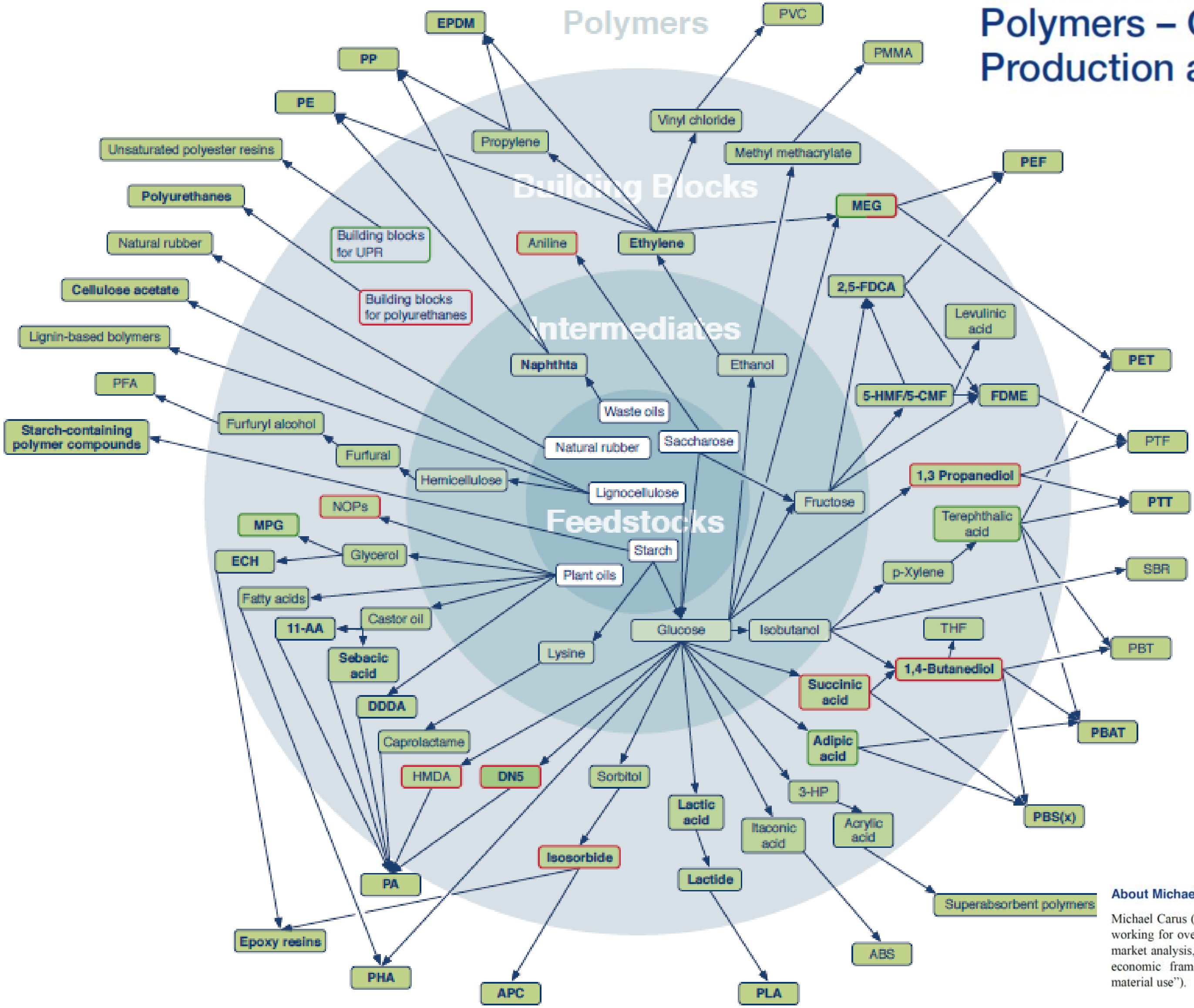
Bio-based polymers

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



About Michael Carus

Michael Carus (MSc) (Germany) physicist, founder and managing director of the nova-Institute, is working for over 20 years in the field of bio- and CO₂-based economy. The focus of his work are market analysis, marketing, techno-economic and ecological evaluation as well as the political and economic framework for bio- and CO₂-based economy ("level playing field for industrial material use").

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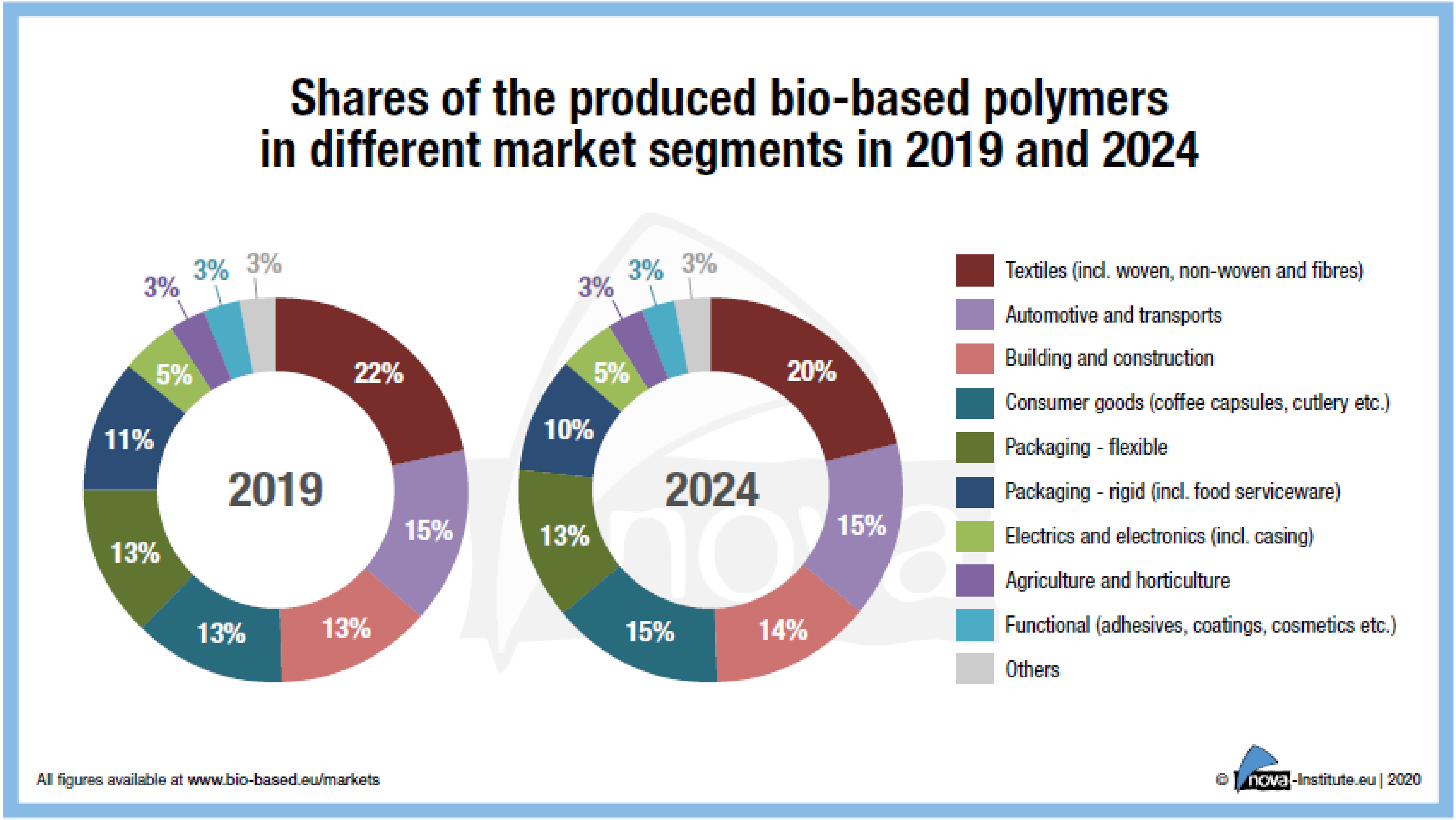


Figure 9: Shares of the produced bio-based polymers in different market segments in 2019 and 2024

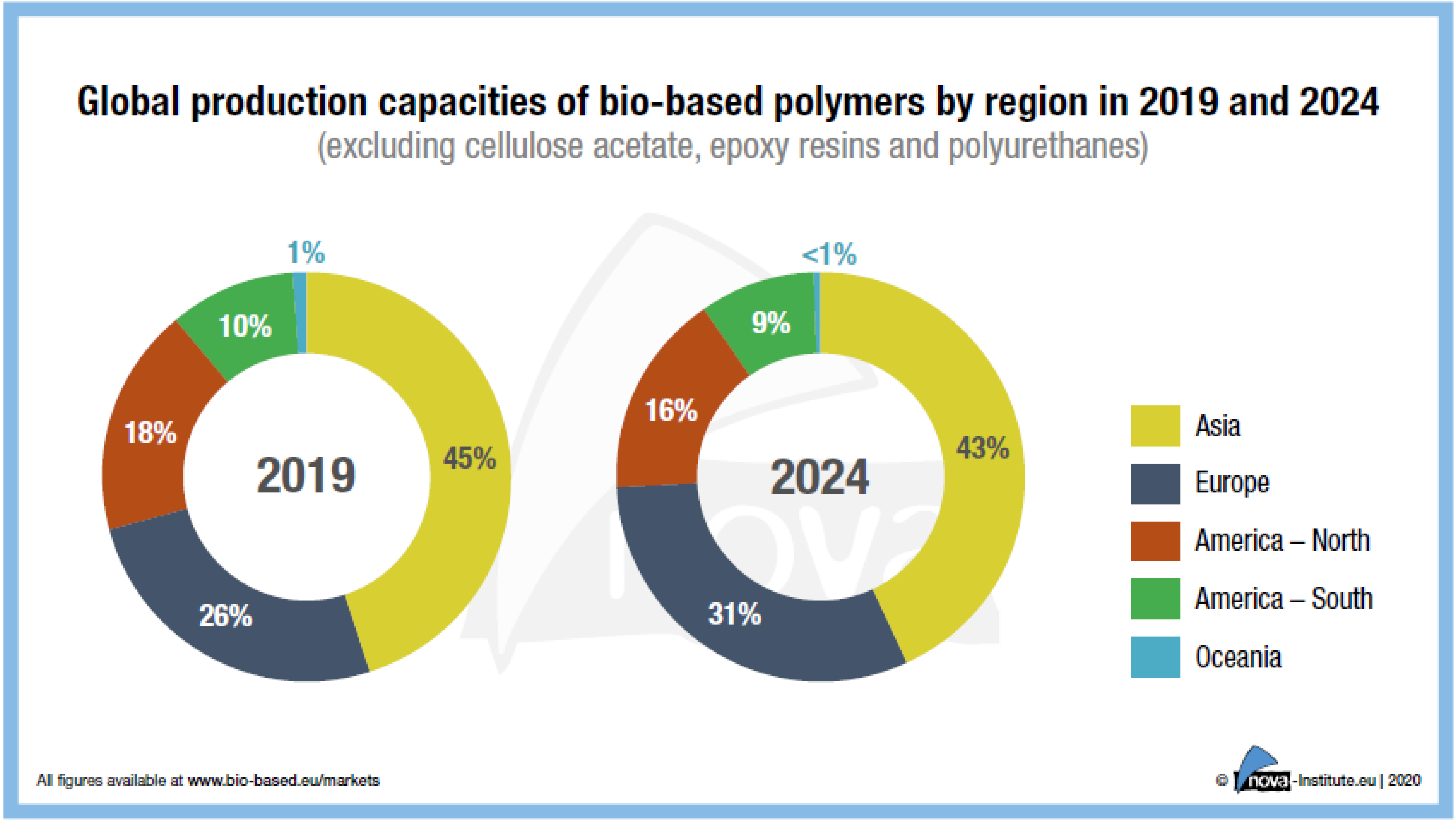


Figure 8: Global production capacities of bio-based polymers by region in 2019 and 2024 (excluding cellulose acetate, epoxy resins and polyurethanes)

Renewable Carbon is the Key

Definition

Renewable Carbon entails all carbon sources that **avoid or substitute the use of any additional fossil carbon from the geosphere.**

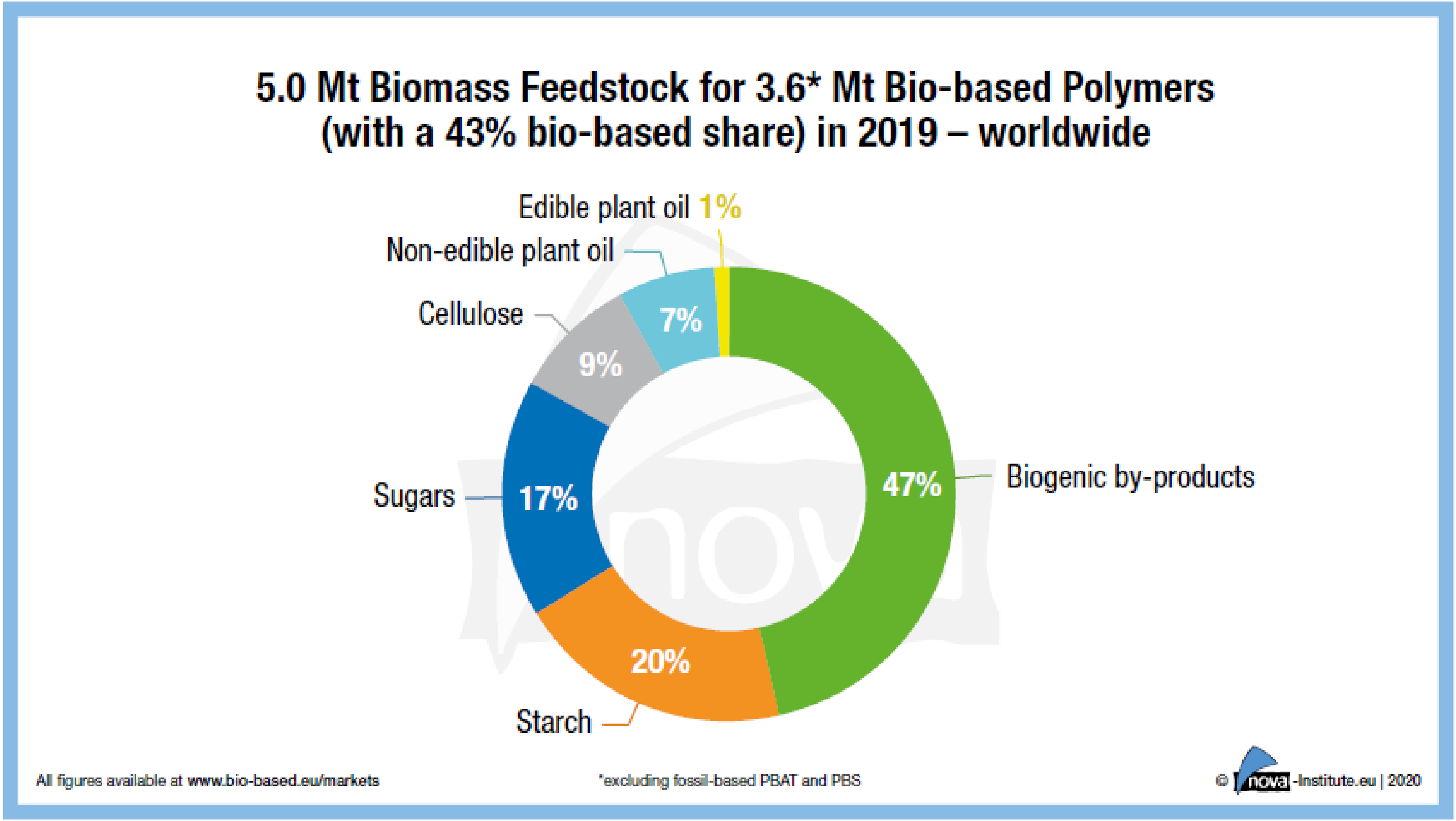
Renewable carbon can come from the **atmosphere**, **biosphere** or **technosphere** – but not from the geosphere. Renewable carbon circulates between atmosphere, biosphere and technosphere, creating a carbon circular economy.

There are only three sources of renewable carbon

- Renewable carbon gained from all types of **biomass**, from the *Biosphere*

- Renewable carbon from **direct CO_2 utilisation**, from the *Technosphere* and *Atmosphere*

- Renewable carbon from **recycling** of already existing plastics and other organic chemistry products, from the *Technosphere*


5.0 Mt Biomass Feedstock for 3.6* Mt Bio-based Polymers (with a 43% bio-based share) in 2019 – worldwide

All figures available at www.bio-based.eu/markets

*excluding fossil-based PBAT and PBS

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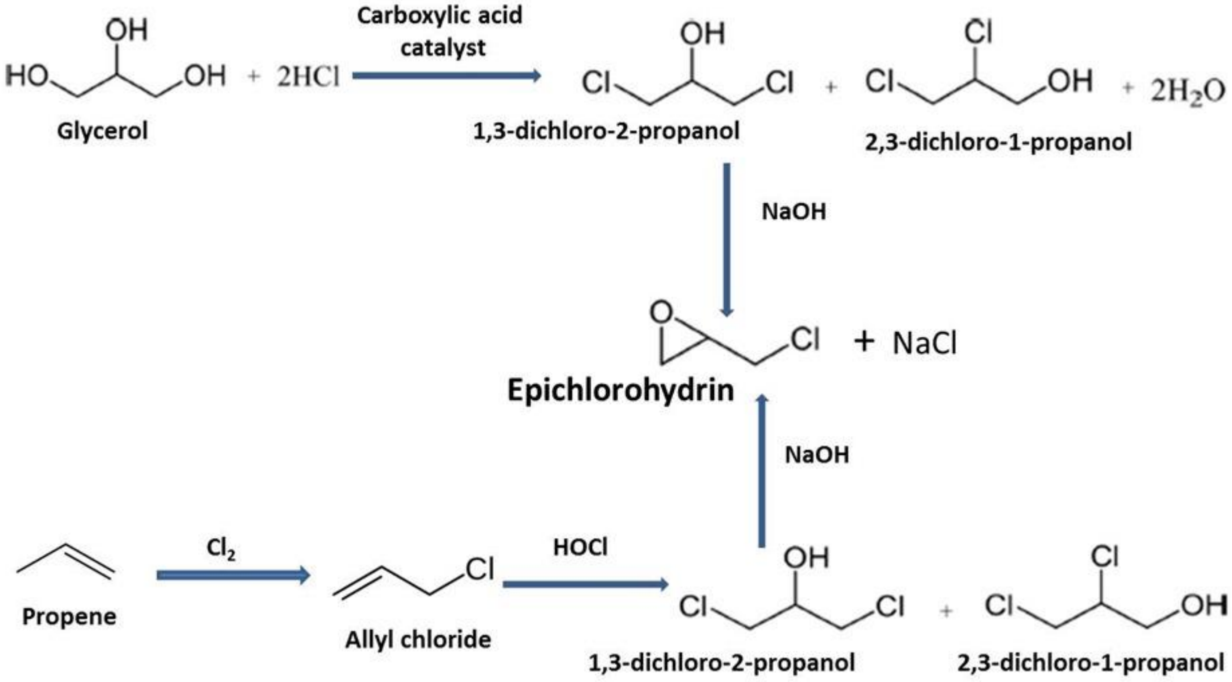
Figure 2: Worldwide biomass requirement for bio-based polymer production in 2019

The major biomass feedstock used for bio-based polymer production are biogenic by-products (46%), especially the by-product **glycerol from the biodiesel** production, which is mainly used for epoxy resin production via epichlorohydrin as an intermediate.

Figure 3. Renewable and Petroleum-Based Routes to Epichlorohydrin



37% of the required biomass are made up by starch and sugars,
8% by cellulose (mainly for cellulose acetate) and
9% by edible and non-edible plant oils, such as castor oil.

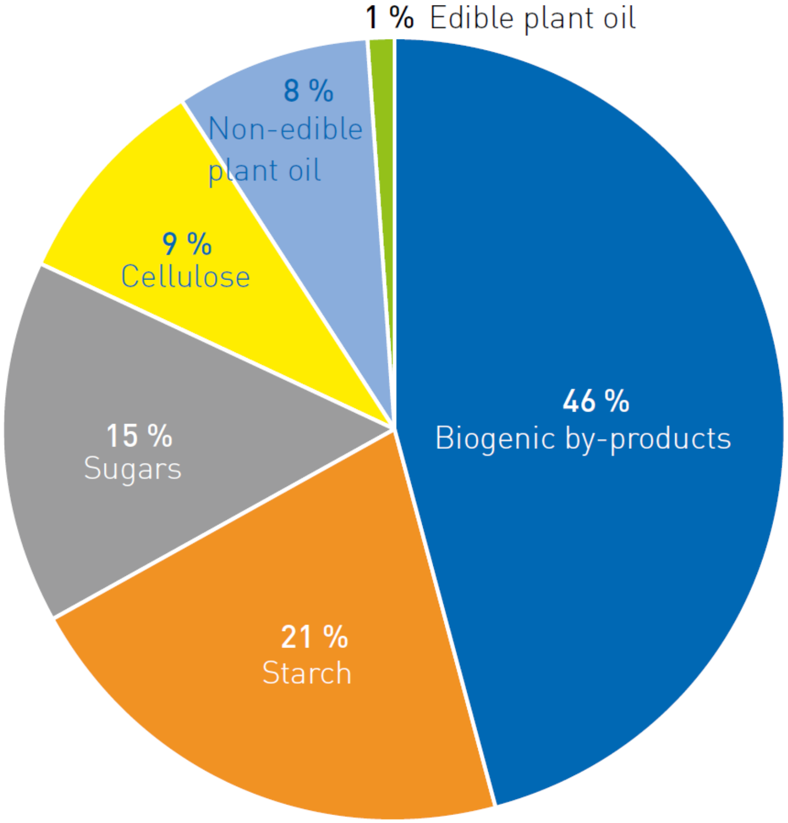
From the 3.6 million tonnes of produced bio-based polymers (fully and partly bio-based, excluding fossil-based biodegradable PBAT and PBS) only 1.6 million tonnes are actual bio-based parts of the polymers (43%).

Considering this fact, 3 times more feedstock is needed than used for product formation.

Moreover, 68% of feedstock is not ending up in the product is due to high number of conversion steps and related feedstock and intermediate losses.

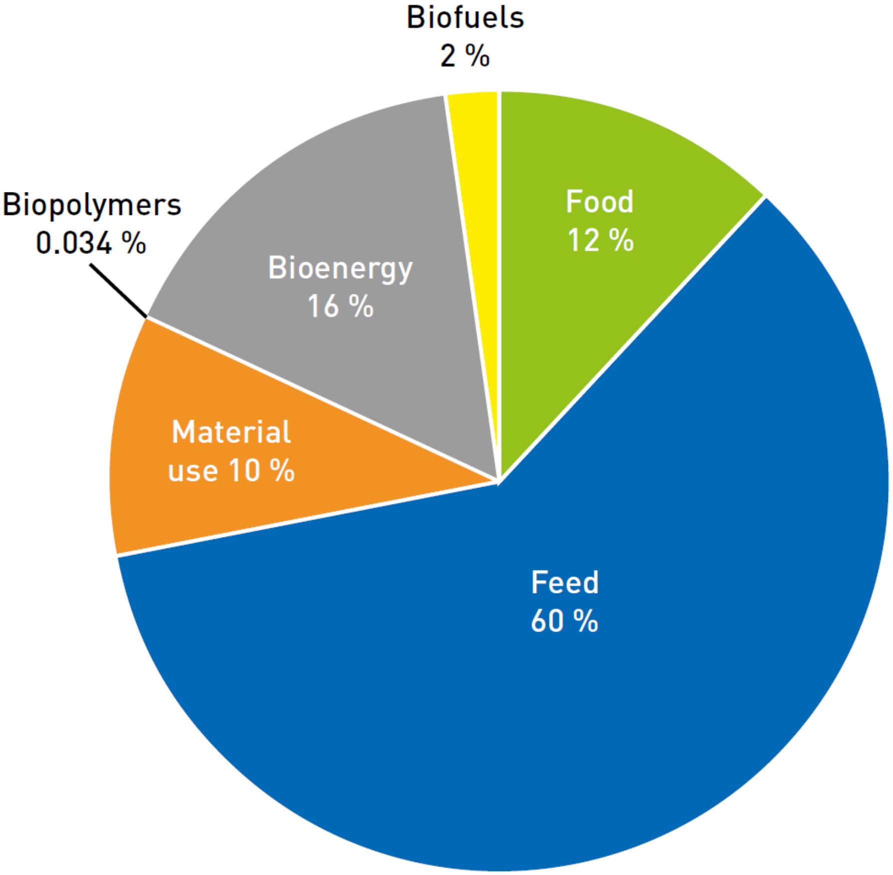
Biomass for bio-based plastics

Fig. 1: 4,3 million tonnes biomass feedstock for 3,4 million tonnes bio-based polymers (with a 43 % bio-based share) in 2018



Biomass for all productive processes

Fig. 2: Worldwide biomass demand 2018, total: 12,3 billion tonnes



Pathways to different kinds of bio-based chemicals

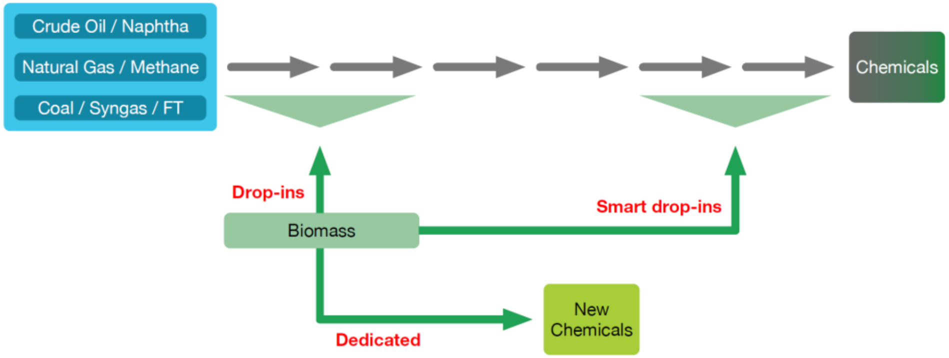


Figure 1: Schematic differentiation of pathways of drop-in, smart drop-in and dedicated bio-based chemicals

Bio-based **drop-in chemicals** are bio-based versions of existing petrochemicals which have established markets. They are chemically identical to existing fossil-based chemicals

Smart drop-in chemicals are a special sub-group of drop-in chemicals. They are also chemically identical to existing chemicals based on fossil hydrocarbons, but their bio-based pathways provide advantages compared to the conventional pathways.

Dedicated bio-based chemicals are chemicals which are produced via a dedicated pathway and do not have an identical fossil-based counterpart. As such, they “can be used to produce products that cannot be obtained through traditional chemical reactions and products that may offer unique and superior properties that are unattainable with fossil-based alternatives”

Example of a smart drop-in chemical

(±)-Epichlorohydrin, a highly reactive building block used in the manufacture of plastics and epoxy resins, is industrially produced from propylene in a three-step process. An alternative two-step process starts from glycerol, a readily available chemical from biodiesel production, which is produced through saponification of triglycerides from plants and animal sources. Glycerol is converted to dichloropropanol with hydrochloric acid in the presence of an acidic catalyst. This smart route avoids the chlorination of propylene using toxic chlorine at 500 °C and yielding many other chlorinated by-products (Hirth et al. 2015).

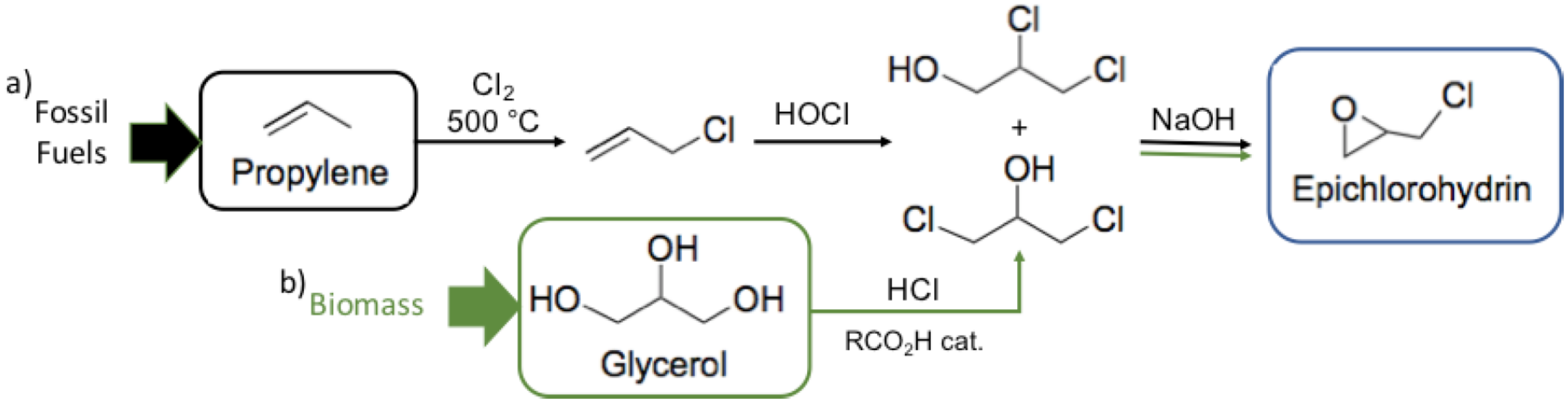


Figure 2: Synthesis of epichlorohydrin following a petrochemical a) or a bio-based b) pathway

Example of a dedicated chemical

Dihydrolevoglucosenone (Cyrene^{TM}), a dipolar aprotic solvent, is an example of a dedicated bio-based chemical. It can be directly derived from waste cellulose in two simple steps, having therefore a high stoichiometric Biomass Utilization Efficiency (BUEs) of 79%. Cyrene^{TM} has demonstrated a similar solvent performance as toxic petrochemically derived solvents such as *N*-2-methyl pyrrolidone (NMP), whose industrial synthesis involves multiple reaction steps starting from acetylene and acetaldehyde (Figure 3) (Clark et al. 2014).

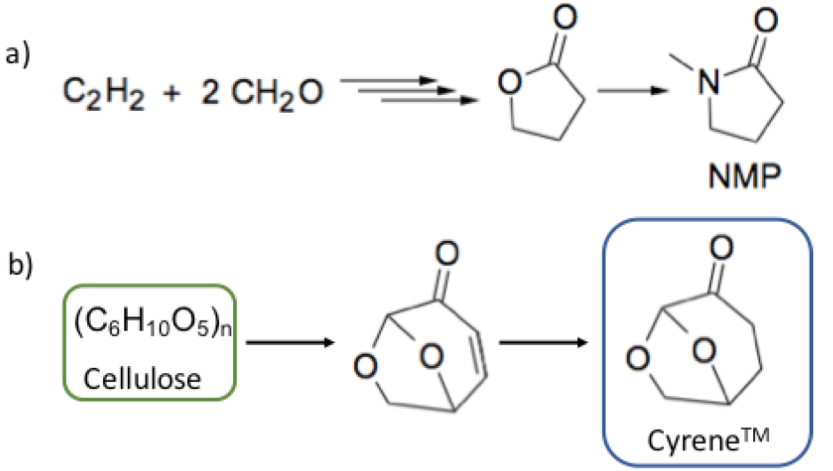
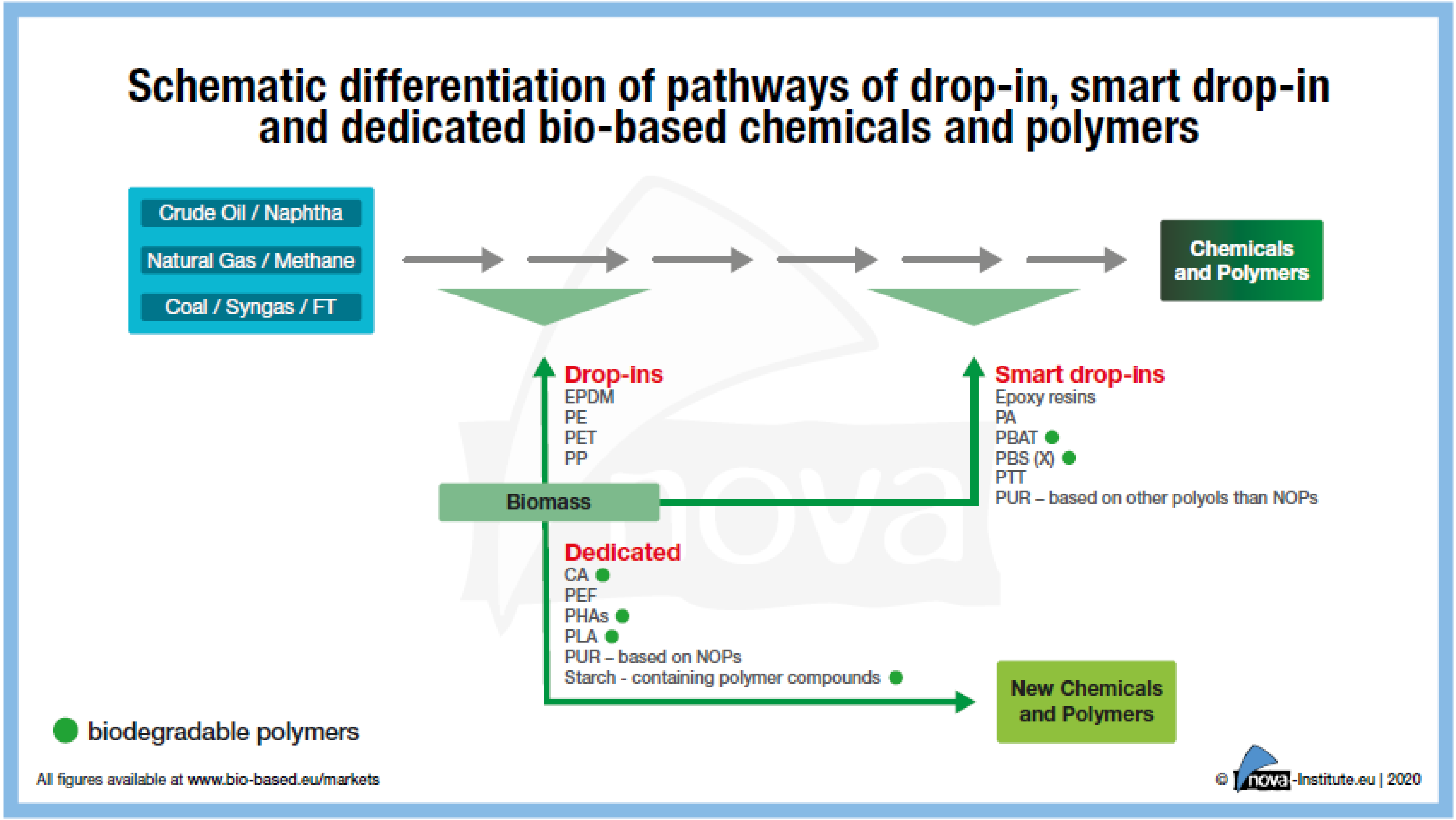


Figure 3: Scheme of the production of a) *N*-2-methyl pyrrolidone (NMP) and b) dihydrolevogluocosenone (Cyrene^{TM})



Schematic differentiation of pathways of drop-in, smart drop-in and dedicated bio-based chemicals and polymers

All figures available at www.bio-based.eu/markets

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Figure 5: Schematic differentiation of pathways of drop-in, smart drop-in and dedicated bio-based chemicals. Selected bio-based polymer examples are shown for each classification group. Biodegradable polymers are highlighted with a green dot.[1]

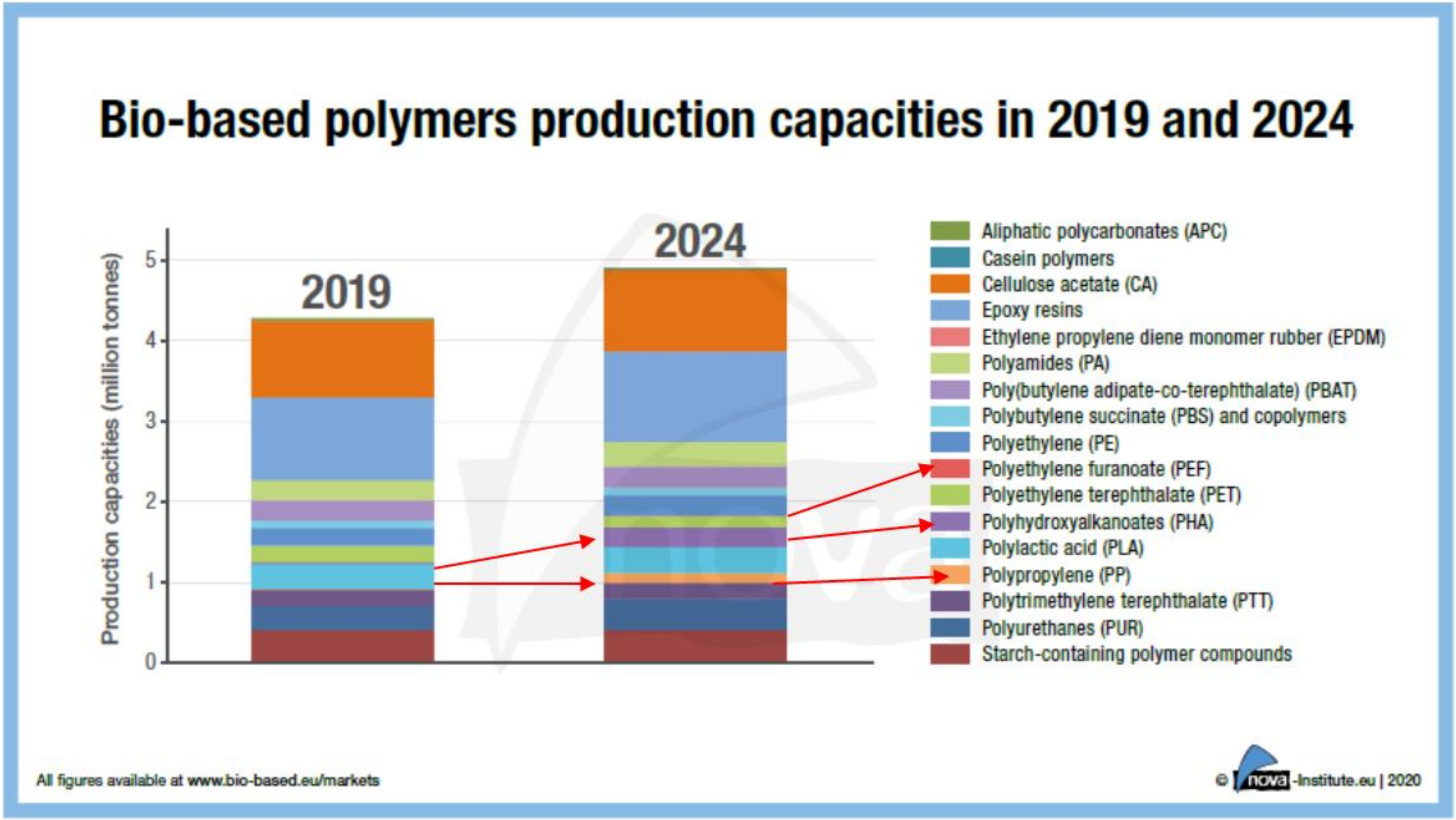


Figure 6: Bio-based polymers production capacities in 2019 and 2024

Glossary of terms

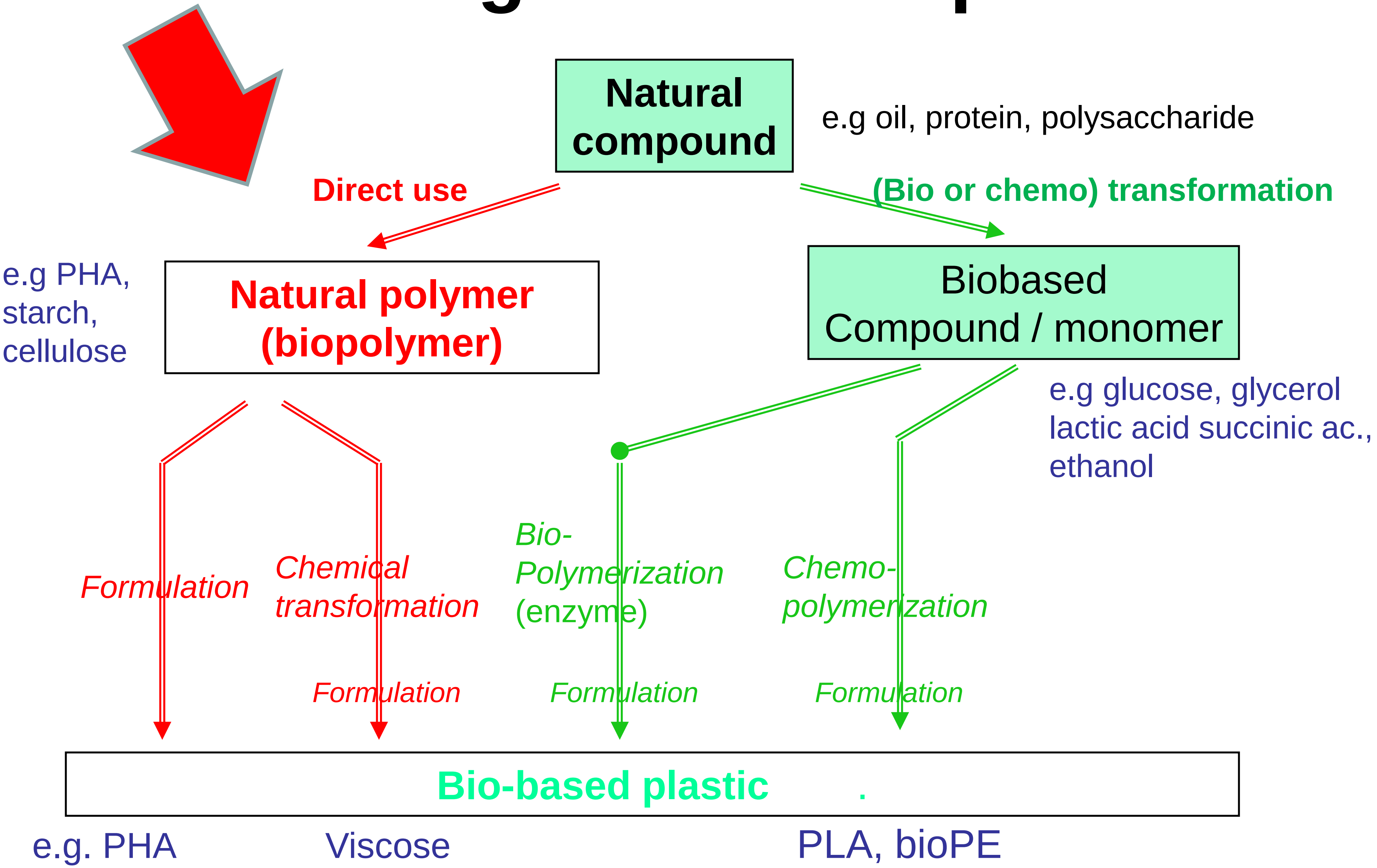
ABS	Acrylonitrile butadiene styrene resin
ASA	Acrylonitrile styrene acrylate resin
bn	billion
CH	Switzerland
CIS	Commonwealth of Independent States
Conversio	Conversio Market & Strategy GmbH
EU	European Union
EPRO	European Association of Plastics Recycling and Recovery Organisations
ETP	Engineering Thermoplastics
GDP	Gross domestic product
m t	Million tonnes
NAFTA	North American Free Trade Agreement
NO	Norway
Other plastics	Thermosets, adhesives, coatings and sealants
PA	Polyamides
PBT	Polybutylene terephthalate
PC	Polycarbonate
PE	Polyethylene
PEEK	Polyetheretherketone
PE-HD	Polyethylene, high density
PE-LD	Polyethylene, low density
PE-LLD	Polyethylene, linear low density
PE-MD	Polyethylene, medium density
PEMRG	PlasticsEurope Market Research Group
PET	Polyethylene terephthalate
Plastic materials	Thermoplastics + Polyurethanes
PMMA	Polymethyl methacrylate
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene
PS-E	Polystyrene, expandable
PTFE	Polytetrafluoroethylene
PUR	Polyurethane
PVC	Polyvinyl chloride
SAN	Styrene-acrylonitrile copolymer
Thermoplastics	Standard plastics (PE, PP, PVC, PS, EPS, PET (bottle grade)) + Engineering plastics (ABS, SAN, PA, PC, PBT, POM, PMMA, Blends, and others including High Performance Polymers)
Thermosets	Urea-formaldehyde foam, melamine resin, polyester resins, epoxy resins, etc.

Bio-based polymers are widely different in terms of chemical structure and biological origin. The EN 17228:2019 document underlines how polymers derived from biomass have to be distinguished into two groups:

the first group includes **polymers, which have been synthesized by living organisms** (plants, algae, microorganisms) and have been extracted and purified. The initial chemical structure is used (e.g. thermoplastic starch, polyhydroxyalkanoate) or is slightly modified to obtain specific functionalities (e.g. cellulose acetates).

The second group consists of **materials where the chemical structure of the biomass feedstock is not maintained.** For example, materials like starch or cellulose are hydrolysed and the generated monomeric sugars are used to produce building blocks (usually by fermentation processes), which can then be polymerised . Examples are lactic acid (to produce poly(lactic acid)) or bio-based succinic acid (used for poly(butylene succinate)). It is also possible to use low-molecular weight biomass feedstock such as ricinoleic acid from castor oil (for bio-based polyamides). These polymers are bio-based, because the original feedstock comes from biomass, but they are non-natural polymers, i.e. they are not extracted from a plant or a bacterium. All these bio-based monomers can be chemically modified to create further chemical variety and complexity in order to confer specific functional properties to the final polymeric product.

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

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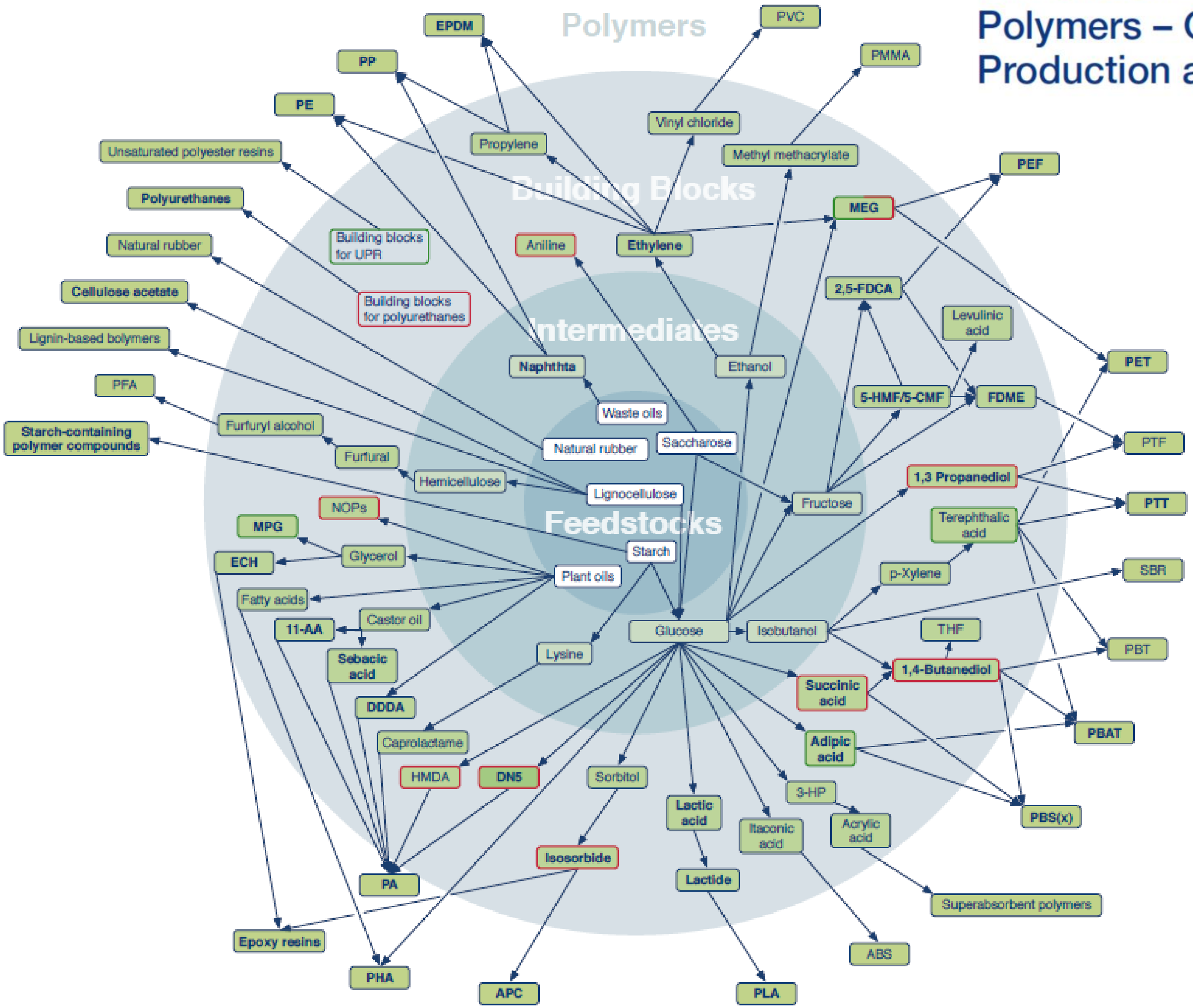

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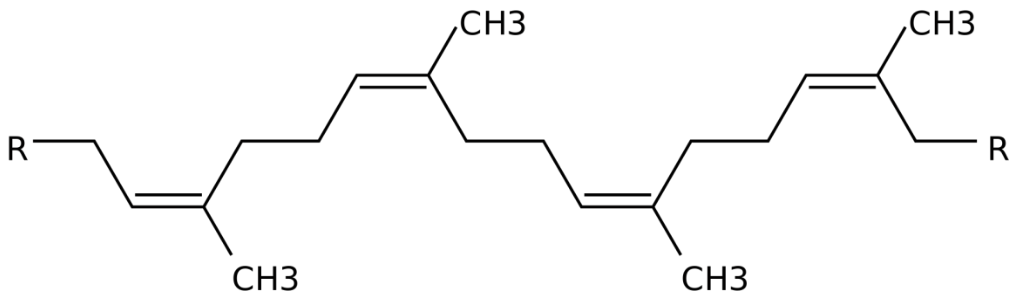
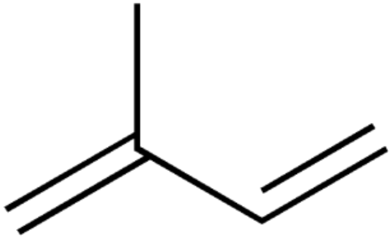
Naturally biosynthesized biopolymers and their chemically modified derivatives.

Chemical classification	Polymer	Properties and applications
Polyisoprene (terpenes)	Natural rubber	Waterproof items, engineering applications in antiseismic buildings or offshore installations for oil extraction,
Polysaccharides	Starch based polymers; thermoplastic starch -TS	Component of biodegradable and biocompostable plastics.
	Cellulose based polymers: Cellulose acetate Cellulose nitrate Acetylphthalylcellulose	Applications in textiles, cigarette filters, surface coatings, ink additive, photographic negatives, motion picture film, microfilm, microfiche, membranes for water desalinization. Chemical modifications decrease the biodegradation of cellulose although derivatives are attacked by both aerobic and anaerobic microorganisms.
	Chitosan	Obtained from deacetylation of chitin. Biodegradable, non-toxic, bacteriostatic and fungistatic with wide application in the pharmaceutical field. Industrially applied as carrier for enzyme immobilization.
Polyphenols	Lignin based polymers	Because of its aromatic and phenolic components, lignin itself is used in polymer blends as compatibilizer, plasticizer, hydrophobizing agent or as a natural antioxidant in active packaging. Employed in flame retardants, optical modifiers, stabilizers. Lignin-based polyols, reacted with diisocyanates, are used as drop-in replacement of fossil polyols in polyurethane foams for their flame-retardant properties.

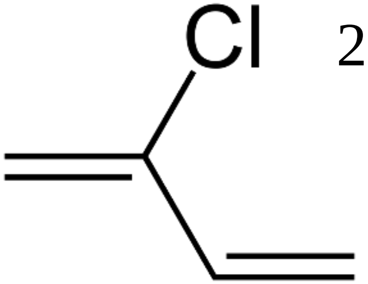
Polimeri naturali idrofobici derivati dall’isoprene





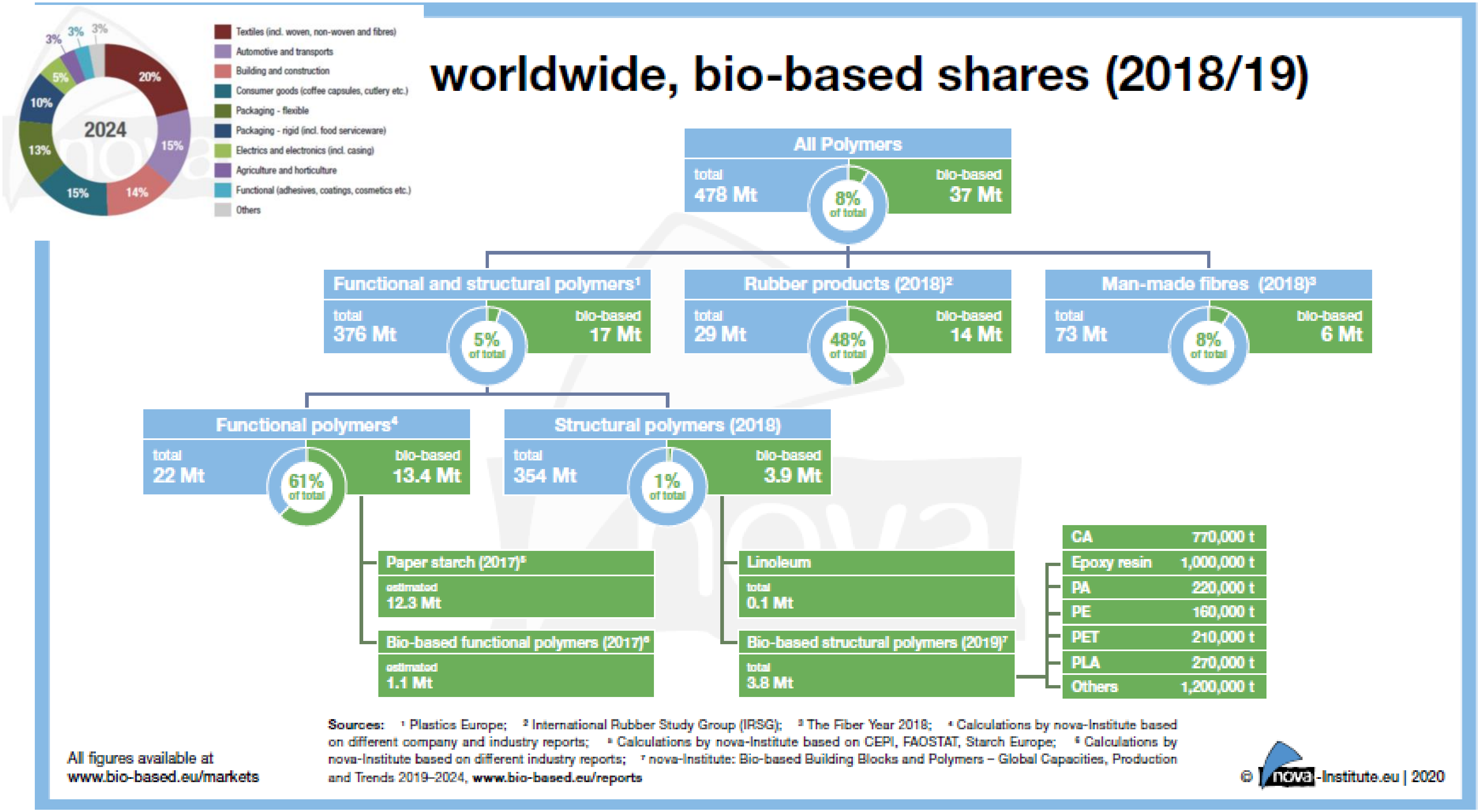
Isoprene (naturale)

Il **caucciù** (o **gomma naturale** o **poliisoprene naturale**) è ottenuto dall'estrazione del lattice di alcune piante quali l’Hevea brasiliensis.
È un elstomero amorfo formato per addizione 1,4-cis dell‘isoprene



2-cloro-1,3-butadiene

Neoprene
(derivato dal petrolio)



worldwide, bio-based shares (2018/19)

All Polymers
total 478 Mt | 8% of total | bio-based 37 Mt

Functional and structural polymers[1]
total 376 Mt | 5% of total | bio-based 17 Mt

Rubber products (2018)[2]
total 29 Mt | 48% of total | bio-based 14 Mt

Man-made fibres (2018)[3]
total 73 Mt | 8% of total | bio-based 6 Mt

Functional polymers[4]
total 22 Mt | 61% of total | bio-based 13.4 Mt

Structural polymers (2018)
total 354 Mt | 1% of total | bio-based 3.9 Mt

Paper starch (2017)[5]
estimated 12.3 Mt

Bio-based functional polymers (2017)[6]
estimated 1.1 Mt

Linoleum
total 0.1 Mt

Bio-based structural polymers (2019)[7]
total 3.8 Mt

CA	770,000 t
Epoxy resin	1,000,000 t
PA	220,000 t
PE	160,000 t
PET	210,000 t
PLA	270,000 t
Others	1,200,000 t

All figures available at
www.bio-based.eu/markets

Sources: [1] Plastics Europe; [2] International Rubber Study Group (IRSG); [3] The Fiber Year 2018; [4] Calculations by nova-Institute based on different company and industry reports; [5] Calculations by nova-Institute based on CEPI, FAOSTAT, Starch Europe; [6] Calculations by nova-Institute based on different industry reports; [7] nova-Institute: Bio-based Building Blocks and Polymers – Global Capacities, Production and Trends 2019–2024, **www.bio-based.eu/reports**

Linoleum: olio di lino, farina di legno, farina di sughero, pigmenti coloranti calandrati su un tessuto di juta naturale.

Elastomeri: sostanze naturali o sintetiche che hanno la capacità di subire grosse deformazioni elastiche, possono essere allungati diverse volte per spostamenti finiti riassumendo la propria dimensione una volta ricreata una situazione di riposo. Possono essere modellati tramite estrusione o stampaggio a caldo.

Come polimeri si suddividono in :
elastomeri termoplastici
elastomeri termoindurenti

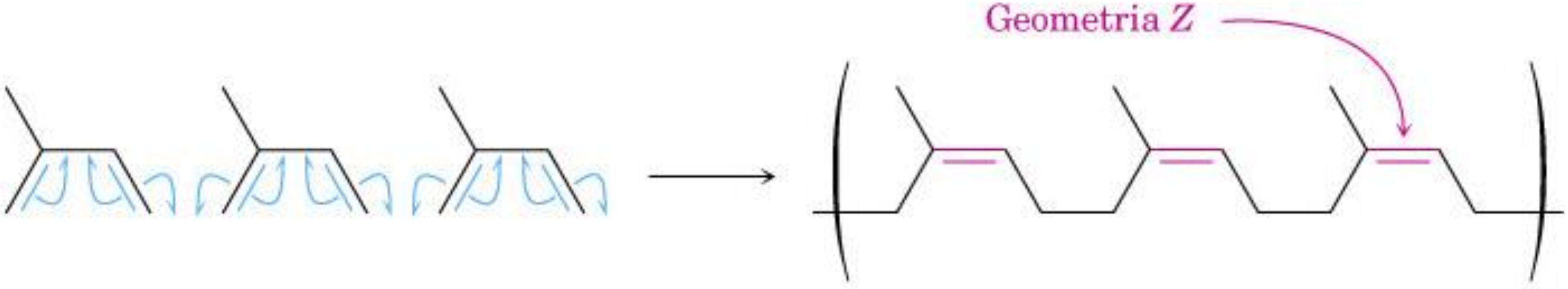
Gli elastomeri termoplastici una volta stampati, se portati alla temperatura di transizione vetrosa possono essere rimodellati.

Gli elastomeri termoindurenti vengono prodotti legando le une alle altre le catene di polimero attraverso l'uso di reattivi chimici, temperatura e pressione in un processo generalmente chiamato vulcanizzazione.Questa modificazione rende impossibile rimodellarli una volta che la vulcanizzazione è avvenuta.

La **temperatura di transizione vetrosa**, T_g, è il valore di temperatura al di sotto della quale un materiale amorfo si comporta da solido vetroso.

Un **solido è amorfo** (per es. vetro) quando nella sua struttura non c'è ordine a lungo raggio nelle posizioni degli atomi o delle molecole che lo costituiscono. Lo stato amorfo è intermedio tra il solido e il liquido.
Relativamente poco frequente in natura, dove la maggior parte dei solidi è di natura cristallina, con molecole disposte con un ordine a lungo raggio che definisce un reticolo cristallino.

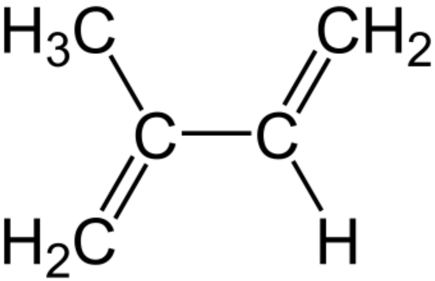
I terpeni sono il prodotto della polimerizzazione delle unità di isoprene



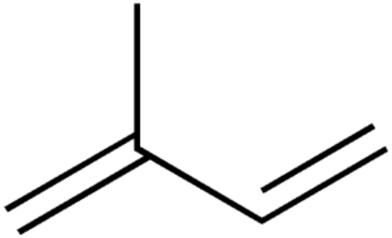
Unità di isoprene

Un segmento di gomma naturale

Prodotti naturali idrofobici derivati dall’isoprene



isoprene



2-metil-1,3-butadiene

Terpeni:
prodotti dai vegetali (600 mil. ton /anno)

I terpeni sono il prodotto della polimerizzazione delle unità di isoprene

Fibre da cellulosa

ORANGE FIBER

A dicembre 2015, grazie anche al finanziamento Smart&Start di Invitalia, viene inaugurato il primo impianto pilota per l’estrazione della cellulosa da agrumi.

IL BREVETTO
Dallo studio di fattibilità condotto con il Politecnico di Milano si sviluppa il brevetto, che viene depositato in Italia ed esteso a PCT internazionale.

ORANGE FIBER X FERRAGAMO

- **Ferragamo Orange Fiber Collection**
- Dall'amore per l'innovazione, il design e la creatività italiana, nasce una collaborazione unica: la *Ferragamo Orange Fiber Collection*.

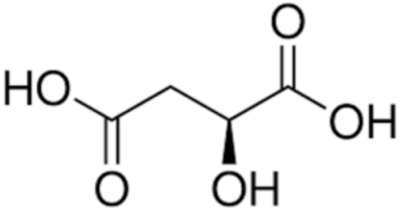
Coerente al proprio motto, *Responsible Passion*, Salvatore Ferragamo ha colto per primo l'essenza e le potenzialità espressive del tessuto da agrumi, dando vita ad una fresca Capsule Collection, omaggio alla creatività mediterranea.

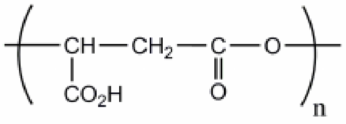
La collezione

Bio-engineered polymers bio-synthesized by microorganisms and plants

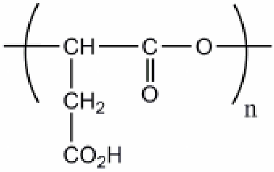
Chemical classification	Polymer	Properties and applications
Polyesters	Polyhydroxy alkanoates - PHAs: poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate -*co*-3-hydroxy-hexanoate)	Biodegradable and compostable. Chain length determines the flexibility of PHA: short chain butyrate provides rigidity, with T_m of 160°C, whereas longer carbon chains confers T_m below 145°C. Sensitivity to thermal degradation makes its processing challenging. Fields of application include agriculture, packaging, biomedical sector.
	Polymalic acid	Linear anionic polyester composed of L-malic acid monomers, with potential applications as drug carriers, surgical suture, and biodegradable plastics.
Polyamides	Poly-γ-glutamic acid - PGA	Water-soluble, anionic, biodegradable, edible. Applications in foods, pharmaceuticals, healthcare, cosmetics, water treatment, curable adhesives.

Some microorganisms naturally produce **β-poly(L-malic acid)** (PMA), which has excellent water solubility, biodegradability, and biocompatibility properties. PMA has broad prospective applications as novel biopolymeric materials and carriers in the drug, food, and biomedical fields.





Poly(β-malic acid)



Poly(α-malic acid)

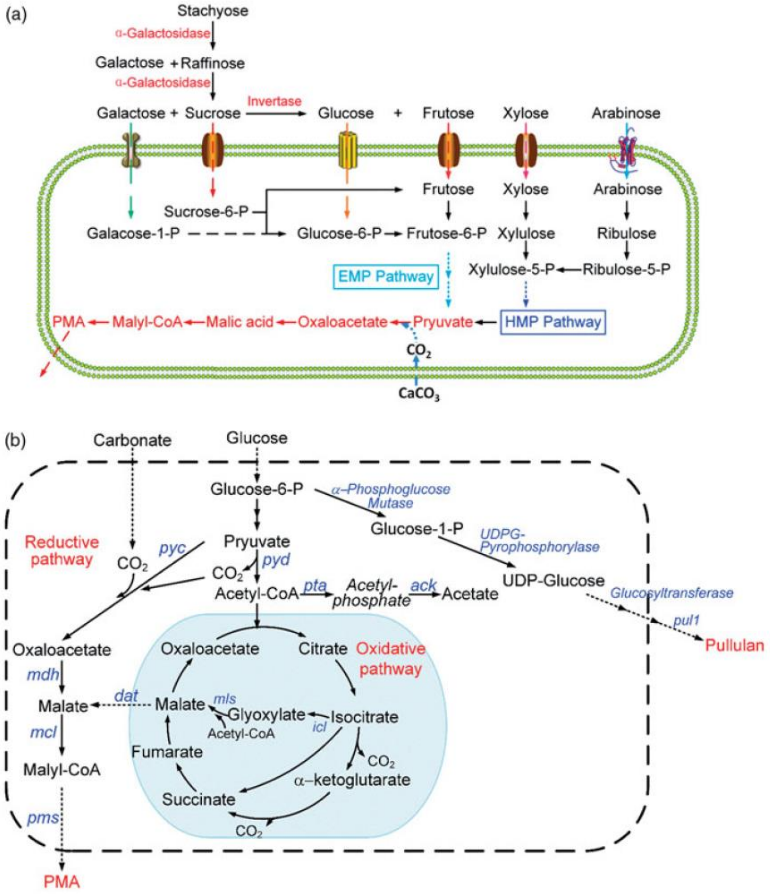


Figure 1. Transport and catabolism of various sugars (A) and metabolic pathways for PMA, pullulan and acetic acid biosyntheses in *Aureobasidium pullulans* (B). Key genes in the pathway: *ack* (acetate kinase), *dat* (dicarboxylate transporter), *icl* (isocitrate lyase) *mcl* (malyl-CoA ligase), *mdh* (malate dehydrogenase), *mls* (malate synthase), *pms* (PMA synthase), *pta* (phosphotransacytylase), *pul*1 (pullulan synthase); *pyc* (pyruvate carboxylase), *pyd* (pyruvate decarboxylase).

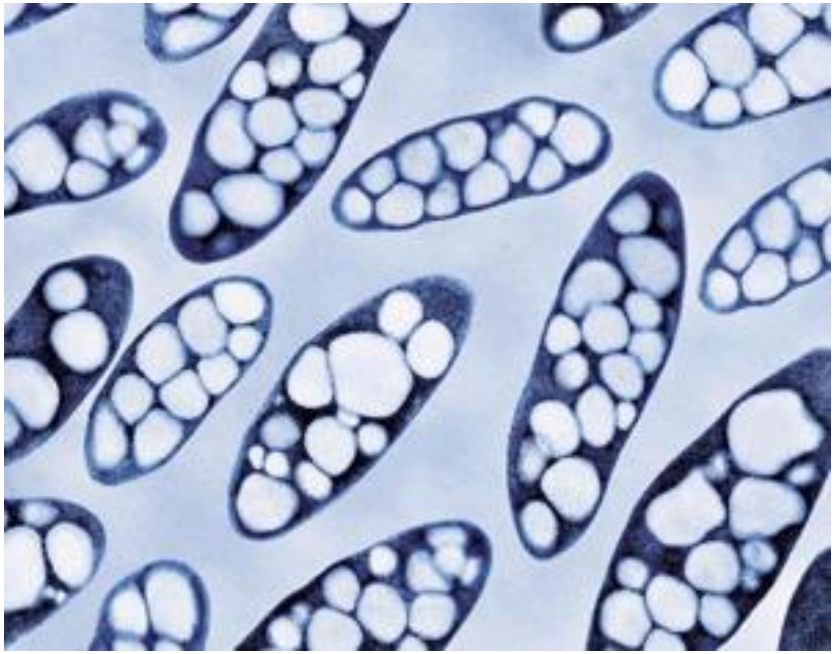
Polyhydroxyalcanoates (PHA)

- Polyester (thermoplastic) produced by microorganisms in response to conditions of physiological stress
- Represent a form of energy storage molecule to be metabolized when other common energy sources are not available

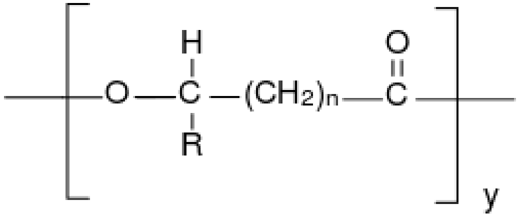
Current production based on sucrose, glucose

Established methodology using waste sources

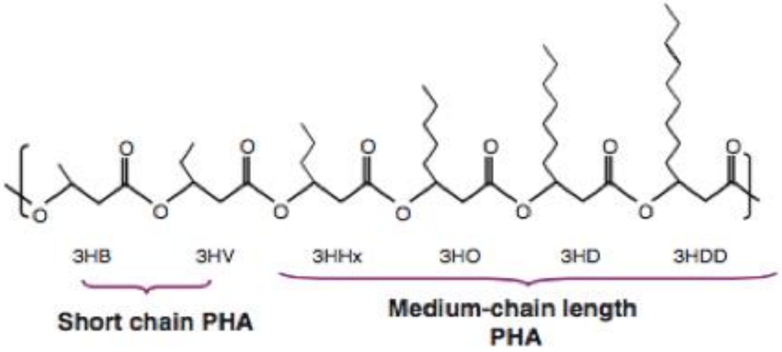
- whey (lactose, salt conditions)
- glycerol
- bone and meat meal (N source)
- animal fats



IPOLIIDROSSIALCANOATI (PHA)



$$\left[-O-\underset{R}{\overset{H}{C}}-(CH_2)_n-\overset{O}{\overset{\|}{C}}- \right]_y$$



Common PHA monomers

- Poliesteri alifatici sintetizzati naturalmente da numerosi batteri sia gram-positivi che gram-negativi.

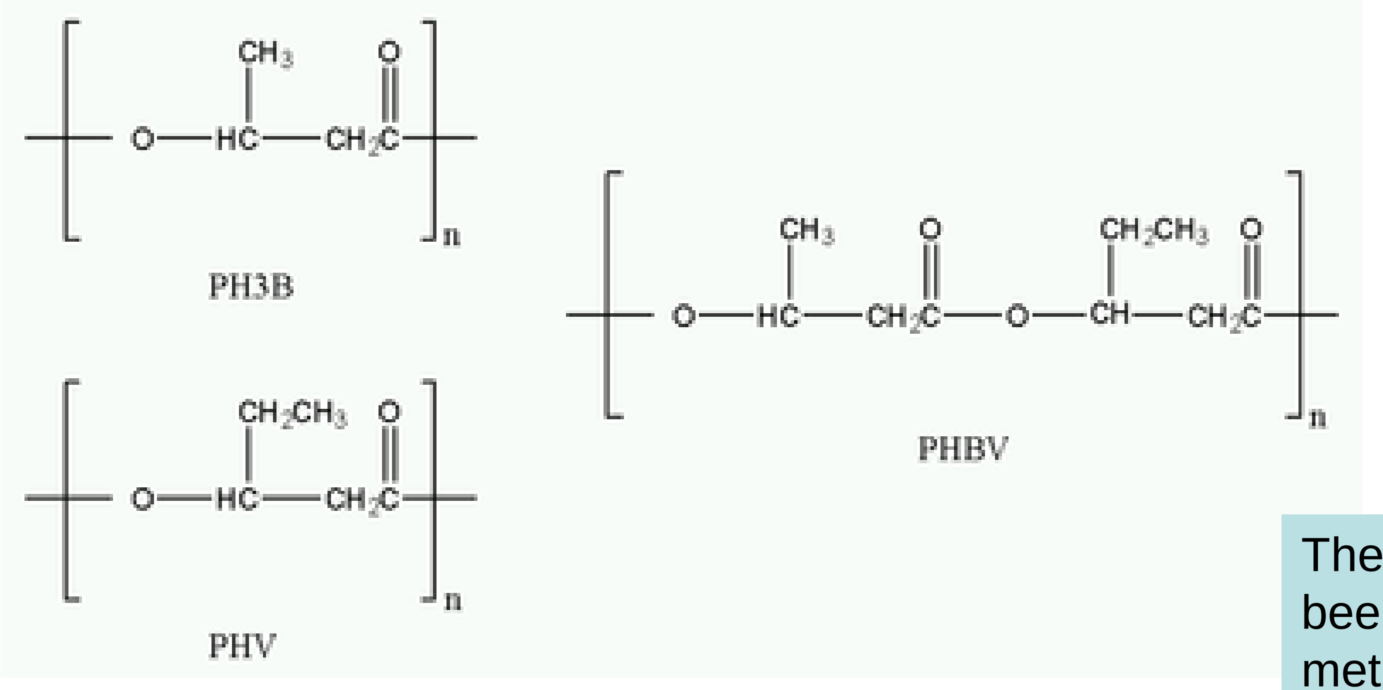
- possiedono proprietà fisico-chimiche, termiche e meccaniche simili a polipropilene (pp) e il polietilene (ldpe).

- **Biodegradabili (anche in ambienti acquatici) e compostabili** negli ambienti naturali a temperature ambiente.

- Disposti in catena lineare, ottenuti soprattutto per condensazione testa-coda di diversi gruppi di 3-idrossiacidi.

- Massa molecolare compresa fra i 20’000 e i 3’000’000 di dalton.

Polyhydroxyalkanoates (PHA)



- Monomer: β-hydroxy acids

→ Large variety of structures

  - Poly(β-hydroxy butyrate)
  - Poly(β-hydroxy butyrate-co-valerate)
  - Poly(β-hydroxy butyrate-co-hexanoate)

  Etc.

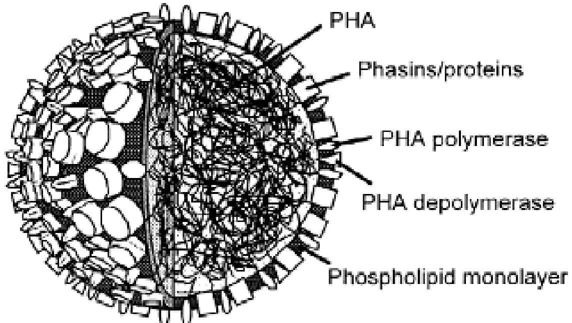
Their properties have been tuned by means of metabolic engineering to produce PHAs with altered monomer compositions and various molecular weights for matching desired thermal and mechanical properties.

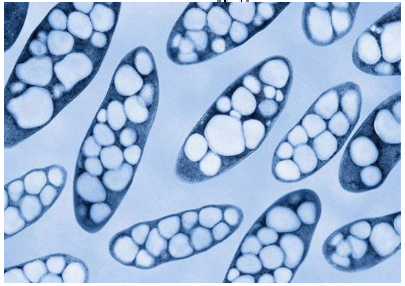
Moreover, the structures of the enzymes that fall under the class defined as PHA synthases have been resolved, enabling the elucidation of the polymerization mechanism. Such knowledge has driven the protein engineering strategy that evolved the substrate specificity of these enzymes towards non-natural substrates, such as 2-hydroxyacylcoenzyme A, thus opening scenarios for the production of new non-natural PHAs.

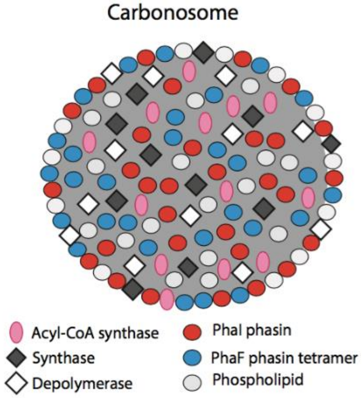
Although there are still some bottlenecks for the large scale production of PHAs connected to the high costs of production, in 2019 the global estimated market of PHAs was calculated at $ 57 million. The successful use of biorefinery by-products, agricultural by-products and industrial wastes as fermentation feedstock has contributed to mitigate the costs.

As the government regulations against single use plastics become more and more stringent, the increasing demand for biodegradable plastics is expected to boost the PHAs market up to $ 98 million by 2024 .

I CARBONOSOMI, GRANULI DI PHA







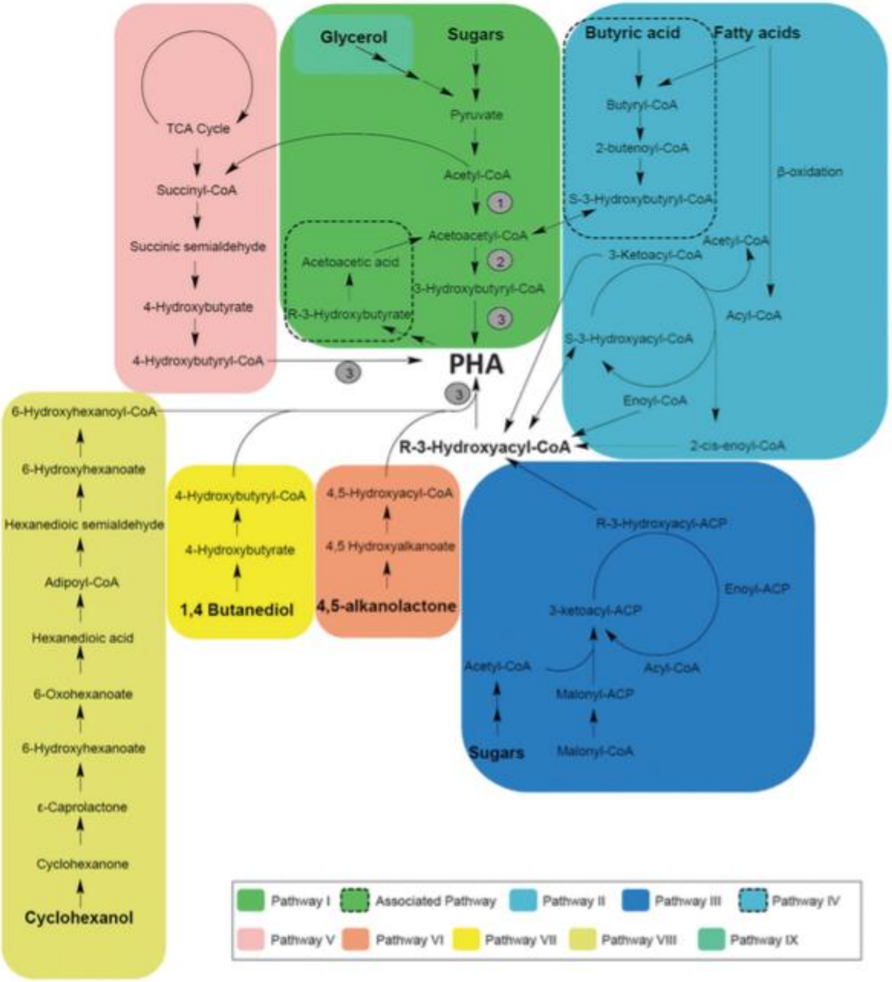
- Un'ampia varietà di batteri è in grado di accumulare PHA sotto forma di granuli intracellulari, come riserve di carbonio e di energia.

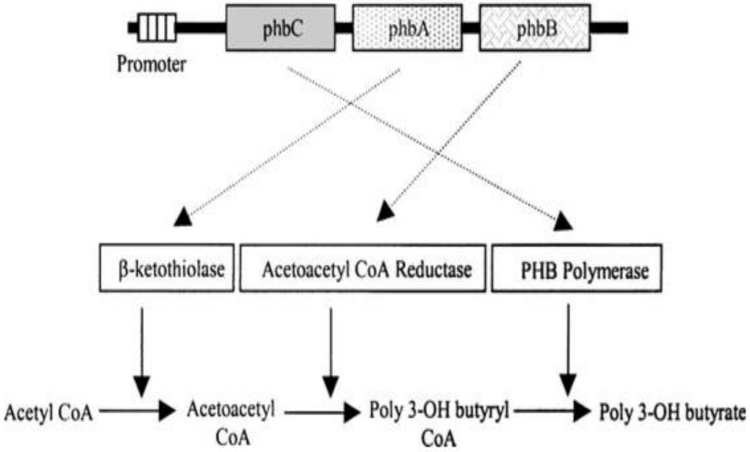
- L'accumulo di PHA viene promosso quando un nutriente essenziale per la crescita è presente in quantità limitata nel mezzo di coltivazione, mentre il carbonio è in eccesso. Il nutriente limitante può essere azoto (N), ma anche zolfo (S), fosfato (P) o ferro (Fe).

- 4 classi principali di enzimi presenti sul carbonosoma:

- **PHA polimerasi**
- **PHA depolimerasi**
- **Fasine ,** proteine strutturali necessarie per la localizzazione dell'organello nel citoplasma e altre funzioni particolari.
- **Gaps**, Proteine associate ai granuli

LE 8 VIE BIOSINTETICHE DEI PHA





Gli enzimi piu' importanti coinvolti in tale processo sono:

- **β-Chetotiolasi**
- **NADPH-dipendente acetoacetil-coA riduttasi**
- **PHA sintasi**

La storia di Bio-On

Bio-on nasce nel 2007 con l'intento di operare nel settore delle moderne Biotecnologie applicate ai materiali di uso comune con lo scopo di dare vita a prodotti e soluzioni completamente naturali, al 100% ottenuti da fonti rinnovabili o scarti della lavorazione agricola.

PHAs: Polidrossialcanoati (plastica veramente biologica) e relative applicazioni strategiche a 360° (packaging generico, packaging alimentare, design, abbigliamento, automotive).

TARGET: Il target di riferimento di Bio-on è operare direttamente nel mondo agro alimentare, nel settore del design e degli accessori, nel settore della cosmetica, nel settore farmaceutico fornendo a tutti la tecnologia necessaria per produrre o utlizzare PHAs con lo sviluppo delle relative caratterizzazioni.

PROGETTO: Intellectual Property Company con sede basata a Bologna e la possibilità di concedere licenze in tutto il mondo. Dalla sede di progettazione al pool di aziende di engineering e laboratori impegnati nella continua progettazione, produzione e distribuzione del know-how **Bio-on**. La produzione di PHAs è limitata territorialmente attraverso contratti di licenza d'uso della tecnologia o partnership industriali dedicate a specifiche aree commerciali. Per l'utilizzo della tecnologia Bio-on contattateci: **info@bio-on.it**

PRODUZIONE: Dal 2017 **Bio-on** opererà nella sua sede produttiva di Bologna dedicata alla creazione e produzione di prodotti PHAs speciali per applicazioni in ambito cosmetico e farmaceutico. Per l'acquisto dei prodotti speciali Bio-on contattateci: **info@bio-on.it**

bio-on
LIFE AFTER PLASTIC

Minerv bio cosmetics formulation type C1
World Wide new patent

Pag. 2

Minerv bio cosmetics formulation type C1 World Wide new patent

http://www.fda.gov/Cosmetics/GuidanceRegulation/LawsRegulations/ucm2005209.

htmhttps://www.congress.gov/bill/114th-congress/house-bill/1321/textEU link

http://eur-lex.europa.eu/legal-content/IT/TXT/?uri=URISERV%3Aco0013

http://ec.europa.eu/growth/sectors/cosmetics/legislation/index_en.htm

Pubblicato il **14 gennaio 2020**

Bio on, parla il fondatore Astorri. "Una rivoluzione, perciò ci hanno fermato"

Intervista esclusiva all'ex presidente (indagato) dopo il fallimento: "Il potenziale tecnologico resta enorme. Vittime di un attacco speculativo ben preparato"

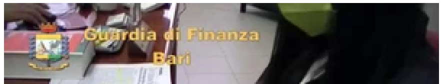
di NICOLA BIANCHI E RICCARDO RIMONDI

Fotogallery / Dall'exploit in Borsa alle misure cautelari. Foto **Video /** Come è partita l'indagine

POTREBBE INTERESSARTI ANCHE

CRONACA

Coronavirus Italia, bollettino della Protezione civile. I dati del 4 maggio



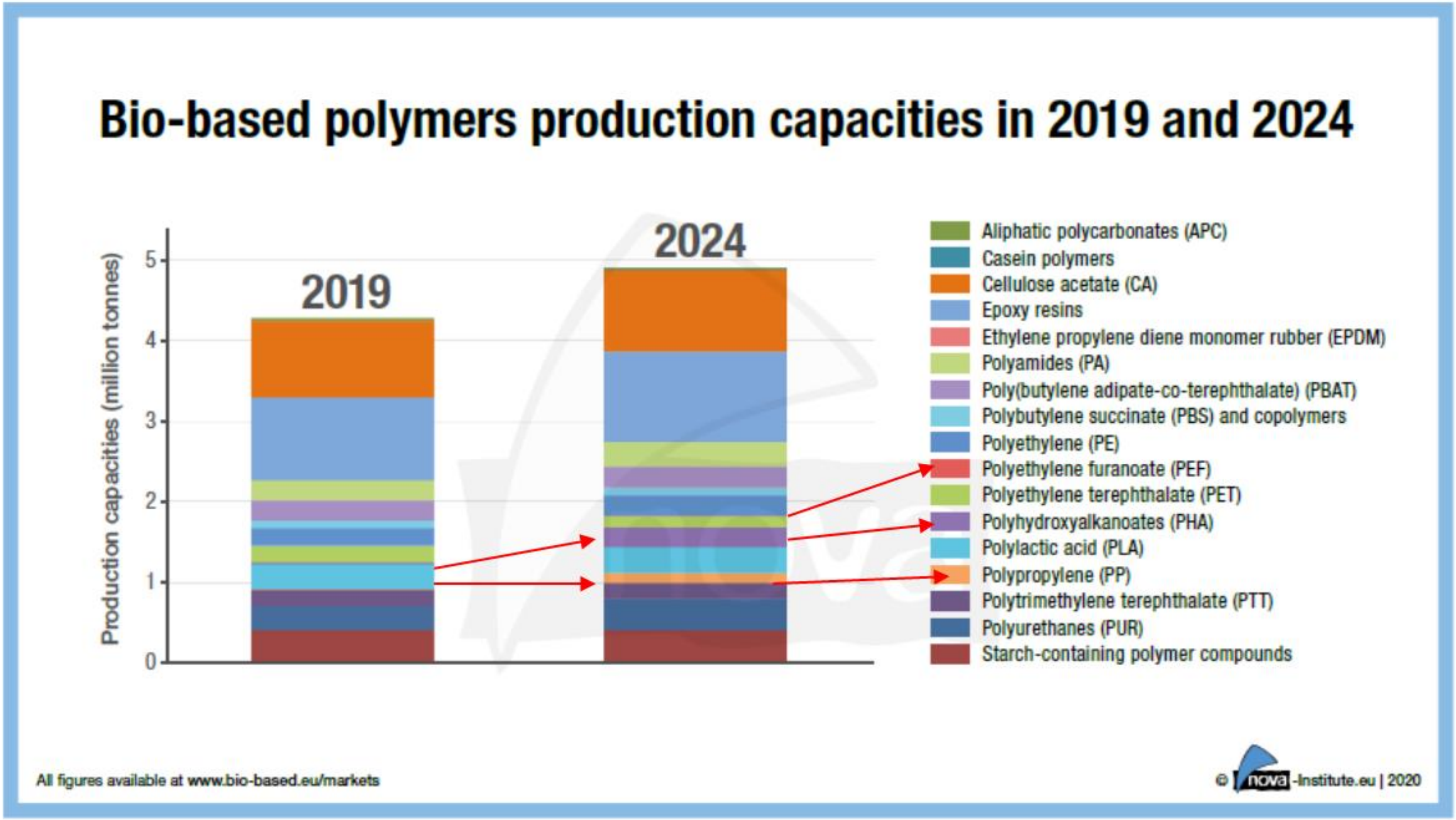


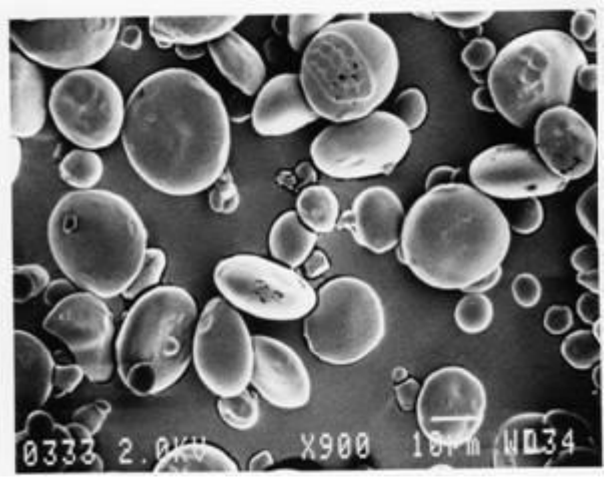
Figure 6: Bio-based polymers production capacities in 2019 and 2024

Thermoplastic starch

based plastics

Starch polymer structure retained while granular structure is destroyed under influence of heat, mixing and plasticizers (e.g. water, glycols)

Used in composites, blends, multilayers



L. Averous, University Strasbourg:
www.biodeg.net/biomaterial.html

Biodegradable

Organic waste collection, vapour permeable packaging

Mater-bi (Novamont) 60.000 t/a cap.
Foamed starch for packaging

COS'E' IL MATER-BI®

Polimero Biodegradabile e Compostabile
Mater-Bi®: la prima famiglia di biopolimeri che utilizza componenti vegetali come l'amido di mais, preservandone la struttura chimica

Attraverso un processo di "complessazione" dell'amido con quantità variabili di agenti complessanti biodegradabili (naturali, da fonte rinnovabile, da fonte sintetica o mista), vengono create diverse sovrastrutture molecolari caratterizzate da un'ampia gamma di proprietà.

Mater-Bi® è prodotto nello stabilimento di Terni, in forma di granulo e può essere lavorato secondo le più comuni tecnologie di trasformazione, per realizzare prodotti dalle caratteristiche analoghe o migliori rispetto alle plastiche tradizionali, ma perfettamente biodegradabili e compostabili, minimizzando l'impatto ambientale. I prodotti in Mater-Bi® dopo l'uso si biodegradano nel tempo di un ciclo di compostaggio.

LA STORIA (1989)

MONTEDISON

Montecatini
Tecnologie
Chimiche

Eridania-Beghin Say
Materie Prime
Agricole

FERTEC Ferruzzi
Research and
Technologies

PROGETTI DI RICERCA&SVILUPPO CON FOCUS SU: MATERIALI, COBUILDERS PER DETERGENZA, BIOCARBURANTI, ADDITIVI PER CARTA, INTERMEDI CHIMICI DA HYDROCRACKING, ETC.

Novamont affonda le proprie radici nella scuola di Scienza dei Materiali Montedison e che nasce nel 1989 per l’integrazione tra chimica, ambiente e agricoltura attraverso l’impiego di fonti rinnovabili per la produzione di bioplastiche per applicazioni specifiche a basso impatto ambientale.

La storia


1990


1992

1998


2001


2002


2003


2005

Lancio di Pneo, innovativo sacchetto in MATER-BI

2007

Premio "European Inventor of the Year"

2012

Prodotti Foodservice in MATER-BI alle Olimpiadi di Londra

Acquisizione Centro Ricerca di Piana di Monte Verna

Raccolta umido con sacchi MATER-BI a Milano


2014

Lancio primi prototipi sacchi di nuova generazione ad Ecomondo

Sacchi Frutta e Verdura in MATER-BI in Unicoop Firenze


2015

Lavazza - Capsula Compostabile

Nuovo Brand

Prodotti Foodservice in MATER-BI per Eataly ad Expo Milano

È stata fondata nel 1990 all'interno del gruppo Montedison (all'epoca della famiglia Ferruzzi) per commercializzare i prodotti della controllante *Fertec - Ferruzzi Ricerca e Tecnologia*, il centro di ricerca voluto nel 1989 da **Raul Gardini** per sviluppare prodotti chimici a basso impatto ambientale utilizzando materie prime di origine agricola. Un'intuizione la sua che aveva sollevato solo sorrisi scettici.

In quel periodo le ricerche avviate dalla Fertec erano due: una riguardava i carburanti e cioè il biodiesel, l'altra le bioplastiche che hanno come base l'amido di mais, il grano e la patata. Su questo secondo progetto si concentrava il lavoro di ricerca del team affidato a Catia Bastioli.

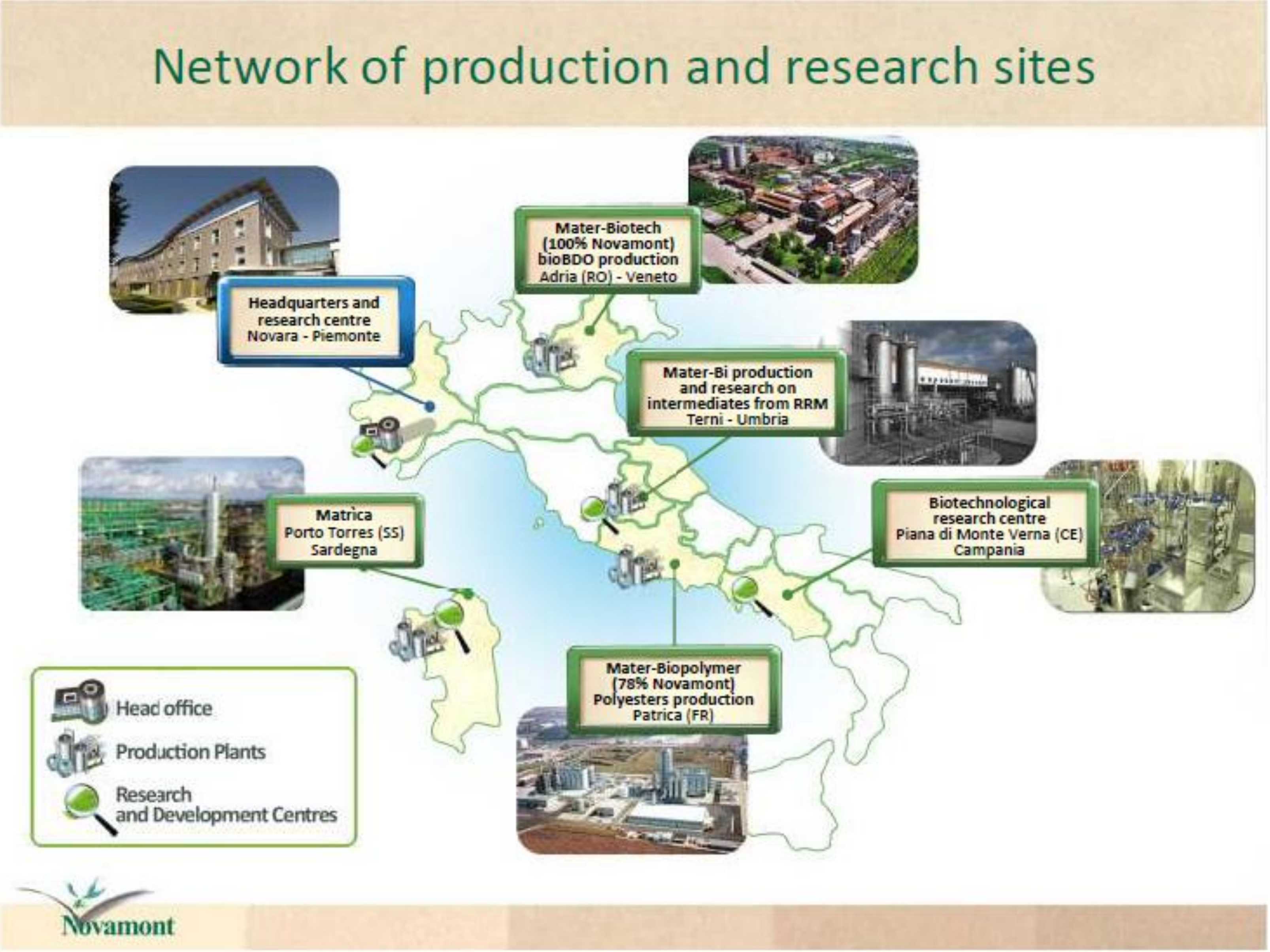
Novamont incorporava la Fertec. e utilizzava il marchio Mater-Bi, madre biodegradabile. In seguito alla crisi del gruppo Ferruzzi-Montedison, nel 1996 Novamont venne acquisita dalla Banca Commerciale Italiana, dalla società di private equity Investitori Associati S.A. e da UBS. Nel 2016 la società è controllata al 25% da Versalis del gruppo ENI e al 75% da Mater-bi SpA, i cui azionisti sono Investitori Associati e altri soci

NOVAMONT SYSTEM

1989	Foundation of NOVAMONT (Fertec research centre)
1991	Fertec incorporated into NOVAMONT
1996	Acquisition of NOVAMONT by Investitori Associati and Banca Commerciale Italiana
1997	1st increase of production capacity of Terni plant
2001	NOVAMONT achieves turnover break-even point
2004	Technological development of biopolyesters ORIGO-BI
2006	Foundation of Sincro, JV with Coldiretti
2011	Conversion of the Patrica site in Lazio region and start of 1st continuous line of biopolyesters
	Creation of Matrìca, JV with Versalis
2012	Conversion of the Adria site in Veneto region for the production of biobutanediol and agreement with Genomatica. Foundation of Mater-Biotech
	Acquisition of Piana di Monte Verna biotechnology research centre in Campania region
2014	Foundation of Mater-Biopolymer with acquisition of 78% of Patrica site
2015	Matrìca: production of first chemical intermediates from renawable resources
	Agreement with Coldiretti for the development of agricultural value-chains
	New brand identity
2016	Grand opening of Mater-Biotech production facilities

MATER-BI PRODUCT

1989	Biodegradable Mickey Mouse watch (Walt Disney)
1992	Green Pen made from MATER-BI
	Production of first biodegradable bag made from MATER-BI
1998	First MATER-BI package with Ecolucart in large-scale retail distribution
2001	Launch of green tyre with Goodyear
2002	Launch of Wave, a foam made from MATER-BI
2005	Launch of Pneo, an innovative bag made from MATER-BI
2009	2nd generation MATER-BI
2012	Foodservice products made from MATER-BI at the London Olympics
	Separate organic waste collection using MATER-BI bags in Milan
2014	Launch of prototypes of 3rd generation MATER-BI bags at Ecomondo
	Fruit and vegetable bags made from MATER-BI at Unicoop Florence
2015	Foodservice products made from MATER-BI for Eataly at Expo Milan
	First compostable Lavazza capsule



Network of production and research sites

Headquarters and research centre
Novara - Piemonte

Mater-Biotech
(100% Novamont)
bioBDO production
Adria (RO) - Veneto

Mater-Bi production and research on intermediates from RRM
Terni - Umbria

Matrìca
Porto Torres (SS)
Sardegna

Biotechnological research centre
Piana di Monte Verna (CE)
Campania

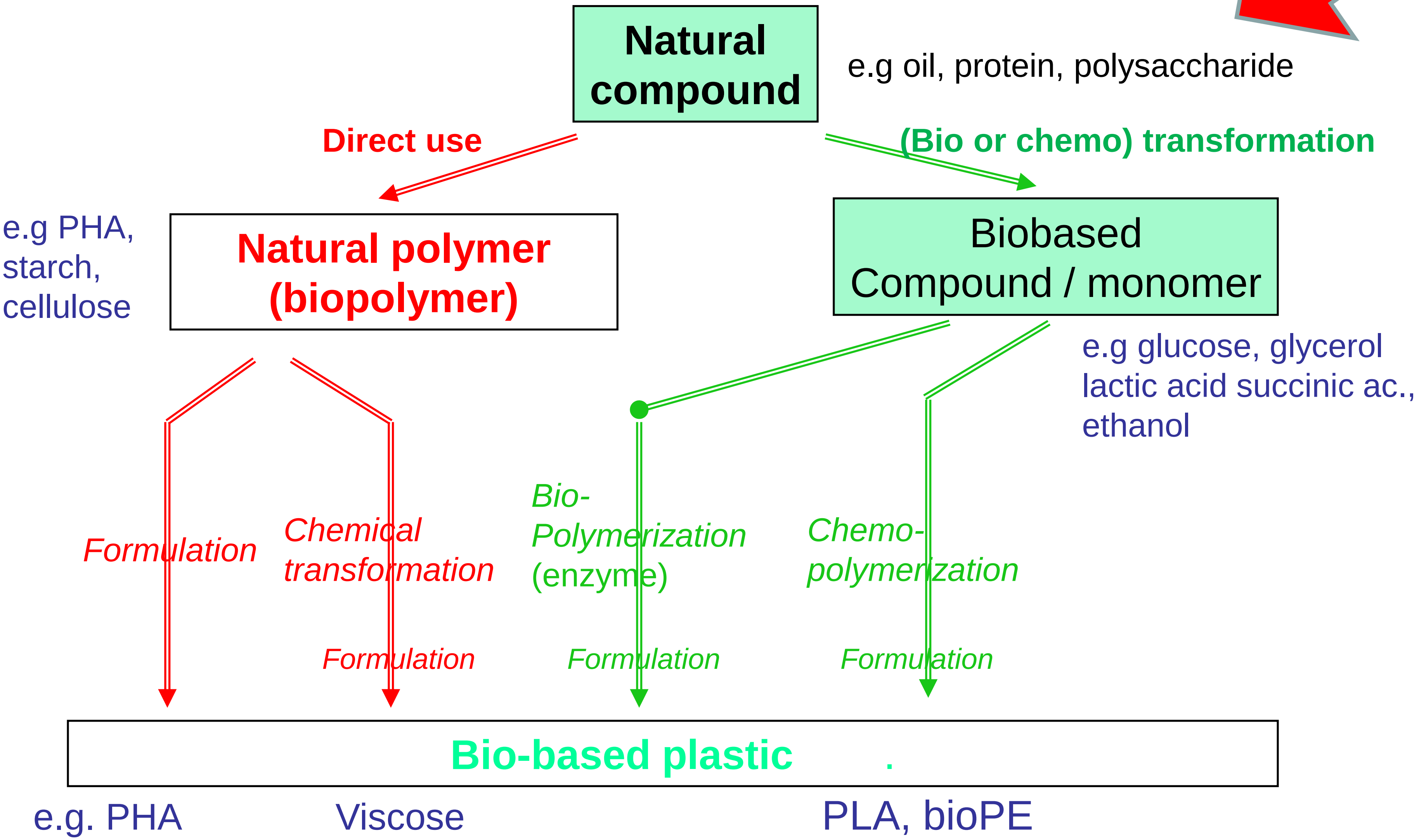
Mater-Biopolymer
(78% Novamont)
Polyesters production
Patrica (FR)

Head office
Production Plants
Research and Development Centres

Novamont

Luigi Capuzzi
luigi.capuzzi@novamont.com

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

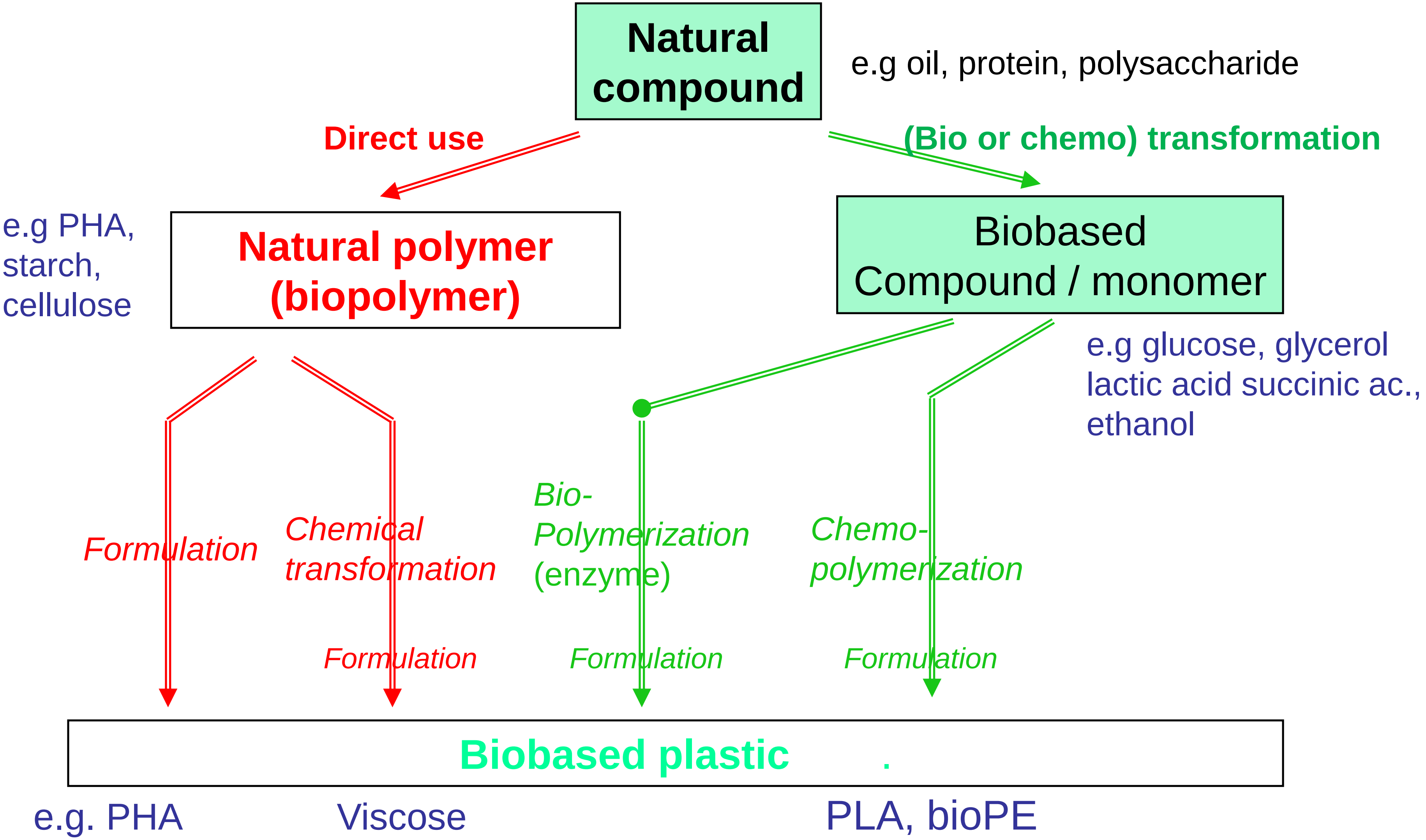
Bio-based plastic .

e.g. PHA

Viscose

PLA, bioPE

Strategies



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

Biobased plastic .

e.g. PHA

Viscose

PLA, bioPE

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

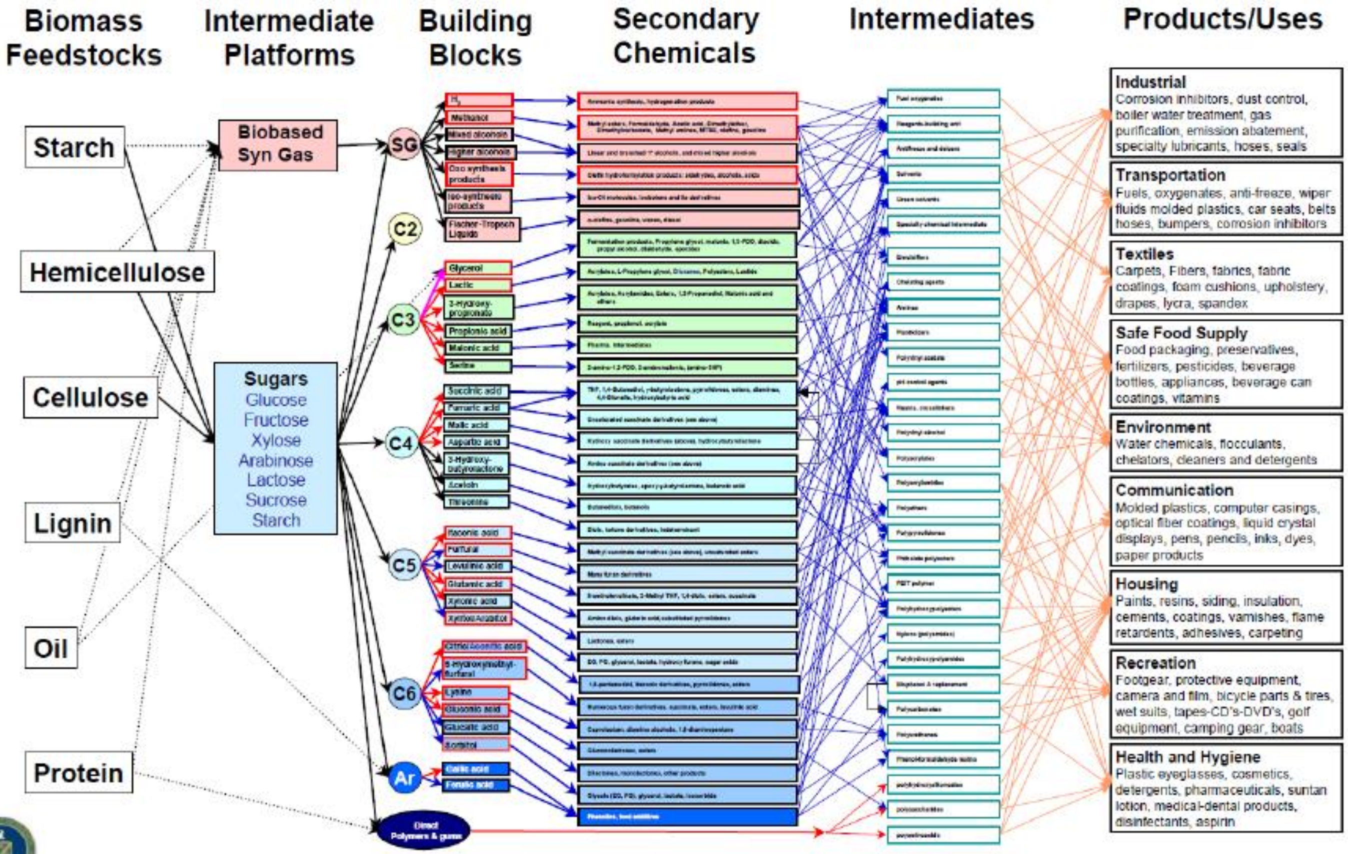
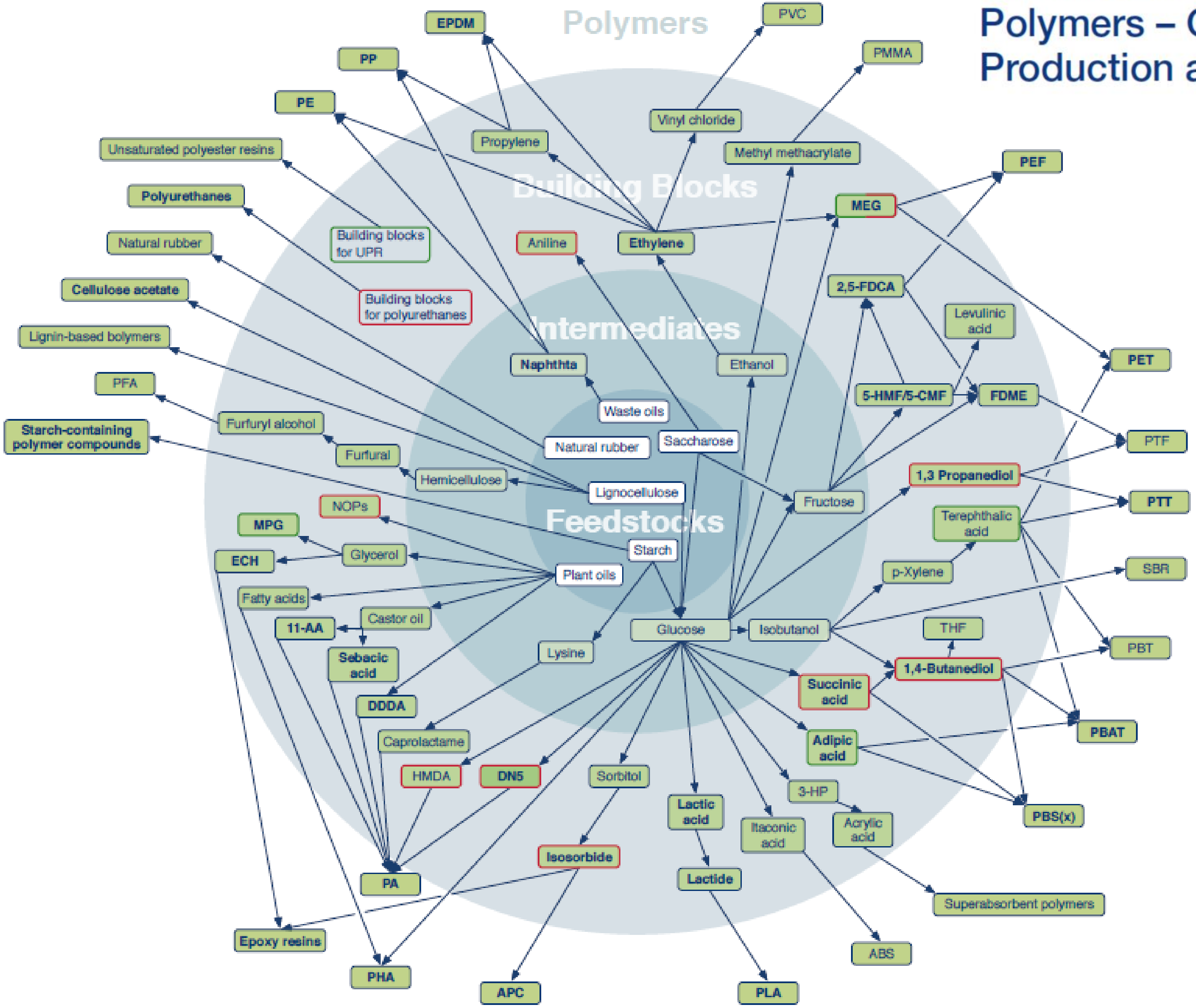


Figure 1 – Analogous Model of a Biobased Product Flow-chart for Biomass Feedstocks

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



Polymers

Building Blocks

Intermediates

Feedstocks

EPDM

PP

PE

PVC

PMMA

PEF

Unsaturated polyester resins

Polyurethanes

Natural rubber

Cellulose acetate

Lignin-based bolymers

PFA

Starch-containing polymer compounds

MPG

ECH

11-AA

PA

Epoxy resins

PHA

APC

PLA

ABS

Superabsorbent polymers

PBS(x)

PBAT

PBT

SBR

PTT

PTF

PET

Propylene

Vinyl chloride

Methyl methacrylate

MEG

Ethylene

Aniline

Building blocks for UPR

Building blocks for polyurethanes

Naphtha

Ethanol

2,5-FDCA

Levulinic acid

5-HMF/5-CMF

FDME

1,3 Propanediol

Terephthalic acid

p-Xylene

THF

1,4-Butanediol

Succinic acid

Adipic acid

3-HP

Acrylic acid

Itaconic acid

Lactic acid

Lactide

Isosorbide

Sorbitol

DN5

HMDA

Caprolactame

Lysine

DDDA

Sebacic acid

Castor oil

Fatty acids

Glycerol

NOPs

Furfuryl alcohol

Furfural

Hemicellulose

Waste oils

Natural rubber

Saccharose

Lignocellulose

Fructose

Starch

Plant oils

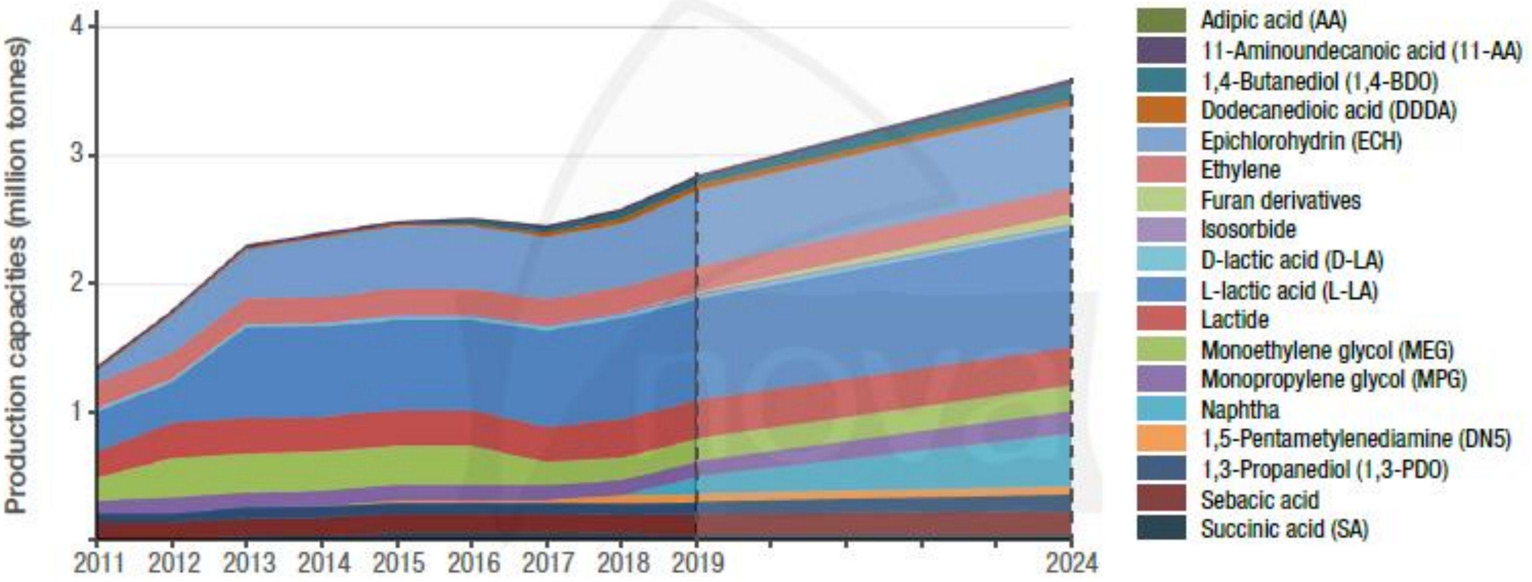
Glucose

Isobutanol

Authors:

Pia Skoczinski, Raj Chinthapalli, Michael Carus, Wolfgang Baltus, Doris de Guzman, Harald Käb, Achim Raschka, Jan Ravenstijn

January 2020



Bio-based building blocks
Evolution of worldwide production capacities from 2011 to 2024

All figures available at www.bio-based.eu/markets

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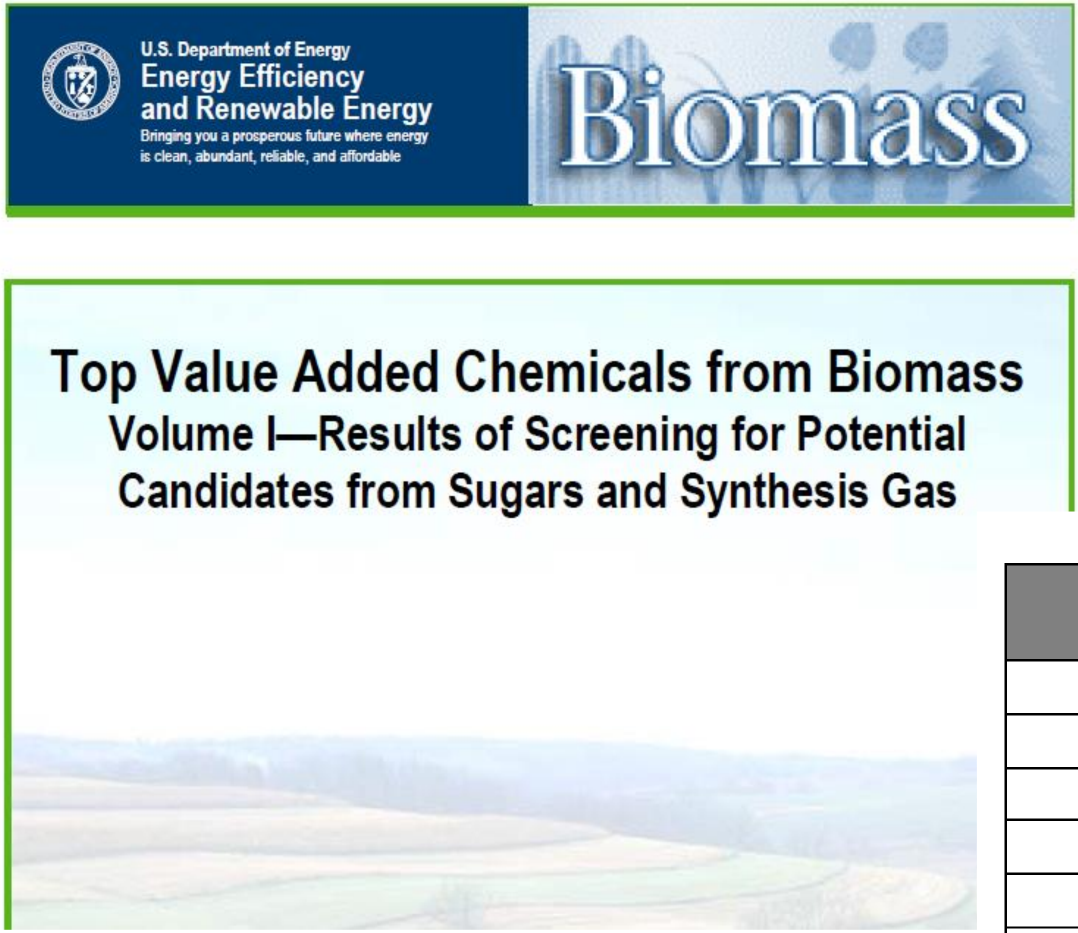
Figure 7: Bio-based building blocks – Evolution of worldwide production capacities from 2011 to 2024



U.S. Department of Energy
Energy Efficiency and Renewable Energy
Bringing you a prosperous future where energy 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.

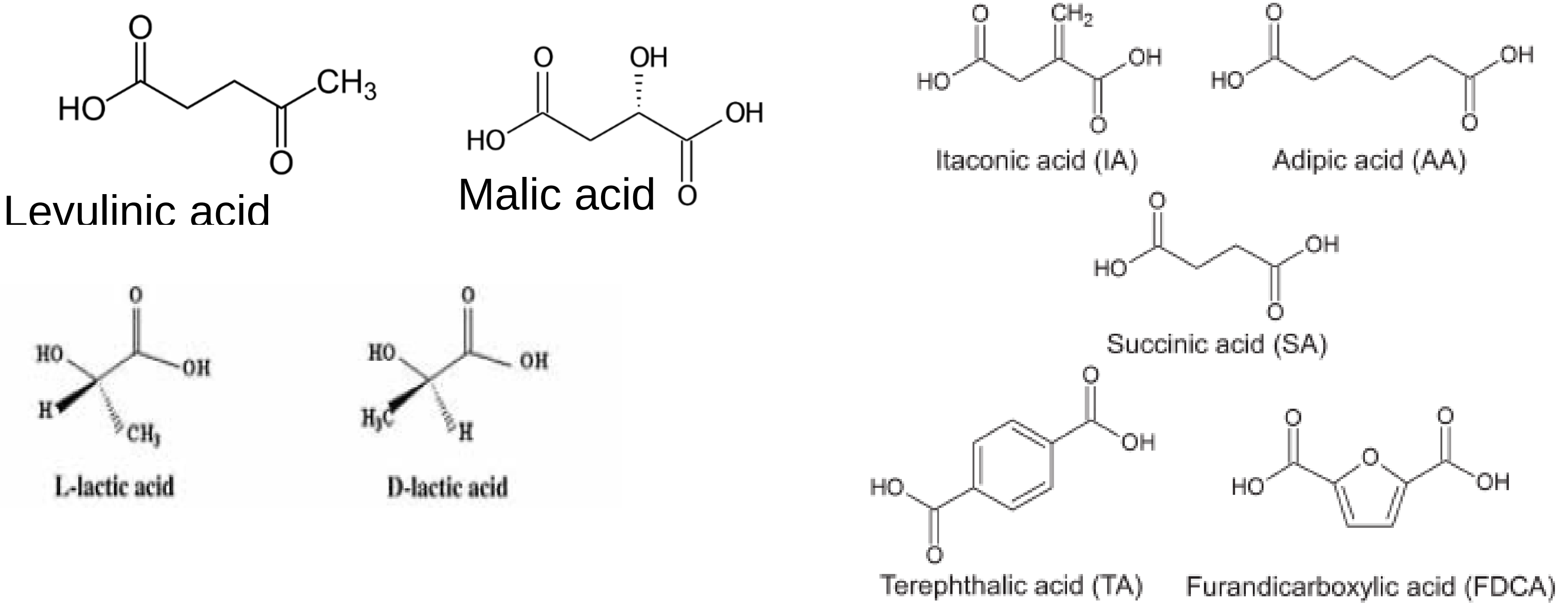
.

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.	[
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.	[
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.	



Levulinic acid

Malic acid

Itaconic acid (IA)

Adipic acid (AA)

Succinic acid (SA)

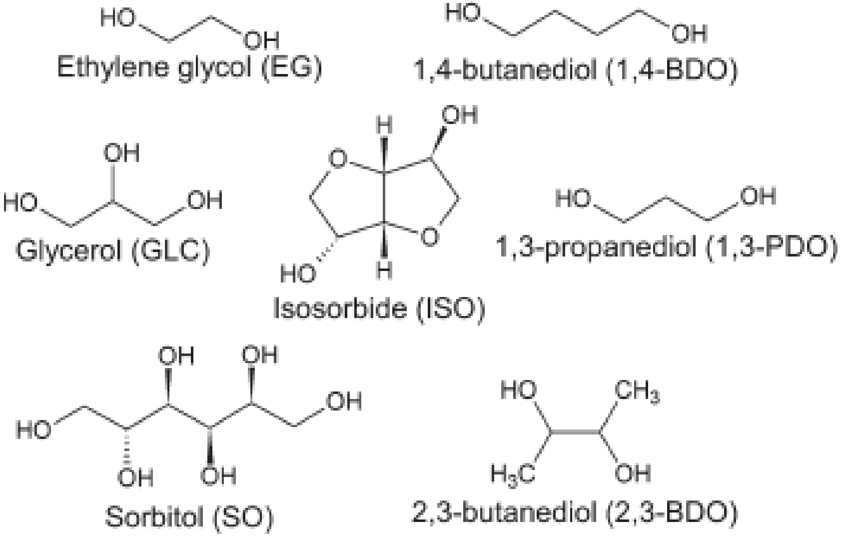
L-lactic acid

D-lactic acid

Terephthalic acid (TA)

Furandicarboxylic acid (FDCA)

Some bio-based monomers for polymer production



Ethylene glycol (EG)

1,4-butanediol (1,4-BDO)

Glycerol (GLC)

Isosorbide (ISO)

1,3-propanediol (1,3-PDO)

Sorbitol (SO)

2,3-butanediol (2,3-BDO)

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

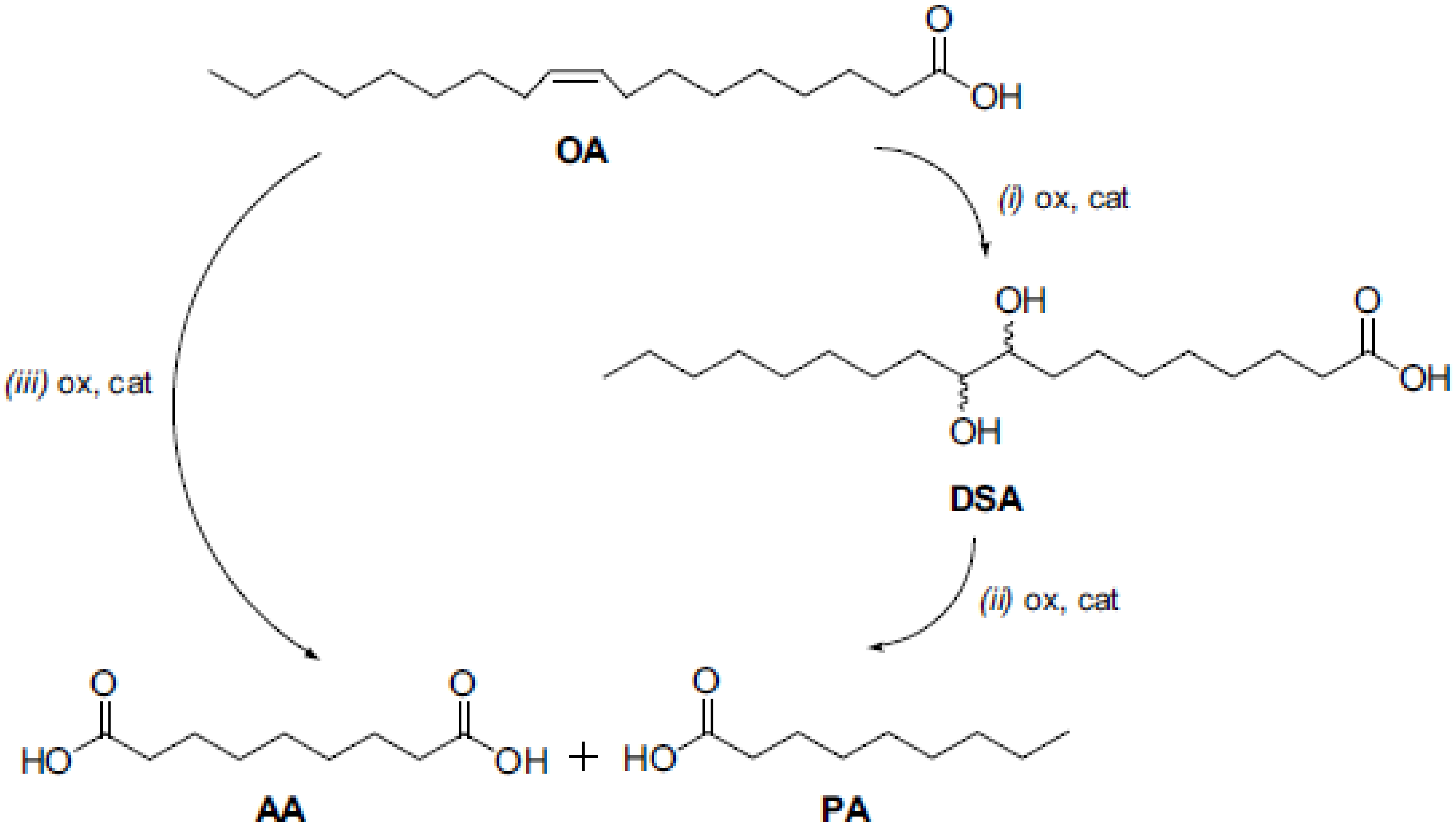
Monomer	Biotechnological route		Company	Status	Application of the corresponding bio-based polyesters	.
Sorbitol	Fermentation + hydrogenation		Roquette, ADM	Market	Functional polyesters; coatings	
Isosorbide	Sorbitol dehydration		Roquette	Market	Thermosetting resins	
Ethylene glycol	Ethanol dehydration		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	

Table 5. New bio-based monomers and chemical strategies for expanding the engineering applications of bio-based polymers.

Building blocks and monomers	Structural evolution	Targeted performance
Modified lactides for improved PLAs	Phenyl-substituted lactide synthesized by cyclic dimerization of bio-based mandelic acid to obtain mandelide (meso stereoisomer), which is polymerized *via* ring opening polymerization (ROP)	Overcoming low T_g and low transparency of PLA by inserting hydrophobic bulky side chains. Polymandelide has T_g> 100°C and is less biodegradable than PLLA.
	Norbornene-substituted lactide obtained by brominating the bio-based lactide. Elimination and Diels Alder reactions yield the norbornene lactide used in ring-opening metathesis polymerization.	Polymers have T_g> 190°C and narrow polydispersity.
Aromatic lignin derivatives	2,4-, 2,5-, and 2,6-pyridinedicarboxylic acid obtained by re-routing the lignin degradation pathways of *Rhodococcus jostii* RHA1	New bio-based aromatic / apliphatic polyesters obtainable via enzymatic polycondensation with Mn around 14000 Da
Succinic acid derivatives	Polyesters obtained by co-polymerization of succinic acid with furan dicarboxylic acid (FDCA)	Modifying soft properties of linear poly(succinates)s by introducing aromatic furan moieties. The corresponding polyesters poly(butylene succinate-co-butylene furandicarboxylate)s (PBSF) have Mw from 39 000 to 89 000 g/mol and display excellent thermal stability. Their structure and properties can be tuned ranging from crystalline polymers with good tensile modulus (360-1800 MPa) and strength (20–35 MPa) to nearly amorphous polymer of low Tg and high elongation (~600%), so that they may find applications in thermoplastics as well as elastomers or impact modifiers.
Furan derivatives	Nucleophilic aromatic substitution polymerization of 2,5- bis(4-fluorobenzoyl)furan (BFBF) derived from FDCA and potassium salts of aromatic bisphenols	Bio-based poly(thioether ketone) (PEEK) with Tm >300 °C, comparable to fossil-based PEEK
Amides	Branched chains of polyamide 4.	Moderation of rigidity. Increased MW. Improved mechanical properties without decreasing T_m.
	{(4,40-diyl-α-truxillic acid dimethyl ester) 4,40-diacetamido-α-truxillamide}, obtained from bio-based 4-aminophenylalanine, UV coupled with cinnamic acid	High-performance biobased polyamide with T_g >250 °C
Phenols	4-hydroxycinnamic acid (4HCA)	The aromatic ring confers liquid crystalline properties to polyesters. The bio-based liquid crystal polymers exhibits remarkable properties (strength = 63 MPa, Young’s modulus = 16 GPa, maximum softening temperature = 169 °C [
Isosorbide	Confers rigidity	Increasing thermos and mechanical properties while preserving the biodegradability.
Ricinoleic acid	Confers biocidal activity to poly(hexamethylene succinate) modified at the chain ends. Imidazolium salt was anchored on C=C bond of ricinoleic acid to improve biocidal activity.	Antimicrobial activity.
Terpenes	Pinene transformed into pinocarvone, which contains a reactive exo-methylene group exploitable for radical polymerization	High molecular weight plytherpenes with excellent thermal properties (Tg > 160 C). Polymerization of pinene would require low temperatures (-70°C) unviable for industrial purposes.
Cyclic diols	Bio-based 1,4-cyclohexanedimethanol (CHDM) is obtainable from renewable terephthalic acid.	As co-monomer in polyesters of 2,5-furandicarboxylic acid-increases rigidity, confers mechanical properties comparable to PET and improves barrier properties. Its polycondensation requires temperature around 240-280 °C due to the high boiling point but such temperatures promote its decomposition. Mild enzymatic polycondensation overcomes this drawback.
Itaconic acid derivatives	Functionalization of the unsaturated double bond of dimethylitaconate by thia-Michael addition reaction using 1-octanethiol.	Improve the stability of itaconic derivative monomers toward common conditions of polycondensation (high temperatures and metal-based catalysts)
	Post-polymerization modification of vinyl group of poly(itaconate) *via* Michael addition of primary amines.	Amine-triggered degradable materials; oligoesters displaying amine functionalities for biomolecules anchoring or covalent crosslinking.
	Michael additions of proline, cysteine and other S-containing nucleophiles to vinyl moiety of poly(itaconate)s.	Addition of pendants to polyester chain. Modifying polymer properties.
	Michael addition of C-nucleophiles (acetylacetone and dimethyl malonate) to vinyl moiety of poly(itaconate)s.	

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

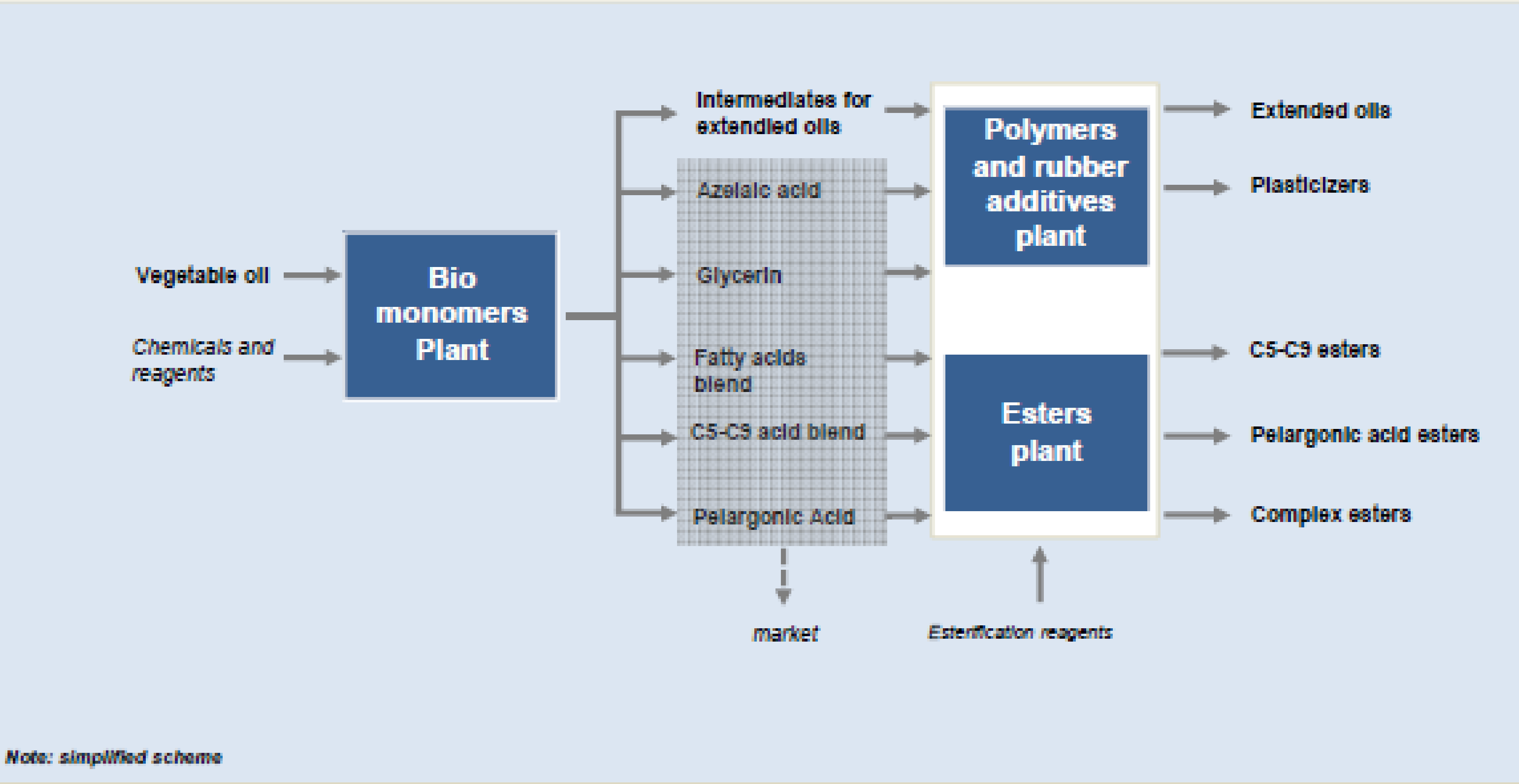
Luigi Capuzzi
luigi.capuzzi@novamont.com

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

Luigi Capuzzi
luigi.capuzzi@novamont.com



Note: simplified scheme

Luigi Capuzzi
luigi.capuzzi@novamont.com

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	

Luigi Capuzzi
luigi.capuzzi@novamont.com

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.

Meccanismo d’azione:

1. Attività inibitoria sulla **tirosinasi**
2. Attività inibitoria sulla **tioredossina reduttasi**
3. Attività inibitoria sulle **ossidoreduttasi mitocondriali**
4. Attività inibitoria sulla sintesi di **DNA** e **RNA**
5. *Free radical scavenger*
6. Inibizione di **NF-kb** (*nuclear factor kappa-light-chain-enhancer of activated B cells*)
7. Inibizione della via delle **MAPK** (*mitogen-activated protein kinase*)
8. Induzione dell’attività di **PPARγ** (*peroxisome proliferator-activated receptor*)
9. Inibizione della via **CD36/Nox**
10. Inibizione dell’espressione genica di **TLR-2** (*toll-like receptor -2*)
11. Inibizione di **CAMP** (*cathelicidin antimicrobial peptide gene*)
12. Inibizione di **KLK5** (*kallikrein-related peptidase 5*)
13. Attività inibitoria di **5α-reduttasi** *in vitro*

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

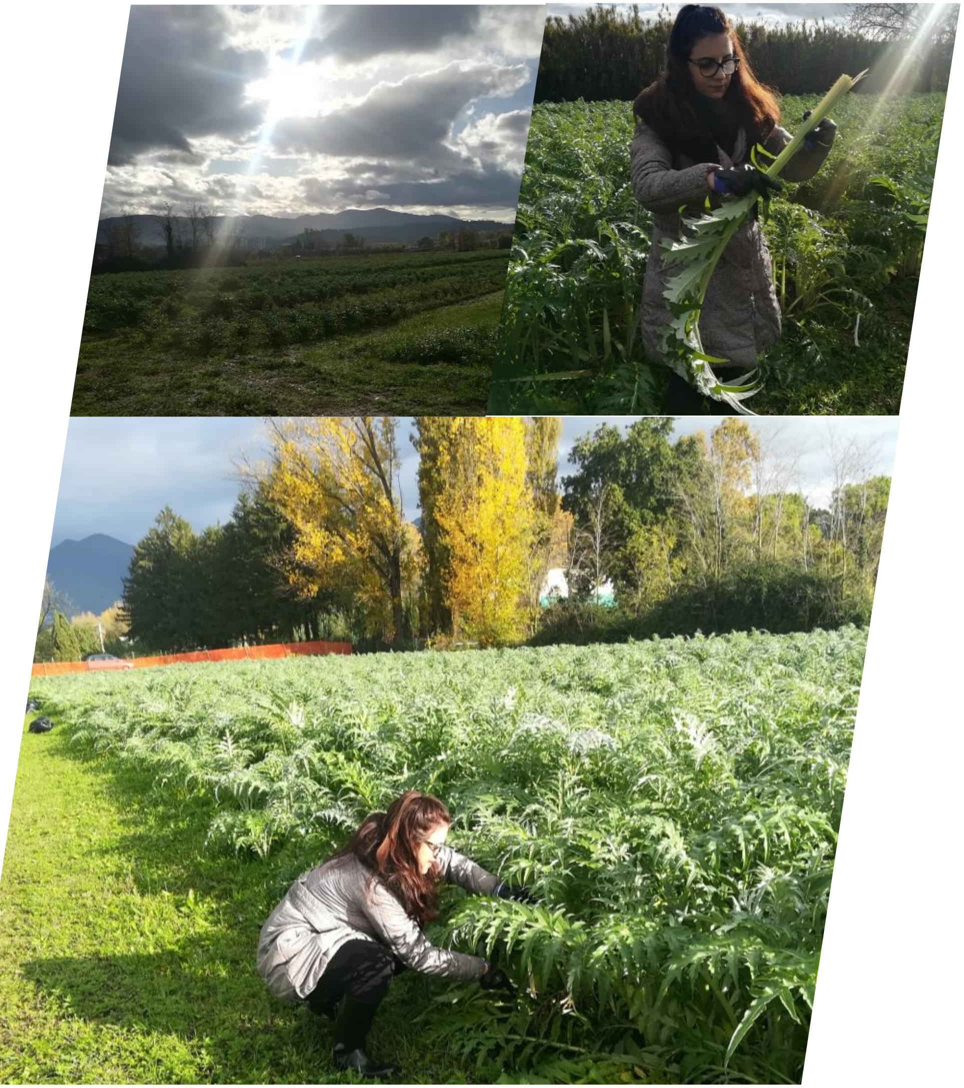
UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II

Consiglio Nazionale delle Ricerche

CARDOON

- ***Cynara cardunculus*** **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)**

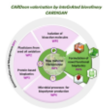
P. Valentão et al. J. Agric. Food Chem. 50(17), (2012), 4989-4993;
C.M. Torres et al. Fuel 111, (2013), 535-542;

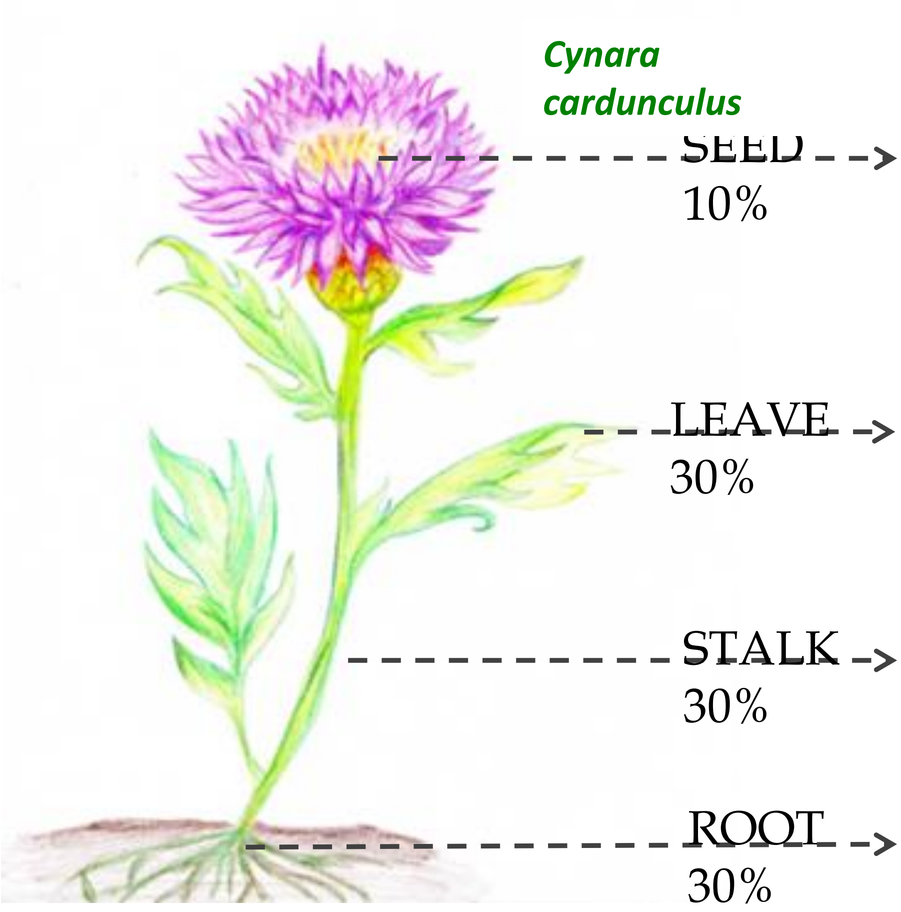


1. Collection of Cardoons

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

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





Cynara cardunculus

SEED
10%

LEAVE
30%

STALK
30%

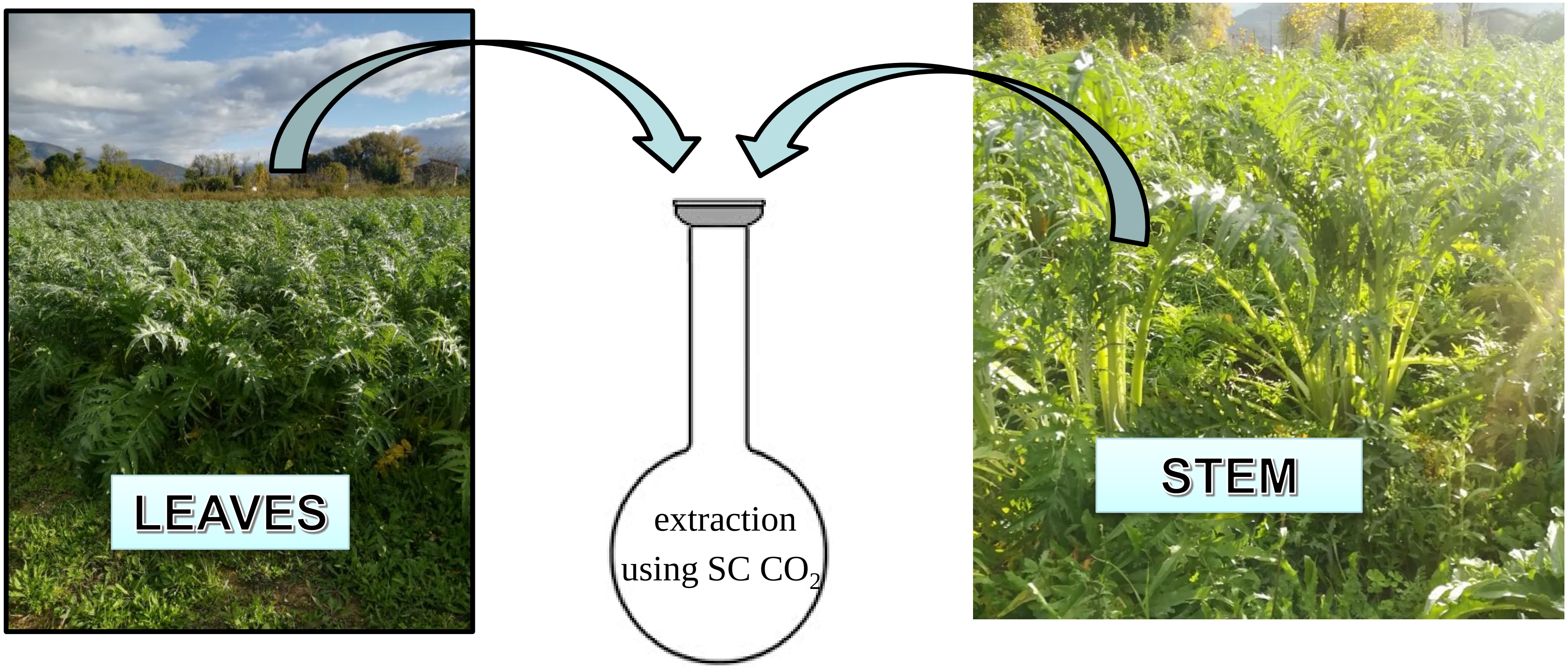
ROOT
30%

Oil
Proteins
Bioactive
Moleculecules

Proteins
Bioactive
molecules
Enzymes

Inulin
PHA
Lactic acid

Extraction of bioactive compounds

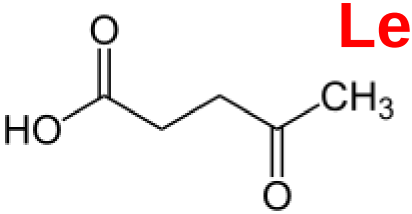


LEAVES

extraction using SC CO_2

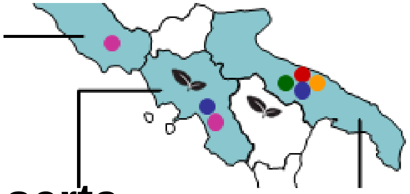
STEM

GF
Biochemicals



Levulinic acid

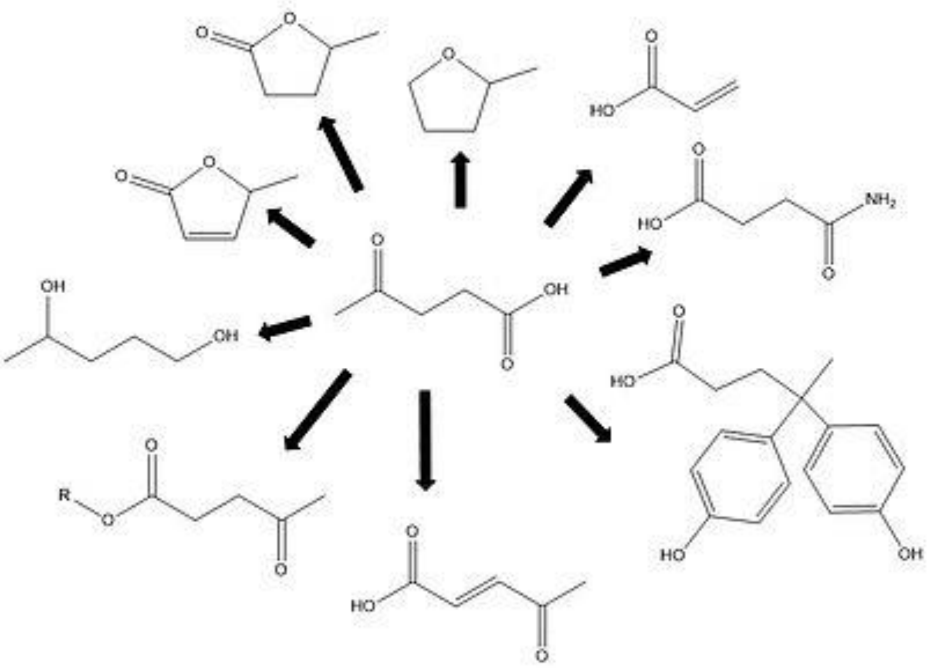
Levulinic acid platform



Caserta

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

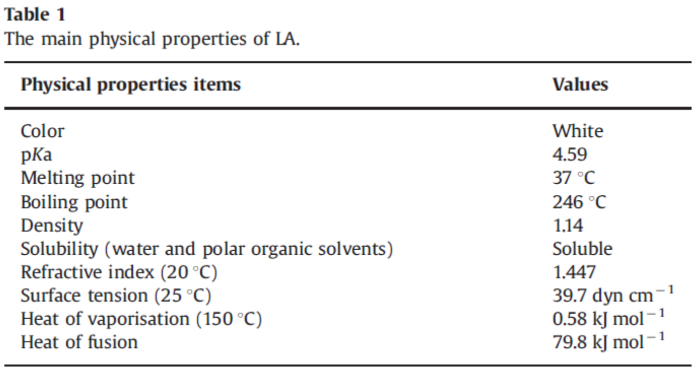


Table 1
The main physical properties of LA.

Physical properties items	Values
Color	White
p*K*a	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

GF Biochemicals

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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+39 344 2379251

17 Februar 2020

Is levulinic acid making a comeback?

GF Biochemicals new joint venture with Oman-based Towell Engineering Group called NXTLEVVEL Biochem to build a levulinate bio-solvent manufacturing plant

It has been a while since we last heard any activities in the levulinic acid space especially as there are…Full text: https://greenchemicalsblog.com/2020/02/11/is-levulinic-acid-making-a-comeback/

Supplier

- GFBiochemicals Ltd.
- nova-Institut GmbH
- NXTLEVVEL Biochem
- Tecnon OrbiChem
- Towell Engineering Group

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.

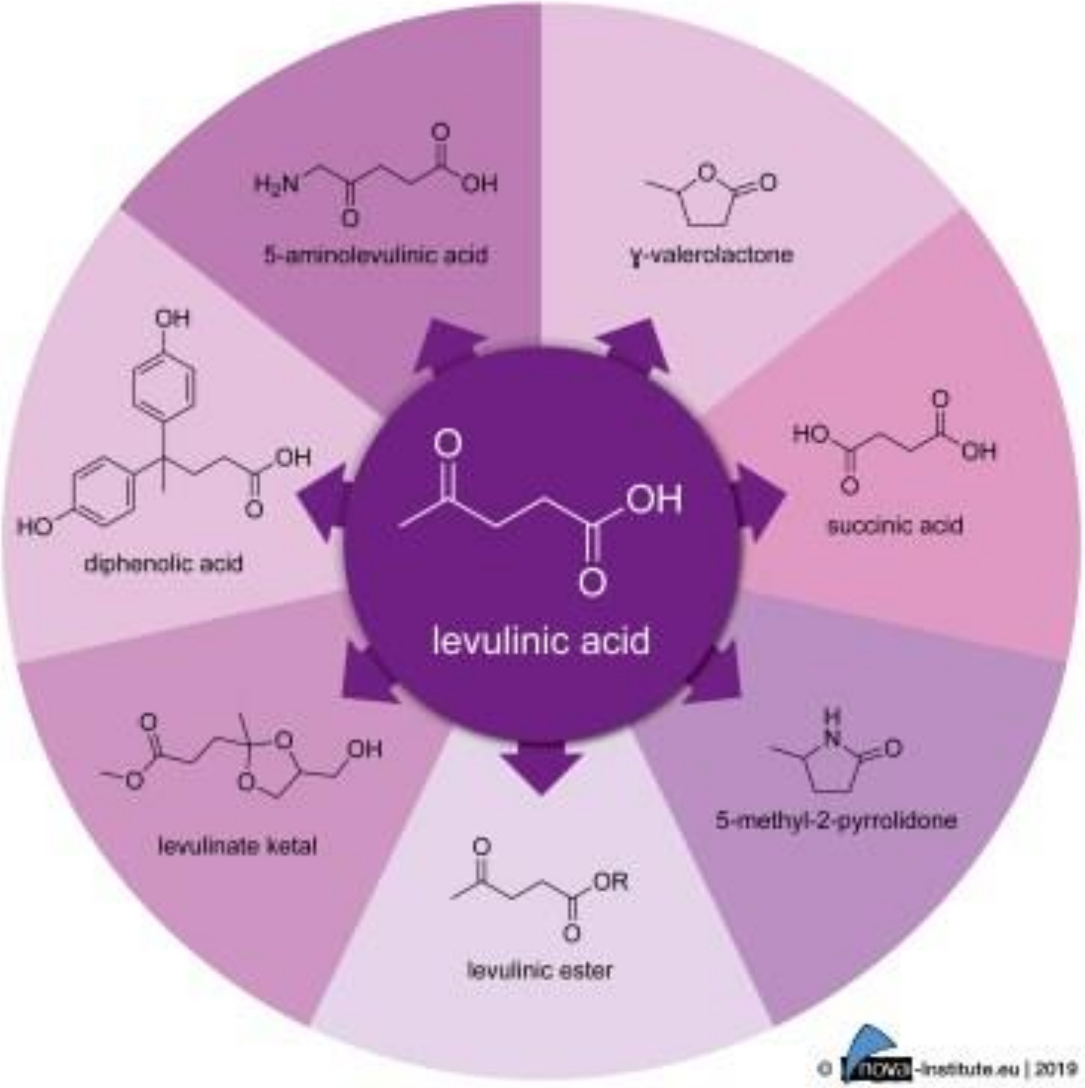

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Table 1
Selected levulinic acid applications

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.

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journal homepage: www.elsevier.com/locate/rser

Production and catalytic transformation of levulinic acid: A platform for speciality chemicals and fuels

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[a] School of Engineering, Brown University, Providence, RI, USA
[b] Department of Chemistry, Lakehead University, Thunder Bay, ON, Canada
[c] Department of Chemistry, Princeton University, Princeton, NJ, USA

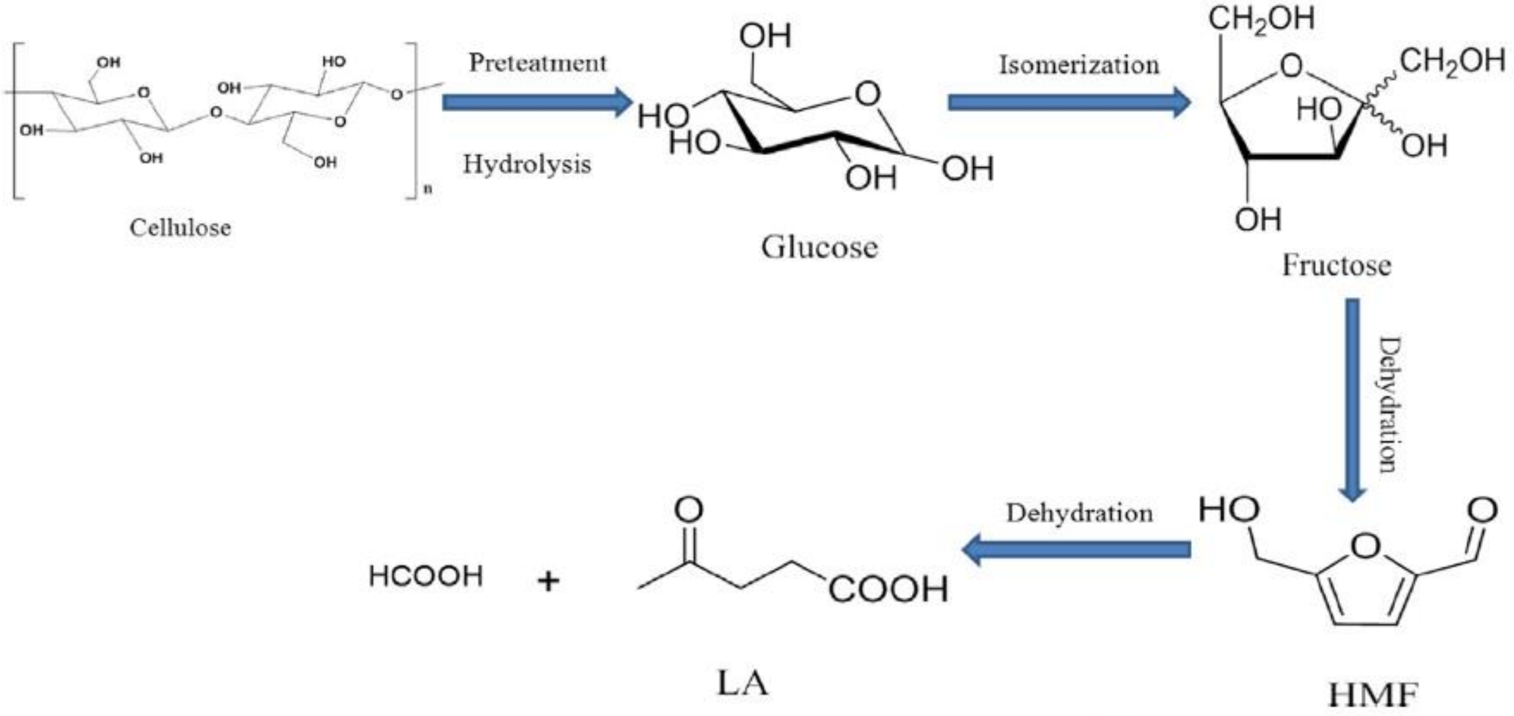


Fig. 2. Production of LA from cellulosic biomass [8,18].

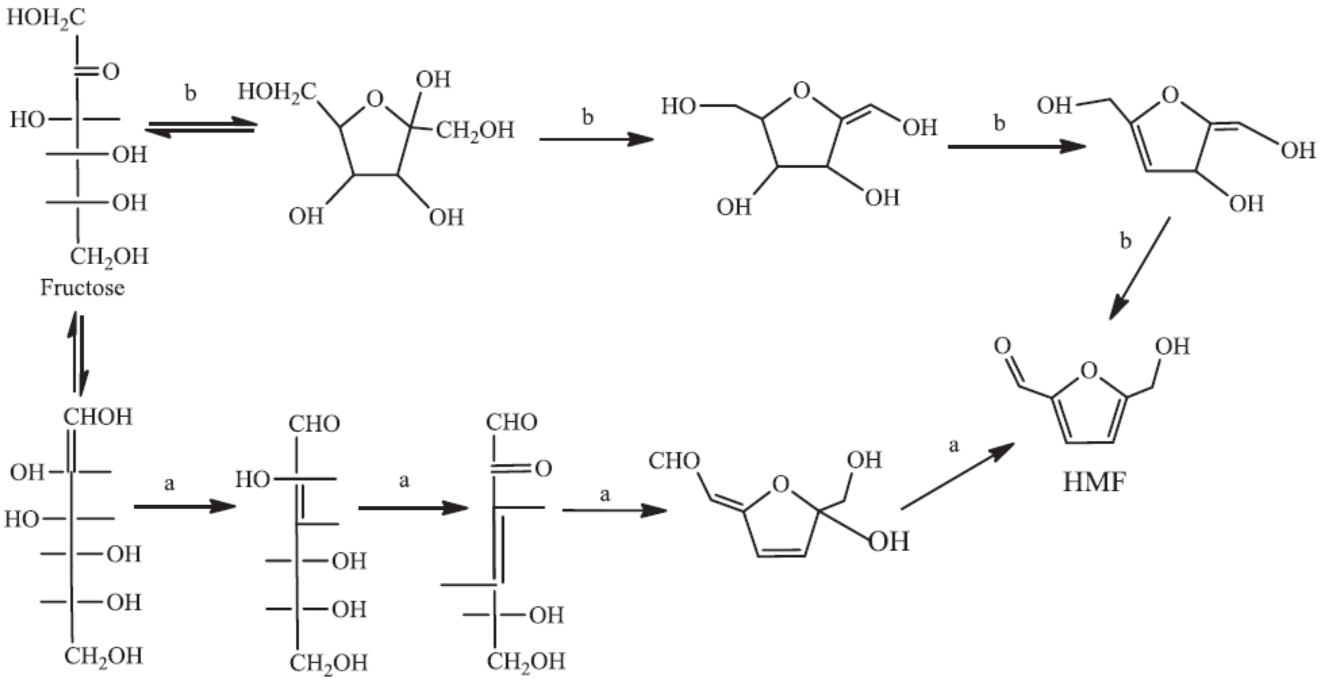


Fig. 4. Possible dehydration mechanisms for formation of HMF (a) acyclic route; (b) cyclic route [40].

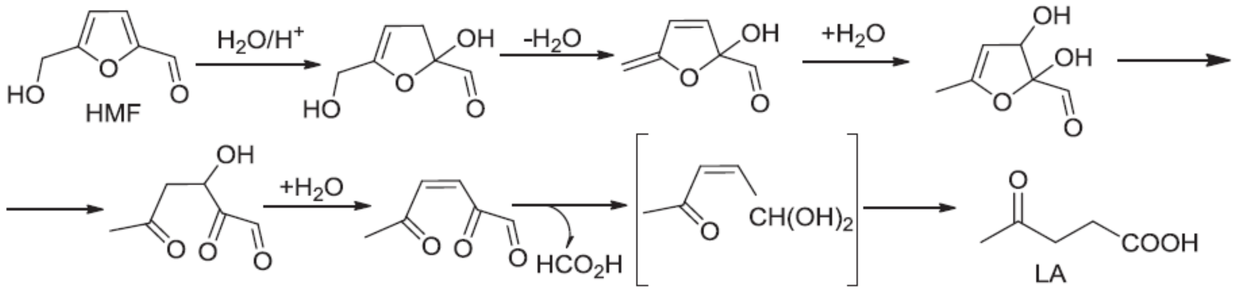


Fig. 5. Proposed mechanisms for the formation of LA from HMF [42].

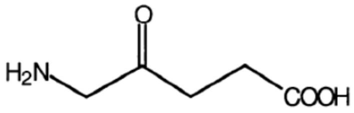
Table 2
Production of LA from carbohydrates substrate[a].

No.	Substrate	Catalyst	Solvent	Time (h)	*T* (°C)	Y_{LA} (%)	Refs.
1	Glucose	$HCl–C_2H_4Cl_2$	–	3	80–100	79	[51]
2	Glucose	$FeCl_3$	H_2O	2	180	30	[56]
3	Glucose	$CrCl_3$	H_2O	2	180	60	[56]
4	Glucose	$CuCl_2$	H_2O	2	180	~23	[56]
5	Glucose	$AlCl_3$	H_2O	2	180	~71	[56]
6	Glucose	$HCl/ClCH_2CH_2$ Cl	$ClCH_2–CH_2Cl$	3	80–100	5–9	[57]
7	Glucose	HCl	H_2O	24	R.T.	15	[58]
8	Glucose	Amberlite IR-120	H_2O		124	5.8	[59]
9	Glucose	HCl	H_2O	0.25	160	41.4	[60]
10	Glucose	Clay	H_2O	24	150	12	[61]
11	Glucose	H_2SO_4	–	1	170–210	80.7	[62]
12	Glucose	HCl	–	1	220	57.7	[63]
13	Glucose	HCl	–	4	90	23	[64]
14	Glucose	H_2SO_4	–	12	98	38	[64]
15	Glucose	Al–Zr oxide	H_2O	2	180	6.1	[65]
16	Fructose	HCl	–	–	98	~75	[64]
17[a]	Fructose	Amberlite IR-120	H_2O	27	R.T.	23.5	[59]
18	Fructose	LZY	H_2O	15	140	43.2	[66]
19	Fructose	Lewatit SPC 108	$H_2O+MIBK$	0.5	80	79	[67]
20	Fructose	H_3PO_4	H_2O	~0.03	280	7	[68]
21	Fructose	$Cs_{2.5}H_{0.5}PWb$	$H_2O+MIBK$	1	115	12.6 ± 0.3	[69]

[a] R.T.: Room temperature.

Table 4
A summary of other biomass feedstocks for production of LA from literatures.

No.	Substrate	Catalyst	Solvent	*T* (°C)	*t* (h)	Y_{LA} (%)	Refs.
1	Starch	HCl	–	220	1	53.7	66
2	Corn stover	$HCl/ClCH_2CH_2Cl$	$ClCH_2–CH_2Cl$	80–100	3	5–9	57
3	Water hyacinth	H_2SO_4	H_2O	175	0.5	53	78
4	Rice straw	$S_2O_8^{2-}/ZrO_2–SiO_2–Sm_2O_3$	H_2O	150	0.25	6.6	79
5	Rice straw	$S_2O_8^{2-}/ZrO_2–SiO_2–Sm_2O_3$	H_2O	180	0.25	8.2	79
6	Rice straw	$S_2O_8^{2-}/ZrO_2–SiO_2–Sm_2O_3$	H_2O	200	~0.17	70	79
7	Rice straw	$S_2O_8^{2-}/ZrO_2–SiO_2–Sm_2O_3$	H_2O	240	0.25	8.6	79
8	Wheat straw	H_2SO_4	–	210	0.6	19.9	77
9	Paper	H_2SO_4	–	< 240	–	59.8	80
10	Pulp residues	H_2SO_4		1st: 210–230 °C, 2nd: 195–215 °C	–	70–80	81
11	Sorghum grain	H_2SO_4		200		45.6	26
12	Bagasse	HCl		220		82.7	83



2, DALA

Table 5
Possible products from LA and potential LA markets demand [85].

Product	Use	Potential LA market (million lb/year)
MTHF	Fuel extender	10,000–100,000
DALA	Biodegradable herbicide	175–350
Diphenolic acid	Monomer	35
THF	Solvent	200

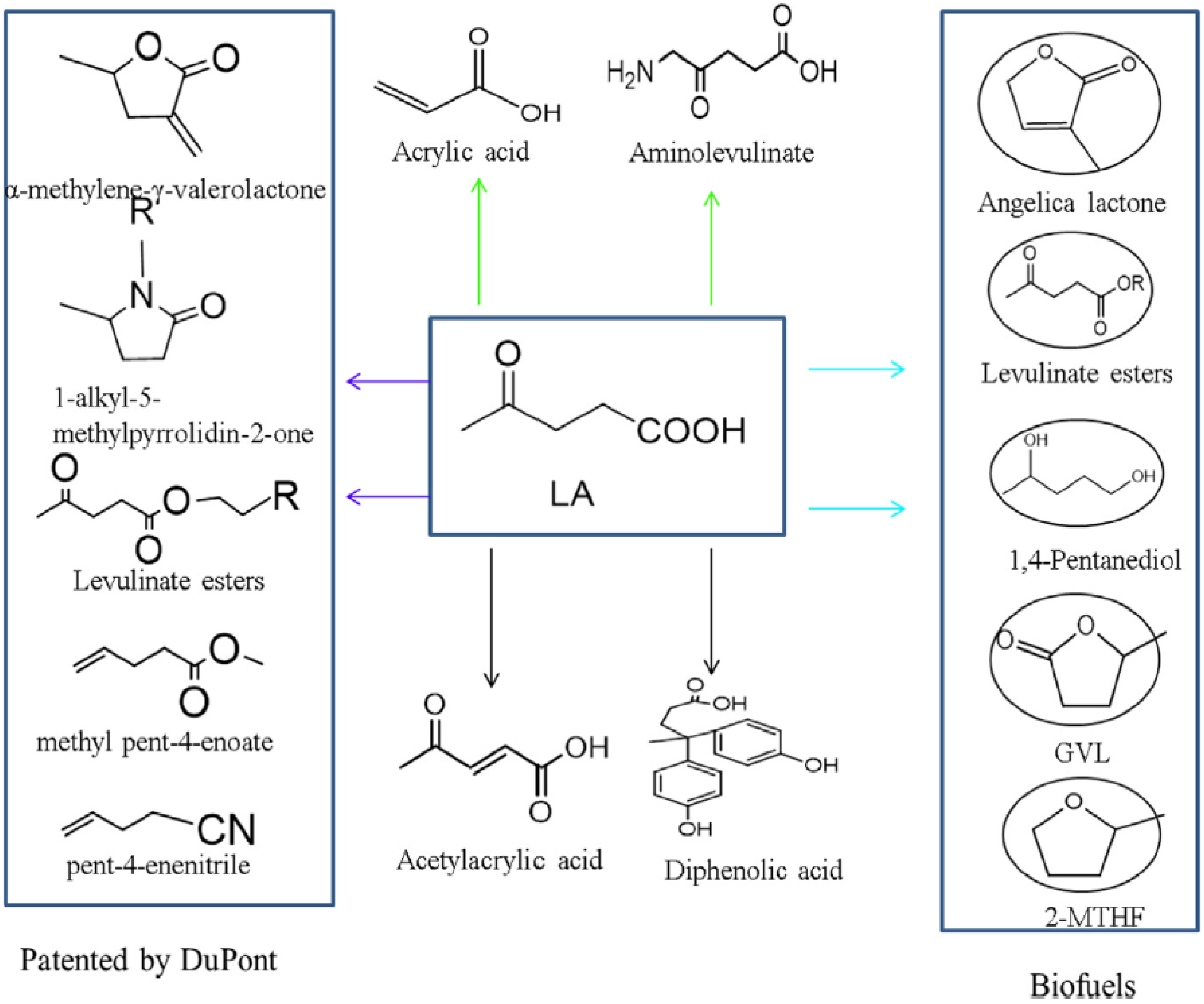
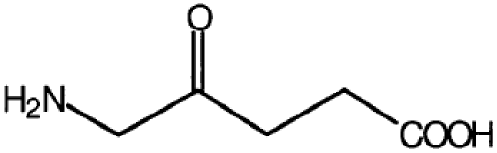


Fig. 3. Importantly value-added chemicals and biofuels from the conversion of LA [23,39].

2.2. Δ-aminolevulinic acid (DALA)

DALA (**2**) is a broad spectrum, biodegradable herbicide that shows high activity toward dicotyledonous weeds while showing little activity toward monocotyledonous crops such as corn, wheat, or barley. DALA is completely biodegradable with a broad spectrum of activity rivaling and possibly exceeding that of Monsanto's Roundup®. DALA exerts its effects by stimulating overproduction of tetrapyrroles in the plant at night. In daylight, the accumulated tetrapyrroles photosensitize the formation of singlet oxygen in the plant, leading to its death [50,51]. More recently, DALA has been found to be useful as an insecticide and as a component in photodynamic therapy as a cancer treatment [52,53].



2, DALA

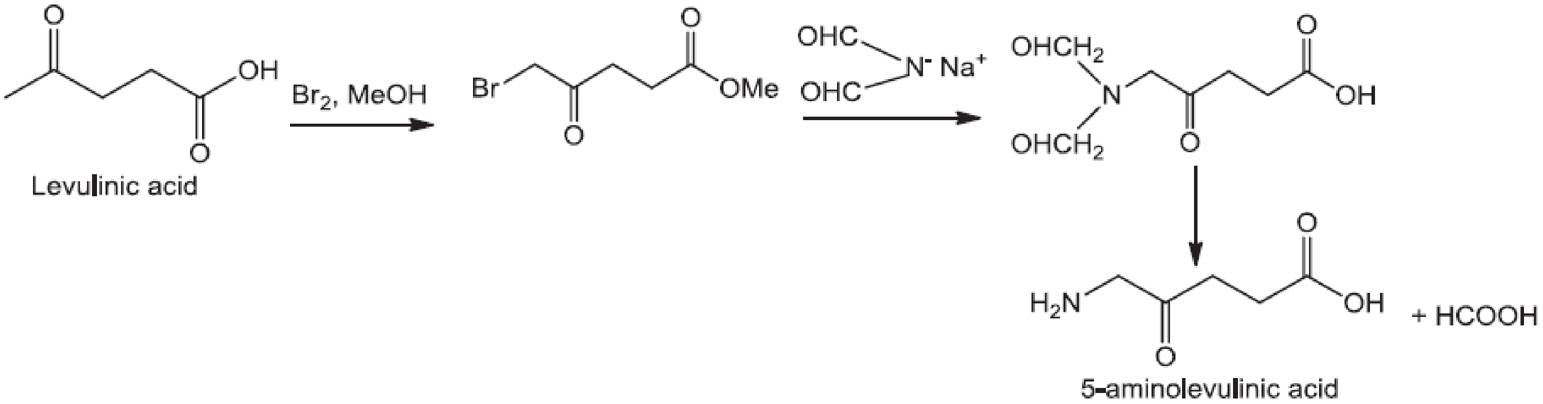


Fig. 8. NREL mechanism for the production of DALA from LA [24].

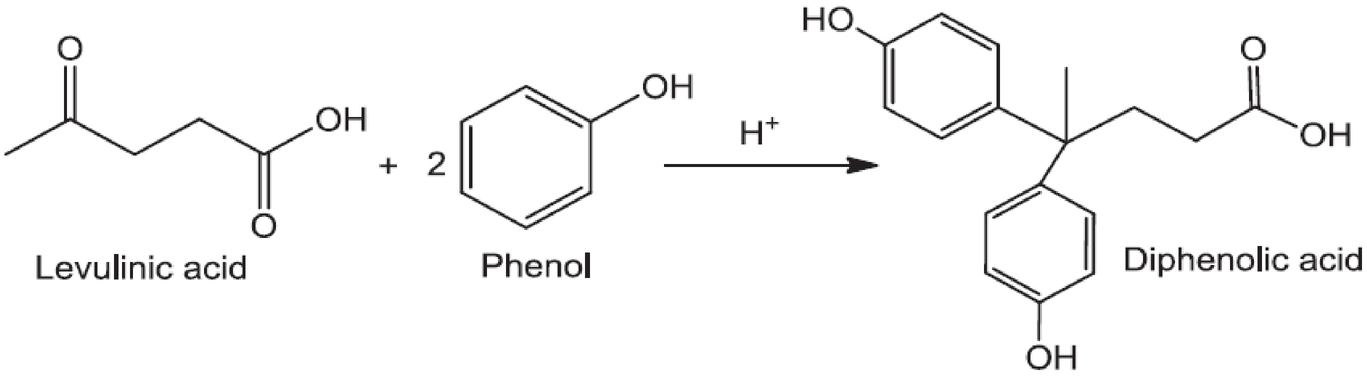


Fig. 7. Production of diphenolic acid from the condensation of LA and phenol.

Table 3
Selected diphenolic acid applications

Application	Reference
Thermoplastics	[69]
Polysulfones	[70]
Polyphenylene ethers	[71]
Hyperbranched and dendrimeric polyesters	[72]
Thermally reversible isocyanates	[73]
Phenolic and polyester resins	[74]
Polycarbonates	[75]
Heat sensitive recording media	[76]
Electronics	[77]
Printing/inks	[78]
Fragrances	[79]
Medicinals	[80]
Dyes/pigments	[81]
Lubricants	[82]
Fire retardant materials	[83]
Polymeric coatings	[84]
Adhesives	[85]
Paints	[86]

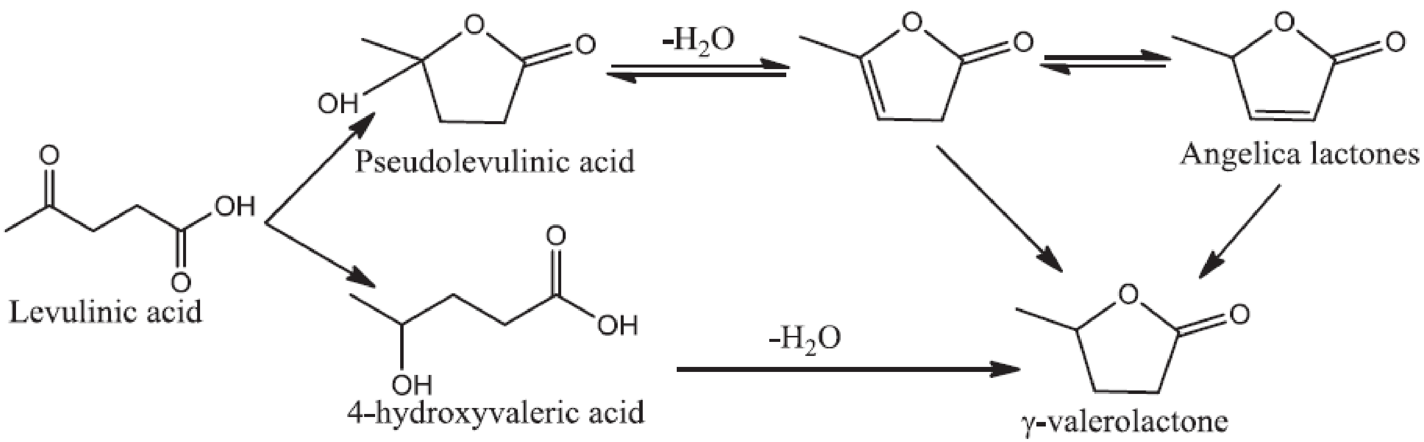


Fig. 9. Reaction pathways for conversion of LA to γ-valeroclatone.

GVL is important and promising **fuel** and also widely used commodity chemical, many studies have been performed to selectively produce GVL and it was shown that GVL can be selectively produced with good activities from LA using the Ru-derived homogeneous catalyst system. Due to the easy recycle and environmentally benign property, heterogeneous catalytic system appeared more promising. Ru- and Cu-derived nanoparticles catalysts have been developed for this purpose

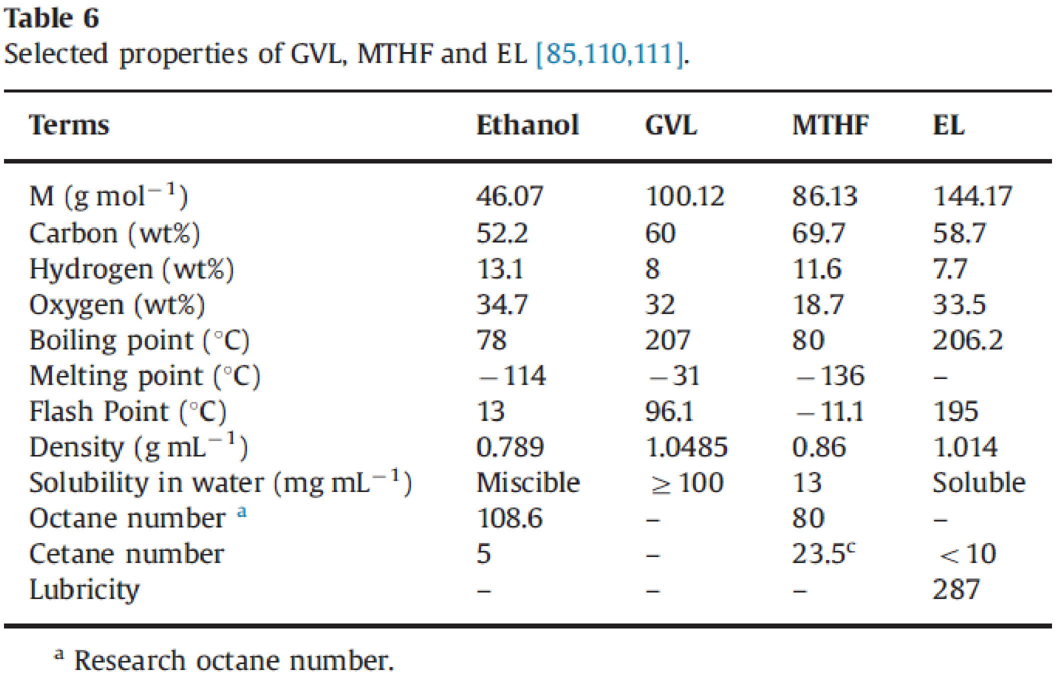


Table 6
Selected properties of GVL, MTHF and EL [85,110,111].

Terms	Ethanol	GVL	MTHF	EL
M (g mol^{-1})	46.07	100.12	86.13	144.17
Carbon (wt%)	52.2	60	69.7	58.7
Hydrogen (wt%)	13.1	8	11.6	7.7
Oxygen (wt%)	34.7	32	18.7	33.5
Boiling point (°C)	78	207	80	206.2
Melting point (°C)	−114	−31	−136	–
Flash Point (°C)	13	96.1	−11.1	195
Density (g mL^{-1})	0.789	1.0485	0.86	1.014
Solubility in water (mg mL^{-1})	Miscible	≥ 100	13	Soluble
Octane number [a]	108.6	–	80	–
Cetane number	5	–	23.5[c]	< 10
Lubricity	–	–	–	287

[a] Research octane number.

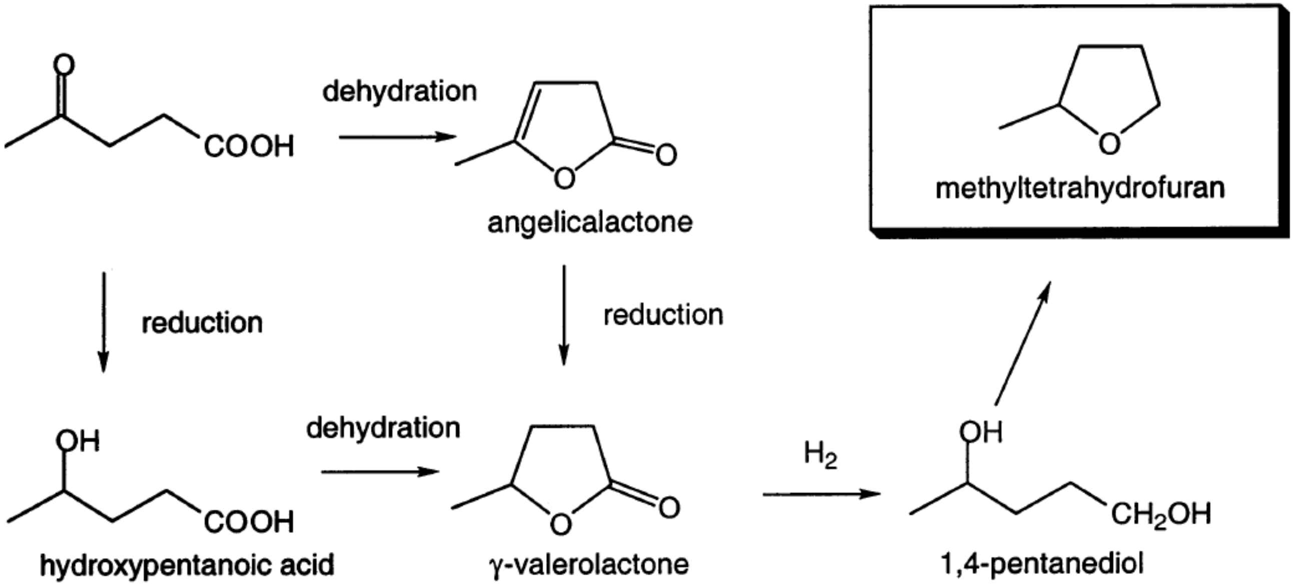


Fig. 2. Conversion of LA to MTHF.

2-Methyltetrahydrofuran (**MTHF**) is a highly flammable mobile liquid.It has reported that the direct application of GVL as a fuel additive is not so ideal and still associates with several issues in the transportation sector, such as high water solubility, blending limits for use in conventional combustion engines, possible corrosiveness in storage and lower energy density compared to petroleum-derived fuels. It has been found that MTHF can be added up to 30% by volume with petroleum with no adverse effects on performance, and engine modifications are not necessary. Different homogenous Ru-derivedcatalysts, heterogeneous Cu-composites and Noble-metalcatalysts have reported for the production of MTHF from LA .

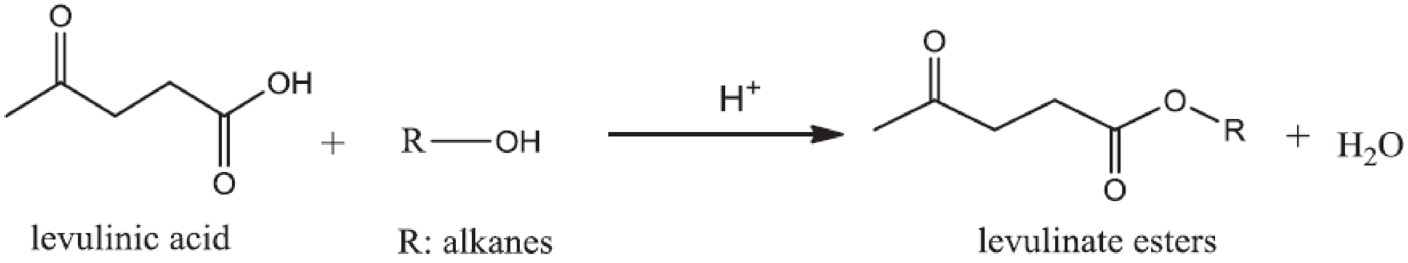
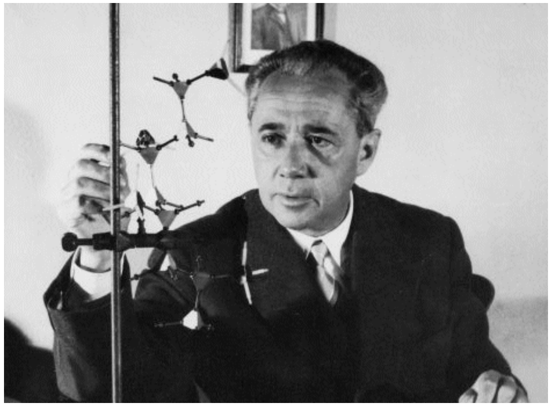


Fig. 11. Esterification synthesis of levulinate esters.

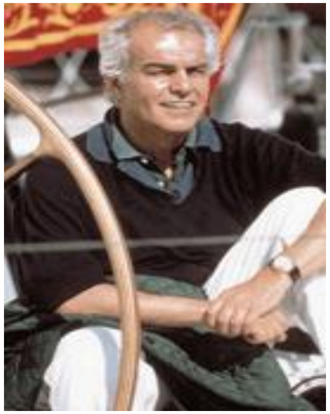
Levulinate esters are certified viable additives for gasoline and diesel transportation fuels.
These levulinate esters, like methyl levulinate, ethyl levulinate, and butyl levulinate, are the kind of short chain fatty esters displaying similar properties to the biodiesel fatty acid methyl esters(FAME). They have manifold excellent performances, such as non-toxic, high-lubricity, flashpoint stability and better flow properties under cold condition.

They can either be used in the flavouring and fragrance industries or as substrates for various kinds of condensation and addition reactions at the ester and keto groups in organic chemistry.

Italian chemistry has a long lasting tradition of visionary innovators



Giulio Natta



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