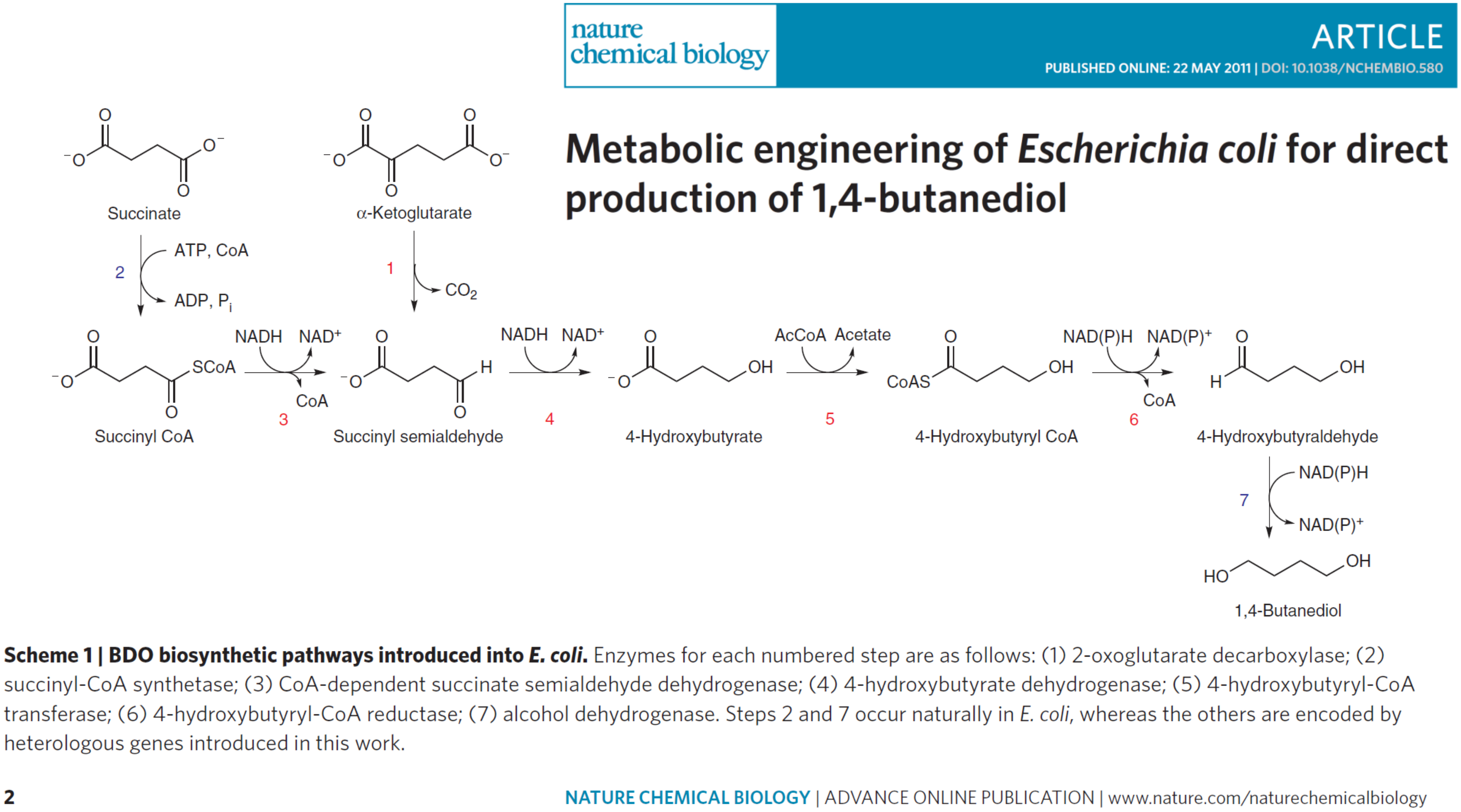
[1]Genomatica, Inc., San Diego, California, USA. [2]Department of Chemical and Biomolecular Engineering (BK21 program), Center for Systems and Synthetic Biotechnology, Institute for the BioCentury, Korea Advanced Institute of Science and Technology, Daejeon, South Korea. [3]These authors contributed equally to this work. *e-mail: svandien@genomatica.com



$C_6H_{12}O_6 + 0.5\ O_2 \rightarrow C_4H_{10}O_2 + 2\ CO_2 + H_2O$
max yield = 1 mol/mol (0.50 g/g, 67 C-mol %)

In September 2016 Novamont opened the first plant at commercial scale in the world for the direct fermentation of sugar to produce 1,4-butandiol.



nature chemical biology

ARTICLE

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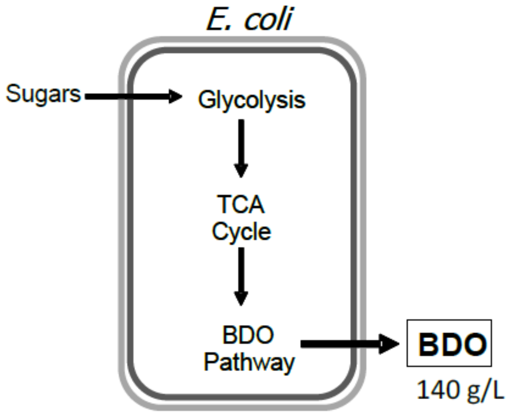
Scheme 1 | BDO biosynthetic pathways introduced into *E. coli*. Enzymes for each numbered step are as follows: (1) 2-oxoglutarate decarboxylase; (2) succinyl-CoA synthetase; (3) CoA-dependent succinate semialdehyde dehydrogenase; (4) 4-hydroxybutyrate dehydrogenase; (5) 4-hydroxybutyryl-CoA transferase; (6) 4-hydroxybutyryl-CoA reductase; (7) alcohol dehydrogenase. Steps 2 and 7 occur naturally in *E. coli*, whereas the others are encoded by heterologous genes introduced in this work.

1,4-BDO **derivatives:**

- tetrahydrofuran
- *γ*-butyrolactone
- *N*-methylpyrrolidone
- 2-pyrrolidone

1,4-BDO is an important chemical that is used for the manufacture of over 2.5 million tons of polymers annually1,4-BDO and its derivatives represent a market ripe for the introduction of a competitive bio-based route



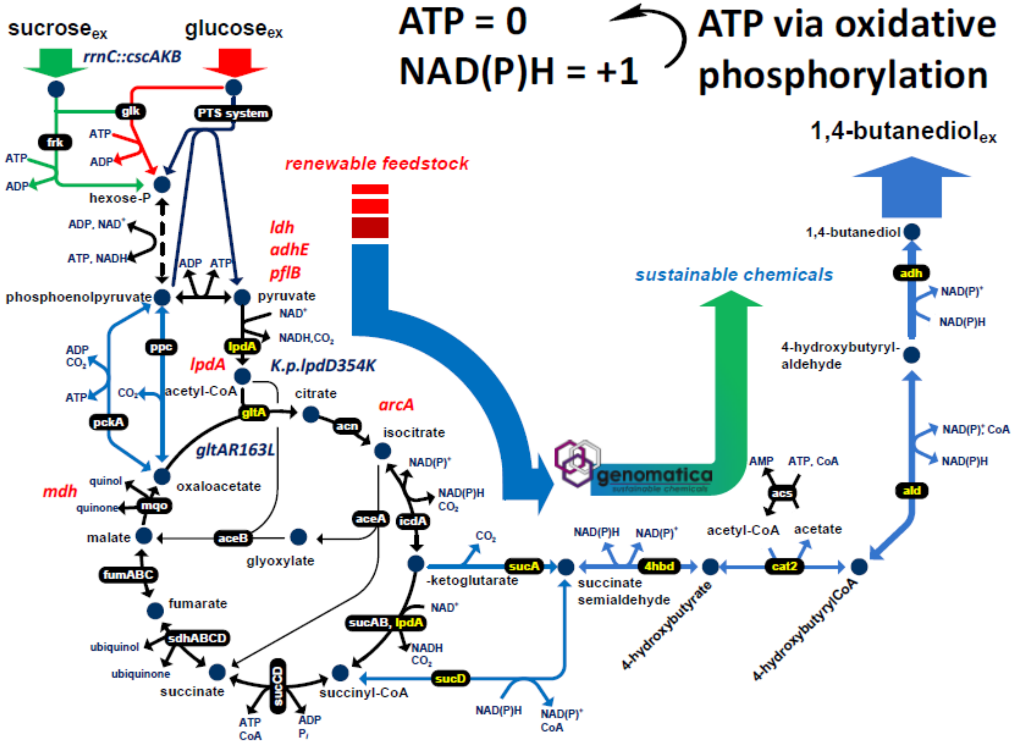
E. coli

Sugars → Glycolysis → TCA Cycle → BDO Pathway → **BDO**

140 g/L

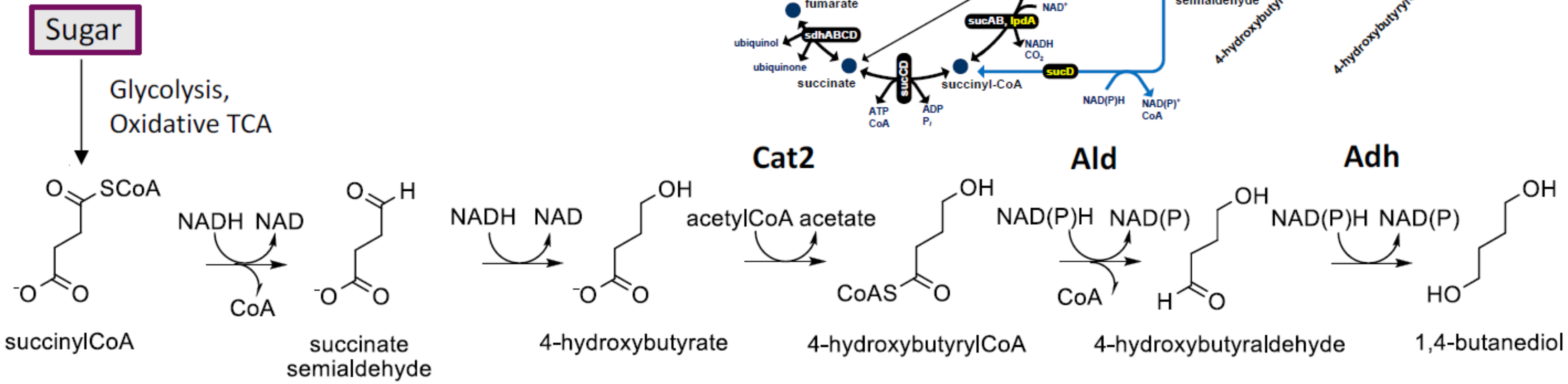
$C_6H_{12}O_6 + 0.5\ O_2 \rightarrow C_4H_{10}O_2 + 2\ CO_2 + H_2O$

max yield = 1 mol/mol (0.50 g/g, 67 C-mol %)



ATP = 0
NAD(P)H = +1

ATP via oxidative phosphorylation



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1,4-Butanediol (BDO) is an important commodity chemical used to manufacture over 2.5 million tons annually of valuable polymers, and it is currently produced exclusively through feedstocks derived from oil and natural gas. Herein we report what are to our knowledge the first direct biocatalytic routes to BDO from renewable carbohydrate feedstocks, leading to a strain of *Escherichia coli* capable of producing 18 g l^{-1} of this highly reduced, non-natural chemical. A pathway-identification algorithm elucidated multiple pathways for the biosynthesis of BDO from common metabolic intermediates. Guided by a genome-scale metabolic model, we engineered the *E. coli* host to enhance anaerobic operation of the oxidative tricarboxylic acid cycle, thereby generating reducing power to drive the BDO pathway. The organism produced BDO from glucose, xylose, sucrose and biomass-derived mixed sugar streams. This work demonstrates a systems-based metabolic engineering approach to strain design and development that can enable new bioprocesses for commodity chemicals that are not naturally produced by living cells.

Thanks to an investment of 100 million euro, Novamont has managed to revive an abandoned manufactory site of Bioitalia, former Ajinomoto, who was acquired in 2012 by Novamont, safeguarding 27 jobs, which later became 51 at the end of 2015.
The plant of Bottrighe di Adria is the first facility in the world capable of producing butanediol (BDO) directly from sugars (30 thousand tons yearly).

BDO produced by the plant enables Novamont to deliver its fourth-generation of Mater-Bi bioplastics with greater sustainability (e.g. renewable components).

The products made with this new BDO will save an estimated 56 percent of greenhouse gas emissions compared to the use of conventional BDO.

https://www.youtube.com/watch?v=cWPcKil4z4M

https://www.youtube.com/watch?v=awxsW2nzsN8


ATTENZIONE

Other monomers for bio-based plastics

Chemical platform for 3-hydroxypropionic acid

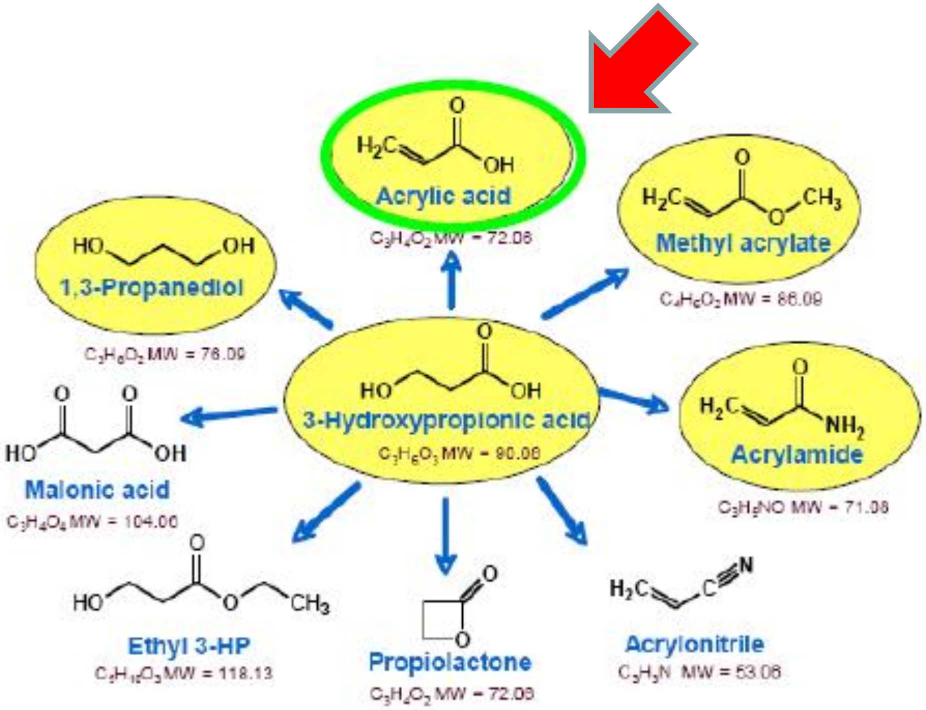
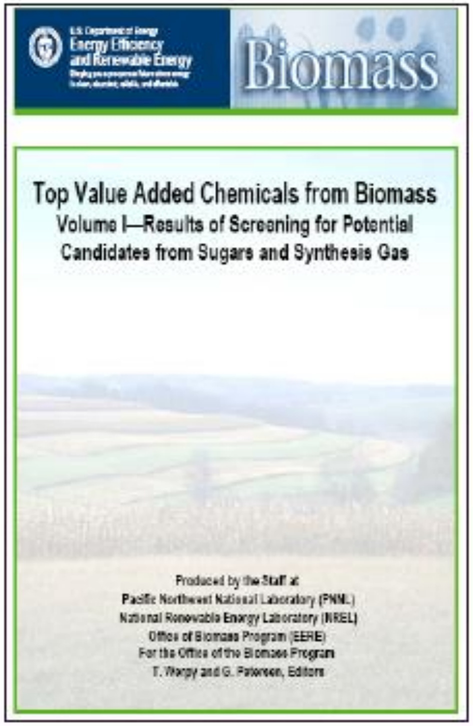


Figure 8 – Derivatives of 3-HPA


U.S. Department of Energy
Energy Efficiency
and Renewable Energy

Biomass

Top Value Added Chemicals from Biomass
Volume I—Results of Screening for Potential
Candidates from Sugars and Synthesis Gas

Produced by the Staff at
Pacific Northwest National Laboratory (PNNL)
National Renewable Energy Laboratory (NREL)
Office of Biomass Program (EERE)
For the Office of the Biomass Program
T. Werpy and G. Petersen, Editors

http://www1.eere.energy.gov/biomass/pdfs/35523.pdf

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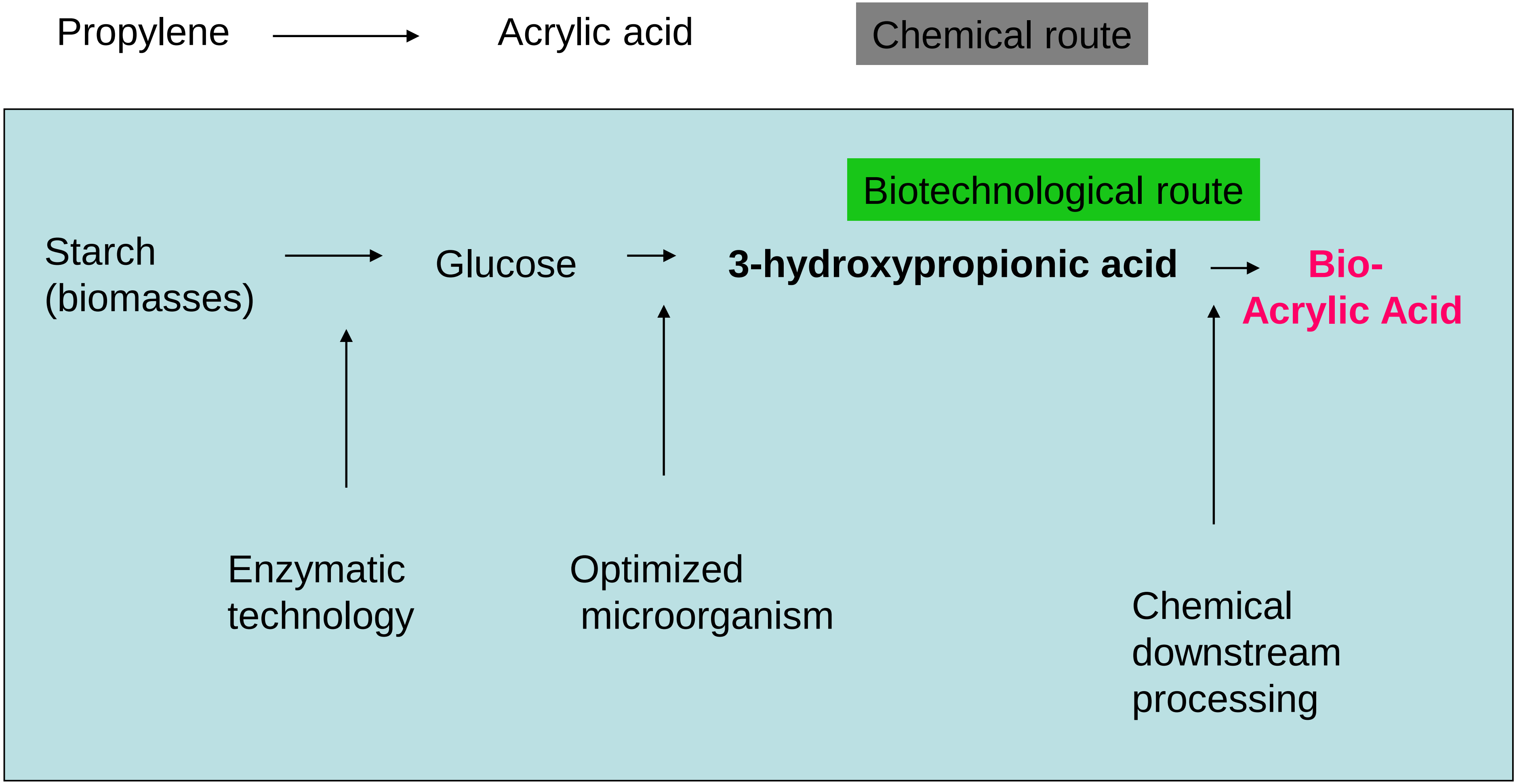
Poly(1,4-butylene succinate) - PBS	Polyester. Biodegradable in soil and biocompostable. Its T_m of 115 °C and tensile strength of 30–35 MPa make PBS suitable for applications in packaging as an alternative to polyolefins.	[5
Poly(ethylene succinate) - PES	Moderately biodegradable. Good oxygen barrier and elongation properties. Used for film applications.	
Poly(ethylene furanoate) - PEF	✹ Polyester. Durable, good oxygen barrier. T_m of 211 °C and T_g of 86 °C. Suitable for packaging, in the food and beverage industry.	[
Poly(trimethylene furanoate) - PTF	✹ Polyester. Not biodegradable. T_m of 172 °C, T_g of 57 °C, good oxygen barrier properties. Employed in light weighting packaging.	
Poly(butylene furanoate) - PBF	Polyester. T_m of 172 °C, T_g of 44 °C. Potential replacer of PET and PBT.	[1
Poly(1,4-butylene adipate-*co*-1,4-butylene terephthalate) - PBAT	Polyester. Biodegradable. Used in blends with PLA and fibers due to low thermo-mechanical properties. Obtained from fossil feedstock or bio-tereftalic acid	
Unsaturated polyester resins - UPR	● Properties varies according the percentage of unsaturated diacid (e.g. itaconic acid) and the curing procedure. Applied in waterborne UV-curable coatings for wood and flooring industry.	
Poly(L-lactide) -PLLA	Polyester. Thermoplastic. Processable by extrusion, injection molding, blow molding. Degradable by hydrolysis rather than microbial attack. Industrially compostable. Crystallinity can be controlled by co-polymerization of selected ratios of L- to D-stereoisomers of lactic acid or lactide. Mechanical, thermal and barrier properties justify applications in food packaging. Used for medical applications and drug delivery because of its biocompatibility.	[1
Polyamides containing four carbons - 4C PAs: 4; 4.6 and 4.10	✹ Not biodegradable. 4C PAs match properties of fossil-based PAs 6 and 6.6, such as thermal durability and mechanical strength, with a Tm above 250°C. All 4C PAs have higher dielectric strength and higher retention of tensile properties as compared to PA 6.6. PA 4.10 has low moisture uptake. Applications range from water management to cable coating, food contact products and automotive.	[1
Polyamides with longer chains. PAs: 6.10; 10.10; 11 and 12	✹ Long chain carbon monomers confer flexibility to these polymers, which find application in fuel lines in cars, offshore pipelines, gas distribution piping systems, electronics, sports equipment, furniture and automobile components.	
Polyvinyl chloride – PVC*	● Not biodegradable and poorly chemically degradable. Same properties as fossil-based PVC. Used in construction profile applications, bottles and non-food packaging. When made more flexible by the addition of plasticizers, it is used in electrical cable insulation, imitation leather, flooring and as rubber replacer.	[2
Polyethylene – PE* (from bio-ethanol)	✹ Polyolefin. Same properties of fossil-based PE. Not biodegradable, recyclable through dedicated infrastructures. Thermoplastic. High Density PE (more crystalline) finds applications in construction sector. Low Density Polyethylene is used in packaging. Ultrahigh Molecular Weight Polyethylene has applications in medical devices and bulletproof vests.	
Polypropylene - PP*	✹ Polyolefin. Same properties as the fossil PP. Not biodegradable, non-polar. Partially crystalline thermoplastic with low density. Used in a large variety of applications and in packaging.	
Poly(methyl methacrylate)–PMMA*	✹ Not biodegradable. Lightweight material used as glass replacement in automotive for shatterproof and UV resistant properties.	[2
Ethylene propylene diene monomer – EPDM (synthetic rubber)	✹ Not biodegradable. Good resistance to hot water and polar solvents but poorly resistant to aromatic and aliphatic hydrocarbons. Chlorine-free synthetic rubber used for technical clothing, elastomers with shock absorption. Ozone and thermal resistant. Electrical insulation properties. Used also for automotive applications.	
Polyurethanes -PURs	Produced through the reaction of a diisocyanate with a polyol. Microbial degradation depends on the chemical structure. Often blended with polyethers to increase flexibility or extensibility. Used as de-halogenated flame retardant foams, paints, powder coatings, medical devices (blood contacting applications). Biodegradable polyurethane scaffolds have been used in tissue regeneration.	[2
Poly(furfuryl a[illegible]l) - PFA	✹ Not biodegradable. Synthesized from bio-based furfuryl alcohol (FA) deriving from sugars. Used in the fabrication of nanoporous carbons structures for molecular sieve adsorbents, membranes and as a component for electrochemical and electronic devices.	
Acrylonitrile butadi[illegible]yrene - ABS	✹ Obtained from butadiene rubber dispersed in a matrix of styrene-acrylonitrile copolymer. Not biodegradable. Thermoplastic, used to make light, rigid, moulded products such as pipes, automotive parts. Used also for its flame retardant properties.	[5
Polyacrylic superabsorbent polymers - PA-SA	Its high swelling capacity is tuneable by controlling the degree of crosslinking. Its biodegradation in soil can be improved under conditions that maximize solubilisation. Find applications in personal disposable hygiene products, such diapers and sanitary napkins.	[3
Poly(itaconic acid) - PIA	● Due to the presence of a vinyl moiety, itaconic acid is structurally similar to acrylic and methacrylic acid, providing a suitable bio-based alternative to poly(meth)acrylates via radical polymerization to yield poly(itaconic acid) (PIA). Applications include fibers, coatings, adhesives, thickeners, binders. As co-monomer itaconic acid gives glass-ionomer dental cement.	

Production of Bio-acrylic acid



Propylene → Acrylic acid

Chemical route

Biotechnological route

Starch (biomasses) → Glucose → **3-hydroxypropionic acid** → **Bio-Acrylic Acid**

Enzymatic technology

Optimized microorganism

Chemical downstream processing

(source Novozymes communication)

Bio-Polyethylene

- Equivalent to fossil based PE

- 100 % biobased (ASTM 6866)

- Not biodegradable

- Braskem 2009, 200.000 t/a
- Dow 2011, 350,000 t/a
- Solvay PVC

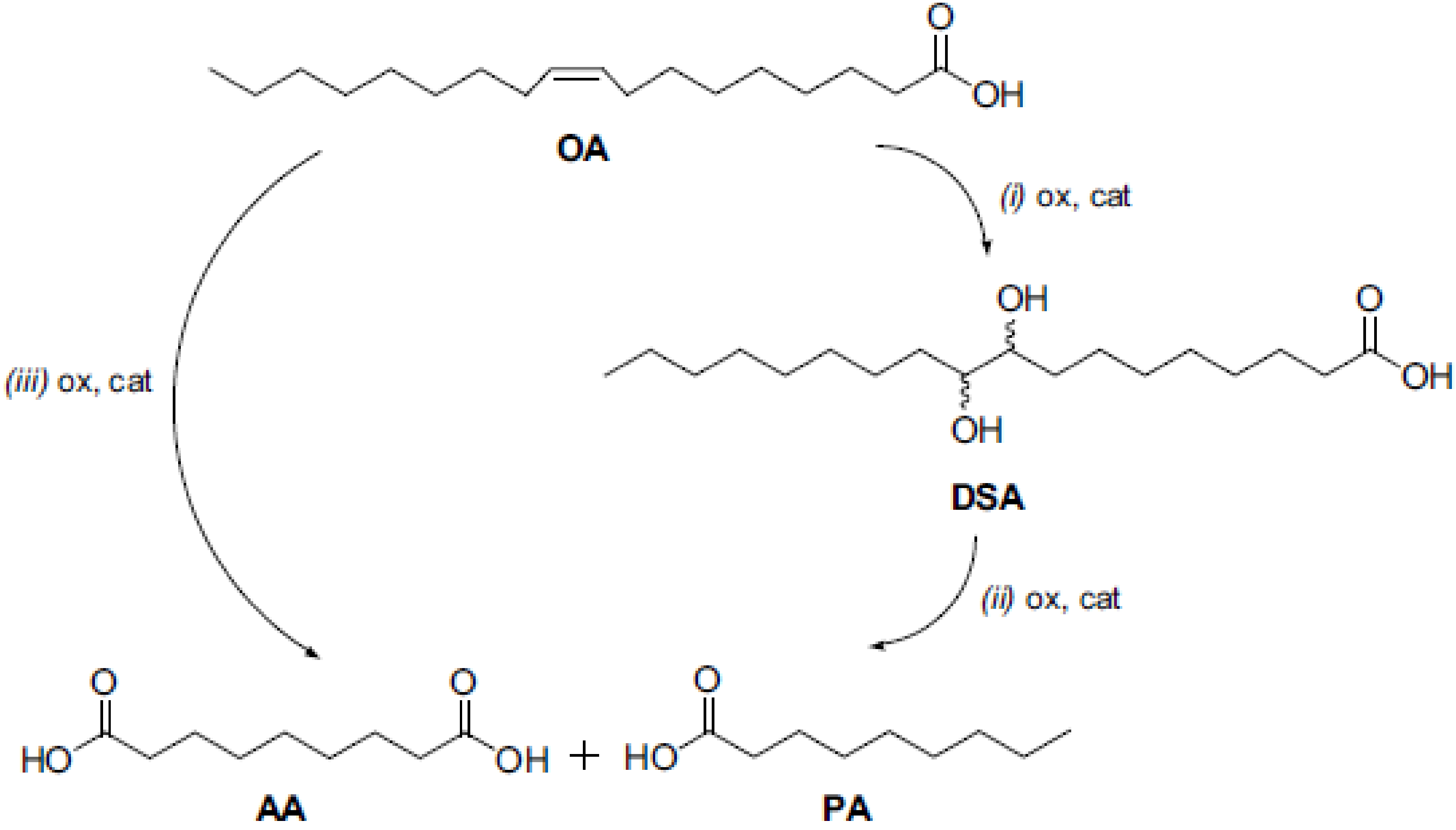
Sugar Cane
↓ fermentation, distillation
Ethanol
↓ chemical dehydration
Ethylene
↓ polymerization
PE

- Ethanol fermentation carbon efficiency?

$$C_6H_{12}O_{6(l)} + H_2O_{(l)} \rightarrow 2C_2H_5OH_{(l)} + 2CO_{2(g)} + H_2O_{(l)} + heat$$

Bio-based monomers and building blocks obtained by chemical routes

Synthesis of azelaic acid and pelargonic acid from oleic acid



Crops from marginal lands

Porto Torres: From a traditional petrochemical site to a biorefinery

Matrica

eni versalis

Novamont
Chimica Vivente per la Qualità della Vita

What crops for Sardinia? : An example : Thistle (Cynara Cardunculus)

- It is a spontaneous polyennial plant
- It needs amount of water compatible with winter rain regime (400 mm)
- It can be grown in marginal areas become a source of extra income for farmers and sheperds
- It produces oil usable as feedstock for the monomers plant
- Proteic meals can be used in feed

- It produces big amount of biomass usable immediately to produce all the energy needed by the plant and in the mid term for the manufacturing of strategic monomers

Luigi Capuzzi
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Some images from thistle harvesting in Matrìca experimental fields (August 2014)

AFTER 3 CONSECUTIVE YEARS OF EXPERIMENTATION:
- BIOMASS PRODUCTION > 15 TON/HA (17 TON/HA IN 2014)
- SEEDS PRODUCTION ~ 1,5 TON/HA (1,74 TON/HA IN 2014)
- ENGINEERING OF SPECIFIC FARMING MACHINES SUITABLE FOR SARDINIAN STONY GROUNDS

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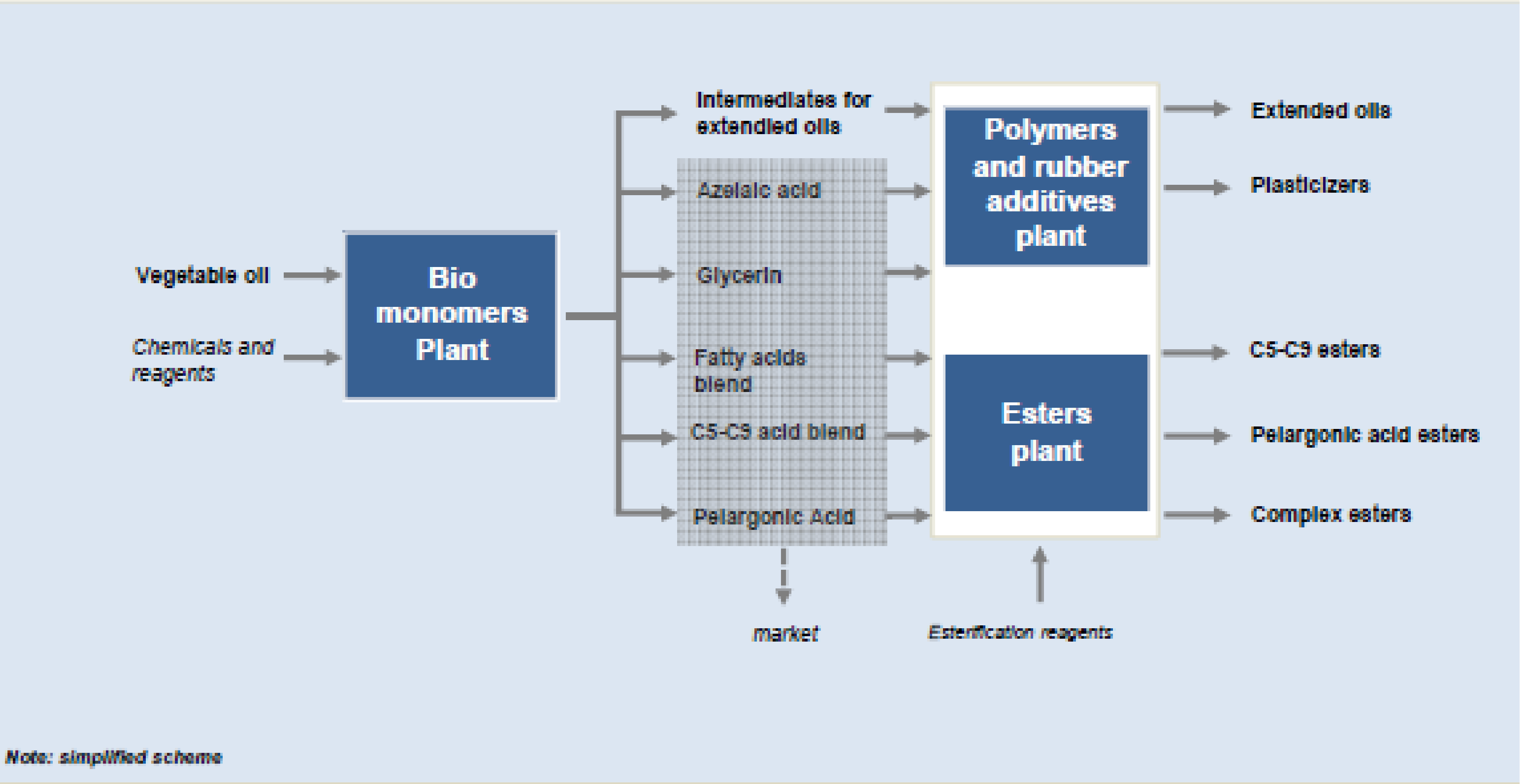

Note: simplified scheme

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Sectors where Matrica Products will Contribute to the Quality of Environment

	PLASTICIZERS FOR PVC AND OTHER POLYMERS AS REPLACEMENT OF PHTALATES	**WORLDWIDE PRODUCTION OF PHTALATES: 5,5 MIO TON**
	BIOLUBRICANTS FOR AGRICULTURE, MARINE AND INDUSTRIAL APPLICATIONS: high lubricity, biodegradability, low flammability	**EU PRODUCTION OF LUBRICANTS: 5,2 MIO TON** **HYDRAULICFLUIDS: 0,7 MIO TON**
	PALM OIL FREE COMPONENTS FOR COSMETICS	
	OIL EXTENDERS FOR RUBBER	**EUROPEAN PRODUCTION: > 0,5MIO TON**
	BIO-HERBICIDES FOR INTEGRATED AGRICULTURE	

Novamont
Luigi Capuzzi
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ACIDO AZELAICO

Uso terapeutico (applicazione topica) nelle patologie:

Acne Vulgaris

Rosacea Papulopustolare

AIFA:

Finacea - 15% (p/p) gel. Tubo da 5, 30, 50 g. Bayer, S.p.A.

Skinoren - 20% (p/p) crema. Tubo da 30 g. Bayer, S.p.A.

Effetti finali:

- Azione sbiancante su aree iperpigmentate
- Azione antiproliferativa tumorale
- Azione citotossica su cellule tumorali
- (a dosi maggiori)
- Azione antiproliferativa virale e micotica *in vitro*
- Azione batteriostatica e battericida
- dose-dipendente
- Azione anticheratinizzante - anticomedonica
- Azione antinfiammatoria
- Riduzione dell’attività serin-proteasica (SPA)

Novel functional bioplastics

Cardigan

CARDoon valorisation by InteGrAted biorefiNery

The construction of the European bioeconomy by designing and developing an integrated process to produce innovative biomaterials, through the valorization of renewable raw materials.

UNIVERSITÀ DEGLI STUDI DI TRIESTE
Dipartimento di
Scienze Chimiche e Farmaceutiche

Laboratory of Computational and Applied Biocatalysis

UNIVERSITA' DEGLI STUDI DI MILANO
BICOCCA

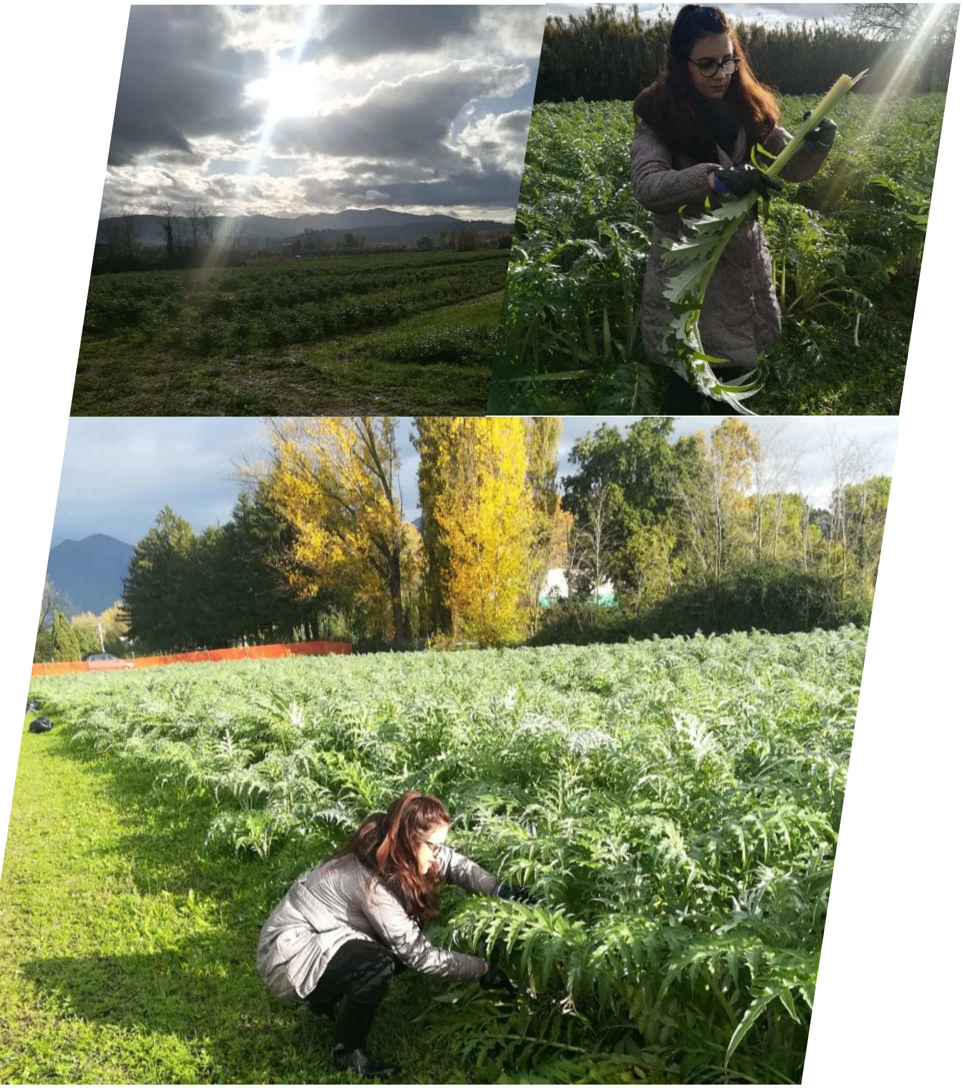
UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II

Consiglio Nazionale delle Ricerche

CARDOON

- ***Cynara carduncululus* L., from Asteraceae family**
- **Wild robust perennial plant**
- **Habitat conditions: high temperature, salinity and drought**
- **High biomass productivities (in the range of 1524 t/ha)**

P. Valentão et al. J. Agric. Food Chem. 50(17), (2012), 4989-4993;
C.M. Torres et al. Fuel 111, (2013), 535-542;

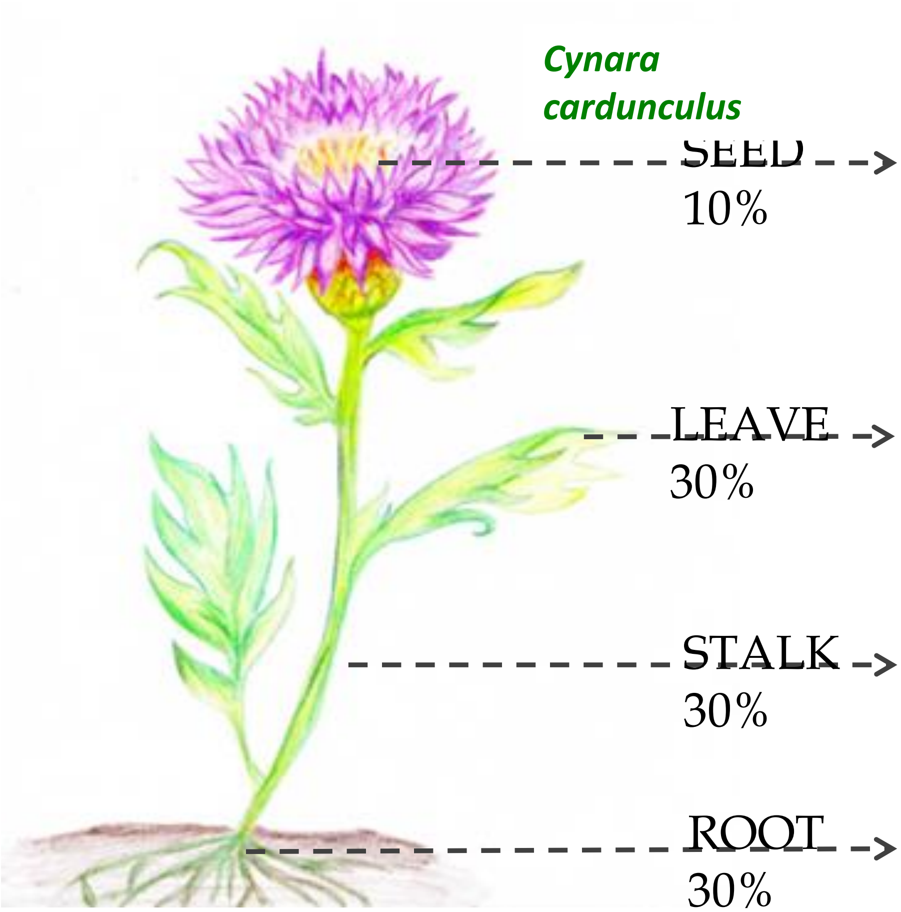


1. Collection of Cardoons

- ***WHERE: Terni***
- ***WHEN: November***

  May-June
- ***CONSERVATION: -20°C***

Cynara carduncullus



SEED
10%

- Oil
- Proteins
- Bioactive
- Moleculecules

LEAVE
30%

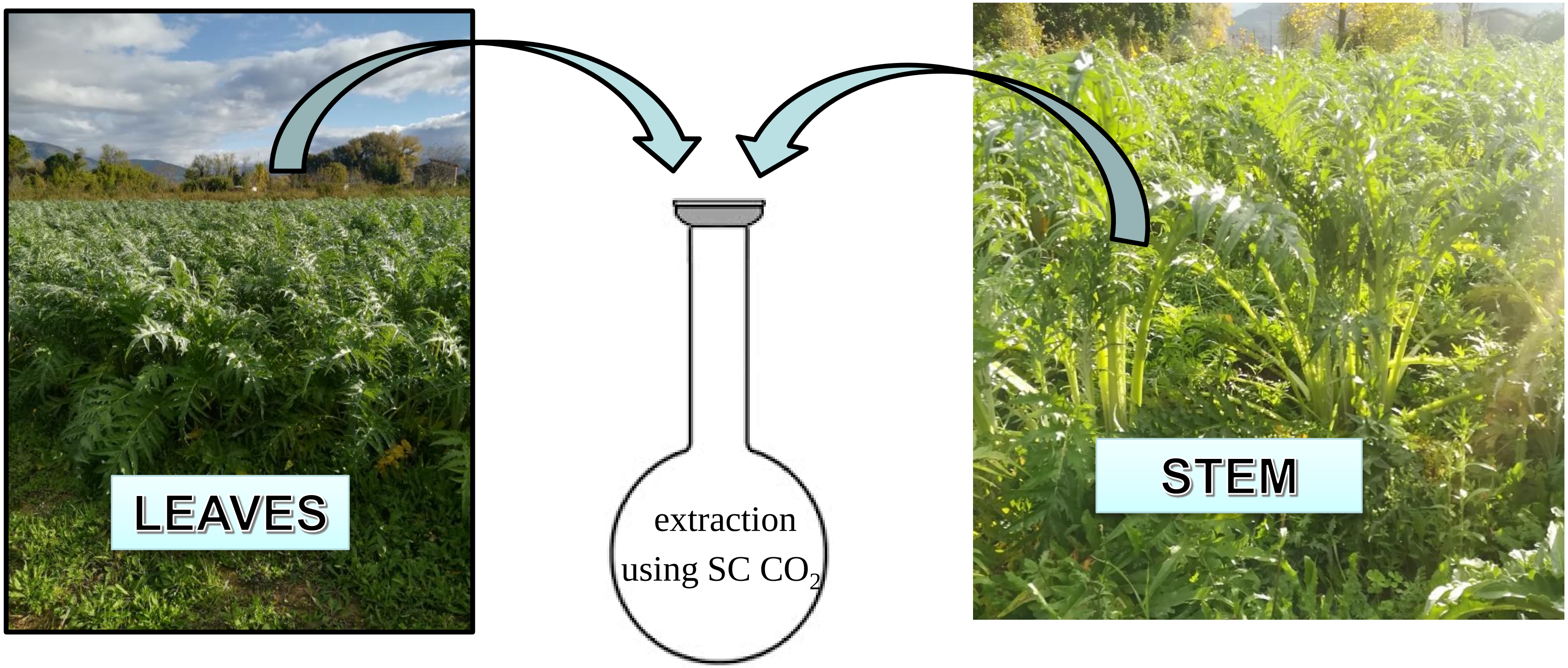
- Proteins
- Bioactive
- molecules
- Enzymes

STALK
30%

ROOT
30%

- Inulin
- PHA
- Lactic acid

Extraction of bioactive compounds

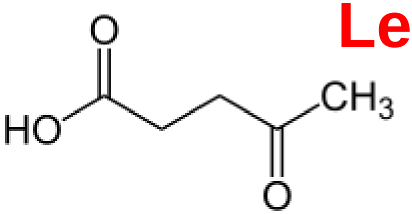


LEAVES

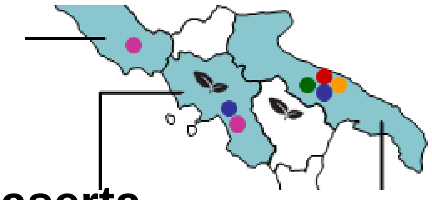
extraction using SC CO_2

STEM

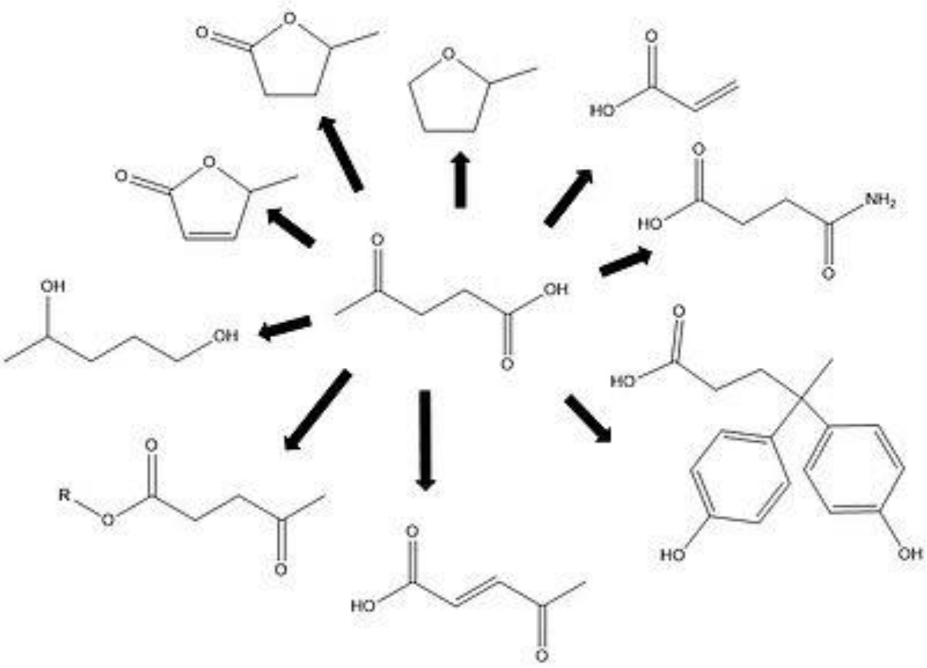
Levulinic acid platform



Levulinic acid



Process developed with the Univ. of Pisa: thermochemical conversion of carbohydrates.
Biomass pre-treatment includes acid hydrolysis for the conversion into C5 and C6 sugars.



pharmaceuticals
agrochemicals
flavours
fragrances
food additives
resins

coatings,
plasticisers
solvents,
fuel additives
biofuels

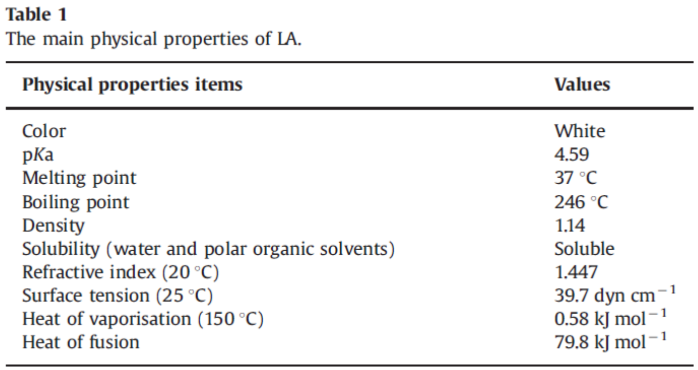


Table 1
The main physical properties of LA.

Physical properties items	Values
Color	White
pKa	4.59
Melting point	37 °C
Boiling point	246 °C
Density	1.14
Solubility (water and polar organic solvents)	Soluble
Refractive index (20 °C)	1.447
Surface tension (25 °C)	39.7 dyn cm^{-1}
Heat of vaporisation (150 °C)	0.58 kJ mol^{-1}
Heat of fusion	79.8 kJ mol^{-1}

GFBiochemicals

FIRST COMPANY TO PRODUCE LEVULINIC ACID DIRECTLY FROM BIOMASS AT COMMERCIAL SCALE

Basics:

- > Proprietary technology portfolio
- > Production assets - Start-up phase
- > Experienced R&D, Engineering & Commercial team
- > Pilot plant and application laboratories

- > Established : 2008
- > Employees : 50

Our Mission:
Bringing levulinic acid to the market by technology innovation

Our locations:

Pilot plant and application lab
Minneapolis, USA

R&D and Marketing & Sales
Geleen, the Netherlands

Headquarters
Milan, Italy

10,000 MT/a levulinic acid plant
Caserta, Italy

In 2016 GF Biochemicals acquired
the American company Segetis

07.04.2017
Italian levulinic acid producer GF Biochemicals and American Process Inc. (API), a **bioprocess** technology firm, have announced plans to jointly build a **cellulosic** biorefinery in the U.S.

Levulinic acid esters can replace solvents of concern like dimethylformamide (DMF), dimethylacetamide (DMA) and N-methylpyrrolidone (NMP) in coatings.

4,4′-azobis (4-cyanovaleric acid) is a common initiator for RAFT (Radical Addition Fragmentation chain Transfer) polymerization of free radical reactions for the production of controlled polymers.

Levulinic acid is a versatile building block for chemicals and materials derived directly from biomass.

ABOUT GFBIOCHEMICALS

Founded in 2008, GFBiochemicals uses breakthrough technology to commercialize levulinic acid – a valuable biobased building block for specialty chemicals and materials. With offices in Milan, Italy and Geleen, the Netherlands, its 10,000 MT/a commercial-scale production plant in Caserta, Italy came online in July 2015.

GF Biochemicals

GFBiochemicals.com

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GF Biochemicals has formed a joint venture with Oman-based Towell Engineering Group called NXTLEVVEL Biochem headquartered in Geleen, the Netherlands. The JV plans to build a levulinate bio-solvent manufacturing plant scheduled to start operations in 2024. Target markets are industrial cleaning, home and personal care, coatings and agriculture.

Aris de Rijke, who joined GFBiochemicals in 2014 after a career at Shell and DSM, will act as Chief Executive Officer of NXTLEVVEL Biochem. Steve Block, former executive of Elevance Renewable Sciences, will be the Vice President of Business Development, Sales & Marketing. Rudy Parton, who has devoted most of his professional life to the development of biomass to levulinic acid and its derivatives technologies, will be the Chief Scientific Officer.

I have reached out to NXTLEVVEL Biochem hoping to learn more about the company, GF Biochemical’s manufacturing status, and revisit the market of levulinic acid and derivatives including other players in this field. All of this information will be coming out on Tecnon OrbiChem’s March Biomaterials newsletter.

In the meantime, check out Nova Institute’s latest report on levulinic acid released late last year. The report indicated that the market is still underdeveloped in terms of production technology and market demand. It is expected that new market segments will open due to the potential of its derivatives, especially and among others: levulinic esters, methyltetrahydrofuran (MTHF), γ-valerolactone (GVL), diphenolic acid (DPA), oligomers for transport fuels and levulinic acid derived ketals. For those markets, a driver for change will be a combination of additional performance and price. Product availability and security of supply are also important decision factors for change.

Table 1
Selected levulinic acid applications

Application	Reference
Chiral reagents	[3]
Biologically active materials	[4]
Polyhydroxyalkanoates	[5]
Polymers	[6,7]
Polymerization initiators	[8]
Antifouling compounds	[9]
Personal care products	[10]
Lubricants	[11]
Adsorbents	[12]
Printing/inks	[13]
Coatings	[14]
Electronics	[15]
Photography	[16]
Batteries	[17]
Drug delivery	[18]
Corrosion inhibitors	[19]

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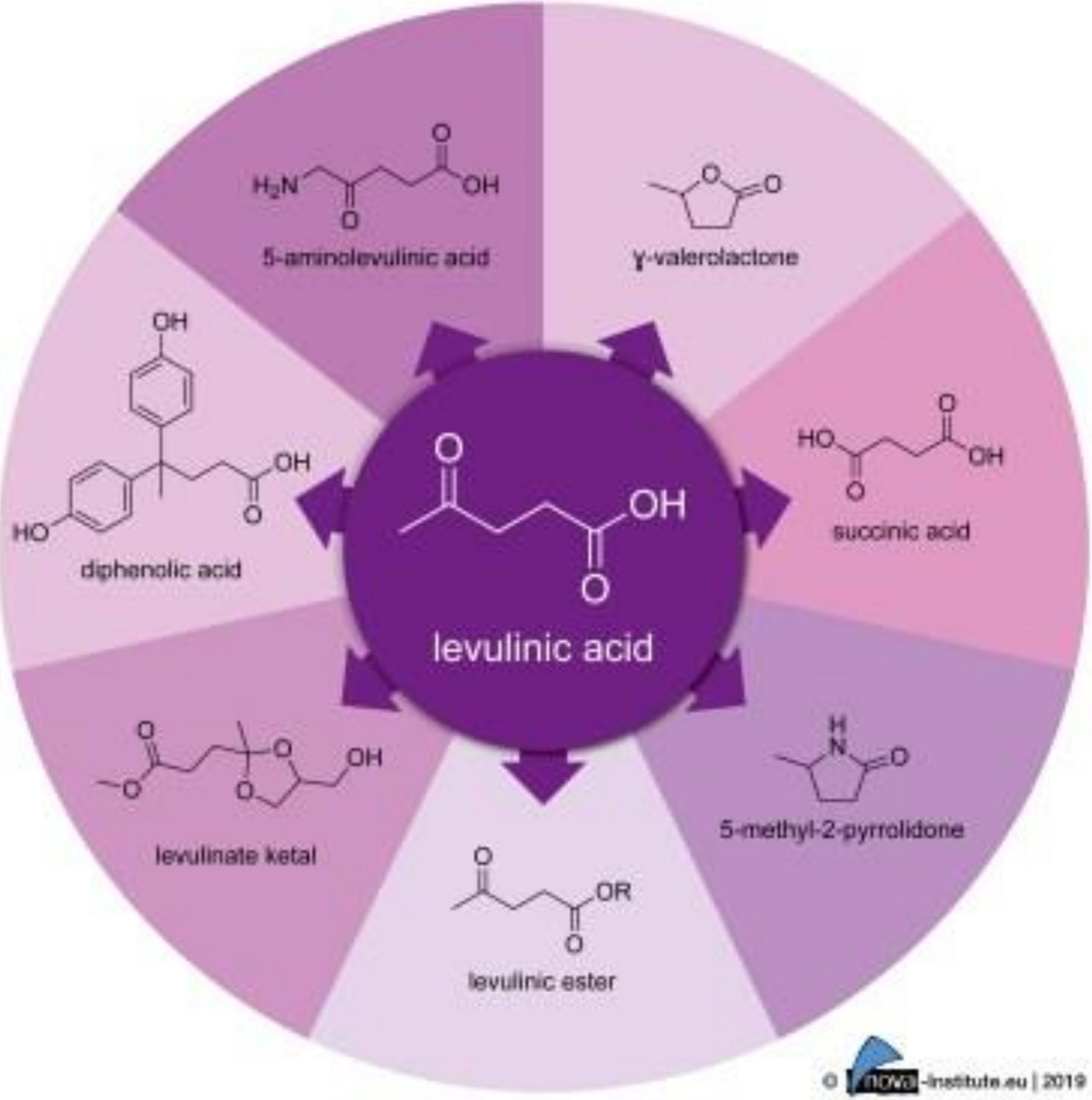
[1] The applications cited in Table 1 and subsequent tables are illustrative but not exhaustive. Many additional examples exist in the patent and open literature. In each case, LA or its derivatives are listed as useable in the given application, but may not be the primary focus of the citation.


levulinic acid
γ-valerolactone
succinic acid
5-methyl-2-pyrrolidone
levulinic ester
levulinate ketal
diphenolic acid
5-aminolevulinic acid