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Market analysis of sugar-lignin platforms

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About S2Biom project

The S2Biom project - Delivery of sustainable supply of non-food biomass to support a “resource-efficient” Bioeconomy in Europe - supports the sustainable delivery of non-food biomass feedstock at local, regional and pan European level through developing strategies, and roadmaps that will be informed by a “computerized and easy to use” toolset (and respective databases) with updated harmonized datasets at local, regional, national and pan European level for EU-28, Western Balkans, Moldova, Turkey and Ukraine. Further information about the project and the partners involved are available under www.s2biom.eu.

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About this document

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Scope of the report and caveats

Numerous potential pathways to biofuels and biochemicals exist via the sugar platform. This report uses literature surveys, market data and stakeholder input to provide:

- i. a classification of most promising value-added chemical production under the sugar-lignin platform;
- ii. insights into the current market trends, industry drivers and challenges of selected typologies of bio-materials and biofuels produced through the sugar-lignin platform to generate a first estimate of the potential additional biomass demand for chemicals, biofuels and materials arising from the sugar-lignin platform and add a further dimension to the RESolve-biomass model.

Scope of this report

The primary focus of the study is the conversion of sugars to biofuels and biochemicals via novel pathways, with an emphasis on applied research and its commercialisation rather than basic research.

Ethanol produced from “first generation” feedstocks (for example corn, wheat, sugarbeet and sugarcane), having non lignocellulosic based biomass as input, is out of the scope of the study.

Lignocellulosic ethanol is nearing commercialisation, with first-of-a-kind commercial plants in operation or currently under construction, and is therefore within the scope of the study, although a great deal is known about this industry already, and therefore less effort is afforded in comparison to more novel pathways to chemicals.

The emphasis of the study is on conversion from sugars, not to sugars, therefore the focus is on the downstream conversion of sugars rather than lignocellulosic biomass pre-treatment processes and sugar production.

Back-end upgrading technologies, such as alcohols to jet/diesel/ETBE fuel for transport are not specifically considered in scope. These routes can be based on the sugar platform, although they take as their input an already finished fuel (sugar-based ethanol).

Lignin is specifically considered in scope, however it should be noted that it is a typical co-product of pulp and paper or lignocellulosic ethanol routes; this means that most of the biomass required to produce lignin is already accounted for in the demand for ethanol (or pulp and paper) hence this PMC should not generate additional biomass demand; in addition, lignin is the main source for aromatics that are investigated in a specific PMC, and potential intermediate product such as ‘phenol’ are included in the section on aromatics.

Routes of biomass to chemicals are diverse and winding: a lot of input biomass typologies and processing technologies can be used to produce an even higher number of intermediates and end products, with a variable percentage of biomass. A clear classification of processing and conversion technologies, intermediates, end products, biobased materials etc is thus required.

The report refers to the demand for sugars in a number of priority pathways, while the allocation of this sugar demand to the lignocellulosic biomass demand is out of the scope of the report; this allocation should take into account that the sugar-based platforms can have as input both lignocellulosic and non-lignocellulosic biomass (in particular starch, sugar crops, vegetable oils, algae).

Other non-sugar based platforms having as input both non lignocellulosic and lignocellulosic biomass and producing intermediate vectors such as vegetable oils, syngas, pyrolysis oils or lignin, are out of scope of this study, even if producing the same typology of end products of the sugar platforms; this should be taken in account when allocating the potential demand of bioproduct to each platform in order to derive the potential biomass demand.

Different feedstocks present different pre-treatment processing efficiencies and related costs, and this should be considered when allocating the sugar demand to the lignocellulosic biomass demand, while the report focuses on conversion efficiency from sugar to intermediate or end product if not further specified.

Most innovative technologies are confidential, industrial strategic plans and expected processing costs are not available and a reliable estimate is out of the scope of this report.

Caveats: key uncertainties and white spots in available information

In the relatively new field of biomass to materials, information is still fragmented and scarce. We'd particularly like to point to the following uncertainties:

- The percentage of biomass to produce a given biobased product or biopolymer can vary in a quite wide range and this should be reflected in a more detailed market assessment.
- An assessment of the current market trends and expected evolution for more traditional uses of lignocellulosic biomass alternative to energy and that can determinate additional biomass demand for the RESolve model should be carried out. The following pathways should be considered: (i) building and particleboards, (ii) pulp and paper, (ii) textile and fibres, (iv) animal feed.

The estimate of additional domestic biomass demand for biomaterials and bioethanol should consider the extra EU trade and in particular the import of biomass from low-cost Countries to fulfil the expected lignocellulosic based sugar processing capacity. In addition, an accurate market assessment of end products demand should consider

the expected trade of biomaterials and biofuels and in particular the percentage of EU demand that will be satisfied by extra EU import (this is relevant not only for bioethanol, but also for most of bio-products, where Brazil, China and US are expected to play a major role).

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1. Sugar platforms and biomaterials

1.1. The sugar-lignin platform

A biorefinery system is described as a conversion pathway from feedstock to products, via platforms and processes [1]. The platforms are intermediates from which final products are derived. They are the most important feature in specifying the type of biorefinery. The platform concept is similar to that used in the petrochemical industry, where the crude oil is fractionated into a large number of intermediates that are further processed to final energy and chemical products. These platforms are recognized as the main ‘pillars’ of this biorefinery classification, since they might be reached via different conversion processes applied to various raw materials. Conversion of these platforms to marketable products can be carried out using different processes.

Biorefineries produce both energetic and non-energetic products, and can be broadly grouped into two main classes: (i) Energy-driven biorefinery systems, where the biomass is primarily used for the production of secondary energy carriers (transportation biofuels, power and/or heat); co-products are sold or can be upgraded to added-value biobased products, to optimize economic and ecological performances of the full biomass supply chain; (ii) material-driven biorefinery systems, which primarily generate biobased products (biomaterials, lubricants, chemicals, food, feed etc.) and process residues that can be further processed or used to produce energy (for internal use or sale).

In this classification approach, biorefinery products are divided into energy products and material products. Some products like biohydrogen or bioethanol might be used either as energy or as a material product (such as bulk chemicals for further processes). In this classification approach, the main market targets must be identified. Material products include fine chemicals (such as amino acids, organic acids and extracts) used in the food, chemical or pharmaceutical industry, or animal feed and fiber products, among others. The selected subgroups of bio-material products proposed by IEA bioenergy Task 42 are: (i) Fertilizers, (ii) Biohydrogen. (iii) Glycerin (from the transesterification of triglycerides) (iv) Chemicals and building blocks (b.b.) (e.g. fine chemicals, aromatics, amino acids, xylitol, polyols, succinic-, lactic-, levulinic- and itaconic acid, phenols, furan dicarboxylic acid, furfural, etc.), (v) Polymers and resins (produced by (bio)chemical conversion of biomass via monomeric intermediates (e.g., PHA, resins, PLA). (vi) Food, (vii) Animal feed, (viii) Biomaterials (fiber and textile products, polysaccharides, pulp and paper, particleboards).

The use of biofuels to reduce greenhouse gas (GHG) emissions and fossil energy depletion is being increasingly contested due to overall sustainability concerns. Ethanol production from lignocellulosic biomass, and in particular biomass wastes,

has the potential to significantly improve sustainability of biofuels for transport by avoiding land-use competition with food crops, achieving higher conversion efficiencies than conventional pathways and reducing impacts related to agricultural inputs. However, high production costs remain the bottleneck for large-scale development of this pathway. In that sense, a huge potential exists in upgrading fuel and energy producing pathways into biorefineries in order to improve the financial performance and long-term sustainability. A biorefinery is a process, based in intensive fractionation scheme of fossil fuel refineries, in which biomass conversion leads to a multifunctional system producing biofuels, value-added chemicals and power generation. Ongoing research is devoted to second-generation lignocellulosic biorefineries with special attention to pathways using agricultural and forestry residues as feedstock. Different platforms are suitable to this end, including thermo-chemical and sugar-based biochemical pathways. Several researches are currently focused on sugar-lignin refineries with special attention to the influence of biomass pre-treatment in down-stream process stages and the potential for process integration and product diversification. In this platform, 5-carbon (C5) and 6-carbon (C6) sugars, issued from lignocellulosic matrix fractionation, are converted into fuels and building block chemicals by biotechnological or chemical pathways. Lignin output can be used as solid fuel for co-generation, with or without previous pelletization, or it can be upgraded into value-added chemicals, as reported in the high level summary of Figure 1, that reflects the IEA Bioenergy Task 42 Biorefinery Classification System [2]. In the sugar-lignin platform, there are several possible combinations of feedstock, pre-treatment options, conversion technologies and downstream processes that can be followed as potential pathways to produce even a larger number of biofuels and intermediates or end products for the chemical sector.

Even following a single pathway from one feedstock to one final product (via sugars), different technologies at different stages of commercialisation are required. The associated co-product streams also mean that integrated biorefinery concepts (multiple input and output synergies) could play an important role in the sugar platform. Today there are scattered examples of studies assessing specific chains or components. No-one has yet conducted a comprehensive study that maps out all the potential value chain options, assessing them on a common basis for a number of important aspects, such as development status, economic competitiveness, environmental sustainability and market potential, in order to answer what is achievable within the next 20-30 years. The broad number of product/market combinations available in the sugar platform does not allow a comprehensive study to map its potential value chains; for this reason, the assessment of the development status of all potential options, economic competitiveness, environmental sustainability and market potential is out of the scope of this report. This study aims to describe the different sugar platform pathways and propose a market analysis of a limited number of products, and in particular the routes that have the largest market share and those

ones that are under development pipeline with industry support, or already commercialised with the potential for growth.

Bio-ethanol is the dominant current sugar platform product, followed by much smaller, but still significant, markets for n-butanol, acetic, succinic and lactic acid.; Xylitol, sorbitol and furfural also show significant markets for chemical conversion of sugars, without petrochemical alternatives. The smallest bio-based markets are, as is to be expected, those of the earliest stage products, such as 3-HPA, acrylic acid, isoprene, adipic acid and 5-HMF. If economically competitive, many bio-based markets could grow to exceed the current demand for the fossil-based product, and expand into new markets, replacing other products.

The most promising lignocellulosic based end products from the sugar platform are reported in Figure 2. They have been selected being at least TRL 5, with at least one EU developer, and significant potential for market expansion.

Figure 1: Sugar-lignin pathways and value-added chemical production options under the biorefinery concept [2]

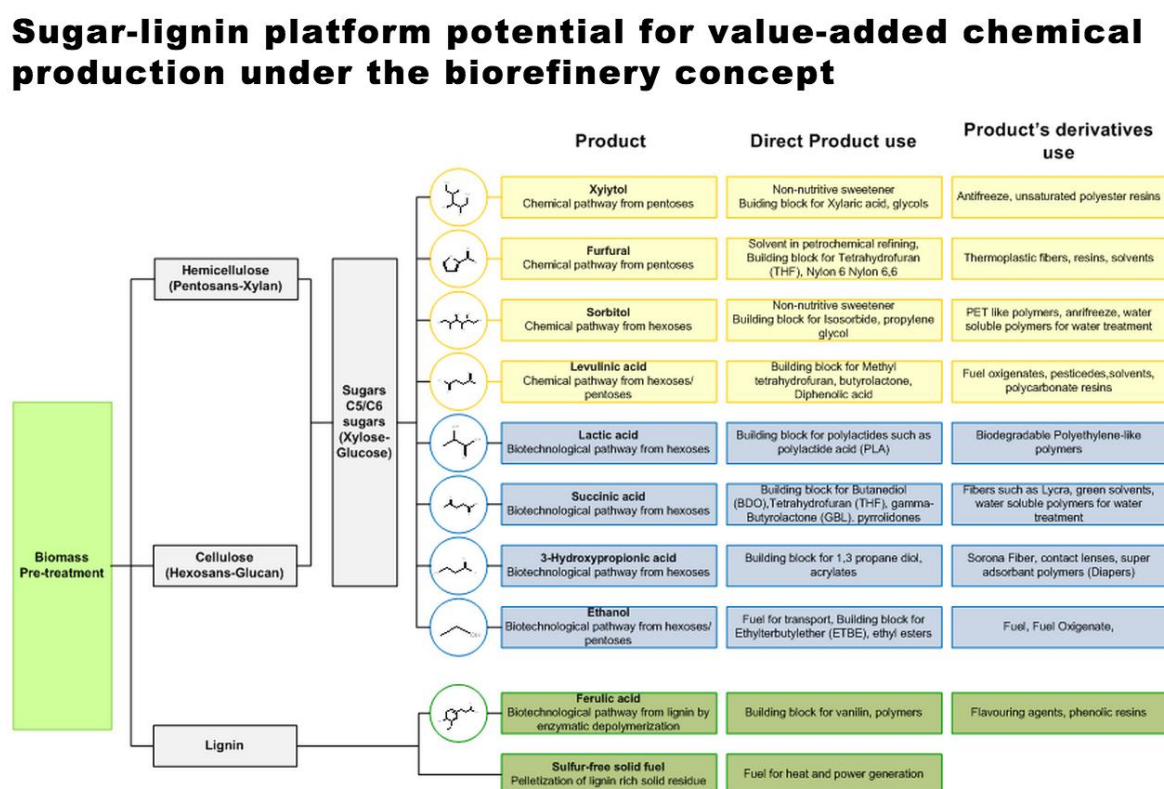


Figure 2: Most promising bio-based products with related key markets and value proposition, [3]

Bio-based product	Actors	Key markets and value proposition	Cost relative to fossil alternative	GHG saved vs. fossil alternative
Acrylic acid	BASF-Cargill-Novozymes (EU) OPXBio-Dow (USA). Both partnerships focusing on 3-HPA route	Drop-in replacement for a widely used chemical intermediate	20 - 48% better than the fossil-based when commercial	>70%
Adipic acid (ADA)	Biochemtex and DSM (EU) Some US projects have reached pilot scale (Rennovia, Verdezyne).	Drop-in replacement meeting demand for nylon 6,6 and polyurethanes	Expected to be cost competitive (lower capex and utilities)	70-95%, depending on N2O intensity of fossil process
1,4 – Butanediol (BDO)	Genomatica (USA) main actor. BASF, Novamont, DSM, Biochemtex making BDO and PBT based on Genomatica technology. JM-Davy BDO is via Myriant's succinic acid	Drop-in replacement for fossil BDO. BDO is used to make GBL, THF and PBT	15-30% lower than fossil and competitive at an oil price of 45 \$/barrel	70-117% depending on the process and electricity co-product substitution
Farnesene	Only one market player, US-based Amyris. There are no major European players.	Moisturiser emollients, durable easy-cast tyres, and jet fuel properties consistent with C15 iso-paraffin	Already attractive in emollients; close to market in tyres; high compared to jet	Up to 80% compared with fossil jet
2,5 furandicarboxylic acid (FDCA)	Development led by Avantium in the EU. Corbion Purac, AVA Biochem and Novozymes also active in this space in Europe	Substitute for TPA to make new class of polyethylene furanoate (PEF) polymers. Application in drinks bottles as superior gas barrier vs PET	High since at small scale, yet to be commercialised	45-68%
Isobutene	Small number of players, only Global Bioenergies and Lanxess in EU. <i>Gevo and Butamax are the main developers of isobutanol</i>	Rubber for automotive, and as a precursor for fuel & lubricant additives and biofuels. Might be used as food antioxidant	Could be profitable under high oil price market conditions	20-80%
Poly-hydroxy-alkanoates (PHAs)	Modest EU activity compared with China and the Americas. Biomer and Bio-on are the key EU players. Metabolix the largest US player	Fully biodegradable, niche use in sutures. Tuneable properties means could be used in most aspects of plastics industry	High costs. May fall via integration with sugar mills	20% with starch feedstocks, 80% with sugarcane and 90% with LC feedstocks
Poly-ethylene (PE)	Braskem in Brazil is the only commercial scale producer	Drop-in replacement for fossil PE, the most commonly produced plastic globally – main application in packaging	Sold at 30-60% above to fossil PE. Higher volumes may see price differential fall	>50% using sugarcane. Higher savings with LC feedstocks
Poly(lactic acid (PLA)	A few large industry participants; NatureWorks (USA) and Corbion Purac (NL) dominate PLA and LA production respectively. ~9 other EU producers of PLA and LA.	Bio routes preferred to fossil. PLA suitable for packaging, insulation, automotive and fibres. Durable, degradable, easily composted, low toxicity	Costs unconfirmed, but improved at scale. Slightly higher market price than fossil PS, PP and PET.	30-70% vs fossil PP, PS and PET. Could rise to 80% with improved conversion
Succinic acid	2 main actors in Europe (Reverdia, Succinity) and a further 2 globally (BioAmber, Myriant)	Drop-in replacement for fossil, and near-drop-in for adipic acid in resins, plasticisers, and polyester polyols	Equal to fossil costs since 2013. Fossil succinic acid now only niche	75-100+%, depending on feedstock production and grid carbon intensity

1.2. Biopolymers and bioplastics from sugars

In the past, plastics have been derived primarily from petrochemicals, but there is a significant expansion in the replacement of synthetics with biobased plastics. Bioplastics are used in an increasing number of markets, from packaging, catering products, consumer electronics, automotive, agriculture/horticulture and toys to textiles and a number of other segments. There are two general types of plastics, i.e., thermoplastics and thermoset plastics, also known as 'thermosets.' Thermosets melt and take the shape of the mold, and, after they have solidified, they maintain that shape. The chemical reaction is irreversible. Conversely, thermoplastics do not undergo changes in their chemical composition when they are heated, so they can be molded again and again. Both types of plastics can be produced from renewable resources.

Bioplastics are plastics made in whole or in part of biogenic resources. A large proportion of certified (EN13432) compostable plastic products available on the market contain a high portion of renewable raw materials. However, bio-based polymers are not in all cases biodegradable and compostable. Existing and emerging bio-based bulk plastics are starch plastics, cellulosic polymers, polylactid acid (PLA), polytrimethylene terephthalate (PTT) from bio-based 1,3-propanediol (PDO), bio-based polyamides (nylon), polyhydroxyalkanoates (PHAs), bio-based polyethylene (PE), polyvinyl chloride (PVC) from bio-based PE, other bio-based thermoplastics (polybutylene terephthalate (PBT), polyphenylene sulphide (PPS), polyethylene terephthalate (PET), polyethylene-co-isosorbide terephthalate polymer (PEIT), further polyesters based on PDO), polyurethane (PUR) from bio-based polyols and bio-based thermosets. New bio-based polymers have been available on the market for approximately one decade and some applications have already gained an established position. Recently, it has also become technically feasible to totally or partially substitute fossil-based raw materials with renewable raw materials in standard polymers like PE, polypropylene, PVC or PET and in high-performance polymers like polyamide or polyester. A summary of conventional biopolymers is reported in Table 1, and in Table 2 the average biomass content of biopolymers is reported. The following paragraphs provide information on some of the most common bioplastics. Newer and niche polymers have had more challenges gaining significant market share, and there is little evidence that they can attain a sustainable premium price.

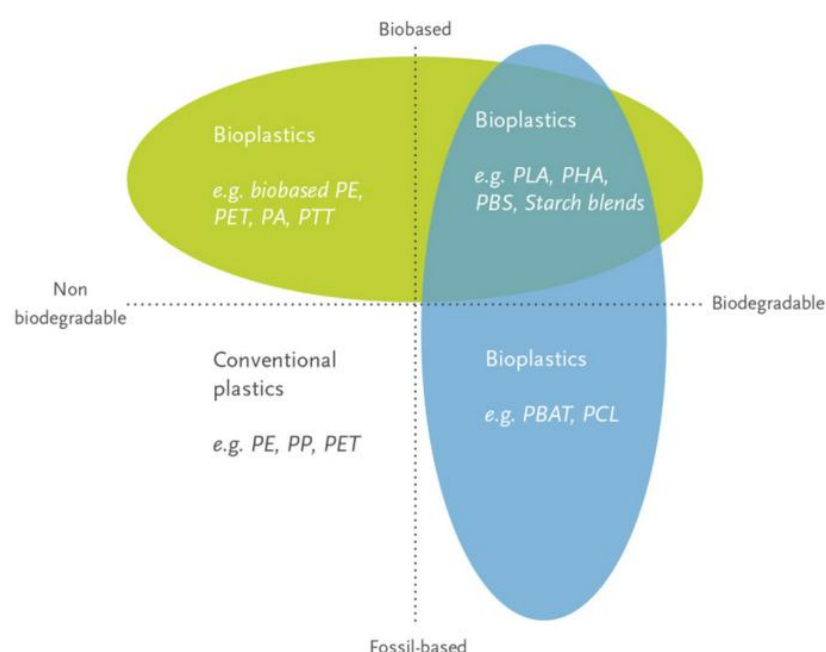
Table 1: Summary of conventional biopolymers [4] Elastomers are polymers with viscosity and elasticity, and very weak inter-molecular forces

Thermoplastics	Thermosets	Elastomers
Polyethylene	Phenolics	Polyisoprene (natural rubber)
Polypropylene	Polyesters (unsaturated)	Polybutadiene (synthetic rubber)
Polyvinyl chloride	Epoxies	Polyurethane (foams, spandex)
Polystyrene	Polyurethanes	Ethylene-propylene-diene terpolymer (EPDM rubber)
Acrylonitrile butadiene styrene (ABS)		Polysiloxanes
Acrylics		
Celluloid		
Cellulose acetate		
Polyacetal		
Polyesters (PET, PBT)		
Polyamides (nylons)		

Table 2: Average biomass content of biopolymers [4]

Biobased Polymers		Average Biomass Content of Polymer
Cellulose Acetate	CA	50%
Polyamide	PA	Rising to 60%
Polybutylene Adipate Terephthalate	PBAT	Rising to 50%
Polybutylene Succinate	PBS	Rising to 80%
Polyethylene	PE	100%
Polyethylene Terephthalate	PET	Up to 35%
Polyhydroxy Alkanoates	PHAs	100%
Polylactic Acid	PLA	100%
Polypropylene	PP	100%
Polyvinyl Chloride	PVC	43%
Polyurethane	PUR	30%
Starch Blends (in plastic compounds)		40%

As can be inferred from this classification and from Figure 3, bioplastics are not a single kind of polymer but rather a family of materials that can vary considerably from one another. There are three groups in the bioplastics family, each with its own individual characteristics: (i) Biobased or partially biobased non-biodegradable plastics such as biobased PE, PP, or PET (so-called drop-ins), (ii) biobased technical performance polymers such as PTT or TPC-ET Plastics that are both biobased and biodegradable, such as PLA and PHA and (iii) PBS Plastics that are based on fossil resources and are biodegradable, such as PBAT, and that are not the scope of this report. It is important to note, that the property of biodegradation does not depend on the resource basis of a material, but is linked to its chemical structure.

Figure 3: Categories of bioplastics [5] Bioplastics Europe, 2015-01-16


Bioplastics are materials whose properties can vary considerably. Biobased or partially biobased durable plastics, such as PE, PET or PVC, possess properties identical to their conventional versions. These bioplastics cannot be distinguished from conventional commodity plastics other than via scientific analyses. Moreover, they can be mechanically recycled in existing recycling streams. New bioplastic types such as starch-based plastics or PHA are potentially biodegradable. This feature is directly linked to the chemical structure of the polymer and can benefit particular applications. Biodegradable plastic types offer new ways of recovery and recycling (organic recycling). If certified compostable according to international standards such as the EN 13432, these plastics can be composted in industrial composting plants. Along with the growth in variety of bioplastic materials, properties such as flexibility, durability, printability, transparency, barrier, heat resistancy, gloss and many more have been significantly enhanced. In Table 3, the reference fossil routes for the main bio-based chemicals are reported.

Table 3: Bio-based chemicals and their reference fossil based routes [1].

Bio-based chemical	Reference petrochemicals
Ethyl lactate	Ethyl acetate
Ethylene	Ethylene
Adipic acid	Adipic acid
Acetic acid	Acetic acid
n-Butanol	n-Butanol
PTT	PTT & Nylon 6
PHA	HDPE
PLA	PET and PS
FDCA	Terephthalic acid
Succinic acid	Maleic anhydride

1.3. Other bio-materials: bio-lubricants, bio-solvents, bio-surfactants

Although usually not produced through sugar-lignin platforms nor from lignocellulosic biomass, it is worth to provide a synthetic overview of the broad categories of biomass based lubricants, solvents and surfactants, since on the longer term these materials could be also produced through chemical processing of cellulose and sugar based feedstocks. The term bio-lubricant refers to plant-derived lubricants, whether they are biodegradable or not, and whether they are blended with biodegradable mineral oils or not. Formulations are very complex and they are blends of different types of oils. The bio-lubricants group therefore covers a very broad commercial range, and is not limited to 100% plant-derived lubricants. Lubricants are used in e.g. automotive, industrial, marine and aviation applications. Plant-based lubricants are commonly used in cutting fluids, chainsaw lubricants, metal working fluids, hydraulic oils, 2-stroke engine oils, marine oils and drilling fluids. There is a renewed interest in bio-lubricants due to their distinct performance properties and environmental benefits (biodegradability, lower toxicity), which enable their use in sensitive environments and contributes to pollution prevention.

Solvents are liquids that possess the ability to dissolve, dilute or extract other substances without modifying the chemical composition of the extracted substances or of the solvent itself. There are eight main solvent groups: aromatic hydrocarbons, petroleum-based solvents, alcohols, ketones, esters, ethers, glycol ethers, halogenated hydrocarbons and so-called special solvents. Based on their properties, solvents are used as degreasing agents (cleaning of metals, textiles), additives and diluting compounds (paints, varnishes, inks, glues, pesticides), stripping agents (paint, varnish, glue removers) and extraction solvents (perfumes, pharmaceuticals). Bio-solvents have applications in cleaning, plant-protection oils and wetting agents and biofluxing agents. The vast majority of bio-based solvents do not emit volatile organic compounds (VOC) which are harmful to human health. Biosolvents can be entirely or partially plant-based. Examples of bio-solvents are soy methyl ester, lactate esters (fermentation derived lactic acid reacted with methanol or ethanol) and D-Limonene (extracted from citrus rinds).

Surfactants lower the surface tension of liquids, allowing chemicals to mix more easily. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Bio-surfactants are surfactants in which at least one of the two groups (hydrophilic or hydrophobic) is obtained from plants: they are therefore not necessarily 100% plant-derived. Surfactants are used in many industries such as household detergents, personal care, industrial cleaners, food processing, agricultural chemicals, textiles, emulsion polymerization, paints and coatings, lubricant and fuel additives, metal working, mining chemicals, pulp and paper production, leather processing, etc. The largest end use market for surfactants is household cleaning detergents. Surfactants are made from oleochemical (bio-based) and/or petrochemical (synthetic) raw materials. Oleochemical surfactants are commonly derived from plant oils such as coconut and palm oils, from plant carbohydrates such as sorbitol, sucrose and glucose or from animal fats such as tallow. Oleochemical feedstock sourcing for surfactants has been changing in recent years as animal fats have lost ground in favour of vegetable oils.

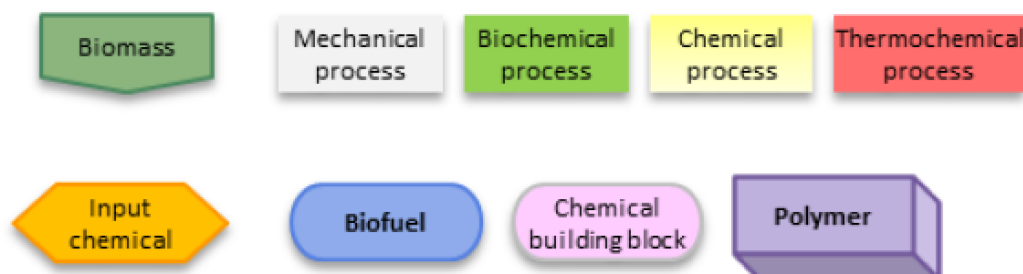
1.4. Sugar platform pathways

This section overviews the main combinations of feedstocks, pre-treatment technologies, sugars, conversion technologies and downstream processing to finished biofuels, biochemicals and bio-based polymers. Pathways for the conversion of feedstocks to fuels and chemicals may be categorised according to the following three main stages: (i) Pre-treatment from feedstock to sugars (ii) Conversion from the sugar platform to a useful product (iii) Upgrading of any intermediate products to final biofuel/biochemical.

Throughout this section, we use the IEA Bioenergy Task 42 Biorefinery Classification System to define raw materials, platforms and output products, and also follow the

same conventions on the construction of flowchart diagrams. These shapes are given in Figure 4.

Figure 4: Legend used for flowchart map [3]



The lignocellulosic (LC) biomass feedstocks can be grouped by agricultural residues (straw and prunings), forestry, products, wood-based wastes, starch crops, annual/pluriannual herbaceous crops and short rotation forestry. Different levels of pre-treatment are required for the different groupings, with starch crops needing to undergo enzymatic hydrolysis to break the starch into sugars, and wood based feedstocks requiring much more extensive pre-treatment to free cellulose and hemicellulose fractions from the lignin.

The pre-treatment technologies can be grouped by process type, with biological, mechanical, chemical and thermo-chemical process options. Ultimately, they are all producing accessible cellulose and hemicellulose materials that will undergo hydrolysis to be transformed into sugars. The chemical building blocks (sugars) can then be grouped into the categories of: (i) C6 or hexose sugars with six carbon atoms (with glucose, fructose and galactose being the most common), (ii) C5 or pentose sugars with five carbon atoms (xylose, pentose and ribose being the most common) and (iii) disaccharides (C12 molecules containing two hexose sugar units), being lactose, sucrose and maltose the most common. Larger molecules such as oligosaccharides and polysaccharides (e.g. starch) are not included within the sugar platform, as they are not easily digestible by a wide range of organisms, whereas monosaccharides and disaccharides are very widely converted.

Once a primary product from sugars has been produced and extracted, there are then an even larger number of downstream process options available, as reported in Figure 5. In several cases these primary compounds are also end products (e.g. hydrogen, ethanol, isobutanol), but they have substantial use as building blocks to other end products. From a technical point of view, almost all industrial materials made from fossil resources could be substituted by their bio-based counterparts, and the main challenge is to assess which conversion processes are most efficient and economically viable.

Bio-based bulk chemicals, fuels and polymers include historic items with a long history of bio-based production (such as citric acid), recently introduced products

(such as propylene glycol), and products currently in the demonstration or pilot stage of development. The report therefore focuses on a limited number of products, either in the development pipeline with supporting industry interest, or already commercialised with the potential for strong growth [3].

Figures 6-11 present exemplary routes arising from some of the highlighted primary product (green “feedstocks”), and also cover at least one method of producing each fuel, chemical and polymer, and are taken from [3]. However, it should be noted that many of these chemical downstream chains could be inverted, so that the intermediate product becomes the final product, and the processes reversed (hydration/dehydration).

The majority of uses of sugars are via microbial fermentation to produce alcohols, organic acids, alkenes, lipids and other chemicals as highlighted in Figure 5. This conversion can be using bacteria, fungi or yeast, genetically modified or not, in a variety of process conditions (e.g. low/high pH, anaerobic/aerobic, nutrient rich/deprived), and this extraction step is assumed to be part of the conversion technology. The list of fermentation products given in Figure 5 is not exhaustive; however it does cover all the initial intermediate products of interest given those fuels, chemicals and polymers discussed later in this report. The other routes using sugars are: (i) Chemical based processes (e.g. hydrogenation of glucose to sorbitol, oxidation of glucose to gluconic then saccharic acid, acid dehydration of xylose to furfural); (ii) Thermo-chemical processes (e.g. Virent's aqueous phase reforming to BTX and a mix of other ketones, furans, acids and paraffins).

Figure 5: Downstream process options from sugars (the majority of which are fermentation based) [3]

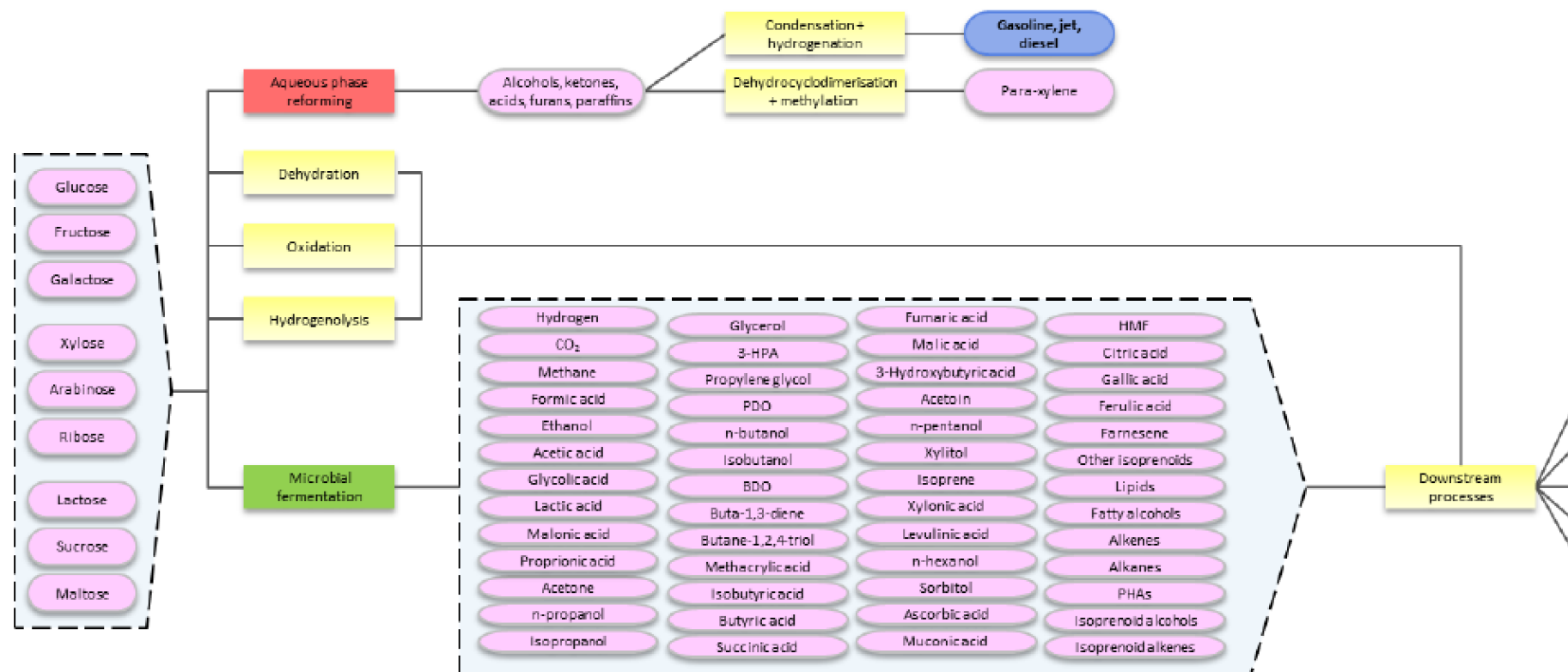


Figure 6: Downstream reactions for ethanol [3]

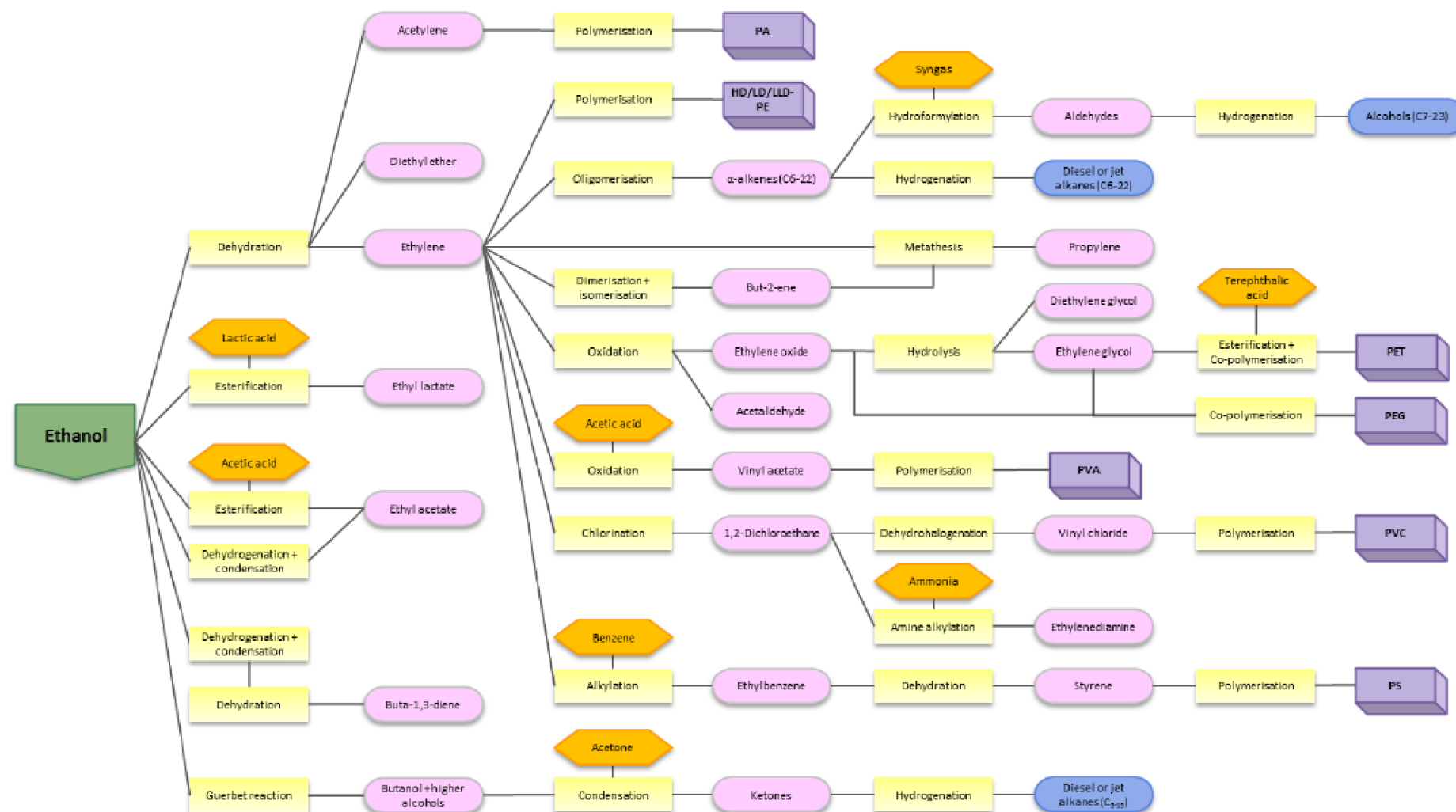


Figure 7: Downstream reaction for C4 intermediate products [3]

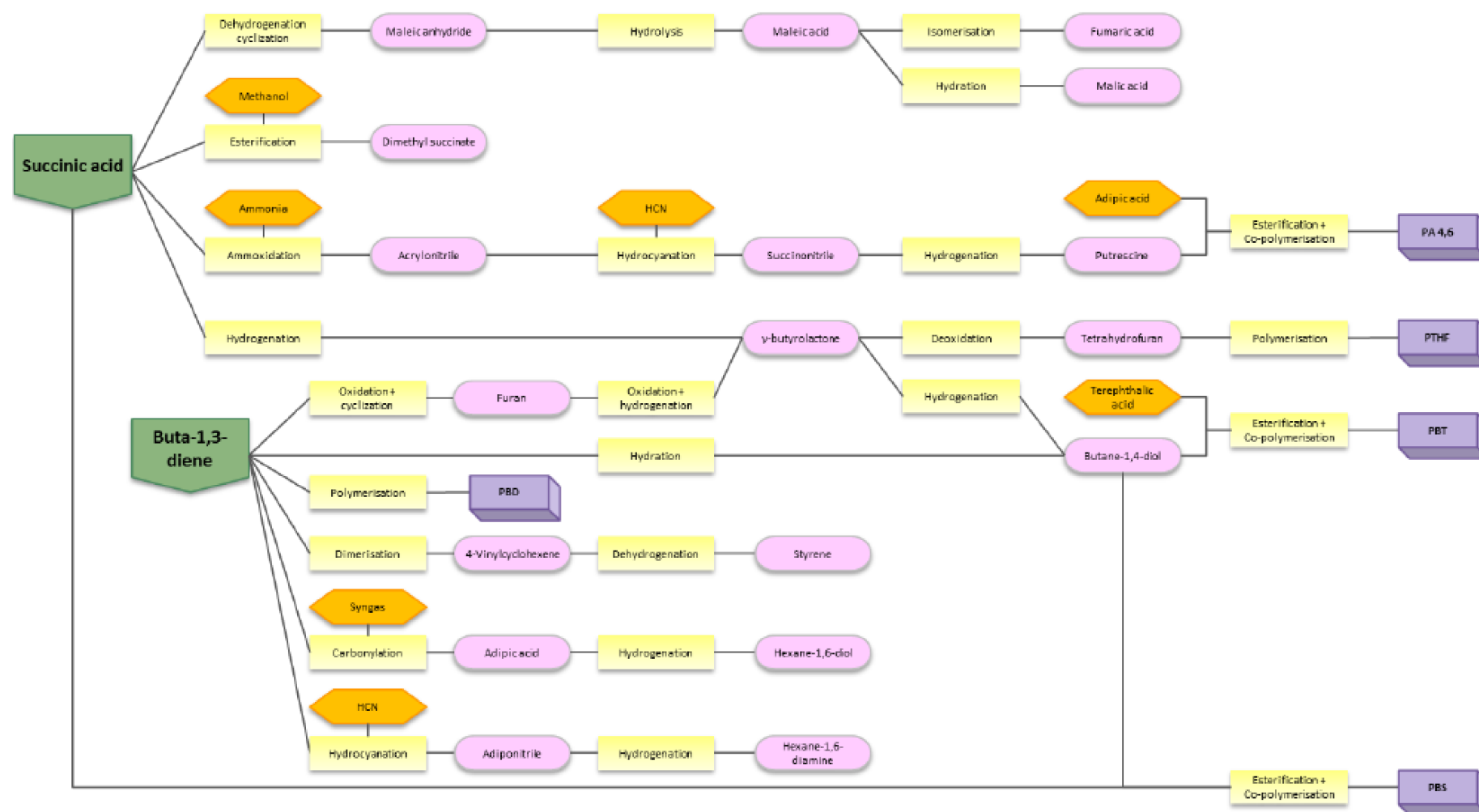


Figure 8: Downstream reaction for C5 sugars and levulinic acid [3]

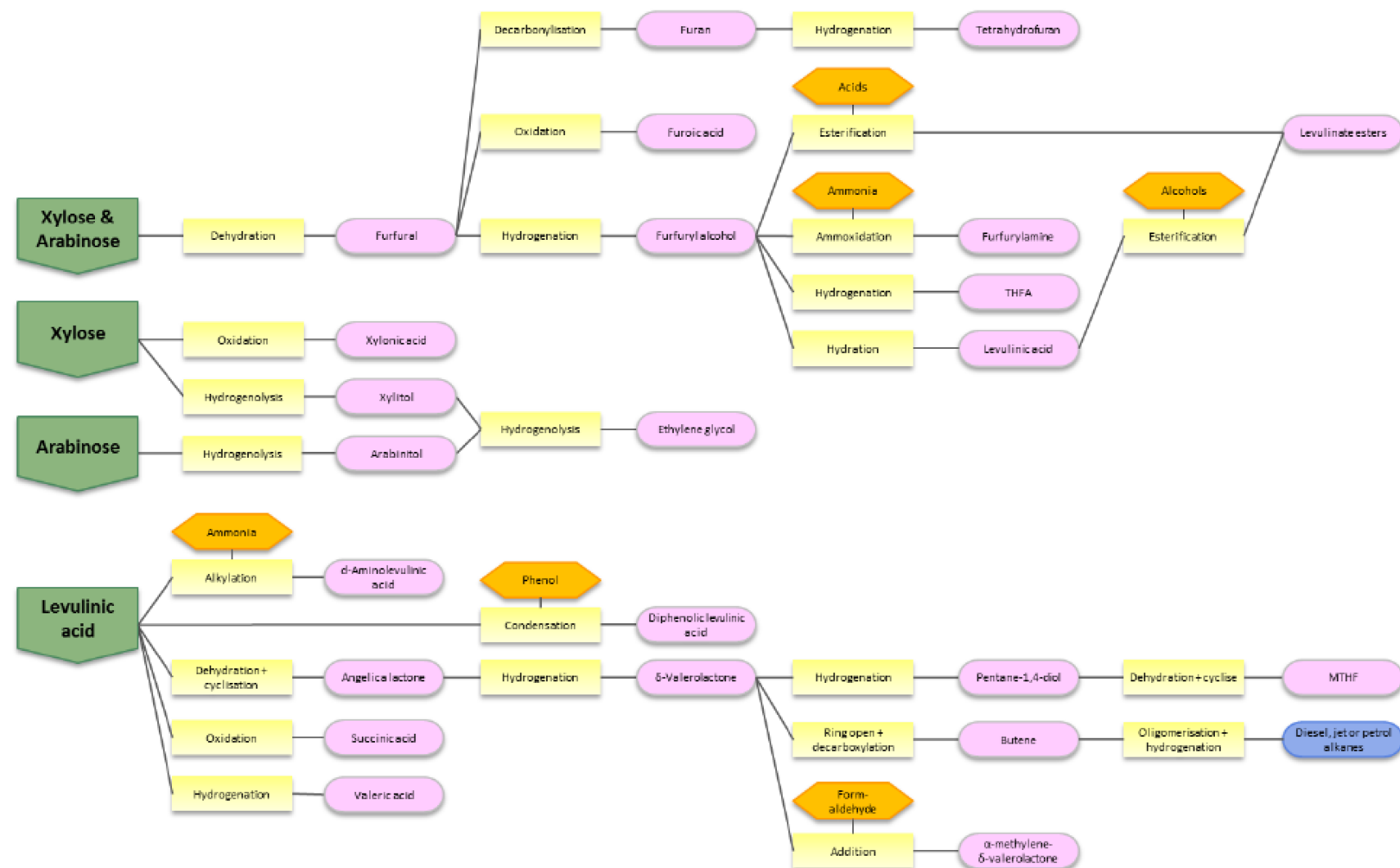


Figure 9: Downstream reaction for C6 sugars [3]

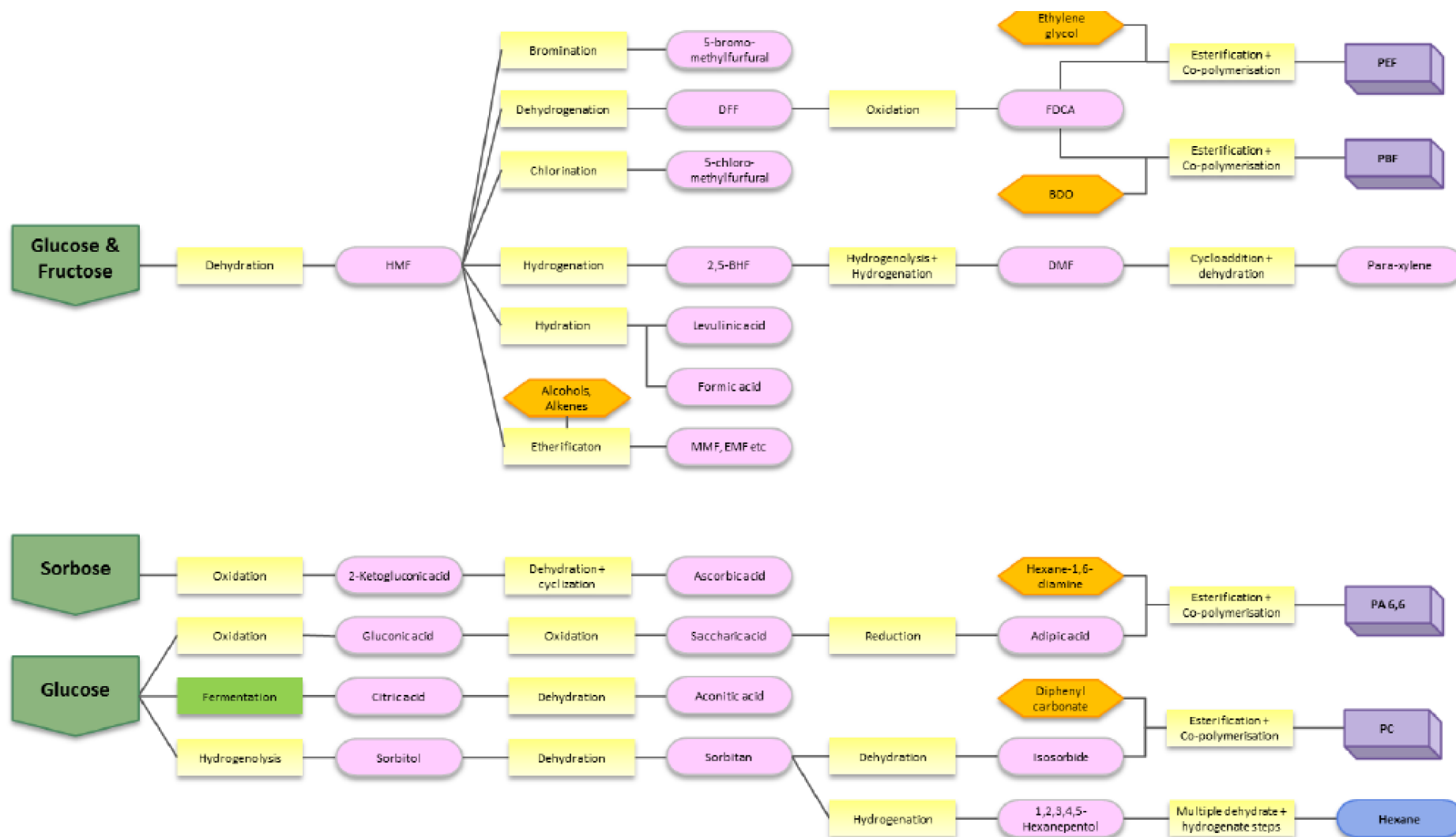


Figure 10: Downstream reaction for glycerol [3]

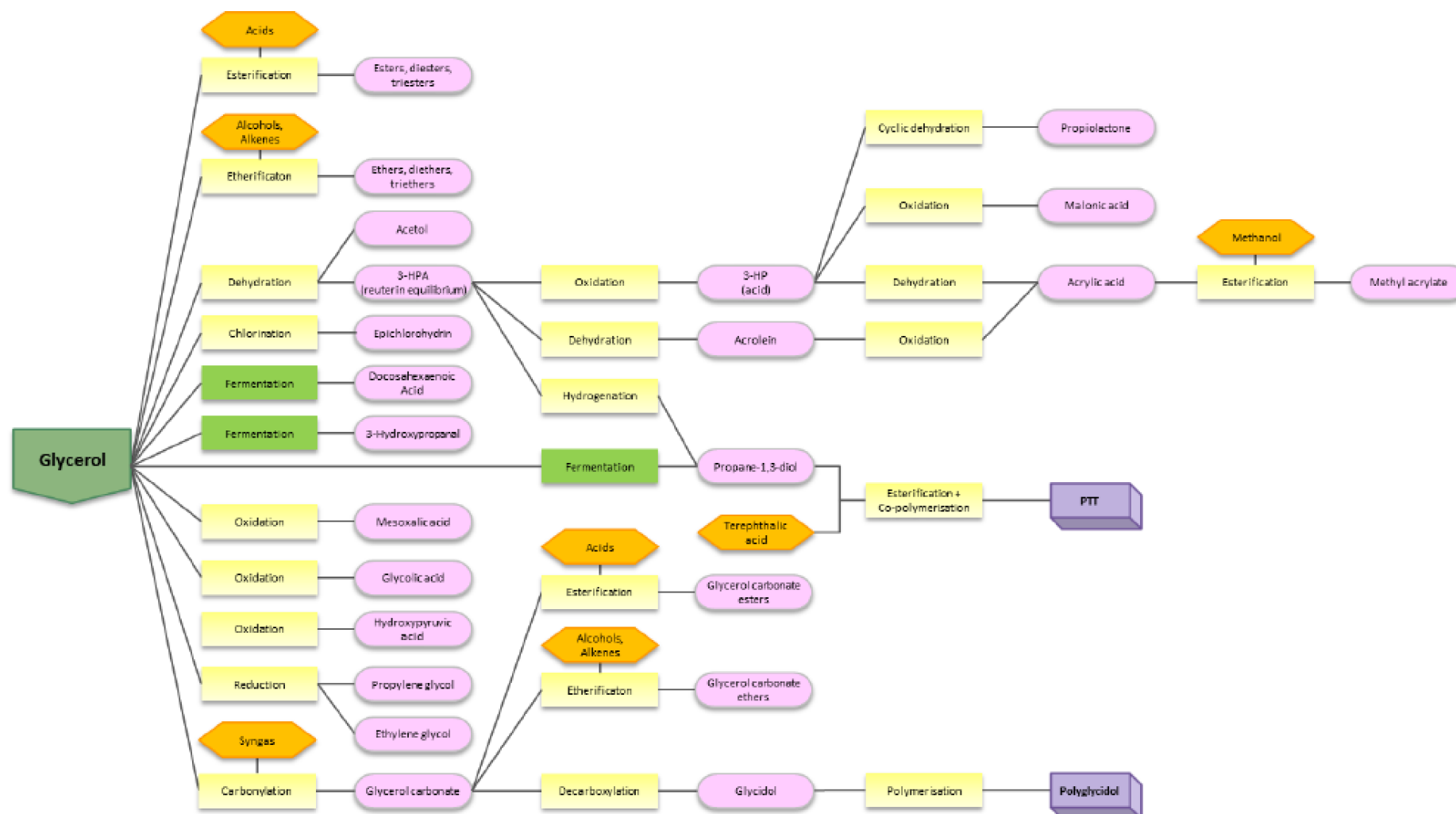
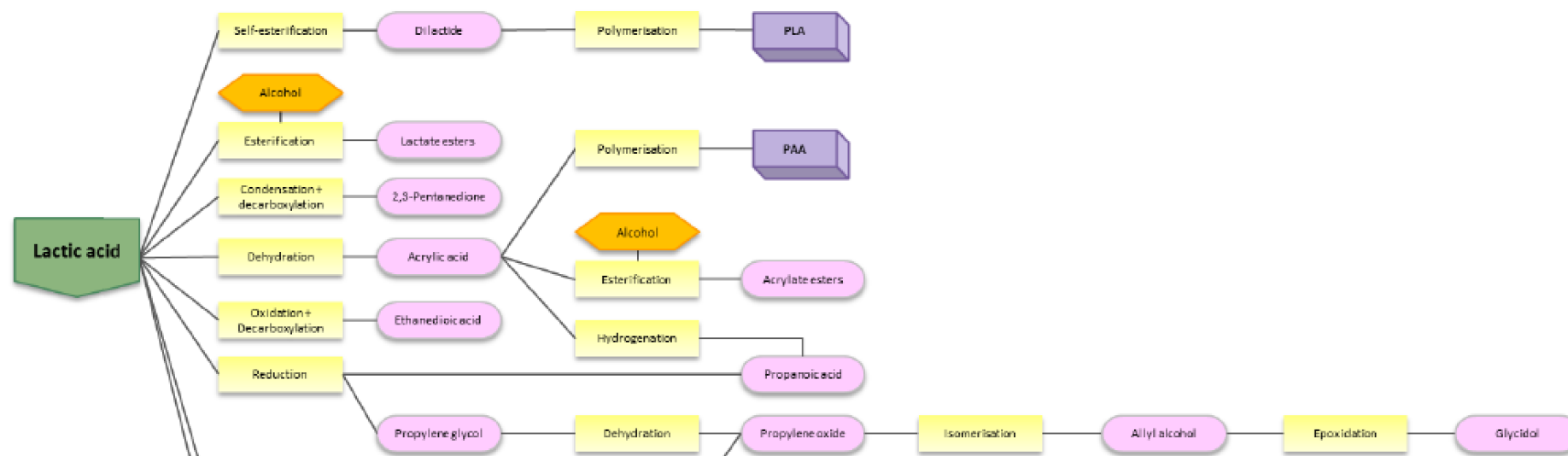


Figure 11: Downstream reaction for lactic acid [3]



A summary of main bulk chemicals produced from sugar platforms is provided in Table 4.

Table 4: main bulk chemicals produced from sugar platforms

Interm. product	Interm. market	Final product	Final Market	Current	2020	2030
C6 sugars	Chemical industry	PLA (via lactic acid)	Food, chemicals			x
C4 sugars	Chemical industry	Butanediol and THF via succinic acid	Fibres, solvents, pharmaceuticals			x
C5 sugars	Chemical industry	Nylon and furfural		x	x	x
C6 sugars	Chemical industry	Propane diol	Bio-plastics, textile fibres, paint industry			
C5 sugars	Chemical industry	Glycol or ethylene glycol (via xylitol)				

Six carbon sugar platforms can be accessed from sucrose or through the hydrolysis of starch or cellulose to give glucose. Glucose serves as feedstock for (biological) fermentation processes providing access to a variety of important chemical building blocks. Glucose can also be converted by chemical processing to useful chemical building blocks. Mixed six and five carbon platforms are produced from the hydrolysis of hemicelluloses. The fermentation of these carbohydrate streams can produce the same products as six carbon sugar streams; however, technical, biological and economic barriers need to be overcome before these opportunities can be exploited. Chemical manipulation of these streams can provide a range of useful molecules.

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2. Market assessment

2.1. Chemicals market

The dimension of fossil based chemicals market is in the range of 330 million tonnes of products per year (IEA, 2014), and the main molecules used are methanol, ethylene, propylene, butadiene, benzene, toluene and xylene. The market of biobased chemicals and polymers accounts for about 50 million tonnes per year (NNFCC The Bioeconomy Consultants, 2014), the main molecules being non-food starch, cellulose fibres/derivatives, tall oils, fatty acids and fermentation products. Key sectors such as bio-plastics are showing annual growth rate in excess of 10% and by 2020 the global market of biobased chemicals and biopolymers is expected to more than triple in value and volume (Biotech support service, India, 2015).

The global chemical industry has grown by 7% annually since 1980, most of this growth being driven by Asia, which represents almost half of global chemical sales, and which presents a fast increasing demand for chemical products and intermediates, due to the increased manufacture of products within the construction, automotive, electronics, textiles and leather, paper, and personal care and cleaning sectors. This means that locating biochemical manufacturing plants in Asia may be particularly attractive in comparison to Europe.

Figure 12 illustrates the production volumes for a selection of key large volume chemical products: nylon (fiber and resin); acrylonitrile & ABS; PVC, PS, PP & PET; PE (different grades); acrylic, adipic & terephthalic acid; ethylene & propylene oxide; and ethylene, propylene, butadiene, para-xylene, styrene and benzene (Bloomberg, 2014). Data is not available for individual countries, but the chart shows Asia already leading the chemical industry, followed by North America and Europe.

Figure 12: Production volumes in 2013 of the leading chemicals (Data from Bloomberg database)

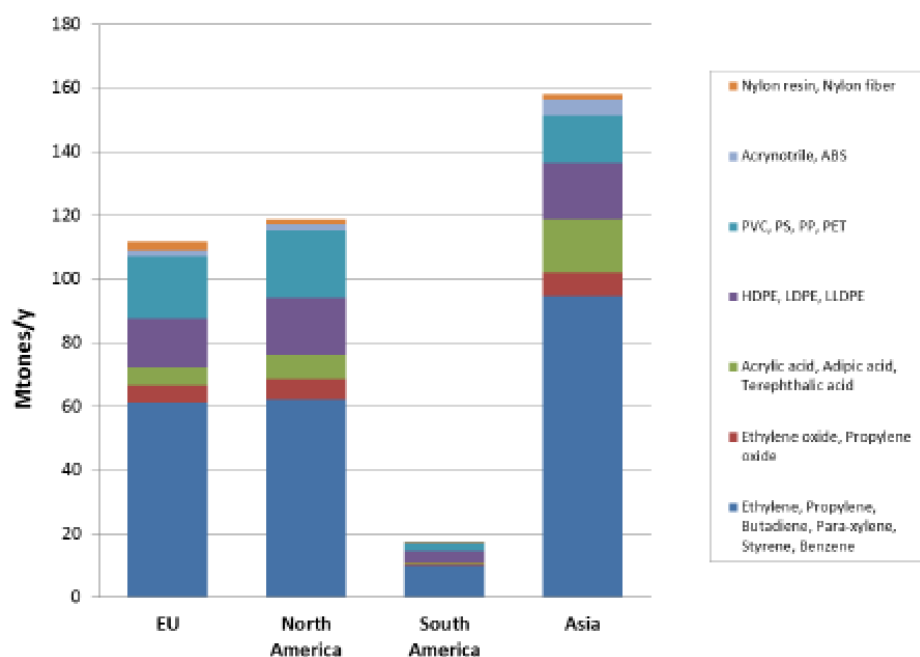
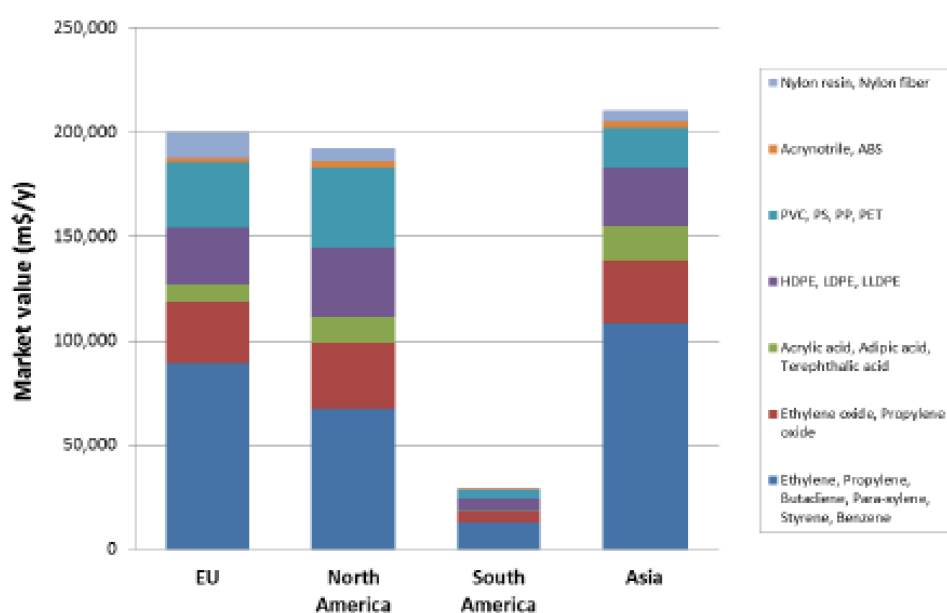


Figure 13 presents the market value in million USD per year for the selected key chemical products in the different regions. According to this data, the value of the chemicals markets in North America, Asia and Europe are quite similar, since higher production in Asia is offset by lower average product prices.

Figure 13: Market value in 2014 of different chemicals (Data from Bloomberg database)



Although price and volume data is available for the majority of fossil-based markets, at various trading hubs, most of the bio-based chemical producers still lack a transparent bio-based commodities market in which to operate, relying instead on bi-lateral agreements. This is in part due to their commercial status, and relative volumes produced vs. fossil counterfactuals.

2.2. Biofuels and biochemical market projections

The forecasts for world market penetration from biobased products vary in a quite broad range, and are affected by a lot of uncertainties, as discussed in the following. In Table 5, the projections from USDA are reported.

Table 5: World wide market penetration from biobased products

Chemical Industry Sector	2010	2025
Commodity Chemicals	1-2%	6-10%
Specialty Chemicals	20-25%	45-50%
Fine Chemicals	20-25%	45-50%
Polymers	5-10%	10-20%

Source: USDA, U.S. Biobased Products Market Potential and Projections Through 2025

Estimates on indicative prices, global production volumes and market sizes for selected primary products, along with their fossil counterparts, have been proposed in [3] and are reported in Table 6. Most of the source data is from 2013 or 2014, so does not reflect the dramatic drop (>50%) in crude oil prices experienced globally in the last six months. The total market size and value presented in Table 5 does not include the potential substitution of other molecules (i.e. non-drop in replacements). Some of the established bio-based products already dominate global production (e.g. ethanol, PDO, lactic acid), and several products do not have an identical fossil-based substitute (e.g. xylitol, FDCA, farnesene). In terms of the largest markets, bio-ethanol dominates at \$58bn a year, followed by much smaller, but still significant, markets for n-butanol, acetic acid and lactic acid. Xylitol, sorbitol and furfural also show significant markets for chemical conversion of sugars, without petrochemical alternatives. The smallest bio-based markets are, as is to be expected, those of the earliest stage products, such as 3-HPA, acrylic acid, isoprene, adipic acid and 5-HMF. Bio-based FDCA, levulinic acid and farnesene have the highest current prices, but could be expected to drop to around \$1,000/tonne (the indicative future bio-based production cost being targeted by several companies [4,5,6]) once the relevant conversion technologies have been successfully commercialised. Bio-based succinic acid is the fastest growing market at present. In many cases, if economically competitive, bio-based products could easily overtake their fossil based alternatives, and expand into new non drop-in markets – they are not necessarily limited by the current demand in the total (bio+fossil) drop-in replacement market. Many bio-based products will however be struggling to compete economically due to significantly lower crude oil prices.

According to data from the Biochem project [7] the total volume growth of major bio-based chemical groups between 2008-2020 is estimated at 2.1 Mt (5.3% pa), with a market value growth from 21 billion EUR in 2008 to 40 billion EUR in 2020. This will increase the market share of bio-based products from 4% in 2008 to 6% in 2020. Future growth will be affected by the cost of biomass feedstocks but also by fossil fuel prices and by the level of public support.

Table 6: Estimated prices and volumes for bio-based and total product markets, Source E4Tech, 2015-01-16 [3]

Product	Bio-based market				Total market (bio+fossil)		
	Price (\$/t)	Volume (ktpa)	Sales (m\$/y)	% of total market	Price (\$/t)	Volume (ktpa)	Sales (m\$/y)
Acetic acid	617	1,357	837	10%	617	13,570	8,373
Ethylene	1,300-2,000	200	260-400	0.2%	1,100-1,600	127,000	140,000-203,000
Ethylene glycol	1,300-1,500	425	553-638	1.5%	900-1,100	28,000	25,200-30,800
Ethanol	815	71,310	58,141	93%	823	76,677	63,141
3-HPA	1,100	0.04	0.04	assumed 100%	1,100	0.04	0.04
Acetone	1,400	174	244	3.2%	1,400	5,500	7,700
Acrylic acid	2,688	0.3	0.9	0.01%	2,469	5,210	12,863
Lactic acid	1,450	472	684	100%	1,450	472	684
PDO	1,760	128	225	100%	1,760	128	225
BDO	>3,000	3.0	9	0.1%	1,800-3,200	2,500	4,500-8,000
Isobutanol	1,721	105	181	21%	1,721	500	860
n-butanol	1,890	590	1,115	20%	1,250-1,550	3,000	3,750-4,650
Iso-butene	>>1,850	0.01	0.02	0.00006%	1,850	15,000	27,750
Succinic acid	2,940	38	111	49%	2,500	76	191
Furfural	1,000-1,450	300-700	300-1,015	assumed 100%	1,000-1,450	300-700	300-1,015
Isoprene	>2,000	0.02	0.04	0.002%	2,000	850	1,700
Itaconic acid	1,900	41	79	assumed 100%	1,900	41.4	79
Levulinic acid	6,500	3.0	20	assumed 100%	6,500	3.0	20
Xylitol	3,900	160	624	assumed 100%	3,900	160	624
FDCA	NA (high)	0.045	~10	assumed 100%	NA (high)	0.045	~10
5-HMF	>2,655	0.02	0.05	20%	2,655	0.1	0.27
Adipic acid	2,150	0.001	0.002	0.00003%	1,850-2,300	3,019	5,600-6,900
Sorbitol	650	164	107	assumed 100%	650	164	107
p-xylene	1,415	1.5	2.1	0.004%	1,350-1,450	35,925	48,500-52,100
Farnesene	5,581	12	68	assumed 100%	5,581	12.2	68
Algal lipids	>>1,000	122	>122	assumed 100%	>>1,000	122	>122
PHAs	6,500	17	111	assumed 100%	6,500	17	111

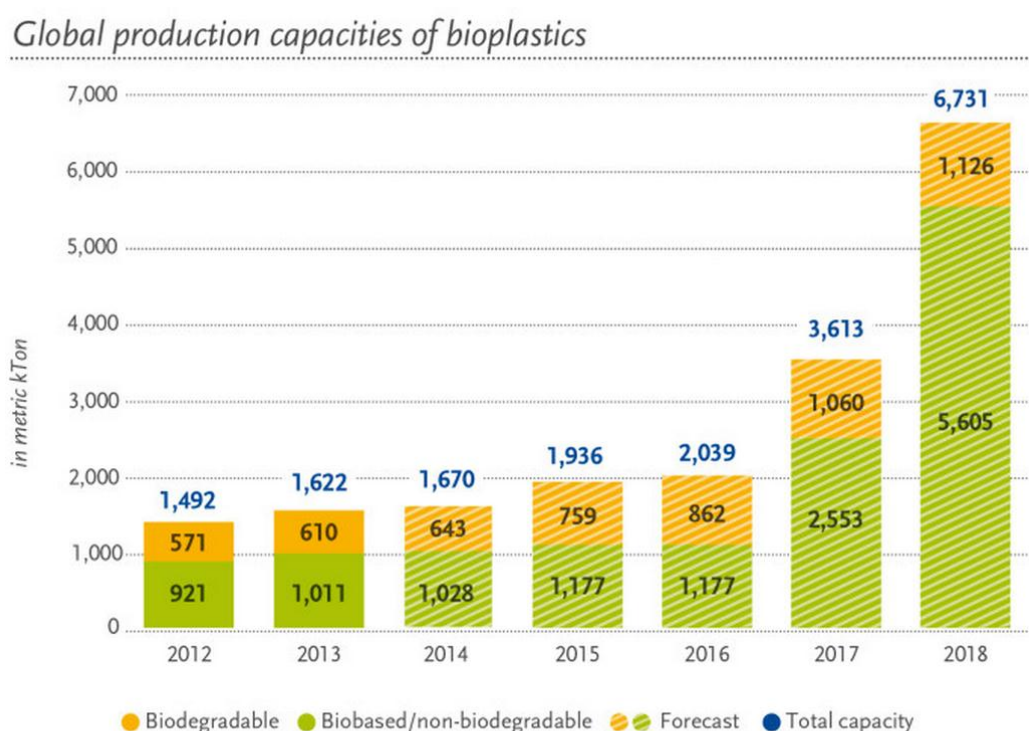
2.3. Bioplastics and biopolymers

Globally, bioplastics make up nearly 300,000 metric tons of the plastics market [8]. While this is a significant quantity, bioplastics account for less than 1% of the 181

million metric tons of synthetic plastics produced worldwide each year. While the bioplastic market is growing by 20–30% per year, and is estimated to grow to 1.5–4.5 Mt by 2020, this growth may not be sufficient to meet demand. Growing demand for more sustainable solutions is reflected in growing production capacities of bioplastics: in 2013 production capacities amounted to 1.6 million tonnes. Market data of European Bioplastics forecasts production capacities will multiply by 2018 – to approximately 6.7 million tonnes. Most bio-plastics have only recently completed the basic development and are thus on the brink of broader market introduction. The EU countries with comparably advanced market development are the UK, Italy, the Netherlands and Germany, followed by Belgium, France, Austria, Switzerland and Scandinavia. Europe is the second important region after USA for bio-based plastics. Asia is the third leading player and South America is an emerging area.

The volume of the European bio-plastics market totalled 0.13 Mt in 2008 and is estimated to grow to 0.9 Mt in 2020 (growth rate 16% pa). In the initial phase of market introduction, products are often used in niche markets, but some bio-based polymer applications have already gained an established position in the market. Recently, it has also become technically feasible to either partially or totally substitute fossil-based raw materials with renewable raw materials in standard and high-performance polymers.

Figure 14: Global production capacity of bioplastics [8]



Source: European Bioplastics, Institute for Bioplastics and Biocomposites, nova-Institute (2014)
More information: www.bio-based.eu/markets and www.downloads.ifbb-hannover.de

Fields of application for bioplastic materials and products are increasing steadily. Today, bioplastics can be found mainly within the following market segments: packaging; food-services; agriculture/horticulture; consumer electronics; automotive; consumer goods and household appliances. But there are a lot more markets starting to use bioplastic materials such as building and construction, household, leisure or fibre applications (clothing, upholstery). Products that show vast growth rates are among others bags, catering products, mulching films or food/beverage packaging.

Figure 15: Global production capacity of bioplastics by material type, 2013 and 2018 [8]

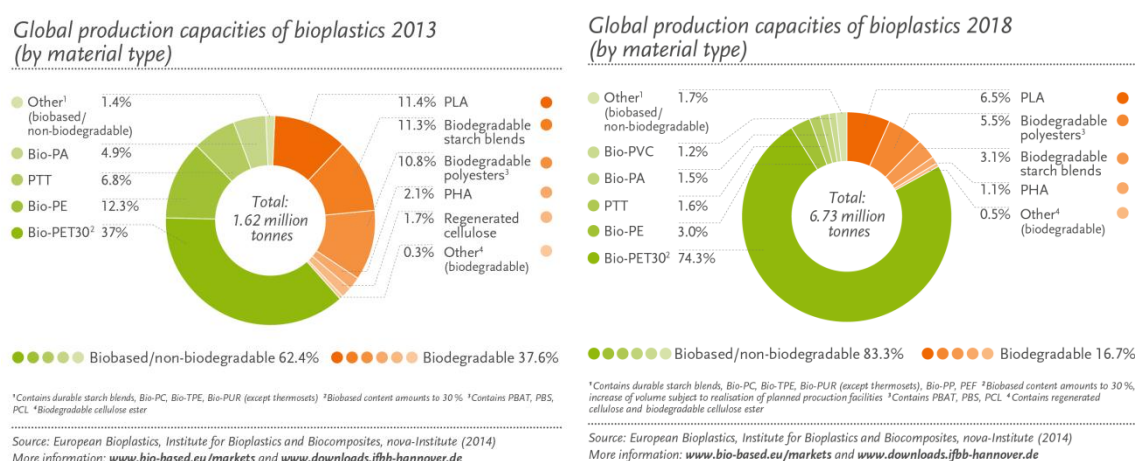


Figure 16: Global production capacity of bioplastics by market segment, 2013 and 2018 [8]

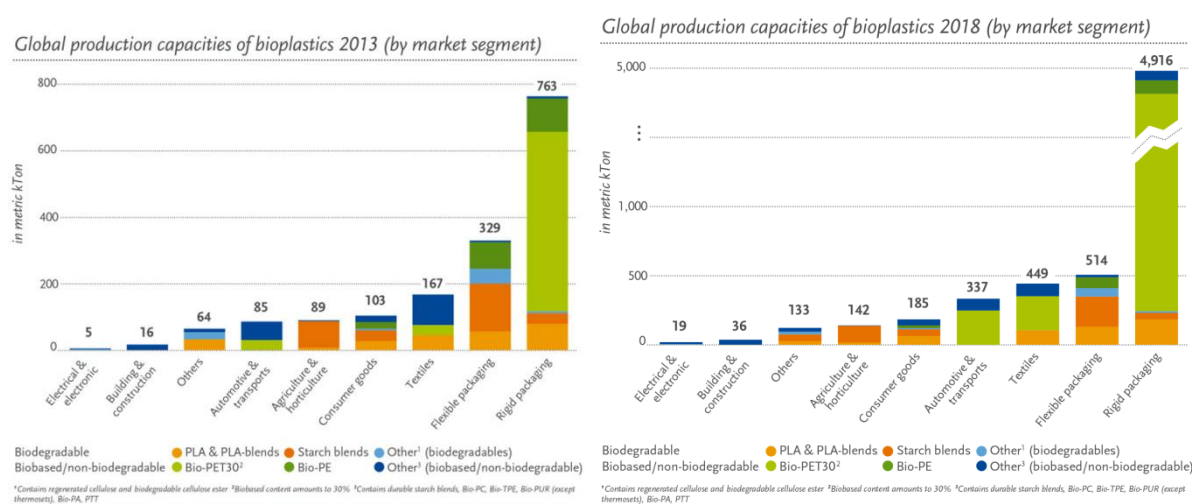


Figure 17: Global land use for bioplastics, 2001 and 2016 [8]

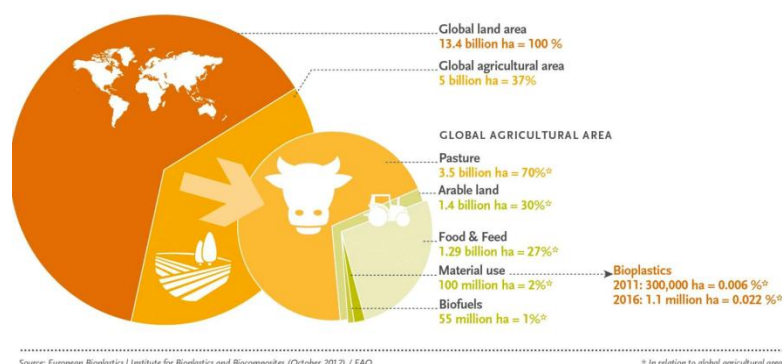
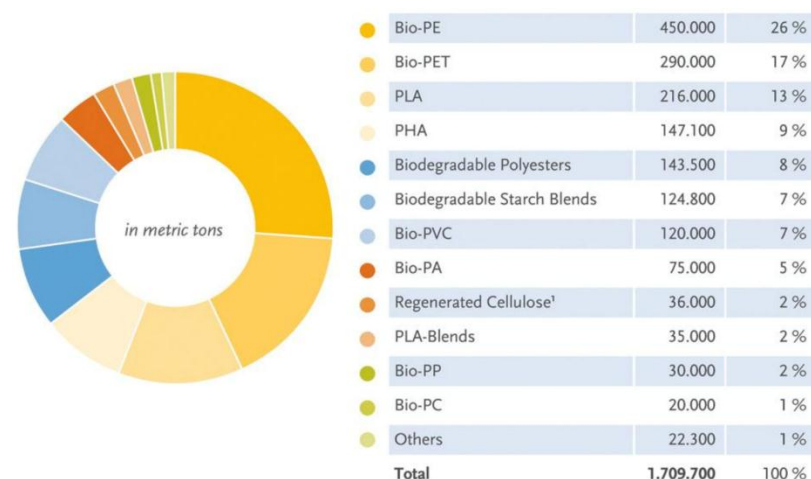


Figure 18: Biopolymers global production capacity by 2015 [8]



According to the BIOCHEM project results, at the current state of technology, 5-10% of the plastics market could theoretically be bio-plastics and the long-term potential (2030 onwards) is significantly higher (70-100%) [7]. This will not only involve replacing conventional plastics in individual application areas, but also development of completely new ones. The market penetration depends on multiple factors, such as environmental regulation, price development of raw materials and the general economic climate. Whilst conventional plastics have experienced strong price increases of 30-80% in recent times as a result of high crude oil prices, bio-plastics prices have in some cases sank considerably. For the most part, the new materials remain more expensive than their crude oil based counterparts, however the relative price difference has clearly diminished. The most important reason for companies not to shift to bio-based production on a large scale is the higher production cost. There are also challenges related to capital availability, scale-up, short-term availability of bio-based feedstocks and to the ability of the plastics conversion sector to adapt to the new plastics. Some important building blocks are not readily available from bio-based feedstocks. The single most important group of plastics precursors, for which bio-based alternatives are still missing, is aromatic compounds. One possible source for aromatic compounds could be lignin derived from wood during pulp and paper

production. The recent technological development in new bio-based plastics has been fast. The first plants are being developed and set up for numerous types of plastics, although technological development is at an early state. Some of the plants are still rather small when compared to petrochemical plants but others are very sizable.

The following applications or product segments are exhibiting high growth rates:

1. Compostable waste bags to collect organic waste and carrier bags, which can also be used as organic waste bags. They can increase the volume of collected organic waste, therefore reduce landfill, and improve the composting process and compost quality. Such bags – most of them are bio-based too - are often regarded to be a key market for bio-plastics with regard to the sizeable market volume and valid arguments in favour of their use.
2. Biodegradable mulch film which can be ploughed into the field once it has been used, offering the opportunity to reduce labour and disposal cost.
3. Catering products for large events or service packaging for snack food sales. They can simply be composted after use along with any remaining food scraps. The available compostable product portfolio includes trays, cups, plates, cutlery and bags amongst others.
4. Film packaging for foods with short shelf life which require attractive presentation, or to extend shelf life. These include compostable pouches, netting and (foam) trays for (organically produced) fruit and vegetables, and recently also fresh meat. The simple disposal and the fact that the sale period could in part be extended are beneficial to retailers. Spoiled foodstuffs can be recovered via composting with no need for separation of packaging and contents at point of sale.
5. Rigid packaging such as containers and bottles. Bottles made from PLA are used for non-sparkling beverages and dairy products.

Many other products make use of their specific functionalities, such as tyres with starch materials incorporated to reduce hysteresis and fuel consumption, diapers with silky soft touch back sheet, urns etc. There is growing interest to source more renewable polymers as builders within personal (shampoo, cosmetics) and home care products, paints and other surface coatings, too. In the initial phase of market introduction, products are often used in niche markets. The level of technical complexity of bio-plastics packaging is increasing: co-extruded double or multiple layer film products have been commercialised recently. This involves an advantageous combination of bioplastics such as starch-based materials, cellulose films and PLA films, which are already available on the market. The development of durable products such as those in consumer electronics (laptop and mobile phone casings etc.), in leisure (sporting shoes, ski boots etc.), and in the automobile industry (interior trim, spare tyre covers) is in an early state of market penetration. The focus is equally on functionality, for example low electrostatic charging, and

sustainability criteria such as reduction of CO₂ emissions. It is estimated that around 2030 it may become possible to imprint bioplastics and thereby make extensive use of them in electronics. An appealing feature of bio-plastics is that they may serve a dual purpose: after use as for instance packaging material they may, by use of certain enzymes, be converted into biofuels. In the field of medical technology, special biodegradable plastics have been in use for some time as stitching materials and for decades for screws or implants (niche products with extremely high prices). Major chemical companies are investing in the production of polymers from renewable sources. Strategies differ between replacement of conventional plastics and monomers using unconventional feedstocks to development of novel monomers using fermentation chemistries from other sectors. Several classes of bio-based polymers are becoming increasingly important: starch chemicals, polylactic acid (PLA), polyhydroxyalkanoates (PHAs), succinic acid, polyurethanes (PURs) and cellulosic polymers.

2.4. Other bio-materials: Bio-lubricants, solvents and surfactants

Trade in lubricants has declined during the past years, and at the same time, lubricant demand has decreased in the EU [7]. This trend is a consequence of a lower level of activity during the financial crisis, but improvements in engine technology have also diminished the consumption of lubricants. Annual lubricant consumption in the EU was estimated at 5.2 Mt in 2008 and the share of bio-lubricants at 0.15 Mt (2.9%). It is estimated that bio-lubricant consumption will grow up to 0.23 million tons by 2020 which represents the growth rate potential of 3.6 %/a [8]. The market penetration of bio-lubricants varies considerably within the EU. It is estimated that their market share is about 15% in Germany and 11% in Scandinavia, but below 1% in France, Spain and the UK. The major vegetable oil in use in Europe for industrial products is rapeseed. However, not all the bio-lubricants are completely vegetable oil-based. In some countries, to get a label only requires that 50% of the oil is renewable. Thus, synthetic esters or even petroleum oils can be used in the formulation. Theoretically around 90% of lubricants currently used could be replaced by plant derived chemicals. The bio-lubricant industry is growing based on environmental concerns and some countries have already banned the use of non-biodegradable lubricants in sensitive areas at least in applications where oils are lost into soil and surface waters. Several studies show that bio-lubricants also have a longer lifespan than mineral lubricants. Other benefits of bio-lubricants include lower toxicity, good lubricating properties, high viscosity index, high ignition temperature and increased equipment service life. Bio-lubricants are more expensive than conventional products, which is the major barrier to market uptake, particularly during the economic recession. The higher cost may be partly offset by reduced need for replacement due to the longer lifespan of bio-lubricants.

Trade in solvents is rather low compared to the consumption of solvents in the EU and import and export volumes have been in decline [7]. The EU solvent market totalled 5.0 Mt in 2008 of which bio-based solvent consumption was 0.63 Mt (12.6%). The consumption of bio-solvents is estimated to grow annually 4.8% up to 1.1 million tons by 2020. The advantage of bio-based solvents is that the vast majority do not emit volatile organic compounds (VOCs) which are harmful to human health. Moreover, they offer the potential to reduce the dependency on crude oil feedstocks. However, bio-solvent production is not currently cost-effective enough to compete with traditional solvents. There are a growing number of companies that supply bio-solvents to the printing industry (HydroDynamic Products, Varn International, Akzo Nobel). These solvents are used to dissolve the pigments themselves, as well as to clean printer rollers, plates and other machinery parts. Such solvents can also be used to de-ink paper so that both the ink and the paper can be recycled. Some bio-solvent based paints and varnishes are now also available. A handful of companies supply them (Livios, EcoDesign) but the main barrier to widespread commercialisation is their cost. Bio-based paint strippers and brush cleaning solvents are also available from other chemical companies, but again the costs are high. As production costs fall and demand grows prices are likely to decrease. Bio-solvents for the home are also growing in number, with a small selection of companies offering cleaning and degreasing products for household and office use (Vindotco, Lord and Partners). These products tend to use citrus oils to cut grease but, even though they are billed as environmentally friendly, they often still include fossil-based additives such as ethylene glycol or amines. Research into the use of bio-solvents in chemical synthesis is advancing, with the successful replacement of organic and halogenated solvents demonstrated for a range of syntheses. Another area of investigation is the production of common organic solvents from biological feedstocks. An example of this is the conversion of succinic acid into tetrahydrofuran (THF). Such research is advantageous, as the production of the solvent would become sustainable and allow established chemistry using THF to continue in a more environmentally friendly way. Described production would not reduce VOC emissions. The evaluation and refining of production methods for bio-solvents is under investigation, with new methods using biological feedstocks being discovered that allow bio-solvent production at lower cost and higher purity. An example of such research is work where using a technique called pervaporation, lactate esters can be produced with cheaper price and using 90% less energy than previously.

The consumption of surfactants totalled 2.7 Mt in the EU in 2008. At the same time, the bio-based surfactant market was estimated at 1.52 Mt, representing 56% of the total surfactant market. Annual surfactant growth potential is estimated to be 3.5 %/a, and bio-surfactant potential 2.3 Mt in 2020. The major drivers in the surfactant market are price, performance and product safety. Environmental drivers can increase the demand for plant-derived surfactants. Several large manufacturers are in operation, for example Huish Detergents Inc., based in Houston, USA, manufacture methyl

ester sulphonate from renewable resources. The plant's capacity is large at around 70,000 tonnes. Advantages of naturally-derived surfactants include biodegradability, low toxicity and raw material availability as they can be produced from industrial waste or by-products. The REACH regulations are estimated to lead towards increased use of bio-based surfactants. Biodegradability standards and their vegetal composition (in whole or in part) confer a distinct advantage to bio-surfactants. However, mineral oil based surfactants are significantly cheaper than plant-derived surfactants. Activities in bio-surfactant market are increasing. The first vegetable oil based sodium lauryl (SLS) was launched by specialty chemicals supplier Rhodia, for use in shampoos, liquid soaps and body washers. New surfactants are being developed using biotech processing. Sophorolipids and rhamnolipids are examples; both are glycolipids that can be used to produce bio-surfactants via a fermentation process applied to starch biomass.

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6. <http://www.altenergystocks.com/archives/biomass/biochemicals/>
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3. Ethanol

Ethanol is a versatile product that finds its application in many fields. Traditionally it is used in the beverage industry, and its most widespread application in the energy sector is as biofuel for transport. Ethanol has industrial uses and is also an essential building block to produce other bio-based products, such as bio-plastics and bio-chemicals.

First generation bioethanol is produced by fermentation and distillation from crops such as wheat, corn, sugar cane and sugar beet. In Europe, wheat is the main crop grown for bioethanol production - accounting for 0.7% of EU agricultural land and 2% of Europe's grain supply¹. The EC has proposed to limit biofuel produced from "food crops" at 7% of energy use in transport, due to concerns about food price and land use impacts. However, there are conflicting studies and opinions on this issue and biofuels producers suggest that the impacts of ethanol production from starch crops may have been exaggerated and the many benefits of biofuels (European fuel security, job and wealth creation, production of valuable by-products, GHG reduction) have not been fully taken into account.

Cellulosic ethanol is chemically identical to first generation bioethanol (i.e. $\text{CH}_3\text{CH}_2\text{OH}$). However, it is produced from different raw materials via the more complex process of cellulose hydrolysis. In contrast to first generation bioethanol, which is derived from sugar or starch produced by food crops (e.g. wheat, corn, sugar beet, sugar cane, etc.), cellulosic ethanol may be produced from agricultural residues (e.g. straw, corn stover), other lignocellulosic raw materials (e.g. wood chips) or energy crops (miscanthus, switchgrass, etc.). These lignocellulosic raw materials are more abundant and generally considered to be more sustainable, however they need to be broken down (hydrolysed) into simple sugars prior to fermentation and distillation. This may be achieved using either acid or enzyme hydrolysis. Both approaches have been the subject of continuing research interest since the 1970s, and large investments are being made in the US and Europe to speed up development of this route to bioethanol.

Perhaps the best-known industrial user of ethanol – after transport – is the drinks industry. Ethanol is used to make many kinds of spirits, such as vodka, gin and anisette, and can also be found in ready-to-drink mixes. It is also used to make perfumes, deodorants, paints, thermometers and cosmetics. Ethanol also has medical uses, and can be found in products such as sanitary wipes and antibacterial hand gels. It is widely used as a solvent, and in many products such as de-icer or anti-freeze used to clear the car windscreen. Ethanol is also an intermediate to produce biopolymers and a large number of biobased materials as shown in previous chapter and it represents a key for the green chemical industry. Transport is also a substantial market outlet for ethanol, particularly in Brazil and the US. Petrol sold in

¹ Source: <http://www.biofuelstp.eu/bioethanol.html>

the EU typically contains up to 5% ethanol by volume. This is referred to as E5, and is widely available as the default petrol of choice. Since 2000 all new petrol cars can also run on a mixture of petrol and up to 10% ethanol, known as E10.

3.1. Market

Figure 19 reports the current production capacity of ethanol in the EU and the historical consumption trend. Although EU ethanol production and consumption have been continually growing since 2003, Europe remains a relatively modest player globally. At 6.7 billion litres and a market value close to 8 billion Euro the EU is the world's third largest producer of ethanol. The US produces and consumes around 50 billion litres annually, followed by Brazil with around 23 billion litres [http://www.unica.com.br], as reported in Figure 20.

Figure 19: Current EU ethanol production capacity and historical consumption trend (Source: <http://www.epure.org/sites/default/files/publication/140612-222-State-of-the-Industry-Report-2014.pdf>)

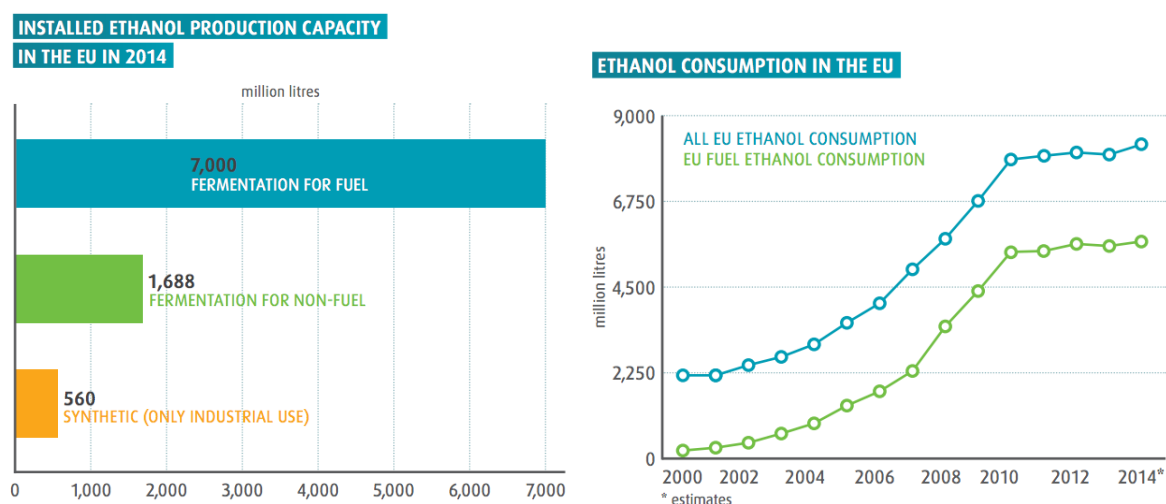


Figure 20: Worldwide ethanol balance, 2013 [Source:F.O. Lichts)

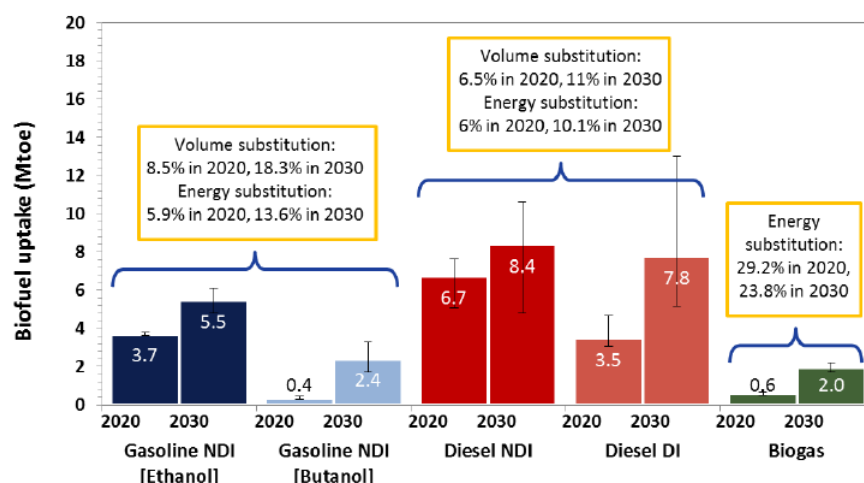
2013 ETHANOL BALANCE (billion litres)

	Production capacity	Production	Consumption	Imports	Imports % of consumption	Exports
U.S.A.	56	51	50	1.6	3.2%	2.9
Brazil	40.7	23.5	20.9	0.3	1.4%	3.6
EU	8.8	6.7	7.9	1.2	15.2%	0.1

Source: F.O. Licht

An extensive review on the potential penetration of biofuels for transport in EU by 2020 and 2030 is provided in (E4tech, 2013, A harmonised Auto-Fuel biofuel roadmap for the EU to 2030). The market forecasts for bioethanol in transport in EU according to this study are of about 7200 M litres (3.7 Mtoe) and 11000 M litres (5.5 Mtoe) respectively by 2020 and 2030, as reported in Figure 21.

Figure 21: Modelled biofuel use in 2020 and 2030 based on maximum uptake capacity and available biofuel supply



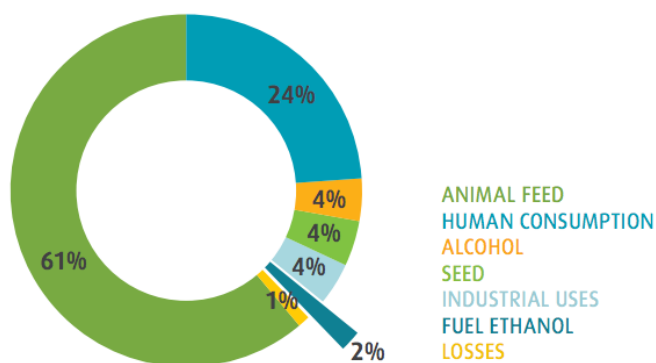
3.2. Typology of biomass feedstocks and biomass uptake forecasts

Since a few years, the research on production of ethanol based on organic materials has increased strongly. As previously mentioned, in long term ethanol can be produced via 2nd generation conversion processes based on cellulose and hemicellulose to ethanol technologies and producing lignin as by-product, and this is the focus of this study, as lignocellulosic biomass is investigated in the S2biom project. These conversion pathways seem to offer higher biomass to ethanol conversion efficiencies and the possibility to use residual and low cost lignocellulosic by-products in comparison to starch and sugar based biomass feedstocks.

In 2013 the EU ethanol industry used 7.83 million tonnes of grains and 1.5 million tonnes of sugar. 93% of the feedstock used to produce ethanol originated in the EU. According to the EU Cereal Balance 2% of the grain grown in the EU is used to produce fuel ethanol, which means that 98% of European grain production is used for other purposes. Production of renewable ethanol in Europe only uses around 0.7% of agricultural land, as reported in Figure 22, while in Figure 23 the feedstock share for EU ethanol production is reported.

Figure 22: End uses of EU cereals and share for ethanol production

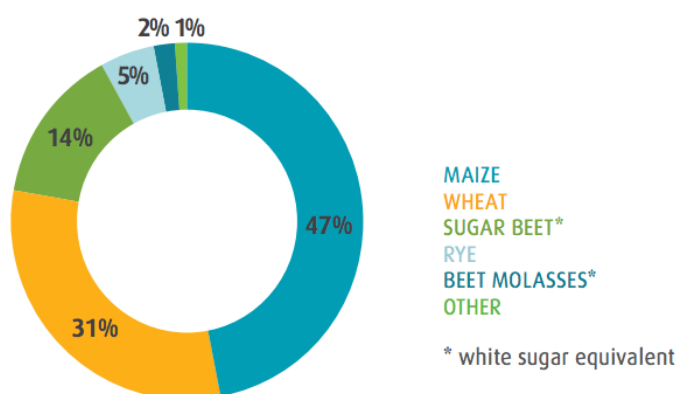
END USE OF EU CEREALS SUPPLY IN 2013/14



Source: EU Cereals Balance, DG AGRI, European Commission

Figure 23: Feedstock share for EU ethanol production

ESTIMATED FEEDSTOCK SHARE OF EU ETHANOL PRODUCTION (2013)



Ethanol can be produced by many different kinds of raw material. Even though most ethanol is still produced from agricultural crops, European production makes use of an ever-increasing variety of feed crops. The biggest share still comes from wheat, but there is also maize, barley, rye, triticale (a hybrid of wheat and rye) and sugar beet. The ability to vary feedstock gives producers flexibility and the possibility to adjust to market circumstances.

The biomass to ethanol conversion efficiency strongly depends on the typology of conversion process and biomass typology, and bioethanol to input biomass ratios can vary in the range of 0.18 to 0.45. In the case of lignocellulosic biomass, the content of cellulose is one of the most important parameters to estimate the bioethanol yield, and the technological improvements in pretreatment steps to separate cellulose and hemicellulose from lignin also play a relevant role.

In order to estimate the potential lignocellulosic biomass demand for EU ethanol in transport sector by 2020 and 2030, the following hypotheses have been done: (i)

ethanol demand forecast for transport by 2020 and 2030 from (E4Tech, 2013), and current EU consumption from European Renewable Ethanol Association (EPURE); (ii) conversion ratio bioethanol/input dry biomass of 38 and 40% for 2020 and 2030 (cellulose average content 45% and conversion efficiency to ethanol 85-90%); (iii) 80% of EU ethanol demand match by domestic biomass; (iv) share of lignocellulosic biomass consumed to produce ethanol of 30 and 50% respectively by 2020 and 2030 (the remaining being sugar and starch crops). Assuming a present consumption of 9.5 Mt/year of starch and sugar biomass for bioethanol, the remaining current lignocellulosic biomass consumption for EU bioethanol is around 0.667 Mt/year dry matter. The lignocellulosic biomass uptake to match respectively 30% and 50% of domestic biomass required according to 2020 and 2030 forecasts will be respectively of 3.5 and 8.7 Mt/year dry matter. It should be noted that, on the other side, the lignocellulosic biomass sustainable supply by 2020, according to Biomass Futures results, is only 0.924 Mt/year. For this reason, the EU bioethanol demand for transport is not expected to be met for 80% from domestic biomass and with a share of 30-50% from lignocellulosics.

4. PLA via lactic acid

4.1. Production route and application

Poly(lactic acid) (PLA), or polylactide, is a thermoplastic polyester, suitable for packaging materials, insulation foam, automotive parts, and fibres (textile and non-woven). It is the most commercially-available biopolymer, fully bio-based and derived from corn starch (in the US), tapioca roots, chips or starch (in Asia) or sugarcane and sugar beets (in the rest of the world). PLA is also biodegradable/compostable under certain circumstances.

Figure 24 illustrates the process chain for PLA production. Lactic acid can be produced via fermentation or chemical synthesis. Industrial lactic acid production utilises the lactic fermentation process rather than chemical synthesis. This is because although synthetic routes produce a high quality product, they use hazardous raw materials (hydrogen cyanide, acetaldehyde), have high energy intensity due to triple distillation, limited output flexibility and high manufacturing costs [1,2].

In general, pure L-Lactic acid is used for to produce PLA²⁸². To produce PLA, there are 3 primary polymerisation routes: direct condensation polymerisation, direct polycondensation in an azeotropic solution, and polymerisation through lactide formation – the current industrial-scale PLA production method. Lactide purification is done via high temperature vacuum-distillation, after which high molecular weight PLA with controlled purity is produced via ring-opening polymerisation. Other PLA methods cannot achieve the same high molecular weight and purity²⁸³. The platform biorenewable chemicals glycerine and lactic acid make up the bulk of biorenewable chemicals being sold in 2010, accounting for 79.2% of the market. There is a large range in market maturity for platform biochemicals, ranging from mature markets such as lactic acid to nascent markets for chemicals such as succinic acid. The strongest growth will be for secondary chemicals such as polylactic acid (PLA), polyhydroxyalkanoate (PHA) and bio-ethylene that are used to manufacture bio-based plastics.

Lactic acid is widely used in the food (as a preservative, acidulant, and flavouring), cosmetic, pharmaceutical, and chemical industries (as a raw material for the production of lactate ester, propylene glycol, 2,3-pentanedione, propanoic acid, acrylic acid, acetaldehyde, and dilactide), and has received increased attention for use as a monomer for the production of biodegradable ploy(lactic acid).

Figure 24: Production pathway for PLA; cellulose can be easily substituted to starch crops to produce C6 sugars through enzymatic hydrolysis [3]



4.2. Market

4.2.1. Current market

The worldwide demand for lactic acid is estimated roughly to be 130-150 ktonnes per year (data from 2005), with the expectation to grow to 500 ktonnes in 2010. The commercial prices of food grade lactic acid range (data 2005) between 1.38 \$/kg (for 50% purity), and 1.54 \$/kg (for 88% purity). Lactic acid consumption in chemical applications, which include PLA polymer and new "green" solvents, such as ethyl lactate, is expected to expand 19% per year [3]. On an industrial scale, the manufacturing cost of lactic acid monomer will be targeted to less than 0.8 \$/kg, because the selling price of PLA should decrease roughly by half from its present (data 2005) price of 2.2 \$/kg [4].

In other references, the global demand for lactic acid (including PLA) is estimated at 472 ktonnes, with revenues of around \$685m, based on market prices for bio-lactic acid of 1,300 – 1,600 \$/tonne [5]. Approximately 45% of lactic acid is used for industrial applications (including lactic acid for PLA), with the more conventional food additive, pharmaceutical and cosmetic markets demanding around 260 ktpa [6]. Global production capacity is estimated to be around 750 ktpa, with a strong presence in China.

In 2014, global production of PLA was estimated as being around 120 ktonnes, with estimated revenues of \$252m, based on a current price of \$ 2,000-2,200/tonne [3,7-8]. The market price for PLA varies by region: US prices have in the recent past been 1,800 - 2,870 \$/tonne, whereas Chinese prices are around 3,500 \$/tonne (due to much smaller PLA facilities) [3,9,10]. According to [10], global PLA production capacity stands at around 200 ktonnes, although with a number of medium sized plants due to come online soon. PLA is primarily used for packaging applications, accounting for around 60% of its total market.

The PLA market is expanding, and although the downstream processing has improved substantially over recent years which has served to lower the price, it is still more expensive than fossil alternatives that serve similar markets. Addressable markets include: (i) Polystyrene (PS) which in 2012 was estimated at 10.5 million tonnes with a market value of \$22 billion (\$2,100/tonne) [11]; (ii) Polypropylene (PP), which in 2011 was estimated at 42 million tonnes with a market value of \$77 billion (\$1,830/tonne) [12,13]; (iii) Polyethylene terephthalate (PET), which in 2013 was estimated at 20 million tonnes with a market value of \$31 billion (\$1,500/tonne) [14]. These fossil-derived plastics prices are however likely to have fallen recently with lower crude oil prices in late 2014, making the economic competitiveness of PLA more challenging.

Other market analysis shows growth per annum to be in the 10-30% range (15-17). Bio-based polymer markets have been dominated by biodegradable food packaging and food service applications.

4.2.2. Market projections

Estimates for the future development of the global PLA market vary quite widely, with either 950 ktpa produced by 2020 [18] (a CAGR of 40%), or more conservatively, only 600 ktpa by the year 2025 (a CAGR of 10%) [19]. At prices of \$2,100/tonne, the market would be valued at \$1.3 – 2.0 bn a year. Packaging is likely to remain the key application segment for PLA. Given Europe's strong drive towards bio-based packaging materials, it is anticipated that Europe will remain a regional leader until 2020 [20]. The share of PLA in Europe's total biopolymer production is expected to be around 13% (216 ktonnes) in 2015.

Demand for more environmentally-friendly packaging products, and the use of PLA in starch-based plastics is expected to drive demand for PLA over the next few years. Further incentives include renewable energy targets and a shift to renewable feedstocks, and health concerns related to chemical toxicity. Previously high oil price rises and price volatility for complex hydrocarbons derived from crude oil [21] have opened a market gap for bio-based chemicals. This may help to increase global PLA demand, and improve the price competitiveness.

4.3. Type of biomass feedstock and percentages in end product

The same feedstock of bioethanol, mainly starch product but with pre-treatments also other lignocellulosic biomass.

Biomass share in PLA is difficult to be assessed, in particular since one of the major advantages of PLA is the capability to produce hybrid paper-plastic packaging with a mix of different typologies of biomass or mixed fossil-biobased materials.

4.4. Conversion efficiency and performance

The production process has favourable yields of up to 80% – better than bio-plastic equivalents such as bio-PP, bio-PET, and bio-PE [22]. The value proposition of PLA is primarily attributed to its environmentally beneficial properties. PLA plastic is durable – offering a viable alternative to traditional thermoplastic products, and disposable – it is degradable and can be composted easily compared to petroleum-based equivalents, and it does not emit toxic gases on incineration. PLA production has multiple advantages, including the ability to recycle back to lactic acid via hydrolysis or alcoholysis and capability to produce hybrid paper-plastic packaging that is compostable [23].

PLA offers a substantial reduction in GHG emissions and energy use compared to competing fossil equivalents such as polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET). The current production of PLA realises GHG emissions savings of between 30 – 70%, and this could be increased to as much as 80% as processing technologies improve [3]. New generation PLAs, using crop residues and renewable energy, promise further reductions.

4.5. Technology maturity

PLA manufacturing technology is mature; however the product itself suffers from performance drawbacks as compared to conventional plastics. For example, PLA typically has a high tensile strength, low toxicity and good appearance (glossy with high transparency), but suffers from brittleness, poor gas barrier performance and is susceptible to distortion at relatively low temperatures (i.e. lower heat resistance). However, PLA producers have been working to develop proprietary processes in order to improve these characteristics and PLA has been shown to have an adjustable set of physical properties. NatureWorks offers 21 grades of PLA resin, each with a different molecular weight and varying lactic acid co-monomer ratio, which have been customised to suit different production techniques and product requirements [24]. Corbion Purac has recently developed a breakthrough stereochemically pure lactide monomer, which can be used in PLA homopolymers to produce polymer blends which show heat resistance properties similar to PP, PS & ABS type materials [25].

In summary, PLA offers a strong environmental incentive for replacement of fossil equivalents. It has a lower carbon footprint and uses less energy, and offers improved end-of-life options because it is biodegradable and low in toxicity. It does have performance drawbacks, including low heat resistance and impact resistance, however these are improving rapidly as manufacturers customise the PLA resin grade to their production method and purpose. It is not yet available in high volumes, and has a slightly higher market price than fossil-based competitors, however there is a strong commercialisation drive which will increase economies of scale.

4.6. Major operators

The PLA market is consolidated in nature, with a few large industry participants. The primary European actors, producing both PLA and lactic acid, are discussed below, with other global players briefly mentioned [3]. The largest global commercial producer of PLA is USA-based NatureWorks, while the largest global lactic acid producer is Corbion Purac.

The main European PLA producers are [3]:

- Futerro, which is: A joint venture between Galactica and Total Petrochemicals, Futerro and it has been operating a 1.5 ktpa demonstration plant in Escanaffles, Belgium since 2010 to produce various PLAs (including PLLA, PDLA and copolymer of L and D lactide); Pyramid Bioplastics: a joint venture between Pyramid Technologies and German Bioplastics to build a PLA plant of 60 ktpa size; Synbra Technology, which developed a new, cost-effective polymerisation process to produce high-quality PLA from a biorenewable resource, and that also uses its own PLA production capacity to produce expanded PLA foam, a biodegradable alternative to expanded polystyrene foam; Uhde Inventa Fischer, part of ThyssenKrupp Industrial group, which constructed a pilot plant in 2010 to produce 0.5 ktpa of PLA in Germany, and it is now able to license its PLA production technology to plants with capacity of up to 60 ktpa. Together with Myriant, in 2013 ThyssenKrupp opened a multi-purpose fermentation pilot plant in Germany to produce 1 ktpa biochemicals annually, including lactic acid.

In addition, Cellulac In 2013 announced plans to convert a brewery in Ireland into a lactic acid and PLA plant, with. Initial capacity of 20 ktpa, ramping up later to 100 ktpa. Corbion Purac announced in October 2014 that it will integrate downstream by becoming a PLA producer, if customers will commit to buying at least one third of the output of a planned 75 ktpa PLA plant in Thailand. Corbion Purac has also announced a collaboration with Japanese Toyobo to produce Vyloecol, an amorphous PLA product for coating and adhesive applications, for the European market.

European lactic acid producers are [3] Corbion Purac, which produces lactic acid, lactic acid derivatives and lactides (including lactide resins for high performance PLA bioplastics), and it is well known for expertise in fermentation of L- and D-lactic acid and subsequent conversion into high purity and 100% biobased L- and D-Lactides. Corbion Purac operates 5 production plants globally, and the largest one has 100 ktpa production capacity. In Thailand, Corbion Purac also operates a 75 ktpa lactide plant. Corbion Purac also operates a demo plant for succinic acid in Spain together with BASF through the Succinity GmbH JV.

Galactica produces lactic acid and lactides in manufacturing plants in Europe (30 ktpa), Asia and America (15 ktpa). Their major shareholder is Finasucre, one of the world's largest producers of sugar. In 2002 Galactica also formed a joint venture with BBKA Biochemical, B&G, in China (Bengbu) for the production of L (+) lactic acid with a capacity of 50 ktpa. Jungbunzlauer, known mainly for the production of citric acid and gluconic acid, has been operating since 2012 a lactic acid plant from its production site in France.

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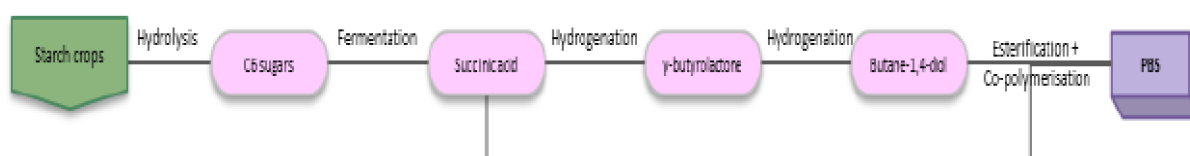
5. Butanediol and THF via succinic acid

5.1. Production route and application

Succinic acid is a 4 carbon platform chemical that has a broad range of applications, from high-value niche applications such as personal care products and food additives (used in the food and beverage industry as an acidity regulator), to large volume applications such as bio-polymers (for example PBS), plasticizers, polyurethanes, resins and coatings.

Petrochemical succinic acid has predominantly been produced from butane through catalytic hydrogenation of maleic acid or maleic anhydride [1]. Bio-based succinic acid (BSA) is most commonly produced through low pH yeast or bacterial fermentation as shown in Figure 25. Other competing routes to produce succinic acid start from glycerol, whilst BDO can also be fermented directly.

Figure 25: Conversion pathway for succinic acid, butanediol and PBF (polybutylene succinate) [2]



Butanediol as a whole may refer to four different isomers of butanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol and 2,3-butanediol. Out of the four compounds mentioned above, 1,4-butanediol (1,4 BDO) is widely used leading to it being commonly referred to as butanediol. The biggest application market for 1, 4-BDO is to manufacture tetrahydrofuran (THF), which is not only used as a solvent in chemical industry, but is also a key raw material for manufacturing spandex via producing polytetramethylene ether glycol. Spandex is a synthetic fiber which is popularly known for its exceptional elasticity and its strength. However it is less durable than its major non-synthetic counterpart, natural latex. The growth of sports apparels market is one of the drivers for tetrahydrofuran demand, which in turn is reflected in global 1,4-butanediol sales. Increasing number of sporting events around the world has been fueling the demand for spandex. The global market for sports apparels was valued over USD 70 billion in 2012 and is expected to grow fast [3]. THF emerged as the leading application segment for 1, 4-butanediol and accounted for 29.94% of total market volume in 2012.

Another key application of 1, 4-BDO is to manufacture polyurethanes, which has immense downstream applications. Increasing footwear demand, mainly in Asia Pacific and Latin America, is expected to contribute to the growth of 1, 4-BDO market. The global footwear market was valued at over USD 180 billion in 2012 and is expected to propel owing to growing disposable income level mainly in BRICS nation.

Polyurethane accounted for 25.2% of total market volume in 2012. However, growing concerns regarding the impact of synthetic 1, 4-BDO on environment is acting as one of the major barrier for the global market. Owing to these concerns, there is shift in consumers demand for eco-friendly bio-based products which are derived from renewable raw materials and are environment friendly. Governments in mainly U.S. and Europe have adopted stringent regulations on the production of 1, 4-BDO and are supporting the use and production of bio-based alternatives to fulfil the growing end use need of 1,4-BDO. Bio-based alternatives for producing 1,4-BDO, not only provide a clean solution, but also enable cost competitiveness to the bio-based 1,4-BDO producers against their conventional counterparts. Synthetic 1,4-BDO is produced from acetylene which is produced by burning hydrocarbons synthesized by crude oil. A number of industry participants such as BASF, Purac, Myriant, Mitsubishi Chemicals, DSM, Genomatica and others have been focusing on development of bio-based 1,4-BDO. Different companies are coming up with different routes to produce bio-based 1, 4-BDO. Some of the upcoming technologies to produce bio-based 1, 4-BDO include sourcing them from raw materials such as bio-based succinic acid and sugar which includes biomass and polyhydroxyalkanoate (PHA) among others.

Polyurethane is also expected to be the fastest growing application market for BDO at an estimated CAGR of 5.1% from 2014 to 2020. Polyurethane was followed by PBT which accounted for 22.1% of total market volume in 2012. PBT is mainly used in household electrical engineering and in the production of plug connectors in the automobile industry. The global demand for BDO in GBL (gamma-butyrolactone) is expected to reach 492 ktons by 2020 at an estimated CAGR of 4.3% from 2014 to 2020. The growth of GBL is primarily due to its downstream applications as a pharmaceutical intermediate, in herbicides and in foundry resins. It is also used as an extraction solvent via N-methyl-2-pyrrolidone.

A process developed by BP Amoco and Lurgi, based on direct oxidation of butane to maleic anhydride, is currently believed to be the low cost technology for THF production [4]. The production of THF can be achieved from any of the technologies that produce 1,4-BDO. BDO is dehydrated to yield THF, with an overall yield generally greater than 90%

5.2. Market

5.2.1. Current market

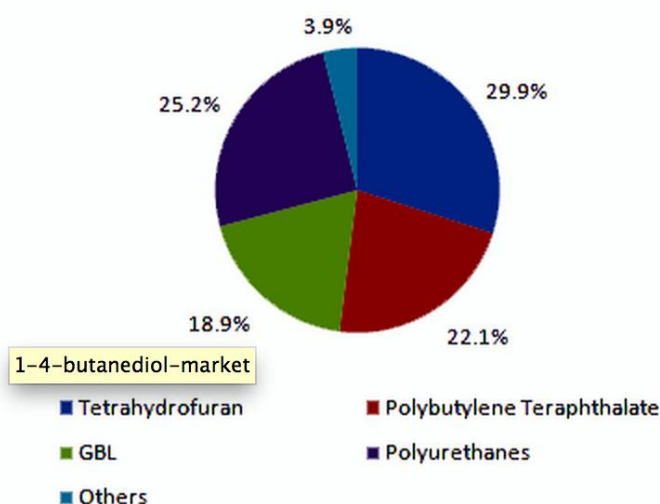
The world market for succinic acid was approximately 30 kTon in 2009, of which less than 5% was produced from bio-based feedstock. Biorenewable succinic acid is just entering the marketplace, but by 2015, will account for two thirds of the estimated 90 kTon/year global succinic acid market [3]. In 2013, global production of bio-based succinic acid was 38 ktonnes at a total bio-based market value of \$108 million.

Fossil-based succinic acid production was approximately 40 ktonnes with a market value of \$100 million [5]. Bio-based succinic acid has a current market price of approximately 2,860 \$/tonne, while the fossil-based equivalent is valued at around 2,500 \$/tonne [6]. At larger scale (typically 50 ktonnes), bio-succinic acid has the potential to be cheaper than fossil-derived succinic acid.

As a platform chemical, bio-based succinic acid has an estimated potential addressable market of \$7- 10 billion [7], including \$4 billion from large volume industrial chemicals such as 1,4 butanediol (BDO), tetrahydrofuran (THF), and gammabutyrolactone (GBL). Another derivative of succinic acid is polybutylene succinate (PBS), a key polymer used in the production of bio-plastics. Bio-based BDO is currently selling at 3,000 \$/tonne with a market volume of 3 ktonnes, which, while more expensive than the fossil-based alternative, is expected to become increasingly competitive as it reaches economies of scale. Bio-based PBS has a current market price of approximately 4,500 \$/tonne, market volume of 5 - 6 ktonnes and a market value of around \$24 million[8]. The global market volume share for butanediol is shown in Figure 26.

Figure 26: Market segmentation and global market volume share of butanediol by application (source Grand View Research, 2012)

Global 1, 4-butanediol market volume share, by application, 2012



5.2.2. Market projections

Several companies have aggressive growth plans in the coming years. BioAmber are currently building a commercial-scale plant in Sarnia, Canada with plans for two additional plants, which will create capacity of around 300 ktonnes by 2020. All of this production is already agreed for sale; BioAmber already have over 19 supply and distribution agreements excluding those with PTT-MCC BioChem and Vinmar [9]. In 2011 Myriant stated plans to expanding operations with a 100 ktpa plant in Nanjing,

China with China National BlueStar, however the status of these plans is unconfirmed. They are also cooperating with Sojitz in Japan. These growth plans are likely tied to the expectation that bio-based succinic acid will open up new markets and applications, especially as a platform chemical for the production of BDO and PBS362. It is expected that the scale benefit and lower costs of raw materials for succinic acid will lead to considerably reduced production costs.

By 2015, up to two-thirds of succinic acid production is expected to be bio-based. Continued collaborations, R&D and cost reduction are therefore likely to create a highly competitive market for bio-based succinic acid, BDO and PBS in the coming years. By 2020 the bio-succinic acid market is projected to reach 600 ktonnes with annual revenues of \$539 million [2], however this translates to an optimistic market price of under 1,000 \$/tonne, which seems somewhat unlikely given today's production costs. The main market demands for bio-based succinic acid are expected from BDO and PBS. Volumes for bio-based PBS are expected to grow at 37% CAGR, reaching 82 ktonnes of succinic acid demand by 2020; bio-based BDO from succinic acid is expected to grow at a CAGR of up to 43%, reaching 316 ktonnes of succinic acid consumed by 2020.

More conservative market estimates only state a total of 250 ktonnes of bio-based succinic acid by 2020 [2].

5.3. Conversion efficiency and performance

The costs of production compared to petroleum-derived succinic acid have been equal as of 2013 [10] and petrochemical succinic acid is now mainly being used only in niche markets due to increasing production costs. BioAmber believes it can competitively produce bio-based succinic acid at a crude oil price above 35 \$/barrel and corn prices of 6.50 \$/bushel [11]. It is therefore expected that a less costly bio-based production of succinic acid will lead to stronger competitiveness and larger market demand [12].

Furthermore, today's technology for the production of succinic acid from biomass can realise a significant reduction in GHG emissions compared to petrochemical equivalents. Succinity has reported 75% GHG savings compared to petrochemical succinic acid, while BioAmber has reported over 100% savings with petro-succinic acid emitting 7.1 kg CO₂e/kg SA compared to -0.18 kg CO₂e/kg SA for the bio-based production route on a cradle/field-to-gate basis. In a detailed footprint study researchers have recently shown that a low-pH yeast route to bio-based succinic acid has the lowest environmental impact in terms of energy use and carbon emissions [13,14]. This is the route Reverdia is using. The two largest factors affecting GHG savings are feedstock production and the carbon intensity of the electricity grid in which the production plant is located, especially if energy intense

downstream processing has been applied (such as electrodialysis of the succinate salt following fermentation).

The physical properties of bio-based succinic such as density, viscosity, molar volume and surface tension are identical to those of petro-based succinic acid and the chemical is therefore considered a drop-in with no additional investment required in new production equipment. The main value propositions offered by bio-based succinic acid are therefore price competitiveness, lower environmental impact and ease of production. Bio-based PBS is becoming steadily more cost-effective compared to its petrochemical counterpart, which is directly linked to recent cost reductions in bio-based succinic acid and BDO. Further, bio-based succinic acid is also considered a near drop-in for fossil adipic acid in applications such as resins, plasticizers and polyester polyols for polyurethanes. It offers additional performance benefits compared to adipic acid, including improved hardness and flexibility of powder coatings, shorter drying times in alkyds and better chemical resistance in polyurethanes based systems.

5.4. Major operators

Unlike some sectors, there is intense competition within the bio-based succinic acid sector, with several EU and non-EU actors at similar levels of development.

Europe [2]:

- Reverdia: JV between Roquette and DSM established in 2008. They started operating a 10ktpa plant in Cassano, Spinola in Italy in 2012. Reverdia is collaborating with players in the PBS, PU, plasticizers, resins and coatings applications including cooperating with Chinese companies active in the area of plasticizers either as a supplier of succinic acid or co-developer of various markets [15]. Next to production, Reverdia has also announced that it offers its Biosuccinium™ low-pH technology for licensing.
- Succinity: JV between Corbion Purac and BASF established in 2013 (with joint R&D since 2009). Headquartered in Dusseldorf, Germany, they started operating a 10ktpa plant in Montmelo, Spain in 2013. Succinity has plans for a second large-scale 50 ktpa facility, the final investment decision for which will be made following a successful market introduction of the Montmelo plant BSA [16].

Rest of world:

- BioAmber: Canadian company who have run a 3ktpa demonstration plant in Pomacle, France since 2010. They are currently constructing a 30 ktpa plant (with 20 ktpa expansion plans to 50 ktpa total capacity) in Sarnia, Canada with JV partner Mitsui & Co. They are also planning a second plant in North America, producing 100 ktpa BDO and 70 ktpa succinic acid, to commence operation in 2017 or 2018 [17], with a third (200 ktpa) for startup in 2020 [18].

- Myriant: A US-based company operating a small production plant (1ktpa) in Leuna, Germany with ThyssenKrupp. Myriant also completed construction of the first commercial bio-succinic acid plant (14 ktpa) in Louisiana, North America in April 2013. A second plant, with 64 ktpa capacity, is being planned for start-up in 2015 [19].

A number of partnerships and joint ventures have developed in the bio-based succinic acid (and associated downstream) industries. BioAmber recently signed a 3-year exclusive supply contract with PTT-MCC Biochem, to supply 80% of their bio-succinic acid needs, for PBS production [20]. The partners also collaborate to test proprietary organisms in BioAmber's production facility in France to further lower production costs [21]. A further take-or-pay supply contract with Vinmar will see annual uptake of 210 ktpa when all three plants are operational. BioAmber has also teamed with NatureWorks to create Amberworks - making polylactic acid (PLA) and PBS composites. Both Showa Denko KK (Japan) and Uhde Inventa Fischer (Europe) make use of Myriant's bio-succinic acid for PBS production. Another partnership BioAmber is involved in is with Evonik on the production of BDO, THF and GBL.

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6. Lignin in lignin chemistry

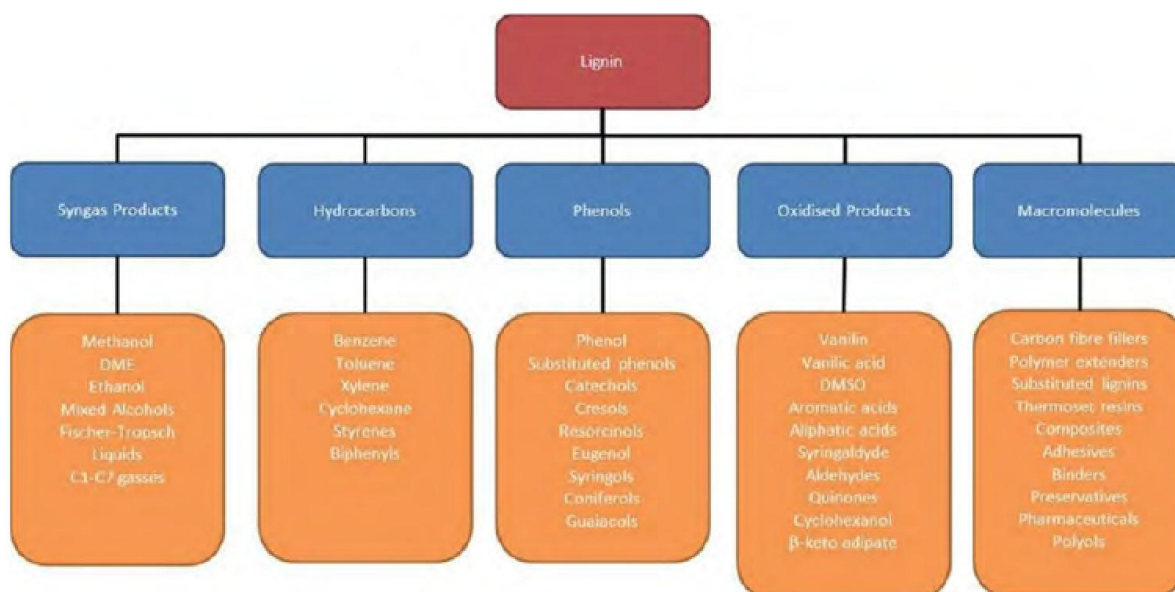
6.1. Production route and application

The dominant force in lignin production is the pulp industry, that produces lignins from forest products. Very recently the technology to produce lignin from bio-refineries is emerging on a commercial scale. Bio-refineries can operate on alternative feedstocks, many from agricultural sources, producing a variety of lignins with properties different to those from pulping. The combined production of lignin and other value-added bio-materials and biofuels offers a significant opportunity for enhancing the operation of a lignocellulosic biorefineries. In fact, lignin is an extremely abundant raw material contributing as much as 30% of the weight and 40% of the energy content of lignocellulosic biomass [1]. As regards potential applications, the innate chemistry of lignin, a phenolic heteropolymer, has allowed it to make inroads into the high value polymer industries whilst continuing to act as feedstock material for the binder industries. Indeed the replacement of phenolics by lignin in resins systems is economically attractive with the phenolic resins market utilising approximately 2.52 M tonnes in 2001. For this reason, lignin could play a central role as a new chemical feedstock, particularly in the formation of supramolecular materials and aromatic chemicals [1,2], as reported in Figure 27. However, lignin derived from different biomass sources and isolation processes have significantly differing reactivity, molecular weight distributions, melting points and polyelectrolyte properties. These will be different in turn from the lignin recoverable from pulp mills. The use of lignin for chemical production has so far been limited due to contamination from salts, carbohydrates, particulates, volatiles and the molecular weight distribution of lignosulfonates. The only industrial exception is the limited production of vanillin from lignosulfonates [3].

Manufacturing of products will thus require some degree of matching the lignin feedstock to its intended final product. The use of lignin as an additive to solid fuels is however one application that can easily use lignin from a variety of sources, while commercial uses of lignin, other than in fuel, is expected to develop after 2020 [1].

A comprehensive overview of potential applications, markets and economics of lignin as a bio-material is provided in [8]. In particular, due to the vastity of the sector, the applications of lignin as bio-material are subdivided into specific subsectors, with some overlap between these, and in particular phenolic resins, epoxies, adhesives, polyolefins and miscellaneous, which includes novel applications. For each subsector, specific examples are highlighted and in some cases the economics are presented.

Figure 27: Potential products from lignin [IEA Bioenergy, Task 42 biorefineries]



The production of bioethanol from lignocellulosic feedstocks could certainly result in new forms of higher quality lignin becoming available for chemical applications. The Canadian company Lignol Energy has announced the production of cellulosic ethanol at their continuous pilot plant at Burnaby, British Columbia. The process is based on a wood pulping process using Canadian wood species but the pilot plant will test a range of feedstocks while optimising equipment configurations, enzyme formulations and other process conditions (4). The Lignol Energy process produces a lignin product (HP-L™ lignin) upon which the company is developing new applications together with industrial partners. Also other lignin types will results from the different biomass pretreatment routes under development and unfortunately there is not one lignin macromolecule which fits all applications. However, if suitable cost-effective and sustainable conversion technologies can be developed, a lignocellulosic biorefinery can largely benefit from the profit obtained from this side stream lignin (5).

The production of more value added chemicals from lignin (e.g. resins, composites and polymers, aromatic compounds, carbon fibres) is viewed as a medium to long term opportunity which depends on the quality and functionality of the lignin that can be obtained. The potential of catalytic conversions of lignin (degradation products) has been recently reviewed (6).

As regards existing and future applications, up to now the vast majority of industrial applications have been developed for lignosulfonates. These sulfonates are isolated from acid sulfite pulping and are used in a wide range of lower value applications where the form but not the quality is important. The solubility of this type of lignin in water is an important requirement for many of these applications. Around 67.5% of world consumption of lignosulfonates in 2008 was for dispersant applications

followed by binder and adhesive applications at 32.5%. Major end-use markets include construction, mining, animal feeds and agriculture uses.

Besides lignosulfonates, lignin is produced as commercial product at about 60 kton/y. New extraction technologies, developed in Sweden, will lead to an increase in Kraft lignin production at the mill side for use as external energy source and for the production of value added applications.

New environmentally friendly chemical pulping technology is being developed using organic solvents (organosolv pulping) that will produce better quality pure lignin, for example: Alcell – ethanol; Acetsolv – acetic acid; Formacell – Formic acid and phenol; Organocell – methanol.

The Alcell process is the most commercially advanced, developed by Repap Industries in New Brunswick, Canada during 1987-97. It produces a natural “organosolv” lignin. Unfortunately Repap collapsed in 1997, and the technology was acquired by Lignol Innovations Corporation, that plans to build a biorefinery technology to produce ethanol and very pure lignin, as previously described.

In the following, the most promising applications for lignin are summarized:

A) Phenolic resins

Lignin can be used as a phenol substitute in phenol formaldehyde resins but its chemical heterogeneity is the limiting factor, and this can be countered via biochemical modifications, addition of filler agents (starch based materials), or novel lignin processing (acetosolv, acid hydrolysis and organosolv processes). On a purely economic basis the introduction of lignin to the phenolics market is promising [8]. Global production of phenol is almost exclusively based on the cumene-based acetone co-product process and produced 8.25 Mtonnes in 2004 of which 30.6% went for use as phenolic resins. Predictions for the future suggest that the current 1380 Eur /tonnes price for phenol is set to increase along with the predicted annual demand. In addition the increasing legislation surrounding waste and effluent management and renewable materials mean that the employment of lignin in this field is eminently logical.

B) Epoxy resins

The use of lignin in this resin field requires high purity levels (no salts, water and sugars). This can be achieved by purifying waste lignins (precipitation, deionisation, etc.) derived from the common pulp and paper processes (Kraft, Soda, etc.) or direct use of lignin from the less condensing pulping processes such as Alcell, non-wood fibres pulping. There have been several developments and reports focussed on lignin–epoxy developments [9,10]. Currently the scale of operation is between the patent and development stage. Conversely, the production of lignin–epoxy resins for moulded composites encompasses the laboratory to industrial scale with the Lenox®

lignin–epoxy resins being produced at 350 kL/annum at their peak prior to liquidation of the company in 2000. The origin and subsequent extraction/processing of the lignin has a distinct effect on the ultimate properties of the composite. Epoxy–lignin blends derived from different lignin types showed that those blends containing hardwood lignin (TomliniteTM and EucalinTM) separated by the Kraft process or isolated by steam explosion crosslinked more efficiently than those derived from softwood lignin. The epoxide resin market is economically vibrant and the three leading producers of epoxy resins are Hexion (formerly Shell's Epoxy Resins and Resolution Performance Products), Dow and Huntsman. Together they account for approximately 75% of the world's capacity. Given that the market is expanding, opportunities for lignin are expected, especially as its inherent properties, also reflected in the end product, are studied and characterised in more detail [8].

C) Adhesives

The principle point of entry for lignin in the adhesives subsector is likely to be in fibreboard production. The fibreboard market has a large turnover but operates on a low-profit margin and this makes the introduction of new technologies notoriously difficult. However, given the increasing legislation surrounding the restriction of chemical usage in fibreboard formation it is likely that alternative, safer sources will be sought and the laccase system should benefit from this.

D) Polyolefins

The polyolefin (PO) subsector may be a welcome home for a lignin feedstock and it would integrate via polymer blends and UV stabilisation. An increasingly important factor surrounding plastics in general but specifically polyolefin-based products is their recalcitrance to biodegradation, and this is one area where there are significant benefits to be achieved by the incorporation of lignin. Variation of the degree of lignin incorporation is reported to be accompanied by increases in the degree and rate of biodegradation. The global market for polyolefins is enormous with PE and PP representing roughly 60% of all the thermoplastics produced and sold in the world with an associated large economic value [11]. Global demand for all types of PE exceeded is projected reach 63.4 Mtonnes in 2006 [11]. Polypropylene (PP) resins are another fast growing category with a predicted consumption of 38 Mtonnes in 2005.

6.2. Market

6.2.1. Current market

There is an estimated 50 million tonnes of lignin available from pulping processes worldwide, but much of this is not available for further processing but burned onsite to provide steam for heat and power production. The global production of isolated lignin for lignosulphonate production from conventional chemical pulping operations

is currently around 1.1 million tonnes, of which 1 million tonnes is derived from the acid sulphite pulping process, and the remaining 100,000 tonnes is derived from the Kraft pulping process.

The current lignin market has instability due to the poor economic health of the chemical pulping companies that produce it. This situation can benefit future biorefineries that will be processing lignocellulosic feedstock. Certain biorefinery pre-treatment technologies, such as organosolv processes, will have the capability to produce a superior form of pure lignin ideal for chemical applications. The marketing of this lignin as a co-product will add substantial revenues and vastly improve the economics of the biorefinery [1].

Major end-use markets of lignin include construction, mining, animal feeds and agriculture. The principal markets for lignosulphonate are summarised in Figure 28.

Figure 28: Principal markets for lignin (7)

Large markets	Dust control	Animal feed	Concrete admixtures
Medium markets	Dye dispersants	Gypsum wallboard dispersant	Vanillin
Small to medium markets	Oil well drilling mud additive	Resins	Binders
Small markets	Carbon black, emulsifier, water treatment, cleaning chemicals, micronutrients, leather tanning, battery expander, pesticides dispersant, rubber additive		

6.2.2. Market projections

Lignin isolated from a fractionation process could be used for the production of chemicals or combusted, either on site or sold to external markets. There is no commodity market in lignin thus it is difficult to elucidate a market and price at which it could be traded. The new biorefineries will more than likely be on a considerably smaller scale than world scale Kraft pulp mills that are now processing 3000 to 4000 tonnes of wood on a dry weight basis per day. Consequently biorefineries will be more flexible and better suited to produce and market some of the specialized lignin that will emerge from them [1].

It is anticipated that a market for these lignins in fuels, especially in fuel pellets is available now. Further technical and market development of chemical products from these lignins is likely to take in excess of twenty years. References [2,8] provide an excellent overview of products that could be developed from lignin and lignosulphonates, also the technical and economic barriers to their establishment in the market.

Some of the products have already been developed, but to date the production of lignins and lignosulphates has been partly unreliable. Until now they have been derived from wood pulping operations whose primary markets of paper type products have declined, with mill closures.

The potential value of lignin in new products and to offset the use of petroleum based materials has now being recognized. However, considerable research, in some cases fundamental research, and development work is required to develop economical lignin production, new products and markets.

The lignocellulosic biofuels sector could result in an increase in lignin availability. The quality and amount of lignin will vary depending on the technologies adopted. Lignin from steam explosion pre-treatment and from pyrolysis is reportedly lower in molecular weight than kraft lignin [5], whilst lignin derived from acid hydrolysis pre-treatments is reportedly unsuitable for chemical use unless non-standard technologies are used [5].

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Annex I: Level of R&D and commercial activities

The geographical distribution of manufacturing, demonstration and research centres for sugar platform bio-products is illustrated in Figure 29, based on the list of companies gathered in the TRL database, as presented in [E4Tech, 2015].

Of the commercial manufacturing plants, approximately 45% are located in China, 30% in the US, 15% in Europe, and 10% in Brazil. China therefore shows the highest average TRL for its facilities. Lignocellulosic bioethanol production already occurs at commercial scale in all four regions, with the US being the main focus of deployment activities at present. Around 20% of the companies in the TRL database operate facilities in more than one world region – companies are increasingly multi-national, and make investments where it is cheapest to do so (and not only in their home region).

Research centers and demonstration facilities of bio-based companies are instead mostly located in the US and Europe, reflecting the academic and research strengths in these regions, the availability of highly skilled personnel capable of carrying out this work, and hence an attractive environment for research investment. Brazil has relatively low levels of activity in R&D, piloting and demonstration, although does have a few early commercial projects.

The EU knowledge base is very well established, but currently mainly being exploited abroad. This is not a recent trend – a historical example quoted in the workshops was that of citric acid, which was established in the EU, but due to production cost competition, all but two plants have moved to China over the decades.

To date, the EU has largely invested in basic and applied research, more so than in demonstration activities, whilst the US has had a more balanced approach, and China has been more focused on commercial activities. Europe's position with regards to demonstration facilities is however set to improve in the coming years with H2020, NER300 and BBI funded plants (once these are identified and constructed), particularly in the area of advanced biofuels.

However, other non EU regions have also recently been investing heavily in basic and applied research. Brazil is researching in the field of bio-based products to realize added value from the availability of cheap sugars. Asia is also improving its position in the R&D arena, demonstrated by the increased number of relevant scientific papers published in the last 5 – 10 years.

Figure 29: Number of commercial, demonstration and research facilities per region, source E4Tech, 2015-01-16

