Chapter 2
Saccharide Biomass for Biofuels, Biomaterials, and Chemicals

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Abstract This chapter is a description of the main applications of saccharides in industry for obtaining energetic and nonenergetic products by means of the biorefinery concept allied to green chemistry principles. A biorefinery seeks to use the entire biomass completely, exploiting polysaccharides, proteins, and lignin in various manufacturing processes, to obtain food, pharmaceutical products, biomaterials, bioproducts, and biopolymers, in addition to energetic products, in a sustainable manner. After analyzing demand aspects, costs, transformation technology to be used, and possibilities for the molecule to be a source for many technological applications, the most promising saccharide applications are succinic acid, bioethanol, and 3-HP (3-hydroxypropionic acid).

Keywords Bioplastics • Biochemical • Biorefinery

2.1 Introduction

Biomass is a renewable resource, as it is part of the natural and repetitive cycles of nature's processes (on a human scale) and is derived from plants starting with the process of photosynthesis, transforming solar light into energy that accumulates in the cells in the form of organic matter. This action is essential to maintain ecological equilibrium and allows biological and soil diversity to be preserved and enriched.

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Since the beginning of the twenty-first century, in Europe, the United States (US), some Latin-American countries, and most recently some Asian countries, projects are being driven by the use of sugars and starch products for carburant bioethanol, and the use of oils and fats from different origins for biodiesel production. These were first-generation projects that were developed from good agricultural management, a known logistic for raw material transportation, and the implementation of technologies already developed for alimentary applications that had excellent performance. But their execution required support from states or governments for exemption of biofuels from taxes if they were to be competitive to gasoil and diesel from fossil origins. Then, environmentalist movements against the first-generation biofuels appeared because of the competition between the use of raw materials to feed the population and their direct bioenergetic use. This conflict drove strong research efforts, from the beginning of this century, to use lignocellulosic materials to produce ethanol, and microalgae and used kitchen or residual oils for biodiesel production, which originated the second, third, and fourth generations of biofuels.

When biomass is seen as a complete system in which every advantage is taken, the concept of biorefinery appears, a term that has been used since the end of the 2000–2010 decade. This concept makes the use of biomass for production of second-, third-, and fourth-generation biofuels more economically sustainable and viable. This concept is in accord with the definition made recently by IEA Bioenergy (Task 42: Biorefineries: adding value to the sustainable utilization of biomass), referring to bioenergy as “the sustainable treatment of biomass in a spectrum of commercial and energy products” (International Energy Agency 2009).

Latin American countries in the north have abundant biomass as the result of their strategic position at the Earth’s equator. This situation provides solar radiation 365 days per year, with 12-h daily cycles of light, abundant rain, and warm temperatures above 24 °C, giving a tropical setting with one of the highest rates of biodiversity. This characteristic influences crop production; for instance, sugarcane cultivated in Colombia has one of the highest performances worldwide, approximately 120–140 ton ha^{-1} per year, of which 40–60% corresponds to agricultural cane residues in a humid base (approximately 13 million tons), and in Brazil this residue can be nearly 300 million tons. These results are significantly close to those of other studies. For example, Central America (another tropical region) reports 60% of field residue, of which 20–40% (w/w) is process residue (BUN-CA 2002).

The biorefinery concept includes an extended range of technologies that are capable of separating biomass from its basic components (carbohydrates, proteins, triglycerides), which can be converted to products with added value (energetic or not energetic). Products can be intermediary or final products, in food, materials, chemicals, or energy (defined as fuel, electricity, or heat). A biorefinery can use every kind of biomass, including wood, agricultural crops, organic residues (vegetal, animal, industrial, or urban), and aquatic biomass (e.g., algae).

An important characteristic for biorefinery implementation is sustainability, which should be evaluated over the entire production chain. This evaluation has to consider possible externalities such as competition between food and biomass resources, impacts on water use and quality, soil changes (fertility) resulting from

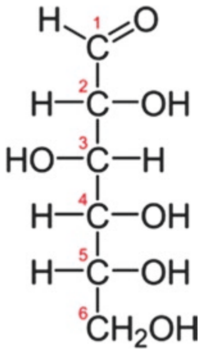

Fig. 2.1 Glucose structure

continuous use, the net balance of greenhouse gases, negative consequences on biodiversity, potential toxic risks, and energetic efficiency. A biorefinery is a concept that depends on continuous innovation, presenting opportunities for all sectors. The construction of a biologically based economy (bioeconomy) has the capacity to face actual difficulties and also provides an environmentally benign industry.

Thus, this chapter focuses on reviewing the application of sugars for bioenergy and non-bioenergy sectors in order to integrate them into a process by the biorefinery concept.

2.2 Chemical Constitution and Physicochemical Properties of Saccharides

Sugars are substances that have the particularity of giving a sweet sensation in the mouth. They are classified as carbohydrates because they contain carbon, hydrogen, and oxygen in their structure. Simple sugars or monosaccharides are classified depending on their number of carbons: as trioses if they have a three-carbon base, as tetroses if they have four, pentoses if they have five, and hexoses if they have six carbons. The most abundant monosaccharide is glucose. As shown in Fig. 2.1, this sugar, as any other, has a chiral structure, all carbons in positions two to five having different substitute radicals, which originate various stereoisomers that show mirror symmetry. Usually, these are called L- (levogyre, levorotatory) and D- (dextrogyre, dextrorotatory). Chemically they behave in a similar manner, even if they are not biologically similar (Pratt and Cornely 2012).

The more common C5–C6 sugars with these structures are D(+)-glucose, D(+)-xylose, and L(+)-arabinose, the physicochemical properties of which are shown in Table 2.1.

As noted in Table 2.1, there is little difference in the properties among these different sugars, except for molecular mass and water solubility.

Table 2.1 Physical and chemical properties of the principal monosaccharides

	Saccharide[a]	D(+)-Glucose[b]	D(+)-Xylose[c]	L(+)-Arabinose[d]
Appearance	White translucent crystals	Crystals or colorless to white crystalline powder	White powder	White powder
Water density at 20 °C (kg m^{-3})	1587	1540	1525	1585
Molar mass (g mol^{-1})	342.3	180.1	150.1	150.1
Fusion point (K)	459	419	419–425	431–436
Water solubility (g 100 ml^{-1} at 298 K)	203.9	91	55	83.4

[a]www.reactivosmeyer.com.mx/pdf/materias/hds_6710.pdf
[b]http://iio.ens.uabc.mx/hojas-seguridad/1593[1]glucosa%20anhidrida.pdf
[c]https://www.applichem.com/fileadmin/datenblaetter/A2241_es_ES.pdf
[d]https://www.carlroth.com/downloads/sdb/es/5/SDB_5118_ES_ES.pdf

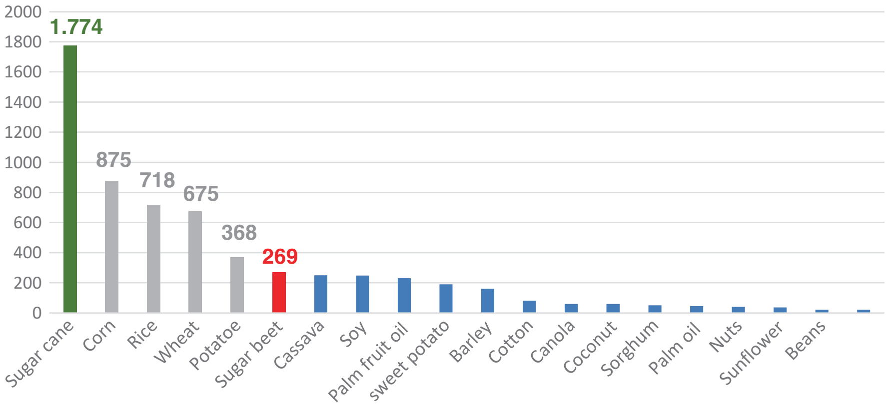

Fig. 2.2 World production of agricultural goods in 2013 (in million tons) (Adapted from Asocaña (2015))

2.3 Economic Aspects: Global Production, Availability, and Distribution of Sucrose

Sugarcane and sugar beet production are the dominant agricultural activity in tropical and subtropical regions around the world. More than 117 countries produce sugar, ethanol, honeys, bagasse, and derived products from these crops, resulting from State policies implemented in various countries that recognize the positive socioeconomic impact associated with the cultivation and processing of cane. Overall, world production of fresh cane in 2013 was 1774 million tons, from 26 million harvested hectares (Food and Agriculture Organization of the United Nations 2017), which bypasses the combined production of maize (875 million tons) and rice (718 million tons) (Fig. 2.2). During the 2014–2015 period,

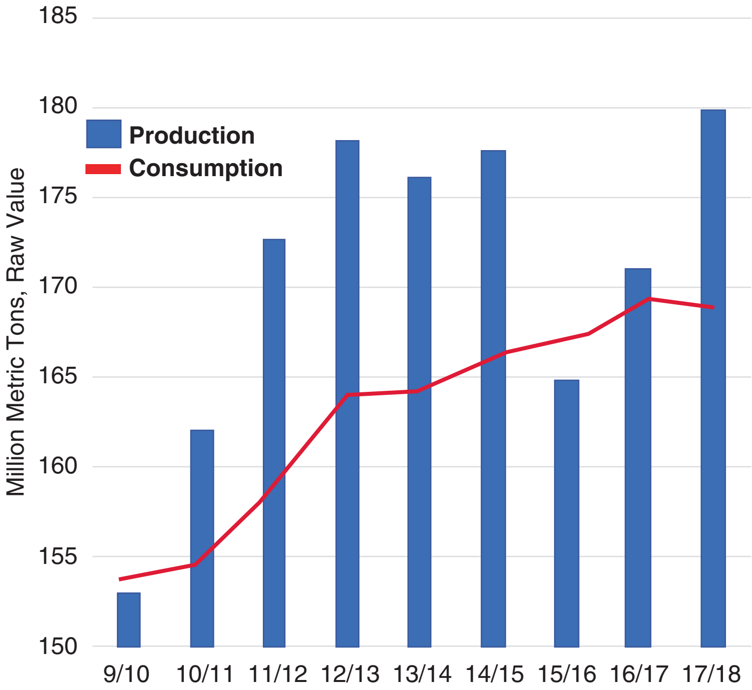

Fig. 2.3 Global consumption and production of sugar during 2009–2018 (*Source:* Adapted from U.S. Department of Agriculture (2017))

sugarcane production increased to 1900 million tons, quadrupling 1965 production (Statistica 2015). Brazil was the first producer (768 million tons), followed by India (341 million tons), China (128 million tons), Thailand (100 million tons), and Pakistan (63 million tons). Other producer countries are Mexico, Colombia, Indonesia, Philippines, and the US (Food and Agriculture Organization of the United Nations 2017). Sugar beet production is much lower, about 14% of cane production in 2014, of which France, US, Germany, and Russia are the main producers worldwide (Statistica 2016).

Worldwide average performance is about 69.8 ton ha^{-1} per year, but it varies from region to region, depending on such factors as weather potential, level of agricultural management, crop cycle, soil quality, and number of harvests (Food and Agriculture Organization of the United Nations 2012). There is a long-term tendency for average global performance to grow about 4 ton ha^{-1} per year. Colombia has the highest production of sugarcane in the world, at 120–140 ton ha^{-1} per year. An important factor on increasing production of sugarcane per hectare is the adoption of new varieties and increasing harvest age, which is maintained over 12.5 months.

Figure 2.3 shows that from 2010 to 2015 sugarcane production increased by 12%, whereas its consumption was 8.8%, creating an oversupply that lowered sugar

Table 2.2 Agricultural and economic value of sugarcane and its products and subproducts

Economic sector	Added-value products from sugarcane residues and the sugarcane industry
Food	Sweeteners, drinks, edible fats and oils, proteins
Health	Chemicals, antibiotics, anti-cholesterol
Fertilizers, compost, food, seeds, concentrates, grass, pesticides	Variety of foods, seeds, concentrates for animals, grass
Industry	Solvents, plastics, bioplastics, chemical products, alcohol-based compounds, anticorrosive compounds, surface-active compounds, biocides
Electric energy, biogas, bagasse fuel, alcohol	Bagasse as fuel, biogas, cogeneration of energy, ethanol from bagasse and sugars
Transport	Ethanol
Education and culture	Books, notebooks, broadsheets, paper
Construction/housing	Boards, alternating current/voltage conduits, decorative plating
Light industry	Textile, wax, bitumen, carbon paper, chemical products
Communication	Isolating materials
Heavy industry	Grout for casting mold
Human resources development	Job creation for rural areas

Source: Solomon (2011)

prices and discouraged its production between 2015 and 2016. It is also important to take into account that after 2010, diverse projects on fuel ethanol were created, particularly in South America, so that sugarcane production was diverted to fuel production. It is expected by projections that for the 2017-2018 that production will reach 180 million metric tons of saccharide, 4.7% more than expected consumption for this same period.

2.4 Main Products: Considering Energy, Biofuels, Biomaterials, and Chemicals

Only after the 1973 world energy crisis did scientists and technicians realize the value of sugarcane and its subproducts and co-products, as it is considered as one of the best plants for converting solar energy to biomass and sugar.

Sugarcane is a versatile crop, being a rich source of food (saccharides, syrup), fiber (cellulose), animal food (green leaves, buds), fuels and chemicals (bagasse, molasses, alcohol), and fertilizers and filter cake. Therefore, almost every country in the world that produces sugar has realized that although its production is profitable, it is better to develop added-value products as obtained by sugarcane industry diversification and the use of its by-products, instead of depending on only one product.

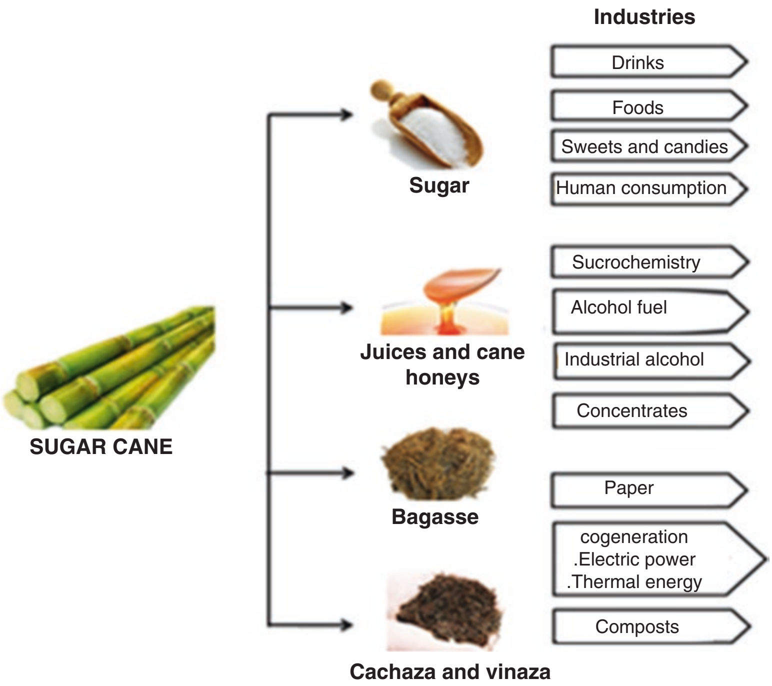

Fig. 2.4 Products and by-products of sugarcane

Sugarcane and its derivatives are raw materials for more than 25 industries: some of the most important are shown in Table 2.2.

Of all the sugarcane products and by-products shown in Table 2.2, those having the highest economic value are sugar (sucrose), juices/honeys (mostly molasses), bagasse, and filter cake (Fig. 2.4). Moreover, other residues produced during harvest and production that have less commercial value, such as green leaves, wax, and ashes, need to be valorized.

In addition to the applications already mentioned, saccharide is the base of the sucrochemical industry, from which bioproducts and other compounds of sugars are obtained and developed.

Bioproducts are made from biological compounds or renewable materials. There is no universally accepted definition for these products, but they can be described as the one that is fabricated in a sustainable manner, total or partially, from renewable resources. Thus, it includes all the processes, from raw material production to every step into the final product fabrication, in addition to processes of investigation, development, and commercialization.

Typically, bioproducts are divided in two categories: bioenergetic and non-bioenergetic. Those categories can be separated into seven segments. Table 2.3 shows the categorization and segmentation of bioproducts.

Table 2.3 Categorization and segmentation of bioproducts

Category	Segment	Products
Bioenergetic	Biofuels	Liquid fuels, such as ethanol, methanol, biobutanol, fuel oil, and biodiesel for means of transport
	Bioenergy	Solid/liquid biomass for combustion to generate heat and electricity
	Biogas	Gaseous fuel, as biogas, biomethane, and synthetic gas to generate heat and electricity
Non-bioenergetic	Bioplastics/biopolymers	Bioplastics from vegetable oils and C6 and C5 sugars
	Biocompounds	Fabricated from agricultural and forest fibers (hemp, linen), that can be used for panels and part production for vehicles, for example
	Biochemicals	Basic chemical products and industrial specialties, including grouts, paints, lubricants, solvents
	Biomedicine	*Pharmaceutical products*: antibodies and vaccines produced by genetically modified plants; medical compounds from a natural origin *Cosmetic products*: soaps, body creams, lotions

Source: Adapted from Gobina (2014)

Among compounds derived from saccharide, ethanol and butanol are important as bioenergetics. From the non-bioenergetics, the most significant are bioplastics/biopolymers and biochemicals. Other products are derived from lignocellulosics, which are discussed in Chap. 5. Hereafter, we examine more deeply the more relevant compounds for the sucrochemical industry.

2.4.1 Energetics Products

Biofuels are those compounds such as alcohols, ethers, and esters that come from sweetened juices or organic compounds of sugar-based cellulosic extracted from plants, cultures, or biomass residues. Since the 1970s, biofuels have been promoted to replace part of the consumption of traditional fossil fuels such as coal, oil, and natural gas. The best developed and most used biofuels are bioethanol and biodiesel; other alternatives are biopropanol and biobutanol, which have been until now less commercially valuable.

According to the study by Gobina (2014), during the period between 2010 and 2011, between 28.8 and 30.6 billion gallons (BG) of biofuels were sold worldwide. His projections show that global consumption of these biofuels could reach 50.9 BG

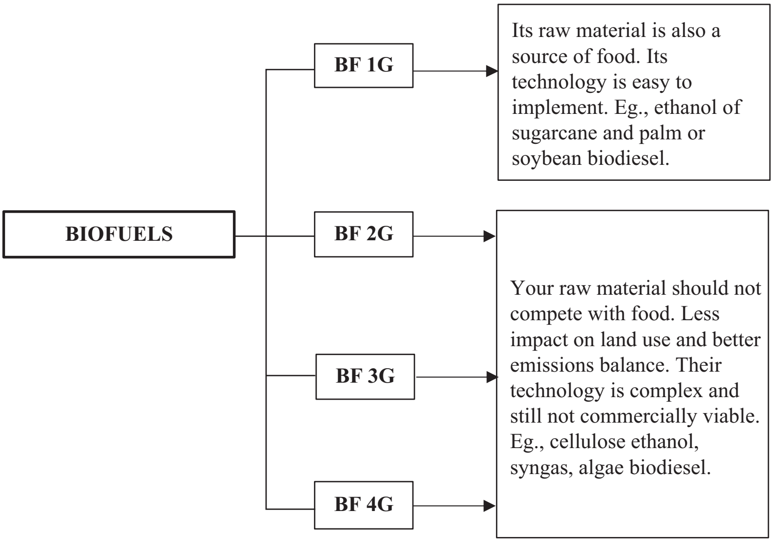

Fig. 2.5 Classification of biofuels (BF) by generations

in 2018, compared to 34.3 BG in 2013. This increase corresponds to an annual growth rate of 8.2% during the forecast period. Energy bioproducts, therefore, can help countries achieve their goals of a secure, reliable, and affordable energy policy, to expand, access, and promote development.

Although the increase is surprising, the production of neither ethanol nor biodiesel is expected to double for the period from 2013 to 2021 (Gobina 2014). Production volumes are expected to decline below the estimated demand of 71.8 billion gallons because of lack of access to low-cost raw materials and difficulties in obtaining financing (Mussattoa et al. 2010). However, this trend is not global, but is particular to each country and the policies implemented in each one. It also depends on the price of oil and the availability of biomass in each region. In Colombia during 2015, 468 million liters bioethanol were produced (Fedebiocombustibles 2017), far below major world powers producers of this biofuel, such as the USA (9000 million gallons) and Brazil (6472.2 million gallons), which covered 89% of the total market in the world in 2008 (Mussatto et al. 2010).

Biofuels can be made from different sources and have different levels of complexity in their processing, depending on the technology required. This variation allows classifying biofuels in four different generations (Fig. 2.5), of which the first two are explained next.

First-generation biofuels (BF 1G) are also called agro-fuels because they come from crops that are used for human consumption, directly or indirectly, and use conventional technologies, which are already produced and marketed in significant quantities by different countries. The US is currently the largest producer of bioethanol, 19.8 billion liters per year, with maize as the main raw material. Sugarcane is used as the main raw material in Brazil, currently the second largest producer in the world (17.8 billion liters per year). The European Union produces 3.44 trillion liters of bioethanol, mainly from sugar beet and starch crops (Food and Agriculture Organization of the United Nations 2007). This ethanol is obtained by processes of fermentation of sugar solutions in which pH value, temperature, type and concentration of inoculum, and quantity and type of micro- and macronutrients are controlled, to obtain musts with an alcohol concentration of 10% (v/v). After that, ethanol is purified by distillation and dehydrated by molecular sieves or pervaporation. Anhydrous bioethanol is thus obtained with a moisture content of only 0.4% (v/v), ready to be used as biofuel. The size of the global ethanol market can be around 86 million ton year^{-1}, of which only 18% is destined for applications other than for energy (Choi et al. 2015).

Second-generation and higher biofuels (BF 2G, 3G, 4G) emerged as the response to the largest critique of first-generation fuels: the dilemma between food and fuels. These biofuels are obtained from biomass that cannot be used as food and are produced with technological innovations that allow a more ecologically sound and more advanced production than that used nowadays. As they are obtained from non-alimentary raw materials, the sources for such biofuels can be cultivated in marginal lands that are not used for growing food, or can be obtained from residues from agricultural, forest, or agro-industrial activities. In that sense, they allow a higher diversification with new raw materials, new technologies, and new final products, promoting agricultural and agro-industrial development.

It has been found that biomass coming from cellulose can be a basic raw material for the production of second-generation biofuels. Biomass from cellulose generates cellulosic bioethanol, which allows the use of sawmill waste, reorienting and expanding the forestry industry to diversify the uses of wood and to protect forests from clearing for agricultural and farming uses.

Second-generation biofuels are in a preoperational stage, but they are not yet produced on a large scale. High manufacturing costs imply that they cannot be commercialized and that these biofuels need incentives and subventions from governments to be able to expand. Demonstration factories of cellulosic ethanol already exist in Sweden, Spain, Germany, US, and Canada. In Latin America, Brazil has a plant under construction in the São Paulo area (Sanford et al. 2016). However, the initial issue represents a potential development to help reduce CO_2 and diminish the consequences of greenhouse gases, braking global warming.

Some companies such as Braskem of Brazil, Dow, and Solvay have announced projects to produce ethylene from ethanol. In the Brazilian case, the plant of Braskem has a production capacity of polyethylene (PE) of 200 ton year^{-1} and a consumption of bioethanol of 462 million liters year^{-1} (Haro et al. 2013). Thereby, ethanol is projected as a commodity for the production of polyethylenes, styrene monomer, and ethylene oxide, from which biopolymers, rubbers, and polyesters are mostly obtained (Fig. 2.6). The world market for ethylene derived from petroleum is booming, with a growth rate around 4.5%. Production is expected to be close to 208.5 million tons by 2017 as the result of the new plants that will go into operation between 2016 and 2017 in the US and China, presently the world leaders for this product (Carvajal medios B2B 2017). This step can give a good margin of growth to

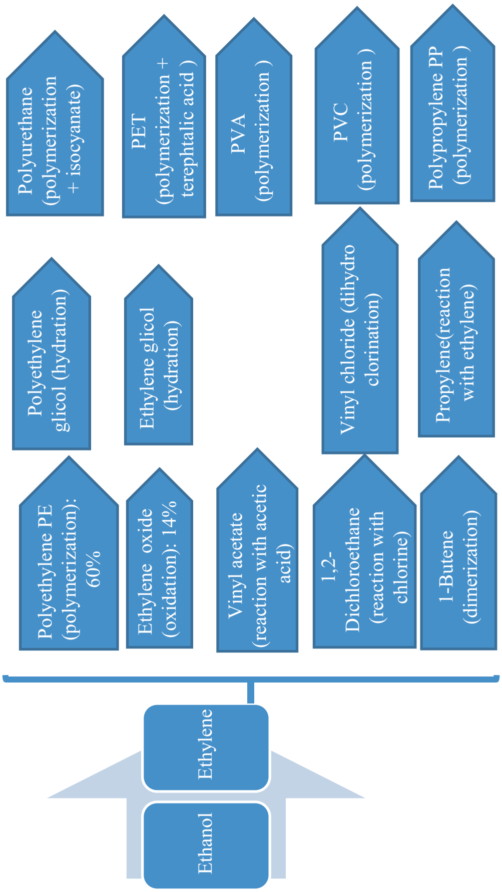

Fig. 2.6 Main products derived from ethylene. Terms in parentheses correspond to the transformation process. *PET* polyethylene terephthalate, *PVA* polyvinyl acetate, *PVC* polyvinylchloride (Adapted from Jong et al. (2007) and Choi et al. (2015))

the bioethylene that is produced from ethanol through a process of dehydration. This process is developed by introducing water and ethanol into a fluidized-bed reactor operating at a temperature of 613 K and a pressure of 0.48 MPa with activated alumina as catalyst. The effluent from this reactor is cooled and compressed to remove the water. The resulting gas then passes through two rectification columns to separate the C3–C4, ethane and propylene, to produce an ethylene with a purity of 99.99% (Haro et al. 2013; Bozell and Petersen 2010). It should be noted that the main product of ethylene is PE, with a participation of 60%, followed by polyethylene terephthalate (PET), with 14% (see Fig. 2.6).

2.4.2 Nonenergetic Products

BCC Research estimates that the world demand of bioproducts will increase at an annual growth rate of 12.6% in 2013 to attain $700.7 billon in 2018, when it will reach a penetration rate of 5.5%. This growth rate is higher than that expected for energetic products, which are expected to increase to an annual growth rate of 8.5% to attain $227.9 billon in 2018, as opposed to an estimated $151.3 billon in 2013. The global market for nonenergetic products is significantly higher; it attained $236.3 billion in 2013. It is expected that for 2018 it may reach $472.8 billon, growing at an annual rate of 14.4% (BCC Research 2014).

Regarding the principal products that can be obtained from the sucrochemical industry, it is important to note that the State Department of Energy of the United States made a study in 2004, identifying by the concept of biorefinery seven potential products that could be produced from sugars by fermentation processes (Werpy and Petersen 2004). This platform was formed by succinic acid, aspartic acid, and 3-HP (3-hydroxypropionic acid) by oxaloacetate, glutamic acid of α-ketoglutarate, itaconic acid from citrate, bioethanol, and bio-hydrocarbons from acetyl-CoA and lactic acid from pyruvate. By chemical means the evaluation of another seven products was also contemplated, such as the production of levulinic acid by acid hydrolysis of saccharides, glucaric acid by oxidation, and sorbitol by glucose hydrogenation. This last process also proposed to obtain arabitol from arabinose and xylitol from xylose. Finally, the furfural of xylose and furfural hydroxymethyl of fructose pass by a dehydration process. Over the years, and after making technical and economic feasibility studies, the range of products was reduced and L-aspartic acid, L-glutamic acid, itaconic acid, and glucaric acid were discarded from the list, because of the limited size of the market, low growth rates, and restrictions on the applications of each product. A large portion of those products comes from fermentation processes, and others from chemical processes (Werpy and Petersen 2004).

2.4.2.1 Bioplastics/Biopolymers

Plastics have become a fundamental part of modern development, to the point that most of the objects we buy are made or packaged with this material, or have at least one plastic part, or have used components of this type in their production or transport. With continued growth for more than 50 years, world production in 2013 reached 299 million tons, an increase of 3.9% as compared to 2012 (PlasticsEurope 2014).

These plastics are generally synthetic and manufactured by polymerization of petroleum derivatives. They are diverse and very versatile in their applications, which indicates that more than 700 types of plastics are produced currently, such as polystyrene, nylon, polyurethane, polyvinyl chloride (PVC), silicones, epoxy resins, and polyamides. Nevertheless, this versatility is accompanied by several environmental disadvantages: inability to biodegrade, high resistance to corrosion and water, and greenhouse gas emissions. Although recycling programs for plastic materials are increasingly efficient and economical, they are applied on residues already generated and, in addition, recycling is not an alternative for all plastics that come from the petrochemical industry. As a result, a significant percentage of residues are discarded as waste, generating serious environmental problems.

Despite this discouraging scenario, one of the alternatives that is gaining strength is the replacement of plastic by bioplastics because they do not constitute a single class of polymers but rather a family of materials with different properties and range of applications. In general terms, the European Bioplastics Association (European Bioplastics 2017) states a bioplastic has one or both of the following characteristics:

- Biological basis materials: these are called biopolymers or materials originated totally or partially from biomass (renewable resources). The biomass used for bioplastics is derived from corn, sugarcane, or cellulose.
- Biodegradable: biodegradation is the ability of a material to decompose into CO_2, methane, water, and organic components, or even biomass, in which the predominant mechanism is the enzymatic action of microorganisms. This property does not depend on the origin of the material, but on its chemical structure.

The classification of bioplastics according to their origin, as biopolymers or from petrochemical biodegradables, can be observed in Fig. 2.7.

An investigation by Jason Chen in June 2014 for BCC Research (Chen 2014) predicted an annual growth rate for bioplastics of 32.7% from 2014 to 2019. In this study, Asia and South America are expected to account for about 90% of the production capacity of bioplastics in 2019 compared to 65% in 2013.

The sugarcane fiber present in residues such as bagasse, leaves, and buds has great potential for development in the field of bioplastics. The degree of commercialization of bioplastics based on renewable resources such as fibers has reached different levels. Some of these have already achieved a certain level of maturity that allows them to be competitive in comparison to petroleum-based plastics. The differences in prices that insulated them from common resins have been significantly

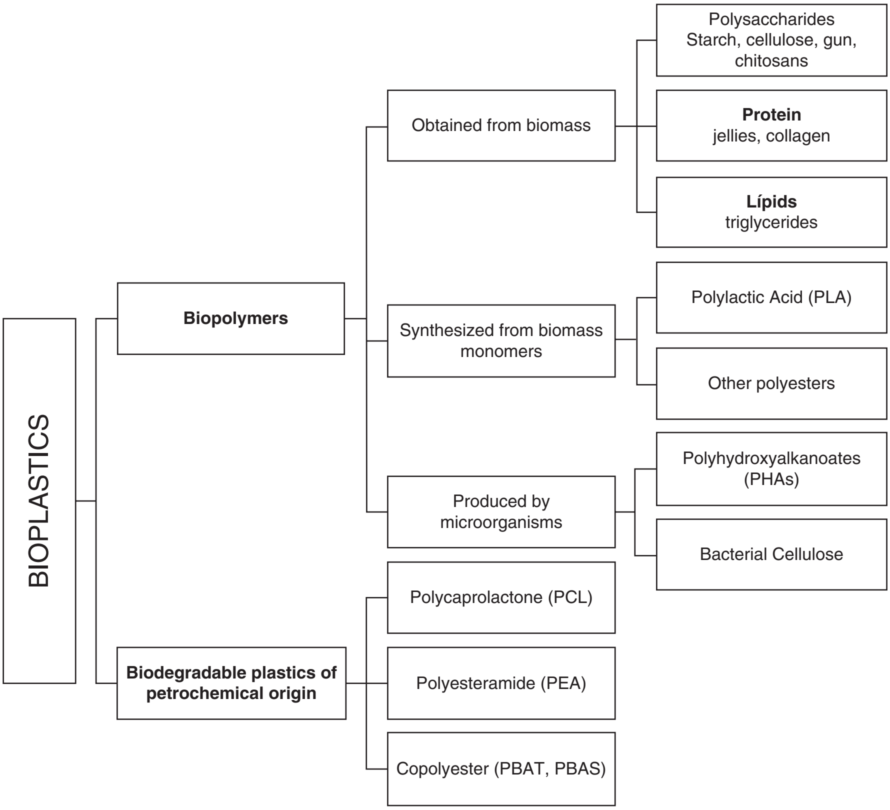

Fig. 2.7 Classification of bioplastics according to their origin

reduced. Furthermore, factors such as the high cost of oil, increasing advances in the processing of these types of materials, the growing number of consumers concerned about protection of the environment, and the creation of new government legislation have allowed consolidation of concrete applications of bioplastics at commercial levels.

Production capacity for biopolymers will triple from 5.7 million tons in 2014 to almost 17 million tons in 2020. Data show a 10% growth rate from 2012 to 2013 and as much as 11% from 2013 to 2014. Bioplastics consolidated in the market will grow at a slower pace because they have already been established for some time. In addition, competition during past years has increased, particularly, for example, for polymers derived from cellulose and starch besides polylactic acid (PLA), which will show a slower growth rate of 26.6% and 18.1% for the first two and 16.7% for the latter. In contrast, bioplastics such as polyethylene (Bio-PE) and polyethylene terephthalate (PET) have noted a significant increase during the past few years. It is expected that from 2014 to 2019, annual growth rates of 38% and 76.5%, respectively,

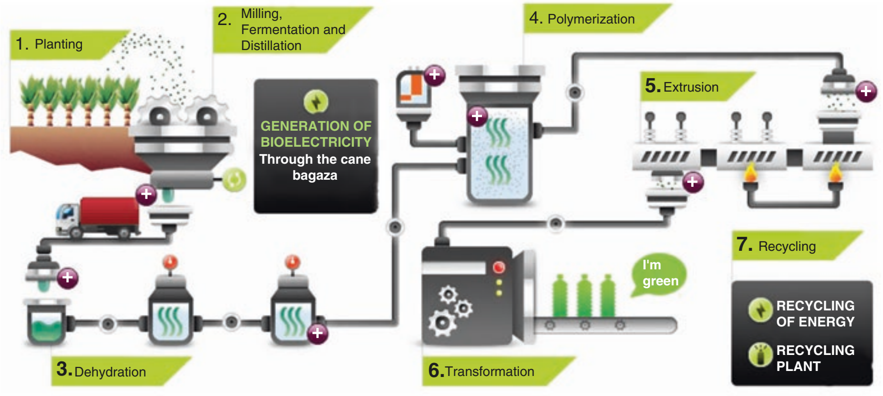

Fig. 2.8 Ecological production of green polyethylene (green PE) (*Source:* Adapted from Braskem (2017))

can be reached (Aeschelmann and Carus 2015). Some examples of bioplastics commercialized in the market are described next.

The renowned Coca-Cola Company launched a new plastic bottle made from materials derived from sugarcane. Since 2009, Coca-Cola has initiated the implementation of this type of new technique to elaborate its containers in the program *PlantBottle* (for PET), with an initial vegetable composition of 30%. Since its introduction, more than 35 million bottles have been distributed in almost 40 countries. The use of these containers has avoided annual emissions equivalent to more than 315,000 metric tons of carbon dioxide. In June 2015, the first 100% sugarcane bottle made was presented in Italy (Procaña 2015).

After years of research and development, Braskem, a Brazilian petrochemical company, launched the green ethylene plant in September 2010, as mentioned previously. This event marked the beginning of the production of *I'm green* polyethylene on a commercial scale, which ensured the company's global leadership position in the field of biopolymers (Fig. 2.8). This industrial plant was constructed by investments of $290 million and has a production capacity of 200,000 ton year^{-1} of green ethylene (Braskem 2017).

Green PE from Braskem is a plastic produced from a renewable raw material source, sugarcane ethanol. Braskem receives ethanol from its suppliers mainly through railways. When ethanol arrives at the ethylene plant, it goes through a dehydration process and is transformed into green ethylene. Then, green ethylene goes to the polymerization step for its transformation into green polyethylene by using the same equipment as used to produce conventional polyethylene (Fig. 2.8). The process and quality of the final product are maintained without the need to invest in new machinery and equipment. For the same reason, it can also be recycled within the company.

In addition to the ethanol mentioned in the previous section, there are other compounds derived from sugars from which plastics can be obtained through different chemical routes, such as polyurethane, polyesters, polyamides, polyacrylamides, and PLA. These compounds, which are used to produce monomers, are succinic acid, 3-hydroxypropionic acid, and lactic acid, explained in detail next.

Succinic Acid

Succinic acid is obtained by the fermentation of sugars (lactose, xylose, arabinose, glucose) by microorganisms such as *Escherichia coli*, *Actinobacillus succinogenes*, *Corynebacterium crenatum*, and *Basfia succiniciproducens* at 37 °C and a pH value between 2.7 and 6.5 (Moussa et al. 2016; Alexandri et al. 2017; Jiang et al. 2017). It is a dicarboxylic acid of four carbons that serves as the base to be transformed in various plastics by applying diverse processes of chemical transformation. In this way, 1,4-butanediol is obtained by hydrogenation. From this process, polyurethanes and polyesters are obtained using polymerization processes with various acids (terephthalic, dicarboxylic) or alkylene oxides. It is also possible to obtain polyamides after reacting succinic acid with ammonia to produce 1,4-butanediamine by hydrogenation, which after polymerization in acid medium produces the plastic (Choi et al. 2015). The size of the succinic acid market is between 30,000 and 38,000 ton year^{-1}. Several companies are currently manufacturing the acid, such as Reverdia, Myriam, Succinity, and Bioamber-Mitsubishi (Alexandri et al. 2017). The expectations for this commodity are to reach an annual growth of 18.7% (Moussa et al. 2016), although most comes from the petrochemical sector (95%) (Gallezot 2012).

3-Hydroxypropionic Acid (3-HP)

The biological production of 3-HP is recent. It is obtained from glucose via malonyl CoA (pathway II), which is expressed in microorganisms of the genus *Lactobacillus* and recombinant *E. coli*. Thus, the glucose is converted to lactic acid and then to 3-HP in a concentration approximately 49 g l^{-1} for 69 h with a 0.46 mol mol^{-1} yield relative to the sugar used (Kumar et al. 2013).

From 3-HP, 1,3-propanediol is obtained by hydrogenation to produce polyester by polymerization. If this polymerization takes place in the presence of terephthalic acid, PTT (polytrimethylene terephthalate) is obtained. Polyacrylamides, polyamides, and polyacrylonitriles are also obtained from the acrylic acid obtained by dehydration of 3-PH. Several companies, such as Cargil-BASF-Novozyme, Opxbio-Dow Chemical, and Perstorp, are already preparing the commercialization of several bio-based products, mainly acrylic acid derivatives with the largest market size, at about 5.5 million ton year^{-1} in 2013 (Choi et al. 2015).

Lactic Acid

Lactic acid is an organic acid with a very important market in the chemical, plastic, pharmaceutical, cosmetic, and food preservation industries (Murillo et al. 2016). PLA, a bioplastic that replaces polyethylene, polystyrene, or polyethylene terephthalate (Gerssen-Gondelach et al. 2014), is obtained from this acid through a polymerization process. About 90% of lactic acid is produced by fermentation from sugars of five or six carbons (Diaz et al. 2017; Murillo et al. 2016), but it has certain limitations in its application as the result of the long reaction times, technical difficulties in the stages of neutralization and purification, and the search of economic raw materials to make it profitable (Abdel-Rahman et al. 2011).

2.4.2.2 Biochemicals

We consider, under this heading, biochemicals as the set of chemicals produced from biomass. Several factors are driving the chemical industry to change its raw materials from petroleum to renewable counterparts for the production of organic chemicals: realization of finite oil resources, the harmful effects of oil derivatives on the environment, the availability of renewable resources, and the latest advances in processing technologies.

It is relevant that throughout the manufacture of chemicals, and in fact for the duration of the product's life cycle, the energy demand must be minimized, the processes applied must be safer, and the use of hazardous chemicals and their production avoided, as preconized by green chemistry (GC) principles. The final product must be nontoxic, and degradable into safe chemicals with minimal waste production; again, GC is closer to these criteria.

Expectations of the market for bio-based chemicals will grow as a result of business initiatives that favor the use of sustainable and renewable raw materials. The biochemical industry was valued at almost $92 billion in 2010. The market reached a value of $155.7 billion in 2013, equivalent to a compound annual rate increase of 19.2%. BCC Research forecasts that the market for biomass-derived chemicals will reach $331.2 billion in 2018, corresponding to an annual composite rate of 16.3% (Gobina 2014).

In 2004, the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL) identified 12 classes of products that could be derived from sugars, as saccharose, to support the production of fuels and energy in an integrated biorefinery both economically and technically. Further, they could identify the challenges and barriers of associated (chemical or biological) conversion processes (Werpy and Petersen 2004). These products are considered "building blocks" or chemical platforms, that is, they have the potential to produce multiple derivatives. Table 2.4 shows the products, the different ways of conversion, and some potential applications.

The products listed in the table represent a small part of the biochemicals studied by different research groups around the world. Several aspects including high oil prices, consumer preference for products from renewable resources, business commitments, mandates, and government support are driving efforts to broaden the spectrum of biochemicals.

In the mid- to long term, biochemical products will share the market with petroleum-based chemicals and eventually replace them as competitively priced products after overcoming the technological challenges they face today, in some cases, from the lack of friendly technologies and green transformations.

According to research done by the U.S. Department of Agriculture (2017), the degree of research, development, and commercialization of chemicals based on

Table 2.4 Main applications of biochemical drivers

Chemical products	Conversion process	Potential applications
1,4-Diacids (succinic, fumaric, malic)	Biological	Green solvents, fibers (such as Lycra), water-soluble polymers, antifreeze, fuel additives, flavorings
2,5-Furandicarboxylic acid	Chemical	PET with new properties (bottles, films, containers), new polyesters, nylon
3-Hydroxypropionic acid	Biological	Contact lenses, diapers, absorbable sutures
Aspartic acid	Biological Chemical	Detergents, absorbent polymers, corrosion inhibitors, water treatment systems
Glucaric acid	Chemical	Solvents, nylon with different properties, detergents
Glutamic acid	Biological	Flavors, monomers for polyesters and polyamides
Itaconic acid	Biological	Paints, adhesives, lubricants, herbicides
Levulinic acid	Chemical	Oxygenated fuels, solvents, synthetic gums, cigarettes
3-Hydroxybutyrolactone	Chemical	Solvents
Glycerol	Biological chemical	Disinfectants, lubricants, cosmetic products, polyester fibers with new/better properties, antifreeze, polyurethane resins
Sorbitol	Chemical	Antifreezes, water-soluble polymers, cosmetic products, sweetener in dietetic foods, source of alcohol in manufacture of resins
Xylitol/arabinitol	Chemical	Flavors, antifreezes, chewing gums, cough syrups, toothpaste, mouthwashes, hard candies

Source: Xu et al. (2008)

renewable resources is at different levels. The most highly developed are derivatives of 1,4-diacids (succinic, fumaric, malic), as well as xylitol, sorbitol, and *y*-3-HP. The world demand for the latter acid was approximately \$832 million in 2013, and it is expected that by the year 2018 this figure will reach \$900 million (Evans 2011).

2.5 Conclusions

Some authors consider that the integration of bio-based products into the production of bioenergy from biomass is still in its first stages of growth. Nevertheless, companies such as Cargil-BASF-Novozyme, Reverdia, Myriam, and Dupont as well as Braskem are making great economic and technical efforts to bring this idea into reality.

There are huge potentials for bio-based products that can be obtained from sugars, but at the moment, those with a more developed platform from the commercial and technical aspects are succinic acid with a market of 30,000–38,000 tons year^{-1}

and acrylic acid, derived from 3-HP, with a market of 5.5 million tons year^{-1}, in addition to biopolymers that can be obtained from bioethanol. However, the expected horizon, in both the short term and medium term, is an increase in the market for these types of renewable chemicals.

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