Synthesis of Green Polymers

Some interesting examples

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- There is an exceptional level of research taking place around the world on “green chemistry”.
- The by-word in all types of industry these days is ‘sustainability’ to conserve resources for future generations and reduce effects of climate change.
- The term ‘green polymer chemistry’ is used to describe production of thermoplastics / elastomers / chemicals from renewable sources.
- This means moving away from ‘fossil fuels’ as sources of basic chemicals and moving to renewable sources like renewable agricultural resources and agricultural waste products. This is no longer just an ideal but a reality as green chemical pathways to produce thermoplastics are now available and coming into commercial production.

1) **Bio Polybutylene Succinate (PBS) & co-polymers PBSA & PBST**
2) **Castor Oil ------- Sebacic Acid -------- Polyamide 610**
3) **Completely bio based & biodegradable co-polyester (Bio based 1,4 Butanediol + Azelaic Acid + FDCA)**
4) **Saccharose ------- Fructose -------- Hydroxymethylfurfural (HMF) --------- 2,5-Furandicarboxylic acid (FDCA) + MEG = Polyethylene Furanoate (PEF)**
5) **Glucose -------- Sorbitol ---------- Isosorbide ---------- Bio based PU or PC**
6) **Bio-based Plasticizers based on vegetable oils (flexible PVC)**
7) **Biobased thermoset resin based on epoxidized vegetable oils**
8) **Biobased Acetic Acid**
9) **Chemically Modified Thermoplastic Starch**

TOP BIO BASED CHEMICALS & MONOMERS FOR THE FUTURE

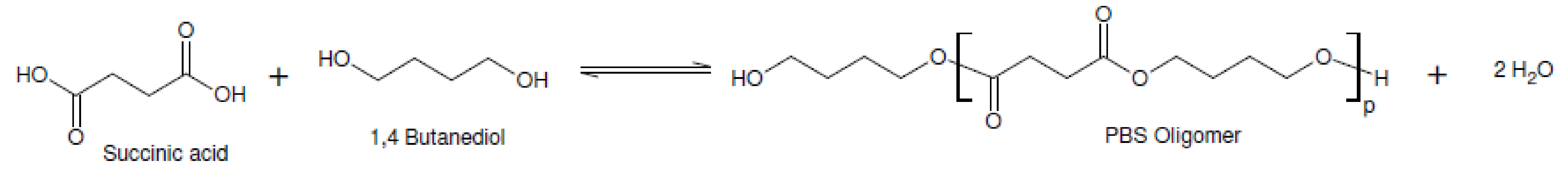
- **Bio Isoprene: **to produce polyisoprene rubber (natural rubber), thermoplastic elastomer and butyl rubber
- **Lactic acid: **Polylactide (PLA)
- **Bio Ethylene**: the chemical industry’s chemical
- **Fumaric acid: **it’s everywhere
- **Bio Propylene**: a major-league petrochemical
- **1,4-butanediol**: the base of the global apparel industry

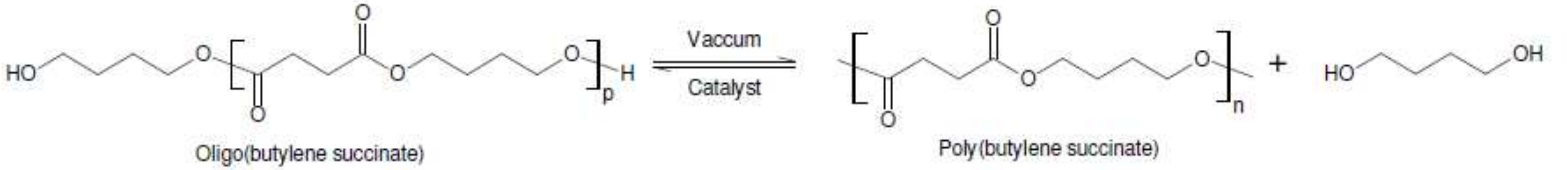
Polybutylene Succinate (PBS)

It is a biodegradable aliphatic polymer with properties that are comparable to polypropylene. Due to its higher cost PBS is blended with other biodegradable polymers like PLA, PBAT, TPS to produce compounds for making end products like packaging films, bags, containers, disposable tableware, disposable medical articles, mulch films, drug encapsulation etc.

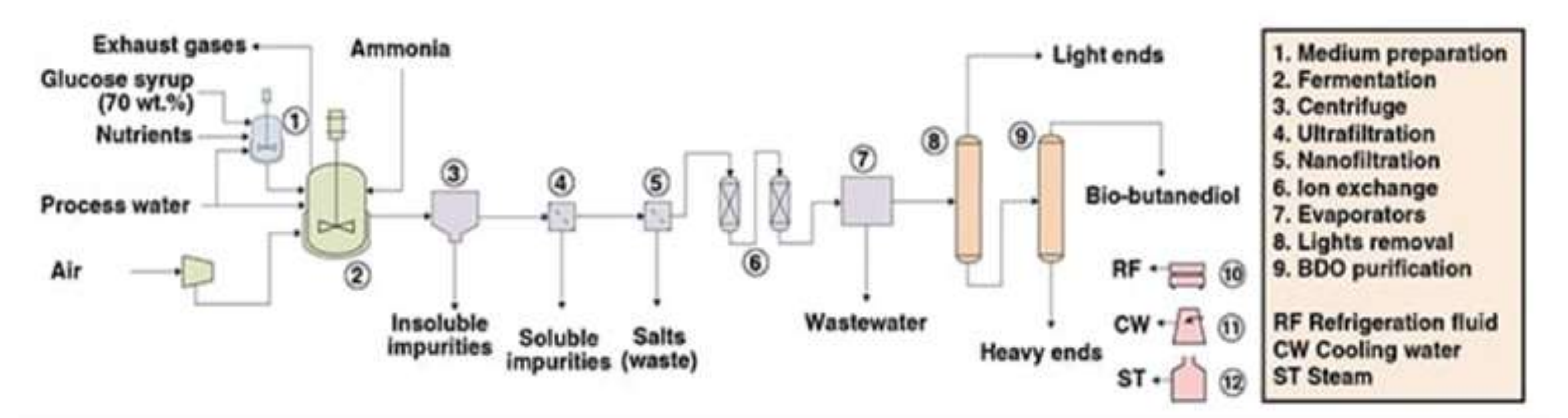
PBS consists of polymerized units of butylene succinate, with repeating $C_8H_{12}O_4$ units and is produced by direct esterification of succinic acid with 1,4 butanediol (with elimination of water) to form oligomers followed by condensation polymerization under vacuum at high temperature to form high molecular weight polymer using catalysts such as titanium or zirconium derivatives.

Oligomer formation and Polycondensation Polymerization of PBS



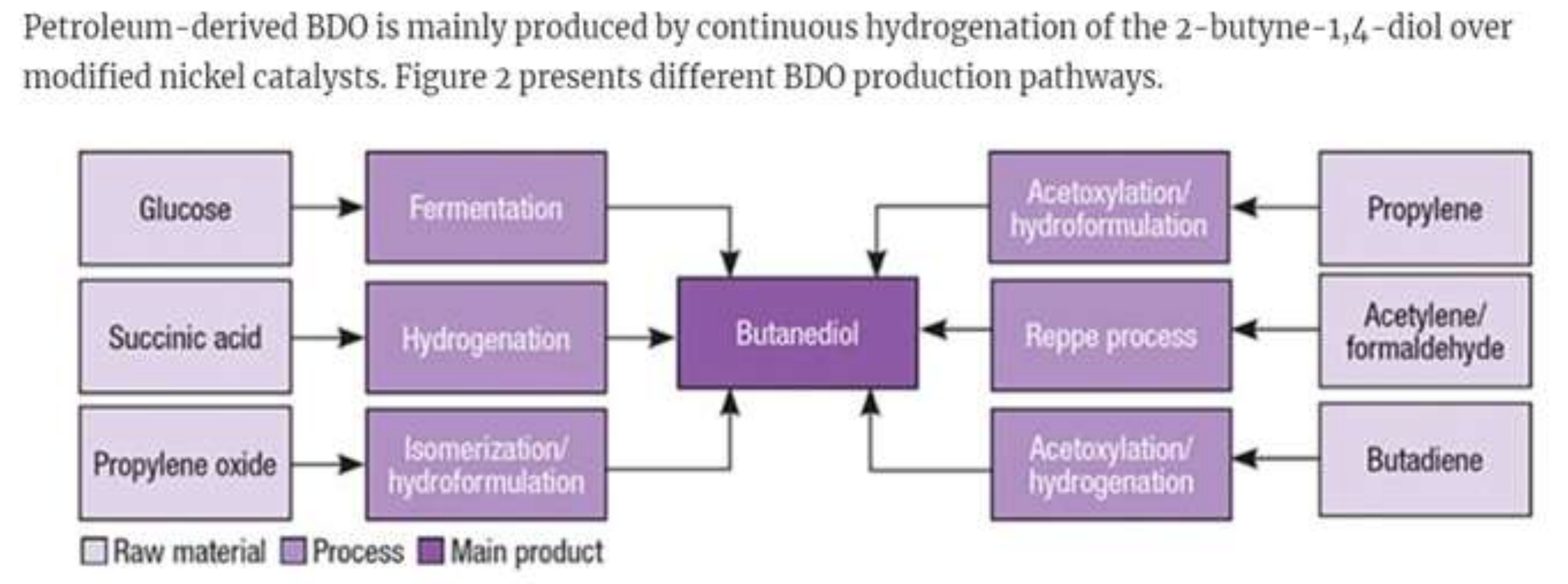


One can consider a bio-based PBS polymer made from bio derived succinic acid and butanediol. An example is Biosuccinium® produced by Roquette under DSM's license. Biosuccinium® is produced via a patented fermentation process from sustainable biomass. In addition to being a drop-in for petro-based succinic acid, it can also replace petro-based adipic acid. Compared to traditional di-acids, BIOSUCCINIUM®'s environmental footprint is much lower, which helps chemicals along the value chain meet sustainability requirements. Bio based 1,4 butanediol can be produced by the fermentation of glucose syrup along with inputs of nutrients & ammonia. An example is the process patented by Genomatica Inc. and used by Novamont to produce bio BDO.



Production of BDO via fermentation of glucose

Source Genenomatica Inc. ™



Petroleum-derived BDO is mainly produced by continuous hydrogenation of the 2-butyne-1,4-diol over modified nickel catalysts. Figure 2 presents different BDO production pathways.

- Co-polymers of PBS can be produced from succinic acid + 1,4 butanediol with either Adipic Acid or Purified Terephthalic Acid.
- Common industrial routes for production of succinic acid include hydrogenation of maleic acid, oxidation of 1,4 Butanediol or carbonylation of ethylene glycol.
- Succinic Acid + 1,4, Butanediol + Adipic Acid = **Polybutylene Succinate Adipate (PBSA)**
- Succinic Acid + 1,4, Butanediol + Terephthalic Acid = **Polybutylene Succinate Terephthalate (PBST)**
- Both PBSA and PBST have better biodegradability & processing behaviour as compared to PBS.

In future, **conversion of biomass components into** **Polybutylene Adipate Terephthalate (PBAT)** like polymers is one of the most promising and economical techniques to replace fossil fuel-based plastics. First biobased BDO obtained through industrial biological fermentation can replace petrochemical BDO in PBAT directly. Secondly, sebacic acid, as a substitute of adipic acid, coming from castor oil can be used as monomer to prepare poly (butylene sebacinate-*co*-butyleneterephthalate) (PBSeT) co-polyesters.

1,4, Butanediol + Sebacic Acid + Terephthalic Acid = **Polybutylene Sebacinate Terephthalate (PBSeT)**

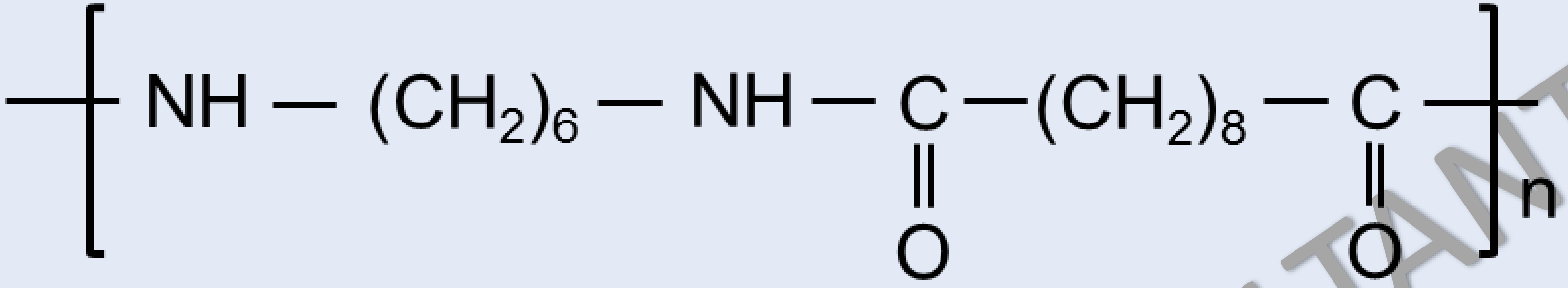
The **DAVY™ butanediol process** can produce in a single reaction train, varying ratios of three products: 1,4 butanediol (BDO), tetrahydrofuran (THF) and gamma butyrolactone (GBL). This flexible process uses maleic anhydride, which can be obtained by the oxidation of butane or benzene, as the feedstock. Maleic anhydride is esterified using a proprietary reaction column and a solid esterification catalyst to form a di-methyl maleate intermediate ester which is then hydrogenated in the vapour phase to produce a mixture of BDO, THF and GBL. By varying the operating conditions and catalyst exposure the ratio between BDO and THF can be changed to suit market conditions. The GBL is always produced and can be either recycled or extracted as required.

Castor Oil ------- Sebacic Acid -------- Polyamide 6,10

Sebacic acid can be produced from castor oil (which is essentially glyceryl ricin-oleate). Castor oil is treated with caustic soda at high temperature (250 °C) to carry out saponification, leading to the formation of ricin-oleic acid, which is followed by a reaction giving sebacic acid and octanol.

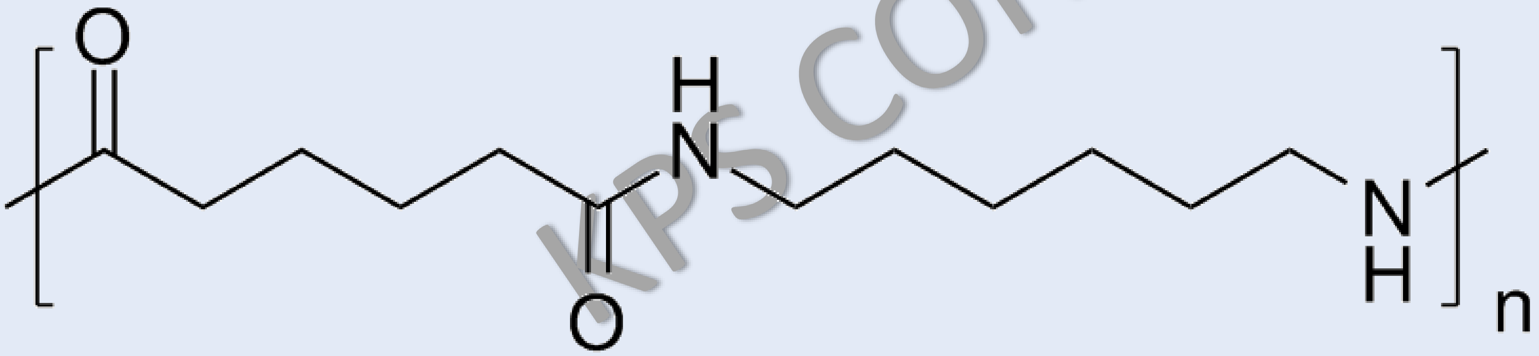
Nylon 6,10 is produced by the reaction of hexamethylenediamine with sebacic acid, initially to form a 1:1 nylon 610 salt, which is then polymerized at about 240 °C. The polymer has a melting point of around 216 °C and a low water absorption, which gives it better dimensional stability and electrical properties than nylon 6 and nylon 6.6. It is a commercially important polymer and is often used in place of nylon 6 and nylon 6.6 in engineering plastics applications. Mechanical properties of the polymer are lower than those for nylon 6 / 6,6 (tensile modulus is typically 70% of the other two polymers).

Polyamide 6-10 or Poly(hexamethylene sebacamide)



$$-\!\!\left[\mathrm{NH} - (\mathrm{CH_2})_6 - \mathrm{NH} - \underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}} - (\mathrm{CH_2})_8 - \underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}} \right]_n\!\!-$$

Polyamide 6,6 or Poly(hexamethylene adipamide)



- Bio-based Rilsan® PA11 from Arkema produced from a renewable source (castor oil) Rilsan® PA11 is used in various applications due to its excellent chemical resistance, easy processing, high and low-temperature performance (-40°C to +130°C), high dimensional stability, and low density.
- automotive, textile, oil & gas, wire & cables, electronics
- extrusion, extrusion-blow moulding, injection moulding, roto moulding, 3D printing
- Pragati initiative (sustainable castor initiative) members are Arkema, BASF, Jayant Agro-Organics, and Solidaridad, an international civil society organization.
- Pragati means 'progress' in Hindi.
- The goals of Pragati are to enhance castor productivity in India, where the majority of the world's supply originates. This is accomplished by training farmers to build capacity, improve yields, and reduce environmental impacts, thus helping them to cultivate castor beans effectively and ecologically.

Some of the key features inherent in the castor crop as a favoured renewable feedstock for polymers & additives:

- Naturally drought resistant
- Does not cause deforestation in India
- Not in competition with human or animal food chains
- Resistant to many insects
- Considered to be a profitable crop with low inputs and high returns
- Harvested 4-6 months after planting
- Grown mainly in India (75% of the world's supply) - Primarily in the state of Gujarat
- Grown by approximately 700,000 farmers in India alone!
- Also used to make ingredients for lubricants, coatings, pharmaceuticals

2, 5-furandicarboxylic acid (FDCA) is regarded as one of the most high-potential biobased aromatic monomers. It is a perfect bio-based alternative to the petroleum-based PTA. Hence, it is foreseeable that whole bio-based aliphatic-aromatic co-polyesters will be formed in a few years. For example, a completely bio based & biodegradable co-polyester can be produced with

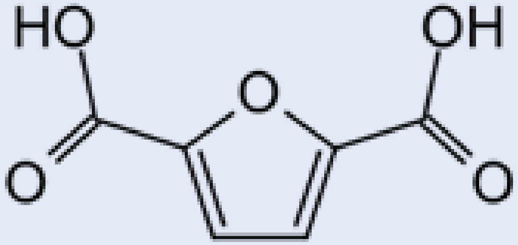
Bio based 1,4 Butanediol + Azelaic Acid + FDCA

Adipic acid is substituted by vegetable oil-based azelaic acid (diacid produced from rancidity of oleic acid) and PTA is replaced by biobased FDCA

Saccharose -------- Fructose --------- Hydroxymethylfurfural (HMF) --------- 2,5-Furandicarboxylic acid (FDCA) + MEG = Polyethylene Furanoate (PEF)

A biobased replacement for PET with better mechanical & barrier properties

Industrial process for production of FDCA involves oxidation of hydroxymethylfurfural (HMF) with air over different catalysts. Oxidation of HMF under strongly alkaline conditions over noble metal catalysts gives highest yield of FDCA. 2,5-Furandicarboxylic acid is an organic chemical compound consisting of two carboxylic acid groups attached to a central furan ring.



FDCA

Poly (tetramethylene ether) glycol or PTMEG is a linear polyether glycol with hydroxyl groups on both ends. As a polyol, it reacts readily with isocyanates to form polyurethanes. The chief uses of PTMEG are in the production of spandex (polyurethane) fibers, polyurethane elastomers, and copolyester -ether elastomers.

The most widely used method of manufacturing PTMEG is based on mixing **tetrahydrofuran (THF)** with a fluorosulfonic acid (FSA) catalyst (HSO_3F). During this reaction, the primary polymerization products formed are poly(tetramethylene ether) chains with sulfate ester groups. The sulfates are then hydrolyzed with water and the acid is removed. In the water extraction step, all water-soluble short polyether chains are also removed and the molecular weight distribution becomes narrower.

Newer PTMEG facilities use variations of the acetic anhydride process. In this type of process, the THF ring is opened by a strong acid catalyst and then reacted with acetic anhydride to form PTMEG diacetate, which is then converted to polyether glycol via alcoholysis.

Spandex is the largest end-use application for PTMEG, accounting for nearly 80% of global demand. The elastomeric fiber is used mainly in apparel, including undergarments, hosiery, and athletic outfits. Polyurethanes are produced mainly from polyols and diisocyanates, where the polyol portion (in this case, PTMEG) forms the soft segment and the diisocyanate provides the hard segment.

PTMEG is used for thermoplastic polyurethane (TPU) and cast urethane elastomers, and in urethane adhesives, sealants, and surface coatings. Products made from PTMEG- based urethane elastomers include automotive and aviation hoses and gaskets, forklift tires and wheels, roller skate wheels, industrial belts, tank and pipe liners, mining and oil production pump liners, shoes (e.g., athletic shoes), apparel such as leather coats, and medical prostheses, catheters, and other medical devices. The advantages of PTMEG-based urethanes are resistance to hydrolysis and fungus, flexibility at low temperatures, low heat buildup, high resiliency, low viscosity, and very low noise characteristics.

Copolyester-ether elastomers (COPE) are high-performance engineering materials that bridge the gap between the more flexible elastomers and the rigid plastics. COPE is relatively easy to process, resistant to oil and many chemicals, and have low-temperature-flexibility characteristics. COPE is used in many automotive applications, such as seating, airbag deployment, air intake ducts, and hoses and tubing, as well as in breathable films for medical applications.

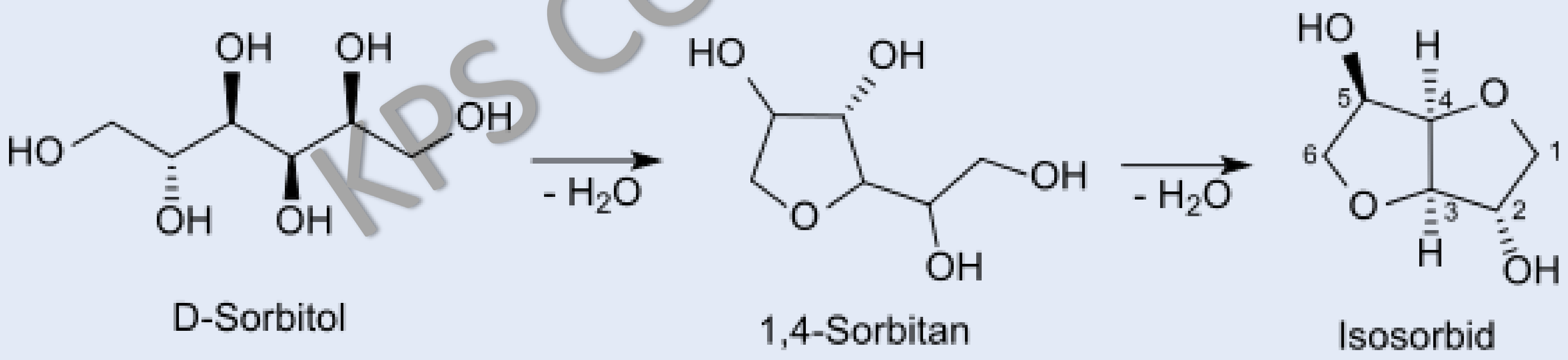
Poly (oxytrimethylene ether) glycol also known as PO3G is a polyol made from 1,3 propanediol. As a polyol, it reacts readily with isocyanates to form polyurethanes. PO3G can be a 100 % biomaterial-based eco-friendly bio polyol that is made by fermenting corn i.e. bio based 1,3 propanediol produced from fermentation of sugars (sugarcane molasses, corn syrup, beet root sugar etc.). PO3G is used mainly for products that require elasticity, such as **polyurethane and spandex**. Products made with PO3G have the advantage of being smoother and having improved elasticity and abrasion resistance over existing products, making them more wearable with less deformation.

The polymer can be based on petrochemical derived or renewably sourced monomer, 1,3-propanediol (PDO), which has a lower environmental footprint compared to the chemically derived monomer, with both lower amount of greenhouse gas emissions and energy use. PO3G is produced by polymerization of 1,3 propanediol using tetrafluoroethane sulfonic acid (TFESA) at high temperatures (around 212 °C). The initial high color (brown) and high unsaturated impurities of the polymer are overcome by careful control of the processing conditions.

Glucose -------- Sorbitol ---------- Isosorbide ---------- PU or PC

Hydrogenation of glucose gives sorbitol. Isosorbide is obtained by acid-catalyzed dehydration of D-sorbitol which yields the monocyclic furanoid sorbitan, which in turn forms by further dehydration into the bicyclic furofuran derivative isosorbide.

The reaction gives about 70 to 80% isosorbide in addition to 30 to 20% of undesirable by-products which must be removed by distillation, recrystallization from alcohols, recrystallization from the melt or by a combination of these methods. A high purity product (> 99.8%) is essential for the use as a monomer when high molecular weight polymers have to be produced.



Isosorbide from renewable raw materials is of interest as a monomer for thermoplastic (bio)polymers such as polyesters and polycarbonates, as well as for thermosets such as polyurethanes and epoxy resins. Isosorbide is of interest as a monomer for polycarbonate where it can replace Bisphenol A (an identified xenoestrogen). Limitations of isosorbide-based polycarbonates are their unsatisfactory temperature resistance and limited impact resistance, which has to be improved by addition of co-monomers to the isosorbide or by polymer blends.

When MEG as a diol is replaced with isosorbide in the polyester PET, polyisosorbide terephthalate (PIT) is obtained, which has high thermal stability. However, the PIT produced has lower molecular weight and high residual content of terephthalic acid leading to insufficient chemical stability of the resulting polymer.

The use of isosorbide as a comonomer in PET as a bottle raw material and as a substitute for bisphenol A, especially in thermosetting polycarbonates, is currently considered particularly promising.

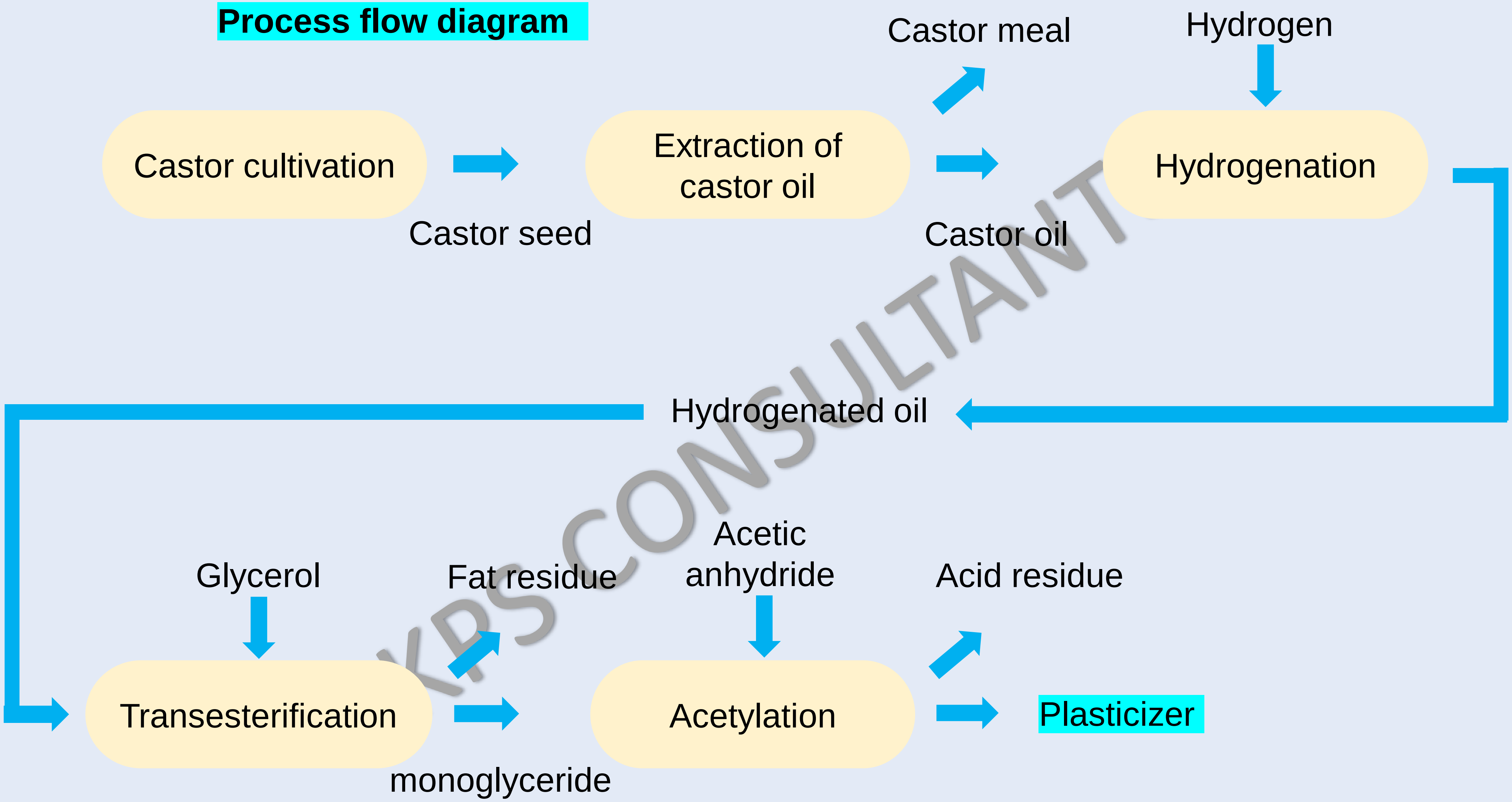
In polyurethanes, isosorbide itself can serve as a diol or as a building block for the polyol as well as for the diisocyanate component or as a chain extender.

Bio-based Plasticizers based on vegetable oils

Plasticizers are compounds incorporated in a polymer to increase its flexibility and improve its process-ability. Earlier phthalate-based plasticizers represented 85% of the total plasticizers market. However, ban on usage of HMW phthalate-based plasticizers in consumer goods, food packaging, toys and medical products have led to the development of eco-friendly bio-based plasticizers. Further, stringent government regulations and rising health concerns are stimulating demand for non-phthalate and bio-plasticizers in other end applications. Flexible PVC product manufacturers are increasingly switching to non-phthalate plasticizers like Epoxy Esters of Soybean Oil & Linseed Oil, Phosphate Esters, Terephthalates, Acid Esters (Sebacates, Adipates) and other bio-based plasticizers.

- Renewable, agricultural, non-edible oil based bio plasticizer is well placed to replace phthalate based and other competing plasticizers in soft PVC compounds without sacrificing product performance at a competitive cost.
- Castor Oil based plasticizer is an ideal choice due to its abundant availability in India, non-edible nature and its chemistry that enables production of plasticizer with superior functionality.
- Basic process of converting castor oil into plasticizer involves two steps. The first step involves Trans-esterification of hydrogenated castor oil with glycerol and the second step involves Acetylation of the product from the first step with acetic anhydride to produce plasticizer. Bio-plasticizers can be also manufactured from other oil-seeds like cottonseed oil, palm oil, rice bran oil, linseed oil etc.
- Food grade plasticizers can be produced from biobased based glycerine derivatives. Examples are Acetylated Monoglycerides (AMG), Acetylated Citric Acid Esters of Monoglyceride (ACMG), Polyglycerol Esters of Fatty Acids (PGE), Calcium or Zinc Stearoyl Lactylate etc.

Process flow diagram



Castor cultivation

Castor seed

Extraction of castor oil

Castor meal

Castor oil

Hydrogen

Hydrogenation

Hydrogenated oil

Glycerol

Transesterification

Fat residue

monoglyceride

Acetic anhydride

Acetylation

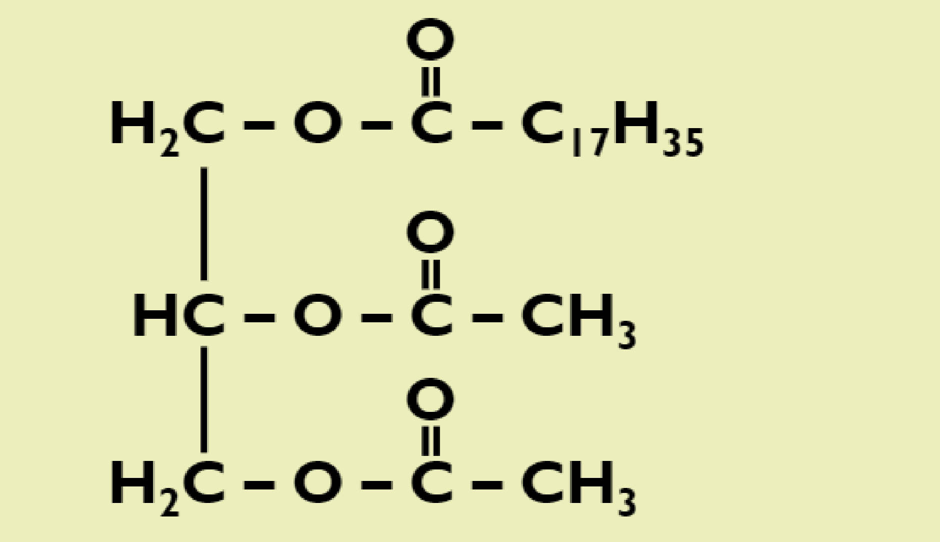
Acid residue

Plasticizer

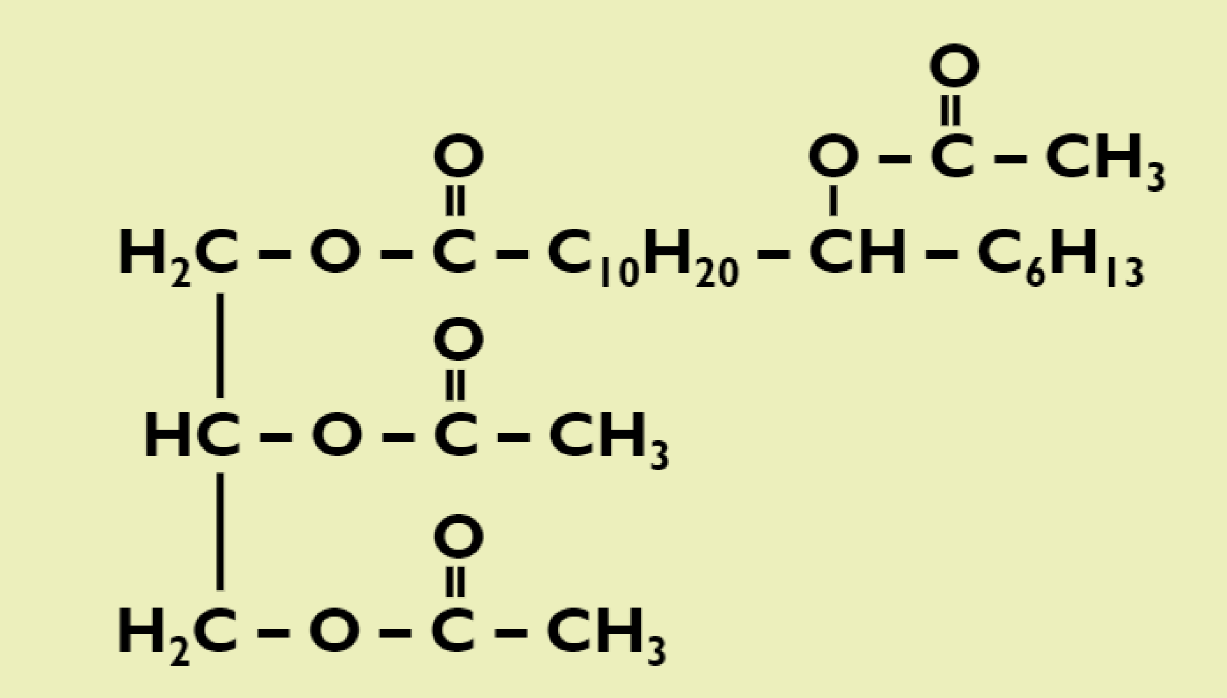
Key target market segments for bio-plasticizers (for flexible PVC products)

- Medical - e.g. infusion bags, blood bags, tubing and various others
- Pharma - e.g. transparent blister packaging for tablets
- Food packaging – film & sheet
- Toys & consumer (skin-contact) goods
- Wire & cable jacketing
- Vinyl flooring, waterproofing sheets, tarpaulins
- Coated fabric & rainwear
- Building construction & irrigation
- Automotive components (specially for export to EU & NA)
- Thermoplastic elastomers like NBR / PVC blends

The Bio-plasticizer is acetic acid ester of monoglycerides made from fully hydrogenated castor oil



Fully acetylated glycerol monostearate



Fully acetylated glycerol monostearate on 12 hydroxystearic acid

Source: Grindstead Soft-N-Safe™ by Danisco

Estolide esters of vegetable oil fatty acid alkyl esters where the vegetable oil has an unsaturation of greater than 90 Iodine Value. Examples include soybean oil, canola oil, rapeseed oil, sunflower oil, corn oil, safflower oil, camelina oil, and linseed oil.

An "estolide ester" is an aliphatic ester esterified to the backbone carbons of a long chain unsaturated fatty acid at the site of unsaturation Vegetable oils contain both saturated and unsaturated fatty acids. The estolide esters are acyl chains attached to the backbone carbons of the fatty acid at the site of unsaturation (eg, linoleic acid, á-linoleic acid, and oleic acid) Each unsaturated fatty acid alkyl ester has greater than one estolide ester functionality.

The vegetable oil fatty acid alkyl esters can be C 1 - C4 alkyl esters. Examples include methyl and isobutyl esters. The unsaturated fatty acid alkyl esters are fully estolided. By "fully estolided" it is meant that all available unsaturated reaction sites are reacted to form an estolide ester functionality e.g., esters derived from carboxylic acids having 1 to 4 carbon atoms - acetate esters

The estolide esters may be prepared by

(a) treating the vegetable oil fatty acid alkyl esters with an oxidizing agent to form a reaction product comprising epoxy and hydroxyl groups covalently bonded to the fatty acid alkyl esters at the site of unsaturation, and

(b) treating the reaction product with an acylating agent to react the epoxy and hydroxyl groups to form estolide esters covalently bonded to the unsaturated fatty acid alkyl esters such that each fatty acid alkyl ester has on average greater than one estolide ester functionality.

Thermoset Polymers from renewable agricultural source like Vegetable Oils

- Epoxidized vegetable oils (EVOs) can be reacted with disulfide-based aromatic dicarboxylic acid (DCA) to produce thermoset materials with high biobased content (50 to 80%)
- Vegetable oils (VOs) are extracted from seeds by solvent extraction or by the pressing process. More than 95% of VOs constitute triglycerides, containing three fatty acids branched to a glycerol unit.
- Considering the growing amount of fiber-reinforced composite materials due to their outstanding properties in terms of lightweight, high weight-to-strength ratio, and long durability, the next generation of bio-based thermosetting resins need to be cost-effective and based on nondepletable bio-based resources.

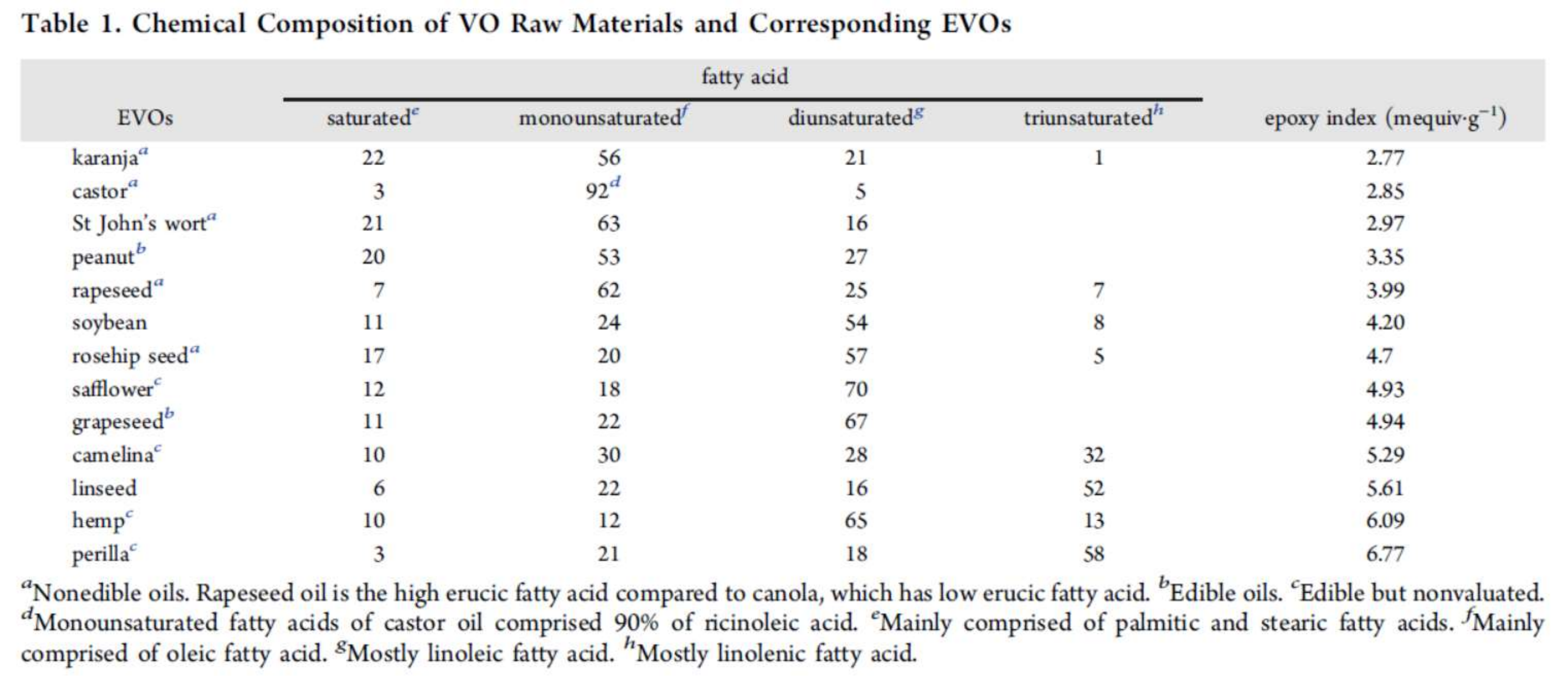
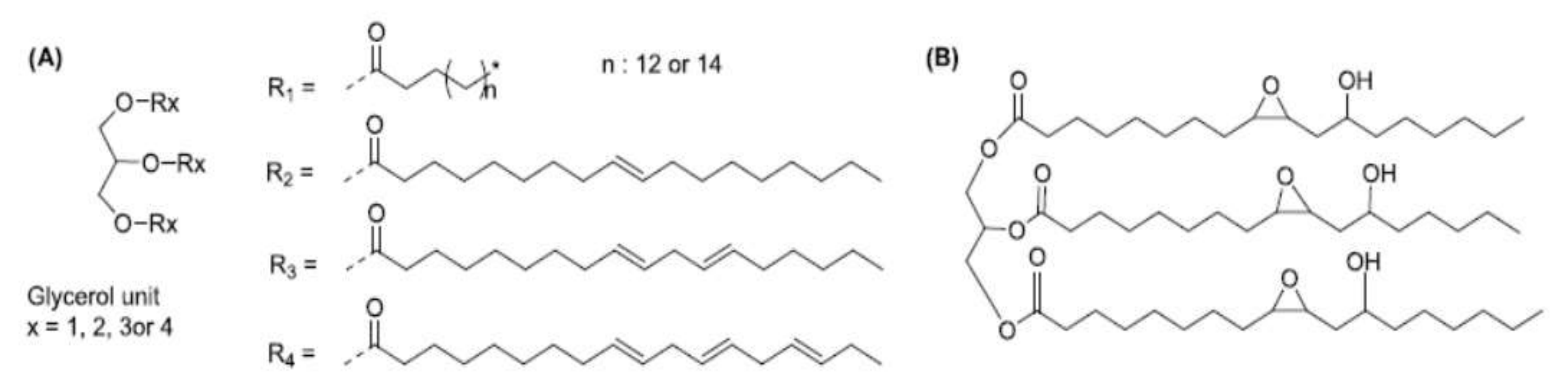


Table 1. Chemical Composition of VO Raw Materials and Corresponding EVOs

EVOs	fatty acid				epoxy index (mequiv·g^{-1})
	saturated[e]	monounsaturated[f]	diunsaturated[g]	triunsaturated[h]	
karanja[a]	22	56	21	1	2.77
castor[a]	3	92[d]	5		2.85
St John's wort[a]	21	63	16		2.97
peanut[b]	20	53	27		3.35
rapeseed[a]	7	62	25	7	3.99
soybean	11	24	54	8	4.20
rosehip seed[a]	17	20	57	5	4.7
safflower[c]	12	18	70		4.93
grapeseed[b]	11	22	67		4.94
camelina[c]	10	30	28	32	5.29
linseed	6	22	16	52	5.61
hemp[c]	10	12	65	13	6.09
perilla[c]	3	21	18	58	6.77

[a] Nonedible oils. Rapeseed oil is the high erucic fatty acid compared to canola, which has low erucic fatty acid. [b] Edible oils. [c] Edible but nonvaluated. [d] Monounsaturated fatty acids of castor oil comprised 90% of ricinoleic acid. [e] Mainly comprised of palmitic and stearic fatty acids. [f] Mainly comprised of oleic fatty acid. [g] Mostly linoleic fatty acid. [h] Mostly linolenic fatty acid.

Ref: Sustainable Series of New Epoxidized Vegetable Oil-Based Thermosets with Chemical Recycling Properties



(A) General structure of epoxidized vegetable oils (EVOs) (B) structure of epoxidized castor oil

Epoxidized linseed oil and epoxidized castor oil (monomer) can be reacted with disulfide-based aromatic dicarboxylic acid (hardener) at required molar ratio between epoxy and acid groups followed by an initiator to produce thermoset materials with high biobased content

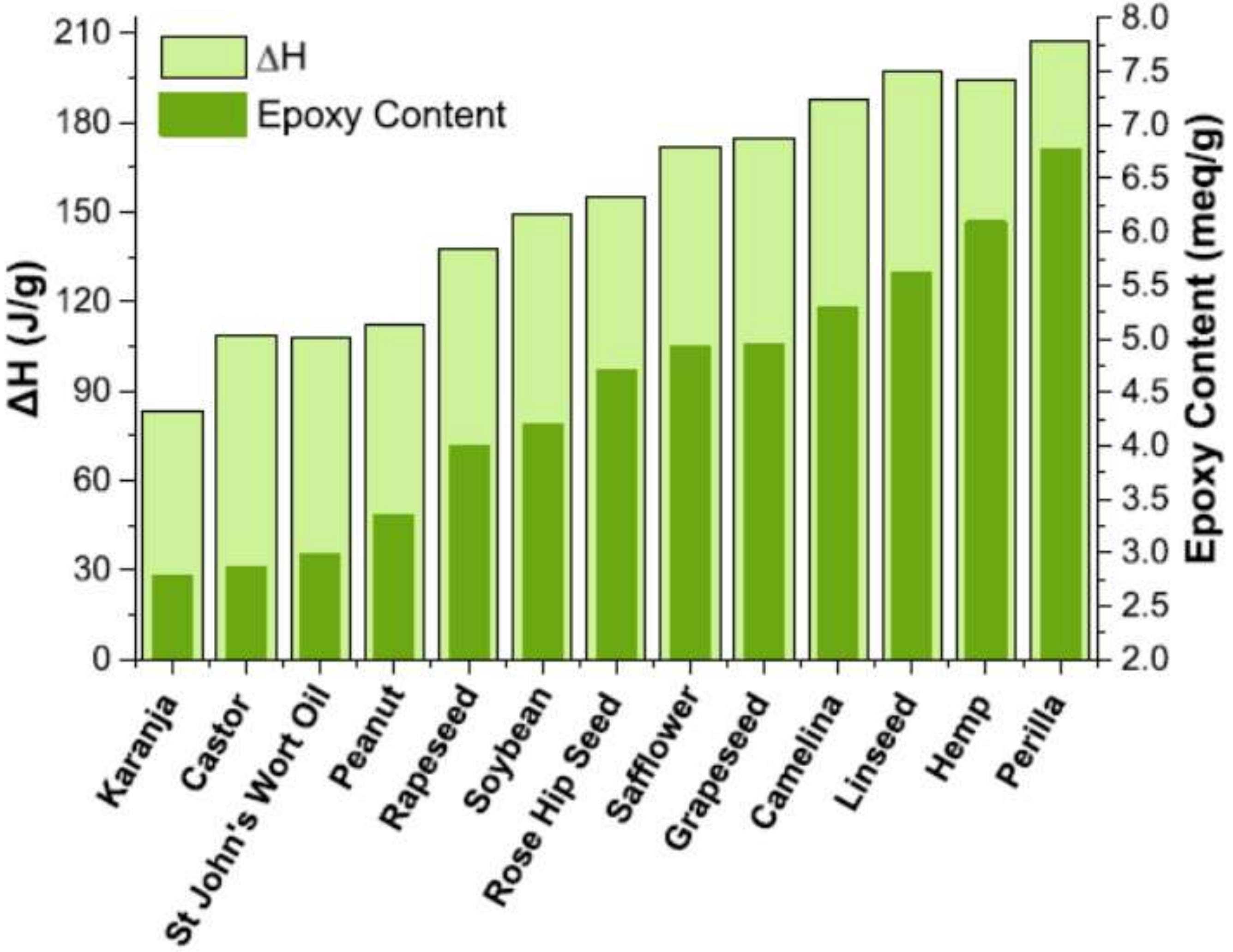


Figure 2. Correlation of the EVOs/DTBA/IM copolymerization enthalpy and monomers' epoxy content.

Ref: Sustainable Series of New Epoxidized Vegetable Oil-Based Thermosets with Chemical Recycling Properties

Epoxidized castor oil

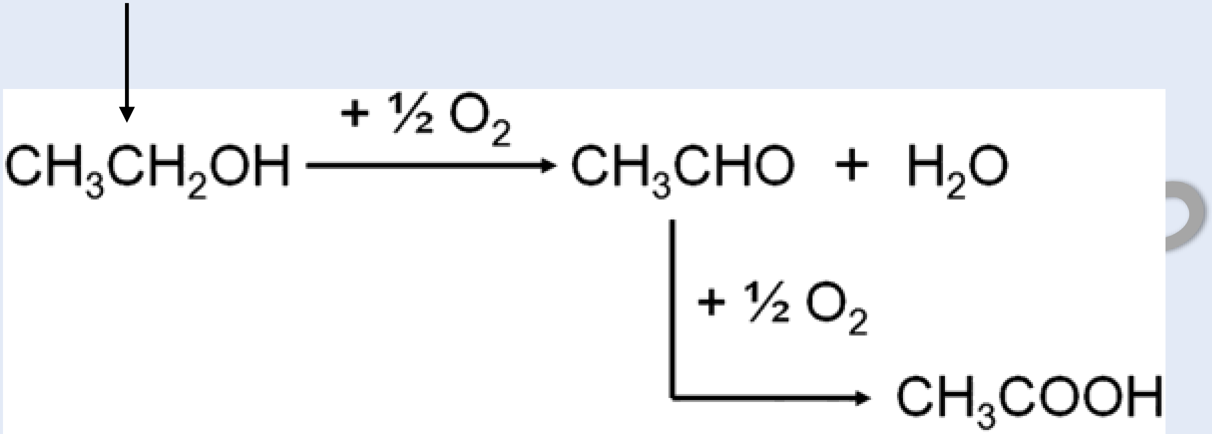
soyabean oil, linseed oil

YM & Stress at break (MPa)

Biobased Acetic Acid

- Acetic acid made by biobased routes for centuries - vinegar (in Latin *acetum*)
- Today, vast majority of acetic acid is made synthetically.
- Historically, derived from petroleum via cracking, yielding ethylene. Ethylene is hydrated using acid catalyst to produce ethanol. Oxidization of ethanol to acetaldehyde, with subsequent oxidization using manganese catalyst, yields AA
- Nowadays acetic acid is produced via carbonylation – reacting methanol and carbon monoxide over a catalyst. Not only is it an energy-intensive route, relies on the fossil-based natural gas as the source of feedstock syngas.
- Worldwide acetic acid production capacity is at almost 21,000 kilotons per annum in 2023, according to Tecnon OrbiChem
- Acetic acid is used in the production of vinyl acetate monomer (VAM) employed in paints, coatings, sealants, adhesives and ink for textile printing. It is also used to manufacture purified terephthalic acid (PTA) that goes into textiles and plastics.

Biobased Ethanol from fermentation of Molasses



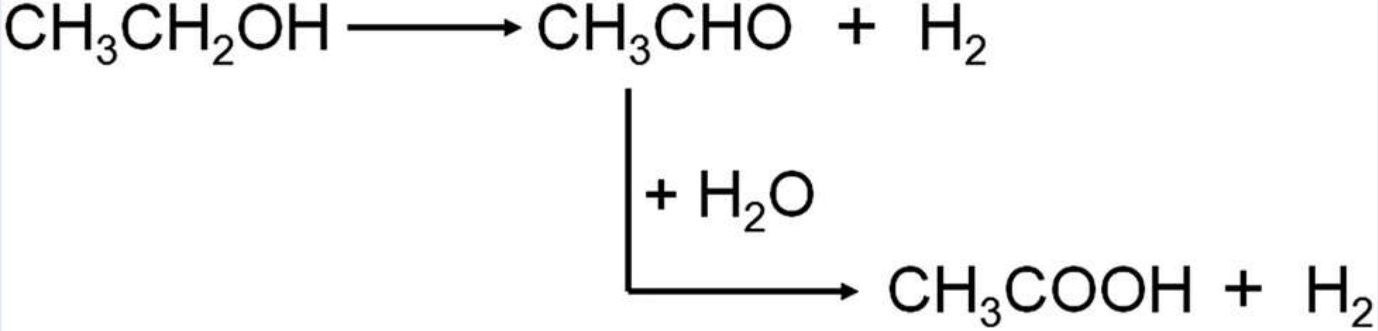
$$CH_3CH_2OH \xrightarrow{+\frac{1}{2}O_2} CH_3CHO + H_2O \xrightarrow{+\frac{1}{2}O_2} CH_3COOH$$

Route1: Two step oxidation of ethanol to acetic acid

Ethanol is firstly oxidized to acetaldehyde and the acetaldehyde is then oxidized to acetic acid. This reaction is considered as a green catalytic process for the only reduction product is water. However, safety is one of the major issues concerning O_2 based oxidation process, in relation to flammability limits and explosion hazards

Examples of catalysts used CuCr based compounds, $K_2Cr_2O_7$ or Potassium dichromate

Biobased Ethanol from fermentation of Molasses



Route 2: “aldehyde–water shift” reaction (AWS)

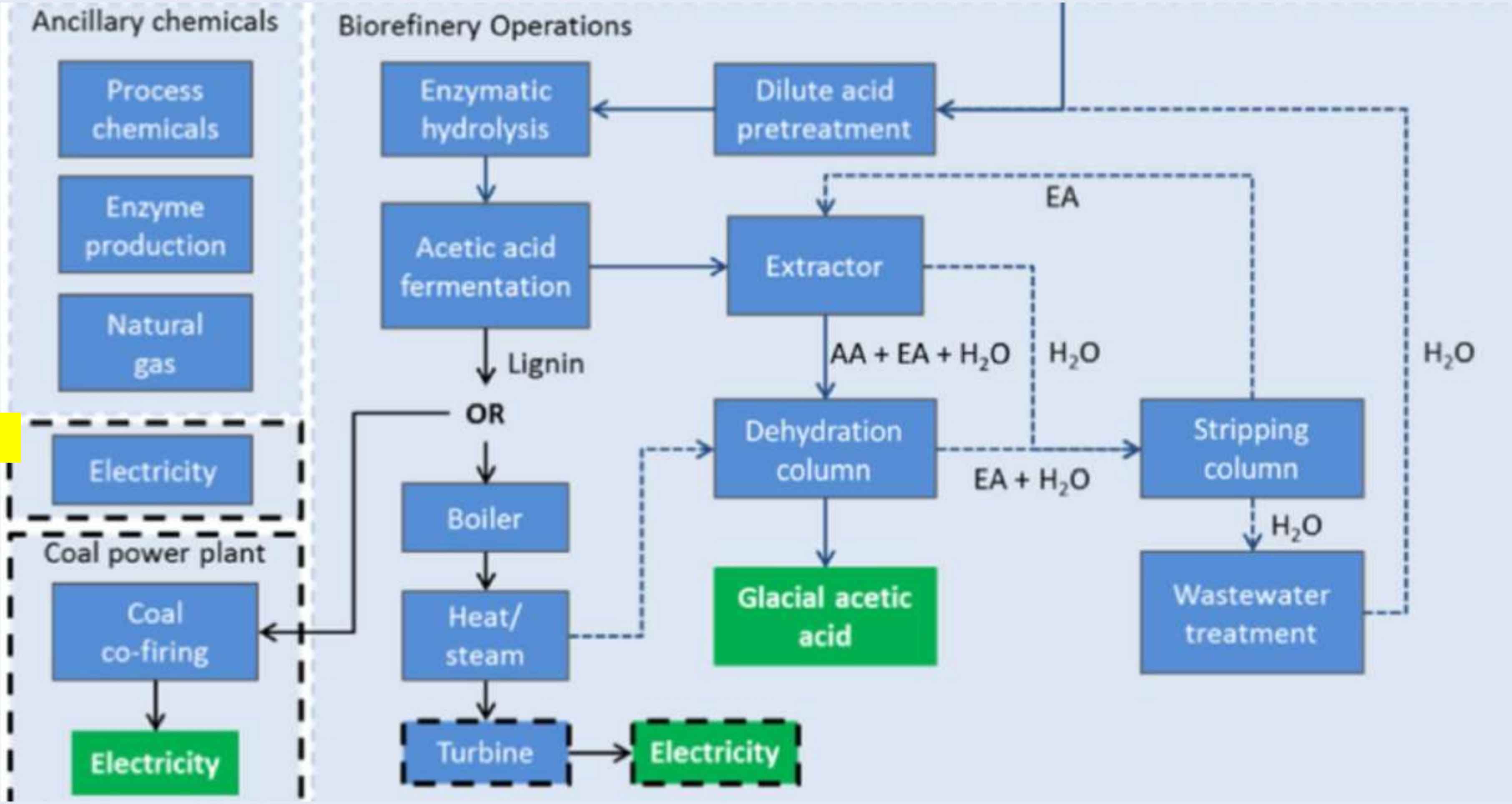
When O_2 is non-existent in the reaction system, ethanol is dehydrogenated to produce acetaldehyde, and then water, acting as the oxidizer, reacts with acetaldehyde to produce acetic acid, concomitantly releasing hydrogen gas.

Examples of catalysts used are SnO_2-supported molybdenum oxides

ZnO catalyst inhibits the acetaldehyde aldol-condensation to crotonaldehyde

Pretreated Biomass Feedstock

Enzymatic
Chemical Route



- Swedish company Sekab produces acetic acid sustainably. The company converts different types of biomass from forestry and agriculture into ethanol. The ethanol yield is then refined to biofuels and chemicals - Acetaldehyde, ethyl acetate and acetic acid
- Using molasses-based ethanol for feedstock, India’s Godavari Biorefineries Ltd. produces biobased acetic acid at its Maharashtra-based facility.
- In Europe, Lenzing – a producer of specialty fibres for the textile and nonwovens industries – commercialised biobased acetic acid along with partners including German specialty chemicals company Evonik 40 years ago. (sourced beech wood)

Chemically Modified Thermoplastic Starch

Starch is renewable, readily biodegradable, easily modified both physically and chemically, available in bulk in all parts of country, making it an attractive raw material for manufacture of “green” plastics.

Bio-based polymer from renewable agricultural crops

The main sources of starch are renewable crops like corn (maize), potato, cassava, rice etc.

Easy and fast Biodegradation

Starch is composed of polysaccharides namely - amylose, a linear polymer of glucose units and amylopectin, a highly branched polymer of glucose units. As thermoplastic starch is made up of polysaccharides, it is easily attacked by microbes leading to fast and complete biodegradation.

Low Cost

Thermoplastic starch has the lowest cost among bioplastics (including biodegradable plastics) as well as compared to petrochemical based plastics

Easy to modify and blend with other biodegradable plastics

Native starch is plasticized (de-structurized) with the help of organic plasticizers by the action of shear force at elevated temperature to produce “thermoplastic starch” (TPS). TPS properties can be improved significantly by blending with other polymers, fillers, and fibers. TPS is blended with other bio-degradable polymers (PBAT, PLA, PBS, PCL) to make it suitable for packaging applications with sufficient strength and moisture resistance that are fully biodegradable and compostable.

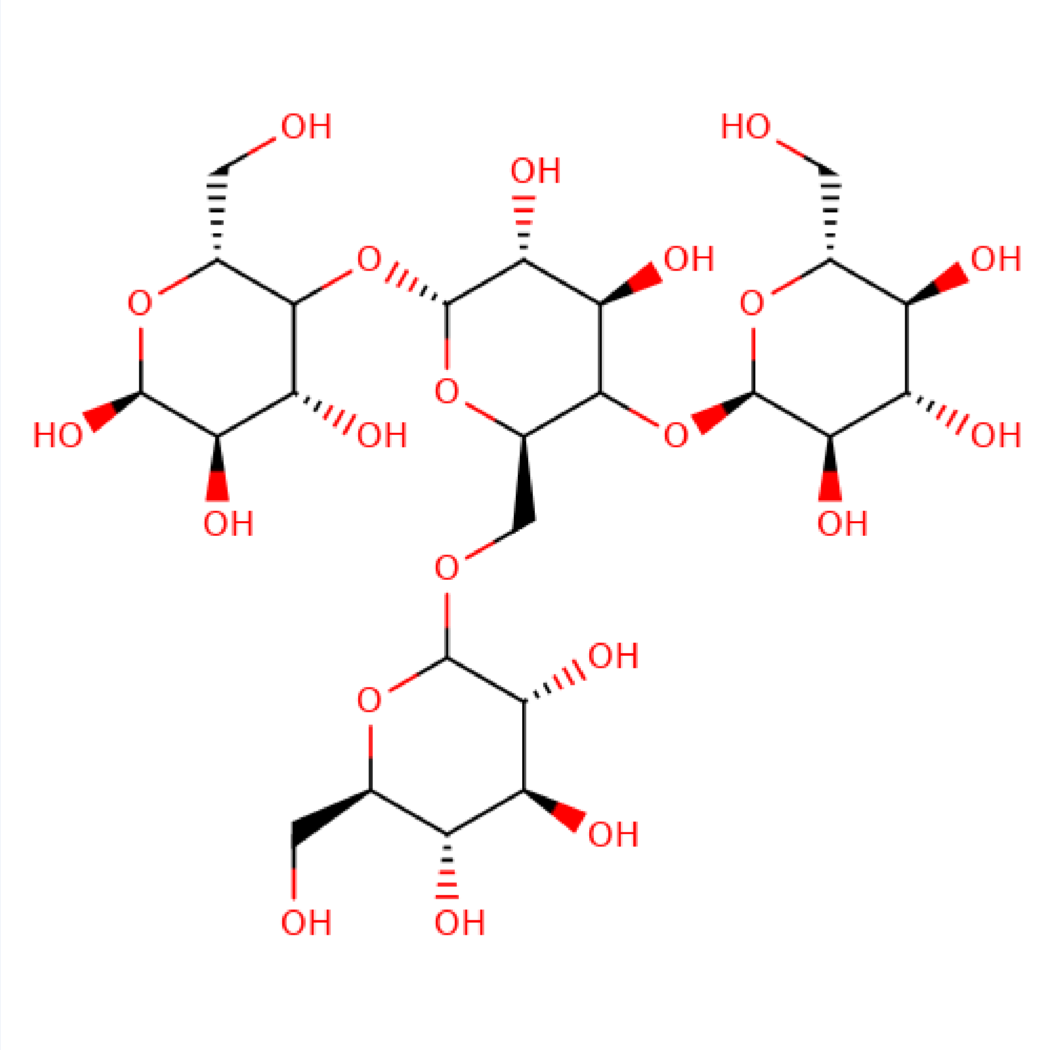
However, thermoplastic starch in itself has poor physical / mechanical properties and resistance to moisture and water. Therefore, chemical modification and crosslinking of native starch improves its usage in various end applications which require biodegradability / compostability, increased bio based content and reduced cost.

Hydroxy-propylated Starch

Hydroxy-propylation is a kind of etherification of starch with propylene oxide in the presence of acid or alkaline catalyst, which lowers gelatinization temperature and enthalpy, increases clarity, freeze-thaw stability and solubility in cold water. Cross-linking alters the viscosity, swelling power and other physical properties and the thermal transition characteristics of starch. Sodium trimetaphosphate (STMP) is and example of non-toxic, safe cross-linking agent

$$\text{Native Starch} \xrightarrow[\text{Propylene oxide}]{\text{Catalyst}} \text{Hydroxy propylated Starch} \xrightarrow[\text{Crosslinking agent}]{} \text{Cross-linked Hydroxy propylated Starch}$$

$$\text{Chemically Modified Cross-linked Starch} \xrightarrow[\text{Heat \& Shear}]{\text{Organic Plasticizer}} \text{Thermoplastic Starch (TPS)}$$



Hydroxypropyl starch is an amorphous, water-soluble polysaccharide with a molecular weight of about 10,000 Daltons. It contains a mixture of linear and branched polymers of glucose, maltose, and other sugars. The product is prepared by reacting starch with propylene oxide in the presence of hydrochloric acid. The reaction mechanism involves breaking of glycosidic bonds in starch by hydrochloric acid and the formation of ester bonds between the hydroxyl groups on propylene oxide and those on the carbohydrate chains.

Plantic Kuraray (Japan, Australia, China) - Plantic’s primary feedstock is naturally high amylose starch (up to 70% amylose), derived from corn which has been hybridised over a number of generations. The high amylose starch currently used by Plantic Technologies Ltd, undergoes a chemical modification process called hydroxypropylation prior to the manufacture of PLANTIC™. This process retards retrogradation and effectively plasticizes the starch, making it behave like a thermoplastic and providing a shelf life of many years. This hydroxypropylated, high amylose starch forms the base of all Plantic Technology products, and its use in packaging applications. https://plantic.com.au/

Isoprene: on the road

Isoprene is used to produce polyisoprene rubber, thermoplastic elastomer, and butyl rubber. These technical-sounding names are present in all manner of essential sectors: in transport, they fill our car tyres while in health, they are used to make surgical gloves. However, it's the lucrative auto tyre market that's behind why the chemical has a market value of around $1-2 billion a year.

Biobased isoprene has reached the market in pockets but companies are still figuring out ways to develop more cost-effective manufacturing processes. In the US, Amyris was an early mover in developing a way to produce the substance, announcing collaborations with buyers through the 2010s around its biobased rubber.

As with many early experiments in the commercialisation of biobased chemicals, Amyris never managed to boost isoprene yields from microbes to profit-turning levels. The company went bankrupt last year.

Still, other companies are trying to become the ones that will tap the market for lower-carbon tyres with a cost-effective manufacturing pathway for biobased isoprene. Last year, it was announced that Ginkgo Bioworks and Visolis were working on a microbial biomanufacturing process for the material. In 2019, US clean tech company Gevo developed a process of converting waste alcohol into renewable isoprene.

Lactic acid: born to be bio

Lactic acid, a global production capacity of over 600, 000 tonnes in 2019,

Is a good example of the kind of chemical that industry should turn bio because so many secondary materials could be derived from it including green solvents, poly-acrylate, specialty chemical intermediates, poly acrylamide, and phthalate polyesters.

A major use for lactic acid is as a food preservative but it is also a vital industrial feedstock for many other industries. One of the major industrial ones is as a feedstock for acrylic acid, an input for superabsorbent polymers, plastics, synthetic rubbers, coatings, paint formulations and leather finishing. It is normally made using petrochemical feedstocks.

One of lactic acid’s highest-growing end-use segments is as an input in the production of biodegradable polymer polylactic acid (PLA) used in food packaging. Commercialisation is in full swing with NatureWorks in Nebraska, USA as well as Corbion in the Netherlands being leading producers.

Ethylene: the chemical industry’s chemical

Ethylene is the chemical industry’s highest-volume molecule worldwide meaning cost-effective biobased options could help support sector-wide decarbonisation efforts.

The substance is used in making high-volume plastics including polyethylenes, the biggest end use for the chemical, as well as polyvinyl chloride, and polyethylene terephthalate (PET). Its production in 2021 was 175 million tonnes globally.

McKinsey estimates that ethylene made from sugar biomass achieves significant reductions in carbon intensity compared to those made from fossil naphtha.

The commercialisation of bio-based ethylene has been relatively smooth as production has been able to piggyback off the bioethanol industry, whose byproduct bio-naphtha is one potential feedstock for the chemical. The major producer here is Braskem which launched a bio-based polyethylene produced from sugar cane-derived bioethanol.

Fumaric acid: it’s everywhere

Fumaric acid is an intermediate for chemical production used in food, chemicals, agriculture and pharmaceuticals. Around 300, 000 tonnes were produced in 2023 making it one of the world’s top workhorse chemicals.

The chemical key to its versatility is that it can be polymerised and made into esters, as well as being nontoxic, a boon for food uses. However, manufacturing it currently involves huge amounts of energy since isomerisation, a step in the petrochemical method, demands very high temperatures.

The biobased production route for fumaric acid has the potential to solve the problem of high energy usage in conventional manufacturing routes, especially if renewable energy sources power the whole process. This is because it uses microbes to ferment some basic biomass into the target chemical – a metabolic process rather than a thermomechanical one.

So far, finding an economically viable way to ferment the substance has been challenging.

BASF is looking into a biobased alternative made using living bacteria from cow stomachs that could turn sugar and carbon dioxide into the substance.

Propylene: a major-league petrochemical

Overall, we can say that biobased propylene is on the cusp of wider commercialisation. It is no surprise why this is the case. The chemical, usually made as a byproduct of petroleum refining, is the second largest petrochemical produced globally by volume and is used to produce many other chemicals that a wide variety of industries depend on including polypropylene (a plastic used in cars, packaging, and medicine) and acrylonitrile (used to make clothing and upholstery fibres).

Shell Chemicals recently started to supply Braskem with bio-attributed and bio-circular propylene feedstocks, based on a mass balance approach and independently certified by a third party.

In 2023, LG Chem signed a Joint Development Agreement with Gevo, Inc., a North American renewable fuel company to develop bio-propylene using bio-ethanol produced from corn and sugarcane. Gevo will supply the source technology with LG Them to advance and verify it through scale-up and commercialisation.

1,4-butanediol: the base of the global apparel industry

This is a spandex precursor that is usually made using coal, another widely used chemical that has acquired major backers to fund the development and commercialisation of biobased alternatives. Geno pioneered intellectual property aimed at the scale-up of biobased versions of this chemical, having developed a metabolically engineered strain of E. coli suitable for making the chemical. Novamont is the leader in making biobased alternatives now after licensing the strains from Geno.

Other large companies working on the chemicals are Cargill and Helm whose joint venture Qore is also set to scale production at Cargill's biotech campus in Eddyville, Iowa. In September 2023 it was announced that BASF obtained long-term access to More's 1,4 butanediol made from renewable feedstock.

Moreover, biobased materials have to be used in the right sectors. This is because natural resources – even biobased ones – are limited. To maximise decarbonisation impacts then, biobased chemicals should be encouraged in sectors where they can make the biggest environmental impact. For producers, it also makes sense to target applications with the highest value proposition.

THANK YOU

THE FUTURE BELONGS TO THOSE WHO SEE POSSIBILITIES BEFORE THEY BECOME OBVIOUS

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