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Chapter 4

² Starch biomass for biofuels, biomaterials

and chemicals

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16 Abstract

The success of modern biorefineries, including those using starch-based feedstocks, 17 18 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 19 20 knowledge of bio-based products obtained mainly from biochemical platforms from starch- and sugar-based feedstocks. After an initial review of starch production sources 21 22 and starch properties as well as starch-based end applications, this chapter reviews the 23 state of the art of starch hydrolytic enzymes, focusing on a bio-based platform for the 24 main value-added (bio)chemicals, biofuels, and biomaterials that can be obtained from sugar-based feedstocks. 25

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
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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 35 36 starch-based raw materials. Although bio-based chemicals and biomaterials still do not 37 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, 38 biolubricants, biosolvents, and biosurfactants) are expected to grow in the near future. 39 Several examples of biological production routes are described in this chapter, namely, 40 for ethanol, lactic acid, and polylactic acid (PLA), polyhydroxyalkanoates (PHAs), 41 succinic acid, 1,4-butanediol (BDO), farnesene, isobutene, acrylic acid, adipic acid, 42 43 ethylene, and polyethylene. One example of using a chemical catalytic route to obtain furan-2,5-dicarboxylic acid (FDCA) is also reported.d sources for starch production due 44 to its high starch content, which represents about 58-70% of the total dry grain weight 45 (Höfer 2015). Proteins are also important components of wheat grains since the higher 46 47 the protein content, the lower the starch content. The starch/protein ratio is highly dependent of the wheat variety, and those varieties selected for having higher starch 48 49 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 50 temperatures of 30–32 °C) and a lot of sunshine (especially during the stage when the 51 grains are filling). Between sowing and harvesting, wheat needs about 3.5-4.5 months 52 depending on the climate, the seed type, and the soil conditions. With the aim of 53 promoting wheat as a viable crop, different techniques - including soil preparation by the 54 55 use of crop rotation and/or the addition of fertilizers and the extensive mechanization of 56 the harvesting processes - have improved plant growth and eased the reaping, threshing 57 and winnowing steps during grain separation. Wheat growth, as any other crop, is highly dependent on climate conditions. In this context, the very high yielding triticale (Triticum 58 aestivum L.) - a cross-breed between wheat and rye with a similar starch content than that 59 for wheat - or hulless **barley** (Hordeum vulgare L.) are appropriate crops for starch 60 production in those places with less favorable climate conditions, such as high latitudes, 61 high altitudes or saline environments (Oettler 2005; Höfer 2015). 62

Rice is another important source of starch worldwide. It contains 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 starches only measure about 7-9 μ m, 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 to be used in decorative cosmetics, and skin and hair care products (Mitchell 2009).

Besides wheat and rice, maize (corn) is one of the most important cereal grains in the 70 world. On each individual corn kernel - the fruits of maize - starch is the major chemical 71 component with about 72% of the kernel weight. Also, 1% to 3% of glucose, fructose 72 73 and/or sucrose can be found in corn kernel. Corn starch usually comprises up to 25-30% amylose and 70-75% amylopectin. However, corn with up to 65-80% can also be found 74 75 in commercial varieties (Schwartz and Whistler 2009). As that for wheat, warm climate is required for maize cultivation, which also can fairly grow in high latitudes. In countries 76 with suitable climatic conditions, maize can now be cultivated with very high yield per 77 78 unit area thanks to current resources and management techniques. Furthermore, the 79 maturing period of this crop is relatively short. As main disadvantage, maize requires plenty of watering, limiting its cultivation in places with low available water capacity. 80

81 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 82 83 as manioc, mandioca, yuca, mogo, tapioca-root or kappa, is extensively cultivated in tropical and subtropical regions. Since starch granules are locked inside cells, a 84 biochemical or mechanical disruption of cassava is first needed for collecting the starch. 85 Higher yields and better starch quality can be obtained by the mechanical process. In this 86 87 method, root cassava is sliced and then rasped, grated or crushed to get a fine pulp with 88 high starch content (Breuninger et al. 2009). In general, cassava starch is primarily used 89 for bioethanol production or cooked to form a clear gel with slightly stringy texture that makes it a suitable food thickener (Shanavas et al. 2011). Potato is another relevant tuber 90 for starch production. The chemical composition of potatoes is very variable and is greatly 91 influenced by variety, environment, and farming practices. Although 80% of its 92 composition is water, starch represents about 65-80% of its dry weight (Höfer 2015). 93 Potato plant is an herbaceous perennial crop that can be adapted to different climates. 94