Chapter 4
Starch Biomass for Biofuels, Biomaterials, and Chemicals

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Abstract The success of modern biorefineries, including those using starch-based feedstocks, should be based on versatile biomass supply chains and on the production of a wide spectrum of competitive bio-based products. This chapter summarizes the current knowledge of bio-based products obtained mainly from biochemical platforms from starch- and sugar-based feedstocks. After an initial review of starch production sources and starch properties as well as starch-based end applications, this chapter reviews the state of the art of starch hydrolytic enzymes, focusing on a bio-based platform for the main value-added (bio)chemicals, biofuels, and biomaterials that can be obtained from sugar-based feedstocks.

At the present time, food and biofuels applications still dominate most of the uses of starch-based raw materials. Although bio-based chemicals and biomaterials still do not account for a significant share of current biomass use, new bioeconomy sectors are emerging such as biomaterials and green chemistry, and several markets (e.g., bioplastics, biolubricants, biosolvents, and biosurfactants) are expected to grow in the near future. Several examples of biological production routes are described in this chapter, namely, for ethanol, lactic acid, and polylactic acid (PLA), polyhydroxyalkanoates (PHAs), succinic acid, 1,4-butanediol (BDO), farnesene, isobutene, acrylic acid, adipic acid, ethylene, and polyethylene. One example of using a chemical catalytic route to obtain furan-2,5-dicarboxylic acid (FDCA) is also reported.

Keywords Starch • Sugar platform • Bio-based products • Biofuels • Biomaterials • Chemicals • Bioeconomy

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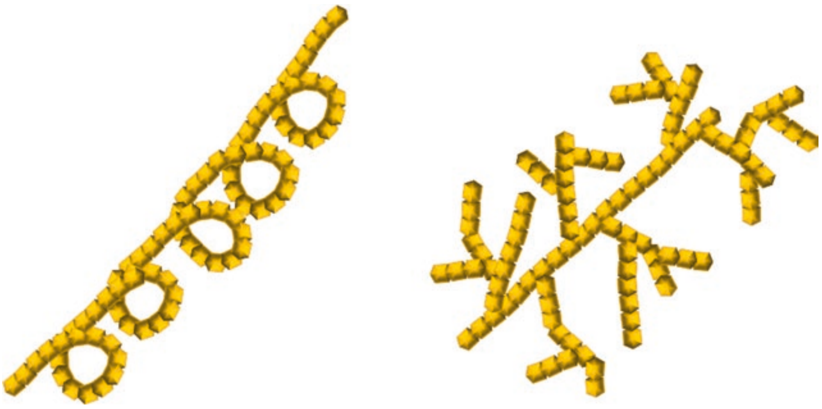
4.1 Introduction

The successful development and implementation of a bio-based economy are important steps in reaching a sustainable society in the long term. A bioeconomy and bio-based products offer several benefits, particularly focusing on carbon sequestration and storage and the need to replace fossil carbon-based chemicals. Analogous to today's petroleum refineries, biorefineries are conversion facilities where biomass feedstocks can be transformed into several fuels, power, heat, and value-added chemicals (Olsson and Saddler 2013).

Biomass, in the context of bioeconomy, constitutes the organic matter, especially plant matter, that can be converted into food, feeds, chemicals, materials, fuel, and energy, including sugar- and starch-based feedstocks and lignocellulose. In the particular case of starch-based materials, grains (such as corn or wheat) and tubers (such as potatoes and cassava) are the most representative feedstocks. Other raw materials such as sago palm, marine algae, and microalgae can also be considered as alternative choices for starch production (Höfer 2015).

Starch is a soft, white, tasteless, and odorless polymer that is not soluble in cold water, alcohol, or other solvents. It comprises glucose monomers linked through α-1,4-glycosidic bonds and branched by α-1,6-glycosidic linkages. The simplest form of starch is the linear polymer amylase; amylopectin is the branched form (Fig. 4.1). Within the biorefinery context, starch biomass can potentially be converted into a wide range of chemical products via chemical/biological processing, with applications not only in the food and pharmaceutical sectors but also in the paper and adhesive industries (Gozzo and Glittenberg 2009). In its native form, starch is mainly used as a raw material for further processing, because of its poor



Amylose

(linear α-1,4-glycosidicbonds)

Amylopectin

$\left[\begin{array}{l}\text{linear } \alpha\text{-1,4-glycosidicbonds}\\ \text{branched } \alpha\text{-1,6-glycosidicbonds}\end{array}\right]$

Fig. 4.1 Linear (amylase) and branched (amylopectin) structures of starch stability, the high viscosity of aqueous solutions, or the formation of precipitates or microgels, or as a cost-effective binder or thickener for industrial applications. When processed, starch-based products include gelatinized starches, thermoplastic biopolymers, starch esters and ethers, maltodextrins, glucose syrups, cyclodextrins, sorbitol, and fermentation-derived products such as ethanol (Gozzo and Glittenberg 2009; Höfer 2015). This chapter reviews the most important advances for the conversion of starch-based feedstocks, from the use of novel raw materials to the investigation of new processing technologies.

4.2 Conventional and Novel Feedstocks for a Starch-Based Biorefinery

The history of industrial conversion of starch-based resources covers more than 200 years, since Kirchhoff first reported the possibility of obtaining glucose and dextrose from potato starch after a cooking process in acidic conditions. The successful development of sugar production from sugar beet, however, initially obstructed further development of the starch industry. This industry is currently growing worldwide, and about 180 million tons of starch and starch derivatives are expected to be produced by 2022 (Global Industry Analysts 2016). In Europe alone, the starch industry produced 10.7 million tons of starch, and the population and other industries consumed 9.3 million tons of starch and starch derivatives, in 2015 (Starch Europe 2017), of which 62% was in food, 1% in feed, and 37% in nonfood applications, mainly paper making (Scarlat et al. 2015).

Starch production is mainly based on cereal grains and tubers. From a quantitative point of view, wheat (*Triticum* spp.), corn (*Zea mays*), rice (*Oryza sativa*, Asian rice; *Oryza glaberrima*, African rice), potato (*Solanum tuberosum*), and cassava (*Manihot esculenta*) are the leading crops for starch production. Wheat is the most important food grain by far, and its cultivation involves more land area than any other commercial crop (Curtis 2002). Wheat grains are good sources for starch production because of the high starch content, which represents about 58–70% of the total dry grain weight (Höfer 2015). Proteins are also important components of wheat grains, because the higher the protein content, the lower the starch content. The starch-to-protein ratio is highly dependent on wheat variety, and those varieties selected for having higher starch content are therefore desirable as raw materials in a biorefinery (Saunders et al. 2011). Wheat cultivation requires warm temperatures (about 25 °C, with maximum growth temperatures of 30–32 °C) and much sunshine (especially during the stage when the grains are filling). From sowing to harvesting, wheat requires about 3.5–4.5 months depending on climate, seed type, and soil conditions. With the aim of promoting wheat as a viable crop, different techniques, including soil preparation through the use of crop rotation, the addition of fertilizers, and extensive mechanization of the harvesting process, have improved plant growth and facilitated the reaping, threshing, and winnowing steps during grain separation. The growth of wheat, as any other crop, is highly dependent on climate conditions. In this context, the very high yielding triticale (*Triticum aestivum* L.), a cross-breed between wheat and rye with a starch content similar to that of wheat, or hulless barley (*Hordeum vulgare* L.) are appropriate crops for starch production in those places with less favorable climate conditions, such as high latitudes, high altitudes, or saline environments (Oettler 2005; Höfer 2015).

Rice is another important source of starch worldwide, containing up to 75% starch depending on the variety. Starch can be isolated from rice with good recovery yields by using alkaline solutions (the so-called wet process) or proteolytic enzymes (Puchongkavarin et al. 2005). Rice starch particles measure only about 7–9 μm and are included among the smallest vegetable powders. This property increases the surface area of rice starches, which results in a soft-touch effect in rice-based products that makes them ideal for use in decorative cosmetics and in skin and hair care products (Mitchell 2009).

Besides wheat and rice, maize (corn) is one of the most important cereal grains in the world. In each individual corn kernel – the fruits of maize – starch is the major chemical component, about 72% of the kernel weight. Also, 1–3% of glucose, fructose, or sucrose can be found in the corn kernel. Corn starch usually comprises up to 25–30% amylose and 70–75% amylopectin in weight. However, corn with as much as 65–80% starch can also be found in commercial varieties (Schwartz and Whistler 2009). As for wheat, a warm climate is required for maize cultivation, which also can grow fairly well in high latitudes. In countries with suitable climatic conditions, maize can now be cultivated with very high yield per unit area as the result of current resources and management techniques. Furthermore, the maturing period of this crop is relatively short. As its main disadvantage, maize requires much water, limiting its cultivation in places with low available water capacity.

Tubers such as cassava and potatoes are also important raw materials for the starch industry. These starchy tuberous roots are native to South America. Cassava, also known as manioc, mandioca, yuca, mogo, tapioca root, or kappa, is cultivated extensively in tropical and subtropical regions. Because the starch granules are locked inside the cells, biochemical or mechanical disruption of the cassava is first needed for collecting the starch. Higher yields and better starch quality can be obtained by the mechanical process. In this method, root cassava is sliced and then rasped, grated, or crushed to get a fine pulp with high starch content (Breuninger et al. 2009). In general, cassava starch is primarily used for bioethanol production or is cooked to form a clear gel with a slightly stringy texture that makes it a suitable food thickener (Shanavas et al. 2011). Potato is another relevant tuber for starch production. The chemical composition of potatoes is quite variable and is greatly influenced by variety, environment, and farming practices. Although 80% of its weight composition is water, starch represents about 65–80% of its dry weight (Höfer 2015). The potato plant is an herbaceous perennial crop that can be adapted to different climates, which has increased its importance from an economic perspective, particularly expanding the suitability of this crop to a larger area, being now cultivated all around the globe. Before mechanization became available in the late nineteenth century, tuber harvesting (both potato and cassava) was tremendously laborious and the work of many helpers was needed. Harvesting machines, however, have boosted this process, shortening it from days to just a few hours.

In 2012, the European starch industry used 23 million tons of agricultural raw materials, which included 7.7 million tons of maize, 7.8 million tons of wheat, and 7.5 million tons of potatoes (Scarlat et al. 2015).

As alternatives to cereal grains and tubers, pulses or grain legumes (belonging to the Leguminosae family) are also significant raw products for the starch industry. Pulses include edible grains and seeds such as beans, peas, or lentils. The starch content in pulse seeds is lower than that for cereals, representing about 22–45% of the dry matter (Höfer 2015). Pulse starches, however, are characterized by their high amylose content (35–39% of weight), conferring to them specific properties for functional texturization and film formation. One of the major benefits of growing pulses is their ability to fix nitrogen, which can be exploited in crop rotation.

In addition to edible crops, sago palm (*Metroxylon sagu*) and different species of algae represent alternative starchy feedstocks. The sago palm is a species of palm native to tropical Southeastern Asia. When mature enough (7–15 years), just one sago palm can yield up to 375 kg starch (Karim et al. 2008). With such starch content, plantations of sago palms might potentially supply about 25 tons of starch per hectare per year. This palm is an extremely hardy plant that can grow in wetlands with acidic or saline soils. However, it requires a moist climate with uniformly high sunshine, heat, and humidity. Another potential starch source that is increasingly gaining attention is algae. Of the algae pool, red algae, green algae, and glaucophytes are known to be capable of synthesizing starch. Starch content in algae varies largely among species, unicellular microalgae being the most interesting option. Among the best starch producers, the green alga *Chlorella* can accumulate starch up to 60% dry weight under specific nutrient-limiting conditions (Brányiková et al. 2011). The main advantage of algae in comparison to terrestrial plants is their more efficient photosynthetic machinery. Moreover, many species of algae can grow in saltwater and/or wastewater, allowing the saving of large amounts of freshwater. Eventually, by using genetic engineering techniques, algae may be manipulated for further development to target starch accumulation (Radakovits et al. 2010).

4.3 Thermoplastic Starch: Challenges and Properties

As already discussed, current research efforts are being directed to replace petroleum-based products to meet sustainability criteria in the future bioeconomy. Among petroleum derivatives, plastics (polypropylene, polyethylene, polystyrene) are polymers highly recalcitrant to microbial degradation because of their high molecular weight, complex three-dimensional structure, and hydrophobic nature (Kale et al. 2015). The global production of plastic is about 150 million tons year^{-1}, and the market is continually growing. Among this, bioplastics consumption and production is foreseen to significantly increase in the near future. Indeed, 5–10% of the plastics currently available on the market could be bio-based plastics and this share can increase up to 70–85% (Scarlat et al. 2015). In this context, starch has been extensively studied as a raw material for the production of alternative biodegradable plastics polymers, as drop-in bioproducts that directly correspond to the petrochemical counterpart. Nevertheless, in spite of the considerable interest from both the academic and industrial sectors, production of starch-based plastics still poses some technical limitations and high costs.

Starch-based thermoplastics have potential applications in vegetable waste composting, in packaging, and in the pharmaceutical sector (e.g., as controlled-release drug carriers) (Leja and Lewandowicz 2010). Thermoplastic starch (TPS) is obtained by subjecting native starch to high temperature and shear stress (extrusion, film blowing, injection molding, etc.) in the presence of a plasticizer (Khan et al. 2016). Several physical and chemical reactions take place, including water diffusion, expansion of granules, gelatinization, melting, and crystallization. The plasticizer is the material that confers flexibility to the plastic polymer and increases its applicability potential. During the process, plasticizers are capable of breaking the intramolecular hydrogen bonds of the starch polymer and thus creating new starch–plasticizer interactions. Water and glycerol are the most commonly used plasticizers, but sorbitol, glycols, maltodextrin, and urea have also been considered (Mohammadi et al. 2013).

TPS can also be blended with other polymers to confer a certain specific property to the final products that allows them to be used in a larger number of applications and to meet market needs (Mohammadi et al. 2013; Khan et al. 2016). For instance, blends with polycapromolactone, polyvinyl alcohol, or other relatively hydrophobic polymers reduce the hydrophilic character of starch-based thermoplastics. In addition, blending biodegradable and nonbiodegradable polymers can effectively reduce the amount of plastic waste by the partial degradation of the biodegradable component. Blends with other plastic materials have therefore more useful application than TPS itself. TPS can be blended with various polymers with different properties and potentials. St-Pierre et al. (1997) prepared blends with low-density polyethylene and linear low-density polyethylene using glycerol as the plasticizer. Blends showed greater elongation properties at the breaking point, even without adding the interfacial modifier. In addition, blends with polyethylene have shown to be relatively easy to process and are capable of decreasing the permeability to water vapor and increasing the toughness and flexibility of the resulting plastic (Khan et al. 2016). Kaseem et al. (2012) blended TPS with polypropylene to study the mechanical and rheological properties of the resulting plastics. The rheological properties showed a reduction in thermoplastic viscosity by increasing the glycerol content, whereas the mechanical properties indicated a lower strain capacity at break in comparison with polypropylene polymer. These properties increase the crystallinity of the resulting plastic, contributing to enhance the tensile strength, hardness, and stiffness. Similarly, Martin and Avérous (2001) studied the mechanical and rheological properties of TPS blends with polylactic acid. It was found that the least plasticized TPS was brittle and rigid, while the most plasticized TPS was ductile and flexible. Furthermore, the authors noticed a lack of affinity between the TPS and polylactic acid, which limited the blending capacity. Nevertheless, blends with polylactic acid represent a promising option—especially for packaging applications—because of low price and availability as compared to other biopolymers. Mihai et al. (2007) reported that blending TPS with polystyrene and using glycerol as plasticizer increased the viscosity ratio between the TPS and polystyrene phase while increasing the glycerol content. Furthermore, the glycerol content in the TPS phase and the TPS content in the overall blend had a firm effect on the blend viscosity and, hence, on the ability to foam the material.

Of the major limitations for the commercialization of starch-based materials, the high costs of the technology and the final products have restricted their applications to those sectors where biodegradability is mandatory. Nevertheless, some products have already reached the market, such as Mater-Bi (Novamont, Italy), a plastic material based on TPS and other polymers that is suitable for composting bags, mulch film, or disposable cutlery.

4.4 Enzymatic Hydrolysis of Starch-Based Feedstocks

In addition to TPS, starch represents an excellent sugar source for the fermentation/chemical industry. Starch can be efficiently hydrolyzed into sugars by acid treatment or by the use of enzymes. Enzymatic hydrolysis is, however, advantageous because of (1) the specificity of enzymes, which allows the production of sugar syrups with well-defined physical and chemical properties, (2) the process takes place at milder reaction conditions and thus results in few side reactions and in formation of no color, and (3) it avoids salts accumulation (Guzmán-Maldonado and Paredes-López 1995; Nigam and Singh 1995). Starch-degrading enzymes, promoting liquefaction and saccharification, include α-amylases (EC 3.2.1.1, also called endo-amylase), β-amylases (EC 3.2.1.2), amylo-glucosidases (EC 3.2.1.3), α-glucosidases (EC 3.2.1.20), pullulanases (EC 3.2.1.41), maltotetraohydrolases (EC 3.2.1.60), and isoamylases (EC 3.2.1.68). α-Amylases catalyze the hydrolysis of internal α-1,4-glycosidic linkages into low molecular weight products, such as glucose, maltose, and short oligomers up to maltohexose units (de Souza and de Oliveira Magalhães 2010). The amylases can be obtained from several sources, including plants, animals, and microorganisms. Among them, a large number of microbial α-amylases, mainly from the fungus *Aspergillus* spp. and the bacterium *Bacillus* spp., are now been commercialized. β-Amylases are exo-hydrolase enzymes that act from the nonreducing end of a polysaccharide chain by hydrolysis of α-1,4-glycosidic linkages to yield successive maltose units (Sundarram and Murthy 2014). Primary sources of β-amylases are sweet potatoes and plant seeds such as wheat, barley, or soybeans. Nevertheless, they can be also obtained from microorganisms such as *Bacillus* spp. or *Pseudomonas* spp. Amyloglucosidases attack α-1,4-glycosidic from the nonreducing end, releasing β-D-glucose (Kumar and Satyanarayana 2009). The huge literature on microbial amyloglucosidases indicates the preference for its production in eukaryotic hosts, being more common the use of fungi strains (particularly *Aspergillus* spp. and *Rhizopus* spp.). α-Glucosidases cleave both α-1,4- and α-1,6-glycosidic bonds on the external glucose residues of amylose or amylopectin from the nonreducing end of the starch molecule (Nigam and Singh 1995; Hii et al. 2012). The main sources for glucosidase production are microorganisms such as *Aspergillus* spp., *Mucor* spp., *Bacillus* spp., or *Pseudomonas* spp. Pullulanases (also known as α-dextrin-6-glucanohydrolases or amylopectin-6-glucanohydrolases) catalyze the hydrolysis of α-1,6 linkages in pullulan, a linear α-glucan polymer consisting essentially of maltotriosyl units connected by α-1,6-glycosidic bonds (Hii et al. 2012). These enzymes are derived from various microorganisms such as *Bacillus acidopullulyticus*, *Klebsiella planticola*, *Bacillus* spp., and *Geobacillus stearothermophilus*. Maltotetraohydrolases hydrolyze α-1,4-glucosidic linkages to remove successive maltotetraose residues from the nonreducing chain ends (Mezaki et al. 2001). Finally, isoamylases, similar to pullulanases, are capable of hydrolyzing α-1,6-glycosidic bonds in amylopectins and are the only known enzymes that completely debranch glycogen completely (Hii et al. 2012). In addition to all mentioned enzymes, starch-active lytic polysaccharide monooxygenases (LPMOs) have recently been described to contribute to starch hydrolysis (Vu et al. 2014; Lo Leggio et al. 2015). LPMOs are recently discovered enzymes that oxidatively deconstruct polysaccharides (Lo Leggio et al. 2015). These enzymes utilize molecular oxygen and an electron donor to oxidize polysaccharides at C1 or C4 positions in the carbohydrate chain, promoting the corresponding breakage and thus rendering the substrate more susceptible to hydrolysis by glycoside hydrolases. All this group of enzymes is needed for the complete hydrolysis of the starch polymer. Moreover, these specific activities have a synergistic action during the hydrolysis process, boosting the release of single sugars.

Enzymatic properties such as optimal temperature, optimal pH value, thermostability, and stability are very much dependent on the enzyme source and are therefore important factors to consider for the proper selection of a certain enzyme. Thus, for starch hydrolysis, enzymes must be active and stable at slightly acidic condition (pH value of 5–7) and at relatively high temperatures (up to 100 °C), given the industrial processes conditions.

4.5 Value-Added Biofuels, Biochemicals, and Biomaterials from a Sugar Platform Perspective

The sugar solutions obtained by enzymatic hydrolysis of starch-rich crops can subsequently be converted into biofuels, biochemicals, or biomaterials through a wide range of biological and chemical technologies.

The simplest biorefineries, typically called “first generation,” are based on the use of sugar-rich or starch-rich crops as raw materials. Some of these biorefineries are already maturely established, and the most significant commercial facilities belonging to this category are biofuel-driven biorefineries, producing first-generation (1G) bioethanol, the most common renewable biofuel. Indeed, despite the potential competition with food that favors the development of lignocellulosic-based plants (Searchinger and Heimlich 2015), date sugar and starch crops are still the most often used biomass feedstock, and the main product of sugar- or starch-based biorefineries is ethanol (Gnansounou and Pandey 2017). According to Scarlat et al. (2015), the European Union (EU) is one of the world's largest producers of cereals, with an estimated production of 285 million tons in 2012. The largest share of European cereals is used for feed (more than 60%) and food (23%). However, a significant share of cereals is also used for processing (3.5%) and another for biofuel (ethanol) production (3%).

Novel chemicals and materials produced from starch-based raw materials are also currently available, but the technologies for conversion into some bioproducts are still in R&D, pilot, or demo stage. However, in addition to biofuels, there are some important examples of product-driven biorefineries producing bio-based products that are already commercialized or near market (Gírio et al. 2017). Although bio-based chemicals and materials do not yet account for a significant share of biomass use (Scarlat et al. 2015), new sectors are emerging, such as biomaterials and green chemistry, and this market (including bioplastics, biolubricants, biosolvents, and biosurfactants) is expected to grow in the near future. This growth rate should, however, be lower than in biofuels and biopower because it is not driven by any mandates or incentive schemes (Sir David King et al. 2010). According to Scarlat et al. (2015), it is foreseen that more than 20% of all chemicals coming from the traditional chemistry sector could be produced from biological sources in 2020. Indeed, there are already several bio-based products on the market, and the European chemical industry used approximately 8.6 million tons of renewable raw materials (including starch) in 2011, among a total of 90 million tons of feedstock used (Scarlat et al. 2015). As an example of success, steady increase is reported for lactic acid, with a 10% annual growth, from its use as precursor of PLA (polylactic acid), which is mainly used for production of sustainable biopolymers. European demand for PLA in 2015 was 25,000 tons per year and could reach 650,000 tons per year in 2025 (Mikkola et al. 2016).

In contrast to drop-in bioproducts, which are bio-based versions (chemically equivalent) of existing petrochemical products and thus can easily replace fossil-based products, some bio-based products have novel functionality and slower access to markets. Also, promising novel chemical intermediates are difficult to integrate into current production networks when no established large-scale chemical processes exist for their conversion, such as the case of levulinic acid. In addition, novel products based on new intermediates may offer unique properties unattainable with fossil-based alternatives (e.g., biodegradability), but they also bear higher risks and usually require a complex process until commercialization. This sequence typically happens with bio-based polymers as substitutes of existing polymers. For instance, PLA and PHAs (polyhydroxyalkanoates) have been known for a long time and only recently have been commercialized, but currently several companies are running large-scale production of PLA and PHA with success (King et al. 2010).

The development of a successful biorefinery should be guided by two concepts: (1) to take maximum advantage of intermediate and by-products to manufacture additional chemicals and materials; and (2) to balance high-value/low-volume bio-based chemicals and materials with high-volume/low-value biofuels (King et al. 2010). Indeed, specialty chemicals from biomass, fitted to specific "niche" markets (e.g., for the pharmaceutical, cosmetics, and food sectors), are sold at relatively high prices because of their limited production (<1000 tons per year), "green credentials," and unique quality and properties (Mikkola et al. 2016). In contrast, the production of bulk chemicals (>1000 tons per year) from biomass remains rather limited, with the majority of organic chemicals and polymers still being derived from fossil-based feedstocks (Mikkola et al. 2016).

Among bioproducts, primary building blocks exhibiting multiple functionalities, suitable for further conversion, are really interesting. The US Department of Energy (DOE) carried out a study in 2004, leading to the identification of a group of 12 (albeit it has been known as the DOE "Top 10" report) target sugar-derived building blocks coming to the market (Werpy and Petersen 2004). This list of candidates was revised by Bozell and Petersen (2010) based on the balance among nine criteria boosting their opportunities (listed by approximate order of importance): (1) extensive recent literature demonstrating research activity; (2) multiple product applicability; (3) direct substitute for existing petrochemicals; (4) high-volume product; (5) platform potential; (6) industrial scale-up; (7) existing commercial product; (8) primary building block; (9) commercial bio-based product. Cost evaluation was not included in this evaluation because cost structures will change with the technology development that is rapidly occurring, driven by the intensive ongoing research activities.

More recently, in 2015, *Biofuels Digest* (Lane 2015) has updated this assessment. Taking into account this recent study, based on the previous US DOE's "Top 10" biochemicals (Werpy and Petersen 2004) and IEA Bioenergy Task 42 (2011) reports, and given the current maturity level of industrial activity and market size, this review focused on ten products that can be obtained using sugar derived from starch that were selected as being of particular interest in a previous report (E4tech, RE-CORD, and WUR 2015). Some of the selected bioproducts are primary products (obtained directly from sugars): succinic acid [also produced via glycerol or FDCA (furan-2,5-dicarboxylic acid), and also intermediate for BDO (1,4-butanediol)], BDO (also produced via succinic acid), farnesene, isobutene, polyhydroxyalkanoates (PHAs), and FDCA (also intermediate for succinic acid). In addition, secondary chemicals are produced from sugars via an intermediate: acrylic acid [via 3-HPA (3-hydroxypropionic acid)], adipic acid (via glucaric acid), polyethylene (PE, via ethanol), and polylactic acid (PLA, via lactic acid).

Some of these established bio-based products already dominate global production, such as is the case of ethanol and lactic acid (E4tech, RE-CORD, and WUR 2015), with the largest markets, and others do not have an identical fossil-based substitute (e.g., FDCA, farnesene). Indeed, bio-based FDCA and farnesene have the highest current prices, but these are expected to drop once the relevant conversion technologies have been successfully commercialized (E4tech, RE-CORD, and WUR 2015). The smallest bio-based markets are, as is to be expected, those of the earliest stage products, such as acrylic acid and its precursor 3-hydroxypropionic acid (3-HPA), and adipic acid. Bio-based succinic acid exhibits the fastest growing market at present, because of the level and breadth of industry activity in the product (E4tech, RE-CORD, and WUR 2015).

Bio-based chemicals and materials can be produced via the sugar platform by different potential pathways that can be grouped into biological or chemical transformation pathways, and each of the bioproducts previously assigned as attractive is highlighted under the most commonly applied route for its production.

4.5.1 The Biological Route

Although there are many possible methods for the transformation of sugars, many products that are familiar today are fermentation based (Zwart 2006). Indeed, sugars can be converted through fermentation, by bacteria, fungi, or yeast (genetically modified or not) into alcohols, organic acids, alkenes, lipids, and other chemicals, under diverse process conditions (e.g., low/high pH value, anaerobic/aerobic, nutrient rich/deprived). The product of interest can also be produced intracellularly (requiring lysis/death of the cell to extract the product, usually via solvents), or extracellularly (simply requiring its separation/extraction from the fermentation broth). Given the wide range of organisms now available, many of them having been recently discovered and exploited, the fermentation of sugars has great potential for the development of new bioproducts (Gírio et al. 2017). Indeed, the fermentation of pure C6 sugars liberated from starch is straightforward, yielding a very large number of products. This chapter focuses only on the most significant biofuels and bioproducts, as previously listed. In addition to the target bioproducts, the fermentation-based processing of many starch crops also delivers valuable animal feed rich in protein and energy as a co-product, for example, distiller's dried grains with solubles (DDGS) (Gnansounou and Pandey 2017).

4.5.1.1 Ethanol

Ethanol is the most common representative of the biochemical transformation of biomass into fuel, and it exhibits good performance against the nine criteria proposed by Bozell and Petersen (2010). Ethanol was omitted from the DOE original list because it might be categorized as a supercommodity by its expected high production volume.

Indeed, bioethanol is currently used as a biofuel when mixed with gasoline, but it is also a useful intermediate platform chemical. Ethanol is of interest as a precursor to the corresponding olefin, ethylene, via dehydration, and thus links the biorefinery with petrochemical industry infrastructures (Mikkola et al. 2016). Ethanol dehydration was the source of most ethylene in the early stage of the twentieth century, but this route was later discarded in favor of steam cracking processes using crude oil with the expansion of the petrochemical industry (Bozell and Petersen

2010). More recently, increasing crude oil prices have renewed interest in ethanol dehydration, with large companies, such as Dow, Braskem, and Solvay, building ethanol-to-ethylene plants. Dow and Braskem manufacture "green" polyethylene whereas Solvay produces polyvinyl chloride (Bozell and Petersen 2010). Ethanol can also be oxidized, over gold nanocatalysts or Mo-V-Nb mixed oxides, yielding commodity chemicals such as acetic acid and ethyl acetate (Bozell and Petersen 2010).

Nowadays, commercial ethanol production is predominantly based on edible sugar and starchy biomass: mainly sugarcane in Brazil, corn grains in the USA, and sugar beet (58%) and wheat (19%) in Europe (Mikkola et al. 2016; Scarlat et al. 2015). Although sucrose conversion into ethanol provides higher yields compared to starch, the share of sugar crops and molasses for world ethanol production is limited by the instability of sucrose price, given the competition with refined sugar. Indeed, in the period 2012–2014, starch crops provided 57% of the ethanol produced worldwide, with the major contribution of corn, especially in the USA, the largest producer country (Gnansounou and Pandey 2017). The use of corn undoubtedly dominates in the USA, whereas wheat and rice are used in Europe and China, respectively, together with a minor share of barley and other coarse grains, for ethanol production from starch (E4tech, RE-CORD, and WUR 2015; ETIP Bioenergy n.d.). Indeed, the USA pioneered the corn industry, with implementation in Jersey City (NJ) of the first dedicated cornstarch plant in the world by Wm. Colgate & Company in 1844. Much later, in the 1970s, the multi-product corn wet mills appeared in their current form, prompted by the development of technology for the production of high fructose corn syrup for use in the soft drinks industry (Mikkola et al. 2016). Nowadays, there are 216 plants producing 59.5 billion liters of ethanol per year from sugar/starch in the USA, and 74 of the largest commercial 1G bioethanol facilities in operation in the USA, belonging to eight companies, produce 50% of this capacity using corn as raw material. Besides corn, sorghum is also used as a relevant sugar feedstock in the USA, and less than 0.2% of 1G ethanol produced in the USA is obtained from wastes (e.g., beverage waste or wheat screenings) (Gírio et al. 2017). The importance assigned to biomass-derived energy production in China has been increasing in the past 10 years, and China has licensed five fuel ethanol plants (mostly state refineries) for operation, all of which are based on starch crops (King et al. 2010).

Indeed, China has traditionally had an important role in biomass biorefining, dating to the early implementation of hydrolysis and acetone-butanol-ethanol (ABE) batch fermentation plants, mostly aimed at producing acetone and ethanol solvents from corn, cassava, potato, and sweet potato. The first industrial facility of continuous ABE fermentation in the world was the Russian Dokshukino plant, which started operation in 1960 using starch for fermentation by Clostridia bacteria, and several ABE plants were built in the Union of Soviet Socialist Republics in the period between 1960 and 1980. However, almost all these plants were closed in response to the strong competition with cheap solvents from the petrochemical industry (Bozell and Petersen 2010; Mikkola et al. 2016).

Although bioethanol is the dominant product, there are a few commercial biorefinery facilities producing other sugar platform products via fermentation of starch raw materials, such as the previously identified lactic acid or succinic acid (E4tech, RE-CORD, and WUR 2015). Other primary bio-based products from sugars, such as 1,4-butanediol (BDO), farnesene, and polyhydroxyalkanoates (PHAs), are currently produced at R&D, pilot, or demonstration scale.

4.5.1.2 Lactic Acid and Polylactic Acid (PLA)

Organic acids are easily produced from biorefinery sugar streams and are thus attractive platform chemicals. Lactic acid is a bio-based chemical produced by glucose fermentation using *Lactobacillus rhamnosus*, or other lactic acid bacteria, and biomass feedstocks (Marques et al. 2017a, b; Gírio et al. 2017). Indeed, lactic acid can be manufactured either by chemical synthesis (by reaction of acetaldehyde with acid cyanide, yielding lactonitrile, which is further hydrolyzed to lactic acid) or by fermentative processes, but the latter have been preferentially used in industrial production, accounting for approximately 90% of the total worldwide production (Hofvendahl and Hahn-Hägerdal 2000). The fermentative route allows the selective production of the desired L-lactic acid stereoisomer, with additional advantages in terms of energy efficiency and yield. Current commercial fermentation gives close to 90% yield of calcium lactate based on glucose feed, which is neutralized to give pure lactic acid. This neutralization produces approximately 1 ton of $CaSO_4$ for every ton of lactic acid, posing a waste disposal problem in commercial operation (Bozell and Petersen 2010). Alternative separation and purification technologies, based on desalting and water-splitting electrodialysis, have been examined to eliminate the neutralization step in the conventional chemical downstream processing scheme that typically consumes 50% of the cost of lactic acid manufacture (Pal et al. 2009).

Worldwide demand for lactic acid is expanding, driven by the more conventional use in the paint, cosmetic, pharmaceutical, and food preservatives markets, and mainly for polylactic acid (PLA) production. PLA, or polylactide, is a biodegradable and recyclable thermoplastic polyester resin (Vaidya et al. 2005), suitable for packaging materials, insulation foam, automotive parts, and fibers (textile and nonwoven) (E4tech, RE-CORD, and WUR 2015), and more recently, because of its biocompatibility, for biomedical applications (Vijayakumar et al. 2008). Packaging is likely to remain the key market for PLA, with the expected increase in demand for environmentally friendly starch-based plastics for this application, as a substitute for PE (polyethylene) and PS (polystyrene) products. Although lactic acid can undergo direct polymerization, the process is more effective if lactic acid is first converted to a low molecular weight pre-polymer and then depolymerized to the lactide. A wide range of catalysts is known to promote lactide polymerization. The resulting polymer exhibits performance properties similar to, or exceeding, those of PS, a storage resistance to fatty foods and dairy products equivalent to PET (polyethylene terephthalate), excellent barrier properties for flavors and aromas, and good heat stability (Gallezot 2007).

High optical purity is a prerequisite for synthesis of the homopolymers poly-L-LA and poly-D-LA, which form regular structures in a crystalline phase in contrast to the amorphous material resulting from copolymerization of D(−)- and L(+)-isomers (Wang et al. 2015). The ratio of poly-L-LA and poly-D-LA modulates the properties and the degradability of PLA; however, D-lactic acid is not suitable for use in the food, drink, and pharmaceutical industries because it can cause metabolic problems and is toxic to the human body. Thereby, the major challenge lies in producing optically pure lactic acid achieving high concentrations, yields, and productivity using cheap renewable resources (Abdel-Rahman and Sonomoto 2016). Indeed, most PLA producers also manufacture lactic acid, and this is mostly produced from cornstarch (in the USA), tapioca roots, chips, or starch (in Asia), or sugarcane and sugar beets (in the rest of the world).

The largest global commercial producer of PLA is the US-based NatureWorks (former Cargill Dow), producing PLA resins under the Ingeo brand, with a commercial production plant in Nebraska (with an annual 150-kton capacity, in 2015), using cornstarch as feedstock, and plans for a new plant in Thailand (E4tech, RE-CORD, and WUR 2015). The largest global lactic acid producer is Corbion Purac (Netherlands). The latter produces lactic acid, lactic acid derivatives, and lactides (including lactide resins for high-performance PLA bioplastics), operating five production plants, in the USA, the Netherlands, Spain, Brazil, and Thailand (the largest plant, with an annual 100-kton capacity) (E4tech, RE-CORD, and WUR 2015).

In Europe, there are other PLA (and lactic acid) producers, including Synbra Technology, which operates a commercial (annual 5-kton capacity) plant in the Netherlands and a pilot production plant in Switzerland (annual 1-kton capacity). Besides Corbion Purac, Galactic and Jungbunzlauer are operating commercial lactic acid production plants in Europe. Other PLA producers include the Chinese Zhejiang Hisun Biomaterial (with an annual 5.5-kton capacity to be expanded to 50 kton, using cassava instead of corn). Other lactic acid producers include Henan Jindan Lactic Acid Technology (with an annual 100-kton capacity, the largest in Asia) (E4tech, RE-CORD, and WUR 2015).

In addition to its use in the synthesis of biodegradable polymers, lactic acid can be regarded as a feedstock for the green chemistry in the future as it is a platform chemical for the production of several downstream bio-based products (Gao et al. 2011) (outlined in Fig. 4.2). Lactic acid readily undergoes esterification to yield lactate esters, of interest as new “green” solvents. Catalytic reduction of lactic acid leads to propylene glycol, which can be further dehydrated to give acrylic acid esters, but in practice this conversion proceeds with low yield. Lactic acid can also be spun using wet, dry, and electrospinning techniques to give biodegradable fibers for apparel, furniture, and biochemical materials, such as dissolving sutures. New nanostructural materials prepared from lactic acid using electrospinning have found use in neural tissue engineering (Bozell and Petersen 2010).

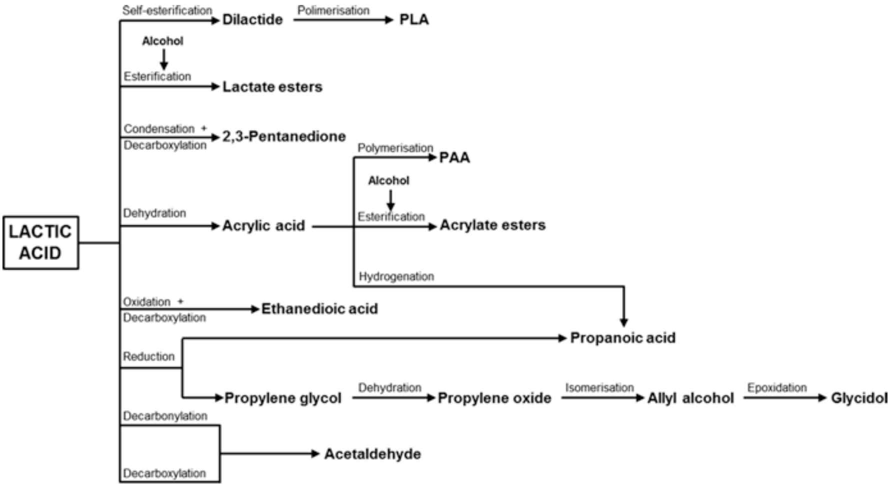


Fig. 4.2 Overview of lactic acid as a platform chemical. *PLA* polylactic acid, *PAA* polyacrylic acid

4.5.1.3 Polyhydroxyalkanoates (PHAs)

Polyhydroxy alkanoates (PHAs) are linear polyesters directly produced by bacterial fermentation of sugars or lipids. PHAs are typically produced by bacteria under physiological stress so as to store carbon and energy. PHAs can be combined with diverse monomers yielding different thermoplastic or elastomeric biodegradable plastics (suitable for home composting) (E4tech, RE-CORD, and WUR 2015). PHAs include polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHBV). PHB exhibits mechanical, physical, and thermal properties similar to those of polypropylene (PP), polyethylene (PE), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyvinylchloride (PVC), PS, and PET, depending on its grade. Given its tunable properties, it might have several applications. Besides its use as plastics/foams substitute (e.g., for packaging, injection molding), it can have niche applications, such as for internal sutures, capsules in pharmacology (as a non-toxic, compatible, and naturally absorbed polymer), and also in automotive, design, and high-tech electronics sectors (E4tech, RE-CORD, and WUR 2015).

PHB is intracellularly produced from glucose under aerobic conditions by certain types of bacteria (e.g., *Alcaligens euthrophus* and *Lactobacillus acidophilus*), and thus PHB should be extracted from bacterial cells using different technologies, some of them based on organic solvents, followed by purification. PHAs thus exhibit very high costs and investment, and activity in their production is relatively low as compared to PLA and other bioplastics. Global production capacity in 2014 was estimated as 54 kton. Once feedstock makes up close to 50% of the production cost of PHA, this is expected to decrease by using cheaper feedstocks, such as starch, for example, hydrolyzed cornstarch, which is less than half the price of glucose. In addition, production costs may decrease via integration with sugar and ethanol mills, by assuring on-site energy production by burning the bagasse by-product and co-producing the solvent (iso-pentanol) for cell extraction. In this context, PHB production is beginning to be associated to the Brazilian sugar industry (E4tech, RE-CORD, and WUR 2015).

When the cost barrier is overcome, enabling mass production, the potential market for PHA may be as much as 50% of the current plastics market. However, nowadays the PHA market keeps focused on niche high-value markets, and there are currently few PHA developers based on sugar fermentation in Europe: these include the German-based Biomer, owner of a demonstration-scale plant producing four different grades of PHB; and KNN, which is considering to produce PHA resin via the sugar platform (using pulp and paper starches) in the Netherlands and Sweden. There are a few more PHA developers in China (Tianjin Green Bio, Yikeman, and TianAn Biopolymer Co.) and the Americas (PHB Industrial in Brazil and Metabolix in the USA) (E4tech, RE-CORD, and WUR 2015).

4.5.1.4 Succinic Acid

Succinic acid, a 1,4-diacid, is also a widely investigated chemical building block that is most commonly biochemically produced by low-pH fermentation of biorefinery sugars by adequate yeasts or bacteria, such as *Anaerobiospirillum succiniciproducens* or engineered *Mannheimia succiniciproducens* (Bozell and Petersen 2010). Recombinant *Escherichia coli* strains have been licensed for commercial production of succinic acid, by Reverdia (Roquette/DSM) in Europe (Italy, with 10 kton of annual capacity), and BioAmber (a Canadian company that is also running a plant in France with an annual capacity of 3 kton) (Bozell and Petersen 2010). Other succinic acid producers include Succinity (joint venture between BASF and Corbion Purac) and Myriant (a US-based company) (Lane 2015). Succinity GmbH is operating a plant in Montmelo (Spain) with an annual capacity of 10 kton; Myriant owns several commercial plants in the USA and also a small demonstration facility (1-kton annual capacity) in Leuna (Germany) (E4tech, RE-CORD, and WUR 2015).

As is lactic acid, succinic acid is initially isolated from fermentation broth as a salt, and electrodialysis has also been successfully investigated as an alternative technology for its recovery. Direct hydrogenation of the aqueous fermentation broth has also been studied (Bozell and Petersen 2010). Competing routes to produce succinic acid include its chemical synthesis starting from glycerol (E4tech, RE-CORD, and WUR 2015).

Succinic acid, previously highlighted as exhibiting the fastest growing market, provides high-value niche applications, for example, personal care products and food additives (as an acidity regulator). In addition, it is a powerful platform chemical that is used for the production of bio-based polymers, such as polybutylene succinate (PBS), polyester polyols for polyurethanes, coating and composite resins, phthalate-free plasticizers, and 1,4-butanediol (BDO), for footwear, packaging, and paints, or personal care ingredients. It is a substitute for maleic anhydride (Werpy and Petersen 2004). Succinate esters are also precursors for known petrochemical

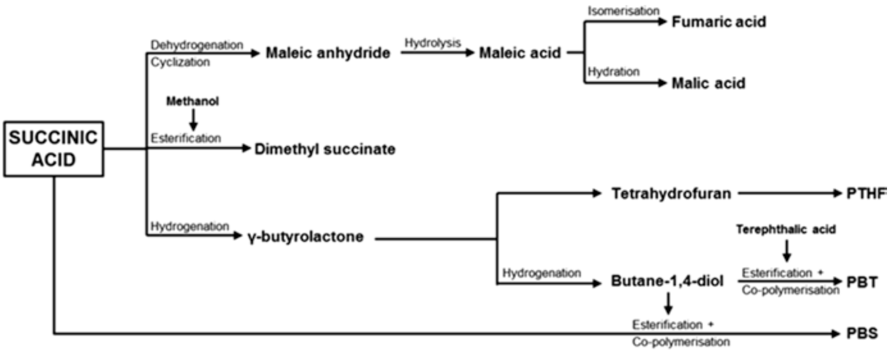


Fig. 4.3 Overview of succinic acid as a platform chemical. *PTHF* polytetrahydrofurane. *PBT* polybutylene terephthalate, *PBS* polybutylene succinate

products such as tetrahydrofuran, γ-butyrolactone, or various pyrrolidinone derivatives (Bozell and Petersen 2010). The use of succinic acid as a platform chemical is summarized in Fig. 4.3 (Bozell and Petersen 2010). Indeed, bio-based succinic acid is a drop-in replacement for petroleum-based succinic acid (Lane 2015) and has the potential to be cheaper than the fossil-based product when produced at large scale (E4tech, RE-CORD, and WUR 2015).

In 2013, global annual production of bio-based succinic acid was 38 kton, corresponding to a market value of 108 million USD, which is comparable to the market of the fossil-based product, but the bio-based product has the potential to significantly increase the share driven by the demand for BDO and PBS. Indeed, by 2020 the bio-succinic acid market is projected to reach 600 kton with annual revenues of 539 million USD (E4tech, RE-CORD, and WUR 2015).

4.5.1.5 1,4-Butanediol (BDO)

BDO is industrially used as a solvent and in the manufacture of some types of plastics, elastic fibers, and polyurethanes, for use in golf balls and skateboard wheels to printing inks and cleaning agents (Lane 2015). The bio-based product can be a direct drop-in replacement for fossil BDO. It can be converted into numerous chemicals, including γ-butyrolactone (GBL), the solvent tetrahydrofuran (THF), and the resin polybutylene terephthalate (PBT) (E4tech, RE-CORD, and WUR 2015). BDO can be produced in the petrochemical industry in various ways from acetylene, maleic anhydride, propylene oxide, and butadiene. Bio-based BDO can be produced via direct fermentation of sugars or via the catalytic hydrogenation of succinic acid, but the first is the dominant industrial route (E4tech, RE-CORD, and WUR 2015).

The market share of bio-based BDO constitutes a very small fraction (less than 0.2% in 2013) of the total BDO market (Lane 2015). The largest application of BDO is in the manufacture of THF, accounting for 30% in 2013, followed by polyurethane at 25%, and PBT, which used about 22% of all BDO worldwide.

The global BDO market is foreseen to reach 2.7 million tons with a market value close to 7000 million USD by 2020, and the bio-based market is expected to increase by 43% from 2014 to 2020 (E4tech, RE-CORD, and WUR 2015).

Genomatica, a California-based company, is the main agent in bio-based BDO production, having patented a GENO BDO process using an engineered microorganism for direct production via fermentation of sugars. Several European companies, such as BASF, Novamont (Mater Biotech), DSM (for PBT production), and Biochemtex (but using cellulosic biomass converted by Proesa technology), are employing the Genomatica technology. Johnson-Matthey-Davy Technologies is producing bio-BDO and THF, in UK, via Myriant's succinic acid. In the USA, Tate & Lyle has also signed a joint development agreement with Genomatica to produce bio-based BDO from dextrose sugars at demonstration scale, whereas BioAmber produces bio-BDO (and bio-THF) from its bio-succinic acid (via chemical processing). The Japanese company Toray produces bio-based BDO (converted into PBT), also based on Genomatica technology (E4tech, RE-CORD, and WUR 2015).

The Genomatica technology enables producing BDO directly from an abundant feedstock, and this company believes that the sugar market is sufficiently robust and can grow to include chemicals production, although currently 50% of global sugar is used for ethanol production (E4tech, RE-CORD, and WUR 2015).

4.5.1.6 Farnesene

Farnesene is a branched-chain alkene with 15 carbon atoms that is found in plants (e.g., in the skin of green apples and other fruits) and some insects. There is no fossil-based substitute, but it is an attractive building block to obtain bio-based products with several niche market applications—solvents, moisturizer emollients, adhesives, fragrances, surfactants, stabilizers, resins, foams, coatings, sealants, emulsifiers, and vitamin precursors. Farnesene has also applicability as a fuel and lubricant feedstock, replacing jet fuel (properties consistent with C15 paraffins but still with higher cost) and diesel and industrial oils (E4tech, RE-CORD, and WUR 2015).

It can be produced from sugars via aerobic microbial fermentation using genetically modified microorganisms (yeasts). The US-based company Amyris, the only player in the market, has developed a pathway enabling the conversion of C6 sugars into farnesene, and its production is already running at demonstration plants in the USA, Spain, and Brazil. The industrial facilities in Brazil are located adjacent to existing sugar and ethanol mills. Farnesene produced by Amyris targets fuel applications, with its use in blends (in diesel and jet fuel) already demonstrated (as diesel for buses in Brazil and as jet fuel in multiple flights) (E4tech, RE-CORD, and WUR 2015).

4.5.1.7 Isobutene

Isobutene (isobutylene or 2-methylpropene) is a four-carbon branched alkene that is a key precursor for chemicals such as fuel and lubricant additives, polymers, and pharmaceuticals. However, because of its toxicity, stringent measures are required to prevent leakage into the environment (E4tech, RE-CORD, and WUR 2015). The addition of isobutene to methanol yields MTBE (methyl tert-butyl ether) and to ethanol gives ETBE (ethyl tert-butyl ether), the most important fuel additives in the market. It is also used to produce isooctane, an additive applied in aviation fuel. In addition, it is used in polymerization reactions, for example, with isoprene to yield butyl rubber for the production of tires, gas masks, baseballs, and chewing gum. It can also yield poly(methyl methacrylate) plastics and tert-butanol and tert-amines for use in various chemical processes and products. A future application of isobutene, with increased demand, could be the production of antioxidants to be used in the food industry (E4tech, RE-CORD, and WUR 2015).

Nowadays, isobutene is commercially produced by petrochemical cracking of crude oil, but it can also be produced by dehydration of isobutanol obtained via biomass digestion. As a biological alternative, the French company Global Bioenergies, owner of three pilot plants in Europe, is developing a process based on direct fermentation of glucose into isobutene using engineered bacterial strains. This completely biological route is advantageous in terms of energy demand for recovery of the gaseous isobutene (instead of isobutanol), which also exhibits lower aqueous solubility than isobutanol and thus decreased product toxicity to the microorganisms. Lanxess is developing in Germany the dehydration process for conversion of bio-based isobutanol into isobutene, targeting production of bio-based butyl rubber for the tire industry. Most isobutanol used by Lanxess is supplied by the US-based biochemicals and biofuels company Gevo, produced from corn-based fermentable sugars. Gevo and Butamax lead the routes via isobutanol (E4tech, RE-CORD, and WUR 2015).

The global annual production of isobutene is around 15 million tons, corresponding to a market of 25–30 million USD, but bio-based isobutene currently accounts only for 10 tons per year produced by a small number of players. Rapid growth of isobutene markets is expected, mostly driven by the aerospace market, together with rubber for the automotive market (E4tech, RE-CORD, and WUR 2015).

4.5.1.8 Acrylic Acid

Acrylic acid is an organic acid with three carbon atoms, systematically named 2-propenoic acid. Acrylic acid and its esters readily combine with themselves (to form, e.g., polyacrylic acid, used mostly in superabsorbent polymers) or other monomers (e.g., acrylamides, acrylonitrile, vinyl, styrene, butadiene) by reacting at their double bond. These homopolymers or copolymers are used in the manufacture of various plastics, coatings, adhesives, fibers and textiles, resins, detergents and cleaners, elastomers (synthetic rubbers), and floor polishes and paints. Acrylic acid is also a drop-in replacement as a chemical intermediate in multiple industrial processes (E4tech, RE-CORD, and WUR 2015; Lane 2015).

Although conventional petrochemical acrylic acid is produced via the oxidation of propylene, bio-based acrylic acid is produced through the dehydration of 3-hydroxypropionic acid (3-HPA), which can be obtained by sugar fermentation (E4tech, RE-CORD, and WUR 2015). As an alternative, acrylic acid can be produced from sugar-derived lactic acid by dehydration. However, none of these processes is yet commercially implemented. The production of acrylic acid in 2013 comprised approximately 5 million tons but the annual production for the bio-based product, still in the pilot phase, accounted only for around 300 tons. The global acrylic acid market is projected to steadily increase, reaching an annual demand of around 7.4 million tons by 2020 (E4tech, RE-CORD, and WUR 2015), partially because of a foreseen increase (4–5%) in the demand for superabsorbent polymers.

Two key strategic partnerships, BASF-Cargill-Novozymes (in Europe) and OPXBio-DOW (in the USA), have been responsible for the development (at pilot scale) of the 3-HPA route for production of bio-based acrylic acid (E4tech, RE-CORD, and WUR 2015). Given the various possible routes to produce bio-based acrylic acid, there is fragmentation among technology developers, with Metabolix together with Cargill-BASF-Novozymes and OPXBio/Dow focusing on the 3-HPA process, and Myriant and SGA Polymers investing on the lactic acid route, also via the sugar platform. In addition, Genomatica have filled a patent from a process to produce acrylic acid via fumaric acid (Genomatica 2009). However, major industrial players have been collaborating toward fast-track commercial development via different processes and feedstocks. The shift from petro-based acrylic acid toward the bio-based equivalent is pulled not only by the demand for reductions in GHG emissions, the result of environmental concerns, but also by the incentive to reduce reliance on crude oil and the associated price volatility (E4tech, RE-CORD, and WUR 2015).

4.5.1.9 Adipic Acid

Adipic acid is the most widely used dicarboxylic acid from an industrial perspective, as a monomer for production of nylon and polyurethane (E4tech, RE-CORD, and WUR 2015). Indeed, 85–90% of adipic acid is used in the production of nylon-6,6, a high performer engineering resin, or is further processed into fibers (polyurethanes, adipic esters) for application in carpeting, automobile tire cord, and clothing. It is also used to manufacture plasticizers and lubricant components. Food-grade adipic acid is used as a gelling aid, an acidulant, and as a buffering agent (E4tech, RE-CORD, and WUR 2015).

As a drop-in chemical (also produced from petrochemicals), bio-based adipic acid can be produced by fermentation, directly from sugars or via hydrogenation of muconic or glucaric acid. Verdezyne has developed a process based on genetically modified microorganisms for direct conversion of glucose into adipic acid. It can also be chemically produced by a two-step chemo-catalytic route involving anaerobic oxidation of glucose into glucaric acid that is finally converted to adipic acid by hydrogenation (E4tech, RE-CORD, and WUR 2015).

The global market of fossil adipic acid was 2.7 million metric tons in 2013 and it is expected to grow, achieving 7240 million USD by 2020, mainly from the increasing demand for nylon-6,6 within the automobile and electronics industries, and for polyurethanes to be used in footwear (E4tech, RE-CORD, and WUR 2015). Despite the environmental benefits, with the potential to provide cost advantage of the equivalent bio-based product, this is not yet commercially produced. Bio-based adipic acid is still at the R&D stage, led by Verdezyne and Rennovia, owners of pilot plants in the USA, and DSM and Biochemtex in Europe. In the USA, BioAmber, Genomatica, Amyris and Aemetis are also developing sugar-based fermentation production processes (E4tech, RE-CORD, and WUR 2015).

4.5.1.10 Ethylene and Polyethylene (PE)

Fossil PE is the most common plastic produced globally [with an annual production volume of 88 million tons and a market share close to 30% (E4tech, RE-CORD, and WUR 2015)], especially used by the automotive industry and manufacturers of cosmetics, packaging, toys, personal hygiene, and cleaning products. There are diverse types and grades of PE, exhibiting different properties and thus applications. Based mostly on its density and branching, PE can be categorized as high-density PE (HDPE), low-density PE (LDPE), and linear low density PE (LLDPE), which results from copolymerization of ethylene with longer polymers (e.g., butylene, hexene, or octane).

Bio-based PE, which can be made by dehydrating bioethanol to ethylene that is further polymerized, is a drop-in equivalent replacement for the fossil product. It is not biodegradable but it can be easily recycled. Nowadays, bioethylene is produced from sugarcane (in Brazil) and sugar beet (in Europe), but also by using cornstarch and wheat starch (in the USA) as raw materials (E4tech, RE-CORD, and WUR 2015). There is no commercial activity of bio-based PE in Europe, and Braskem in Brazil is the only commercial-scale producer (from sugarcane, since 2010) worldwide (E4tech, RE-CORD, and WUR 2015). The production cost of bioethylene (the bio-based PE building block) is obviously dependent on the bioethanol price, and the final polymerization step has a small contribution to the PE production cost. Indeed, the production of bio-PE is expected to increase, reaching 840 kton by 2020, but there are some uncertainties associated with competition with other attractive bio-based packaging polymers, such as PET, PLA, and PEF, as already referred (E4tech, RE-CORD, and WUR 2015).

4.5.2 *The Chemical Catalytic Route*

4.5.2.1 Furan-2,5-Dicarboxylic Acid (FDCA)

Although neither FDCA nor any of its derivatives has yet become a commercial product because of its high price, it is very attractive from its potential as a bio-based replacement for polymers (polyesters). It can substitute terephthalic acid and also PBT and polyamides, providing a new class of polyethylene furanoate (PEF) polymers, with application in drinks bottles with superior gas barrier properties (Werpy and Petersen 2004). FDCA has also the potential to be used in the production of novel solvents, and it can also be converted into levulinic and succinic acid.

It is chemically produced via oxidative dehydration of C6 sugars, such as glucose. Once most of the routes to FDCA proceed via oxidation of 5-hydroxymethylfurfural (HMF), its commercialization might be boosted by the recent achievements on development of more efficient production of HMF by bacterial fermentation (Bozell and Petersen 2010; Lane 2015). Indeed, a significant growth of the current incipient FDCA market is projected, with a volume of 500 kton, corresponding to 498 million USD, foreseen for 2020 (E4tech, RE-CORD, and WUR 2015).

There are only a few companies handling the production and commercialization of FDCA, and the market is dominated by a single key player, Avantium, settled in the EU (Lane 2015). This company has operated, since 2011, a pilot plant in the Netherlands based on development of a two-step catalytic process to convert sugars into FDCA that is used to produce PEF. Corbion Purac, AVA Biochem, and Novozymes are also active in developing FDCA chemical production from glucose in Europe (Bozell and Petersen 2010).

4.6 Concluding Remarks

A large consortium of research organizations has proposed a “Joint European Biorefinery Vision for 2030” (Luguel 2011) based on several key points. The success of modern biorefineries, including starch based, should be based on versatile biomass supply chains and on the production of a wide spectrum of competitive bio-based products. This flexibility – multiple product and multiple feedstock – not only minimizes risks associated with raw material availability and product demand (market) but also allows all-year operation by using feedstocks that mature at different times (E4tech, RE-CORD, and WUR 2015). This flexibility strategy is evident in the typical sugar- and starch-based biorefinery ‘Les Sohettes’ complex, located in Pomacle (France). This biorefinery consists of a sugar beet processing unit, a wheat refinery and a sugar plant, an ethanol distillery (Cristanol), a research center (ARD), a demo-plant for second-generation ethanol (Futurol), a straw-based paper production pilot unit (CIMV), and a succinic acid pilot plant (BioAmber). This facility is a good example of integration in the product networks as two major crops are being used as feedstocks: sugar beet and wheat. The combination of both crops allows year-long biorefining operations, because the harvesting period of sugar beet is rather short (typically only a few months in a year), which would render the sole use of sugar beet for production of ethanol and other bioproducts uneconomical (Gnansounou and Pandey 2017).

As another example of multi-product strategy, NatureWorks LLC has been operating a corn biorefinery since 2002 (Nebraska, USA). This integrated biorefinery processes corn to produce corn oil, sugar, ethanol, lactic acid, and PLA (Gnansounou and Pandey 2017).

More broadly, cluster-based biorefineries constituted by different value chains site plants aggregated as a cluster shall be more competitive, such as demonstrated by the successful implementation of the Chemical Cluster (five-site plants) in Stenungsund (Sweden)—Aga, AkzoNobel, Borealis, Ineos and Perstorp—developing a joint strategy for producing sustainable products. New technologies are being explored for integrating the production of biomass-derived fuels and other products, such as 1,3-propanediol, polylactic acid, and isosorbide, in a single facility (Gírio et al. 2017).

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