

Chapter 2

Feedstocks for First-Generation Bioethanol Production



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Abstract Ethanol from biomass was the first fuel used by man in Otto cycle engines. Its substitution by petroleum derivatives followed naturally due to the logarithmic growth of the world's demand for energy and limitations in agricultural growth. The so-called first generation (1G) ethanol produced from biomass with important levels of easily fermentable sugars or lignocellulosic material that will be hydrolyzed and fermented. The first economically viable materials from saccharine fermentations were sugar cane and sugar beets, starchy fermentations were corn and cassava. The ability to ferment C5 and C6 sugars using classical or GMO yeast strains such as *Saccharomyces cerevisiae* makes it possible nowadays to use almost any type of biomass.

The definition of the use of one of these raw materials depends on factors such as its availability in quantity and frequency, storage organization, tax incentives offered by countries or regions, non-competition with food markets, the price of petroleum derivatives, and the culture of using clean energy that minimizes greenhouse gas (GHG) emissions. The technology for producing ethanol from 1G cereals is well known and there are many plants operating in the world, based on cereals. The interest subsidy for the creation of new ethanol plants is in common use in several countries in Asia, Africa, and the Americas, which justifies the preference for its mixture in gasoline.

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2.1 Introduction

The natural raw material of greatest human interest, since the beginning time, is lignocellulosic biomass due to its versatile and renewable character. This source, which is around 450 million years old, is an indirect way of harnessing solar electromagnetic radiation that chemically converts and stores energy through photosynthesis.

Scientists aiming to replace energy from fossil sources with a clean and renewable energy source are incessantly looking for biomass with high productivity, resistance to climatic variations, easy-to-use technologies, and processing without significant environmental impacts. One of these alternatives uses residues from agroindustry and forestry to produce biofuels. The apex of this vision focuses on technologies known as first and second-generation fuels (e.g., bioethanol).

Engineering and bioengineering studies were needed to define the way to use carbohydrates from biomass, whether by saccharine or starchy processes leading to sucrose and starch fermentation, respectively. After judging your potential of biomass and technology is possible to implement the biological and thermochemical conversion for utilizing biomass to produce bioethanol. Biorefineries in various regions of the world, whether raw sugar mills or those that exclusively produce bioethanol, do not operate year-round, and must adopt other raw materials as a complement. The classic example is sugarcane and sweet sorghum, which have different harvest times, but can be processed into bioethanol using the same industrial equipment.

Over the past 35 years, governments and human society have been following with enthusiasm and concern the growing demand for natural and energy resources. This induced by the consumption of goods and services. Technological development in the production of economically sustainable and environmentally friendly biofuels has been stimulated by the stock and investment market and by governments that have established specific programs for their non-food agricultural matrices. The biggest link in this problem is the population growth that induces a disproportionate consumption in the entire production chain of inputs, following an infinitely worrying spiral.

The agronomic issues throw the proper characterization of a given plant biomass within critical for the optimization of its use for ethanol because this is provided valuable information about properties, storage and handling criteria, theoretical yields and potential environmental problems that are related to large scale industrial operations.

2.2 Production Feedstocks for 1G Ethanol Around Policy and Programs

To start with the correct definition of First-Generation Bioethanol, there is a direct relationship with biomass (raw material) which is a market commodity and used as a food source. Ethanol is produced from the fermentation of sugars (polysaccharides,

C6-glucose sugars) using classical or Genetically Modified Organisms (GMO) yeast strains such as *Saccharomyces cerevisiae*, *Zymomonas mobilis*, and *Escherichia coli* for improved ethanol fermentation (Rosales-Calderon and Arantes 2019).

The production of 1G ethanol occurs through the biological fermentation of hexoses such as glucose. ‘Sugars’ is the name for all types of monosaccharides and disaccharides found in nature. The sugars used in the production of first-generation ethanol are mainly extracted from crops rich in sugars or polymers such as starch. In Brazil, sugarcane juice is used to produce first-generation ethanol, while in other countries other raw materials are used, such as: Sweet potatoes (5.5% sugar), beetroot (8.0% sugar) and sweet corn (6.3% sugar). Other sugars ingredients include molasses, honey, maple syrup, and corn sweeteners, which are composed of varying levels of glucose, fructose, and sucrose (Canadian Sugar Institute 2021).

Therefore, the main raw material used in the 1G ethanol production process are feedstocks such as sugar cane, corn, wheat, among others. Sugar crops, such as sugar cane, sugar beet, and sweet sorghum, can be used as feedstocks for both conventional biofuels process (ethanol via fermentation of sugar) and/or advanced biofuels.

The main differences between corn and sugarcane ethanol are in the form of production. Sugarcane ethanol is simpler to be obtained, requiring fewer unit operations, followed by approximately 10.0 h of fermentation for conversion to bioethanol. However, sugarcane has less sugar than corn, and a one ton of sugarcane produces 89.5 liters of ethanol while corn can produce up to 407 liters of ethanol. The difference is in the chemical conversion of corn starch, leading to the fermentation process which can accept 70 h or more (Barros and Woody 2020).

The world leaders in the production of 1G ethanol are the United States and Brazil, which together produce more than 80% of the world’s ethanol. The 1G ethanol industry in the United States is quite strong and with large technological bases already developed for the efficient production of ethanol from corn. The United States total 1G ethanol production in 2020 was 13,926 million gallons (~63 million L) representing 53% of world production (RFA 2021). Due to the high volume of 1G ethanol production, normally 30% of corn production in the United States is used in ethanol production process (Mohanty and Swain 2019). Corn production in the United States was 347 million tons in 2019, which represents a total of 104.1 million tons of corn directed to the production of 1G ethanol to the production of 1G ethanol (FAO 2020). However, a small percentage (3%) of 1G ethanol could be produced from wheat and since 2021 sorghum is also being used in small quantities as raw material (RFA 2021).

The great production capacity of 1G ethanol in the United States allows it to export large volumes of this biofuel, registering the export of 1463 million gallons (6.6 million L) worldwide in 2019 (U.S. GRAINS 2019). On the other hand, Brazil’s 1G ethanol production in 2019 was 7.93 million gallons (~36 million L), being the second largest producer worldwide with 30% of 1G ethanol produced from sugarcane. According to Brazilian Association of the Sugar Cane Industry (UNICA 2020), in the 2020/2021 season, 657 million tons of sugar cane were produced in Brazil, which allowed a production of 32.0 thousand million liters of 1G ethanol and the production of 41.5 million tons of edible sugar. In addition, new plants to

Table 2.1 Source used in the ethanol 1G production cost by countries and global productivity

Country	Main sources	Ethanol cost (USD/L)	Production (millions of L)	World percentage (%)
Unite State	Corn	0.41	63,308.8	53
Brazil	Sugarcane	0.44	36,050.5	30
European Union	Sugar beet, wheat, and corn	0.47	5682.6	5
China	Corn	0.49	4000.6	3
India	Molasses	0.37	2341.2	2
Canada	Corn and wheat	–	1945.7	2
Thailand	Molasses	–	1818.4	2

produce ethanol from corn are being implemented and the by-products of sugar refining (molasses) are also used as raw material to produce 1G ethanol. Due to its large domestic market, Brazil exports only a part of its ethanol produced, which represents 7.18% of its domestic production (2.3 million liters of 1G ethanol).

The advantage of sugarcane is its productivity, since in one hectare it is possible to obtain up to 90.0 tons of sugarcane, capable of producing up to 8000 liters of ethanol. Corn yields a maximum of 20.0 tons per hectare, which can be transformed into 3500 liters of ethanol.

Although the United States and Brazil concentrate the largest bioethanol production worldwide, the European Union, China, India, Canada, Thailand, and Argentina are emerging as major producers of 1G ethanol from raw materials rich in sugar (FAO 2020).

For example, in the US the cost of raw materials is a major concern in relation to current 1G ethanol production methods, because the raw material cost of corn ethanol is on average 58% of total production, this cost is based on data from the last 15 years (2007–2021) in a typical production plant in the US using the dry milling process.

The production of 1G ethanol in 2020 by the European Union, China, and India was 5.7, 4.0 and 2.2 million liters. Together these three regions/countries account for 10% of world production. The source of raw materials turns out to be truly diverse according to the country and environmental conditions. Especially within the European Union, where corn, wheat, and sugar beet it used for ethanol production. In contrast, China and India produce their alcohol from corn and molasses derived from sugar production respectively (Table 2.1). However, due to their still low productivity, the European Union and Canada are two regions where 1G ethanol is imported, with an approximate of 1.5 billion liters (U.S. GRAINS 2019).

The role of raw materials rich in sugars and starch in the production of 1G ethanol is fundamental and defines the final cost of ethanol, representing 70% of the total process costs. For this reason, the need to increase the productivity of crops reducing their costs is particularly important.

The highest production crop worldwide is corn (1148.5 Mtonne), wheat (765.8 Mtonne), sugar cane (1949.3 Mtonne), rice (755.5 Mtonne) and palm fruits (410.7 Mtonne) (FAO 2020) (Fig. 2.2).

Table 2.1 was assembled using official websites: Canadian Sugar Institute (2021), CONAB (2021), MAPA (2021), FAO (2020), Renewable Fuels Association (2020a, b), and United States Department of Agriculture - Foreign Agricultural Service (2021).

As it might be seen four of the highest ethanol producers' crops are rich in sugars or starch that are used or can serve as raw material to produce 1G ethanol. There is precisely a direct relationship between the largest ethanol producers and the predominant type of crop in each country. The production of ethanol from corn is still slightly more expensive.

In 2020, the green fuel ethanol production was around the world 98.6 million m³. The U.S. and Brazil were the biggest players and producers in the world in our century for green fuel ethanol were with a participation of 53.0 and 30.0% of world production, respectively. The European Union accounted for 5.0% of the world production followed by India (2.0%), Canada (2.0%), Thailand (2.0%) and Argentina (1.0%). The rest of the world reached only 2.0% of the fuel ethanol world production Renewable Fuels Association (2020a, b) (Fig. 2.1).

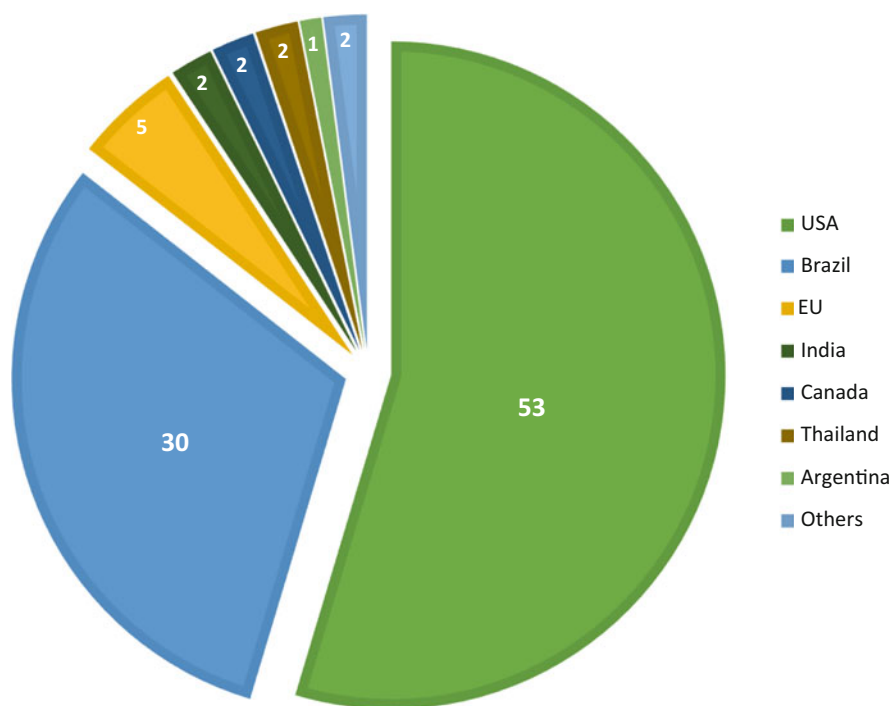


Fig. 2.1 Global ethanol 1G production, by regions/countries (in % of total production)—adapted from Renewable Fuels Association (2020a, b)

According to Renewable Fuels Association (RFA), the main feedstock type for ethanol production in the U.S. are corn starch (94.0%), corn/sorghum/cellulosic biomass/waste (3.4%), corn/sorghum (2.1%), cellulosic biomass (0.5%) and waste sugars/alcohol/starch (0.1%) (Renewable Fuels Association 2020a, b).

In Brazil, the two major feedstocks employed in bioethanol production are sugarcane and corn. In 2019, 96% of the ethanol produced came from sugarcane (USDA 2020). However, the ethanol produced using corn as feedstock has been growing fast during 2020/21 (being sugar cane responsible for 90.8% of ethanol production and corn for the remaining 9.2%) (<https://www.conab.gov.br/info-agro/safras/cana>).

In 2020, 49.5% of the ethanol produced in the European Union was from corn, followed by wheat (18.5%) and sugar (17.8%). The ethanol produced using other cereals and starch-rich crops accounted for only 6.3% (European Renewable Ethanol 2020).

Now after understanding this projection is possible to represent the data's such as in Fig. 2.2, Data were selected and worked from FAOSTAT with the aim of illustrating the world agricultural production based on green energy sources, either of oilseed or lignocellulosic origin. It is evident that in the main producing countries in the Southern hemisphere and below the Tropic of Cancer (South America, Central America and Mexico) sugarcane production is in the majority (green color) while in the Northern hemisphere wheat and maize production stand out (blue and yellow). Also noteworthy is the growth of rice production (purple) in Asia (FAO 2020).

Businesses and government institutions around the world are migrating their sugar production plants to produce bioethanol as well. Following the treadmill, gasoline should have a higher percentage of ethanol in the mixture, as is already the case in Brazil.

Brazil is moving, in some regions, to replace sugarcane with corn, taking advantage of the infrastructure of sugarcane mills that are idle between harvests and expands the opportunity to purchase raw materials at competitive prices in regions with production surplus and that present high logistical costs for the disposal of a product with low added value.

The use of regional biomass makes bioethanol an important substitute for fossil fuels, with advantages such as sustainability, and good adaptability. Over the past 30 years, the development of green fuels has been driven by government policies. Many countries and areas have authorized laws and regulations to ensure the minimization of environmental impacts and reduction of the greenhouse effect. With the support of governments, many projects were commercialized, and raw materials boosted the economy (Soccol et al. 2010; Barros 2020).

Governments provided privileges and financed investments and production costs, reducing subsidies for the entire process of the agro- and sugar-alcohol industry, to reduce the investment risk. As a result of this support, bioethanol started to be marketed in several states, districts, and countries.

Political debate and market reserves continue to be discussed among partner countries about the impact of green fuels on climate change, the extension of plantation areas, and food security.

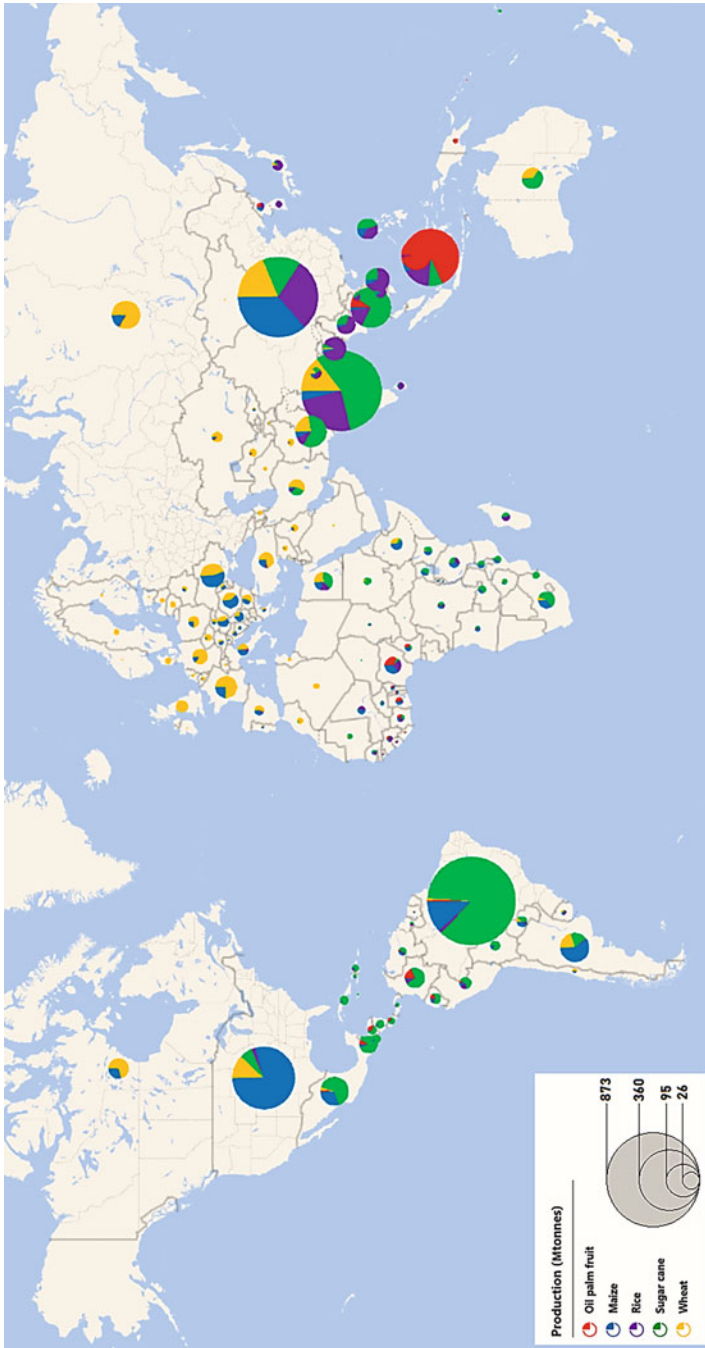


Fig. 2.2 Mains crops distribution by country around of the world (FAO 2020)

Although the production of biofuels is a positive alternative to fossil fuels, there is still a debate regarding food security. As we have seen, for the production of 1G ethanol the raw materials used are also important in the food industry, generating a conflict between the energetic and food industries (Mohanty and Swain 2019). In addition, the fluctuations in supply and demand within the energy market can greatly affect the prices of raw materials destined for the food industry and increase the price of food. This dilemma is even more serious in cereal crops such as corn, since the energy produced by the combustion of 1G ethanol from it commonly represents three times the energy required to produce it, which does not generate a substantial energy gain compared to other biofuels. On the other hand, ethanol produced from sugar cane yields 8.0 times the energy needed to produce it, also reducing greenhouse gases by up to 50% compared to gasoline (Chum et al. 2014).

It is necessary to highlight that the application of published policies of the different governments are necessary to promote the production of 1G ethanol as a biofuel. The United States Environmental Protection Agency set a minimum limit of 15% ethanol in the sale of gasoline. However, the limitation of combustion engines that would not support that level of ethanol, made the measure optional, stating that establishments selling gasoline with 15% ethanol would have to inform and signal this measure, while it was mandatory to maintain 10% ethanol minimum in the mixture with gasoline.

For its part, Brazil has a more robust ethanol industry, since starting in 1933, the combination of ethanol in gasoline was mandatorily established. Later, in 1975, the national alcohol program was established with the aim of reducing dependence on petroleum. However, it was not until 2003 that the Brazilian ethanol industry became more robust with the appearance of flex-fuel cars, which allowed the massive use of ethanol as a biofuel within the transportation sector (Leite and Cortez 2007).

Since 2001, the European Union has required all its members to establish legislation for the use of renewable biofuels. In 2010 the minimum level for the member countries was 5.75% with a significant increase in the following years (Mojović et al. 2006).

Many developed and developing countries prioritize biomass energy generation through policy mechanisms and financial incentives. Feed-in tariff schemes were introduced as a policy mechanism to accelerate investment in the renewable energy sector.

The renewable energy sector continued to perform well despite the global economic slowdown, caused by the COVID-19 pandemic, leading to cuts in tax incentives and commodity market prices. The World Bank's forecast for the global economy is that there will be a 5.2% contraction in 2021, the biggest recession since the end of World War II. With the outbreak of the new coronavirus pandemic in the United States in mid-March/20, the American fuel sector was strongly affected (Barros 2020; EPA 2020). The feedstock used as raw material for 1G ethanol production is synthesized in Fig. 2.3.

News of growth in market consumption after the Coronavirus pandemic in 2021 points to a gradual reopening of world economies, especially the US. The corn futures market is a clear response to the increase in demand for this cereal, also

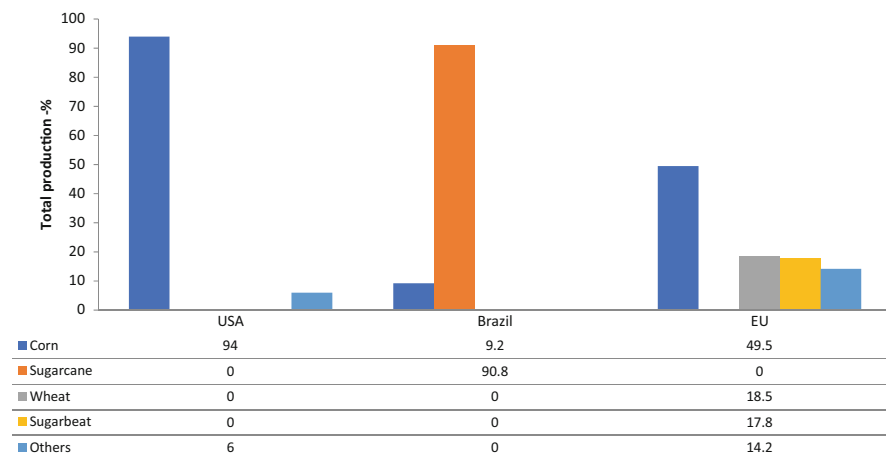


Fig. 2.3 Feedstock used as raw material for 1G ethanol production—distribution in the main countries/regions (data given in % for total production for each country/region)

aiming at the fuel market. According to the USDA greater domestic availability of corn and the uncertainties surrounding the market, at this time after COVID-19, the scenarios for the demand for ethanol production stood out because the sector is responsible for the consumption of more than one-third of the US corn crop (FAO 2020; U.S. GRAINS 2019; Barros 2020).

2.3 Sugar-Based Feedstocks

2.3.1 Sugarcane

Sugarcane processing for 1G ethanol production consists in milling and extracting the sugarcane juice. In general, ethanol can be produced from cane saccharides such as glucans (cellulose and β -glucans), hemicelluloses (xyloglucans and heteroxylans) and pectin after hydrolysis and fermentation. However, some monosaccharides (mostly pentoses) are more difficult to ferment to fuel ethanol than hexoses such as glucose. The juice is sent to a juice treatment system to remove impurities (minerals, salts, organic acids, dirt and fine particles) prior to fermentation (Oliveira et al. 2015). Juice treatment consists of separation of fibers and sand in screens, heating of juice from 30 °C to 70 °C, lime addition with a second heating (up to 105 °C), air removal (flash), and flocculant polymer addition and final removal of impurities through clarification process. Clarified juice is then concentrated to achieve adequate sugar concentration for fermentation. Besides ethanol, a sub-product from distillation process is potassium-rich vinasse, which can be employed for ferti-irrigation of the fields, reducing costs of chemical fertilizers (Lopes et al. 2016). Currently, some sugarcane ethanol plants have implemented a

process for anaerobic production of biogas from the vinasse. Raizen company recently implemented a biogas producing plant in 2020. The biogas plant, located in Sao Paulo (Brazil), can make use of vinasse and filtration cake from sugarcane juice extraction as raw material. The plant possesses an energy producing capacity of 21 MW (Raizen 2020).

In Brazil, from the entire production of sugarcane, around 50% is destined for ethanol production, while the remaining sugarcane is employed for sugar production (this ratio can vary from year to year tough, according to market offer and demand). Approximately, each ton of sugarcane yields 85 liters of ethanol and Brazilian plants produce 10–15 L of vinasse for each liter of ethanol generated. The volumes may vary depending on the technology used in the fermentation process (Pazuch et al. 2017).

2.3.2 Sugar Beet

Sugar beets require more energy to produce sugar from than sugarcane, because unlike sugarcane sugar beet does not have a by-product like bagasse that can be burned to produce energy. On the hand, the tops of sugar beets and the pulp left after extraction of sugar are by-products used as animal feed for cows and sheep.

Ethanol production process from sugar beets starts shredding the beets into thin chips, called cossettes, to facilitate sugar extraction. The cossettes are washed in a counter-current continuously agitated tank (for 1 h) with high temperature water to draw the sugar into a solution called juice. Then, the washed cossettes are pressed to remove the remaining juice. The residual pressed beets, known as pulp, sent to a drying plant to use it as animal feed. Impurities are removed from the crude juice adding lime and bubbling CO₂ before the spent material is filtrated out. After carbonation, SO₂ is pumped through the juice to neutralize the solution. The juice may require to be concentrated to be an adequate substrate for the yeast that would use it during fermentation. The recovery of ethanol is done by distillation (Bowen et al. 2010; NNFCC 2019).

2.4 Starch-Based Feedstocks

2.4.1 Corn

In the U.S., the two major processes for 1G ethanol production from corn are: dry mill (90.9%) and wet mill process (9.1%). Dry milling is preferred over wet mill process due to the low capital and operating costs (Bušić et al. 2018). Dry milling grounds the corn to fine particles to ease subsequent liquefaction step. In the liquefaction step (85 °C, 1–2 h), the milled substrate is mixed with water and α -amylase enzymes. Then, the mixture cooled down to 30–35 °C and supplemented

with glucoamylase enzymes and yeast for simultaneous saccharification and fermentation (SSF) process for 40–50 h. After distillation, ethanol is obtained as the main product. On the other hand, the protein-rich stillage is dried to a 27% protein product known as distillers dried grains with soluble (DDGS), commercialized as animal feeding (Susmozas et al. 2020). In wet milling, the grain is first separated into its basic components through soaking. After steeping, the slurry is processed through grinders to separate the corn germ. The remaining fiber, gluten and starch components are further segregated. The gluten component (protein) is filtered and dried to produce animal feed. The remaining starch can then be fermented into ethanol, using a process like the dry mill process (Renewable Fuels Association 2020a, b).

On average, 100 kg of corn processed by a dry mill ethanol plant produces: 43.2 L of denatured fuel ethanol, 28.2 kg of distillers' grain animal feed (10% moisture), 1.4 kg of corn distillers' oil and 29.5 kg of captured biogenic carbon dioxide (further employed in bottling, food processing, dry ice production, among others). Additionally, ethanol biorefineries produce distiller's grains, gluten feed and gluten meal (Renewable Fuels Association 2020a, b).

2.4.2 *Wheat*

Wheat processing for ethanol production starts with milling as in traditional flour mills. Once the wheat has been milled into flour, water is added to it forming a slurry. Then, the slurry is cooked using steam and enzymes are incorporated to thin the mixture and convert starch into sugar. The fermentation process is similar to conventional brewery but on a larger scale. After fermentation, distillation takes place to separate ethanol from the protein and fiber. The proteins and fiber obtained from distillation step are pressed to remove most of the water. Some of the solid can be commercialized in a moist form or as a syrup feed. Other portion can be dried and pelletized to form an animal feed product (Vivergo Fuels 2017).

2.4.3 *Cassava*

Cassava is the third source of carbohydrates for human consumption in the world. Cassava is cultivated in countries with warm and moist tropical climate. The tubers grow well on soils of relatively low fertility where the cultivation of other crops would be difficult or uneconomical.

After harvesting cassava, the roots are chopped into chips and dried usually in the sun. Dried chips can be stored for months. However, depending on the storage temperature, approximately a 5% reduction of starch yield is obtained in 8-month storage.

The ethanol production process from cassava is very similar to those of corn and wheat. As in corn processing, on an industrial scale, cassava processing can be

Table 2.2 Main co-products generated during the processing of feedstock for 1G ethanol production, their co-products and main destination

Feedstock	Main co-products	Main destination of co-products	References
Sugarcane	Bagasse and vinasse	Ethanol 2G, biogas, fertirrigation	Pazuch et al. (2017)
Sugarbeet	Sugar beet tops and pulp	Animal feed	Bowen et al. (2010), NNFCC (2019)
Corn	Distiller dried grain	Animal feed, biogenic CO ₂	RFA (2021)
Wheat	Protein and fiber rich residues	Syrup feed, animal feed	Vivergo Fuels (2017)
Cassava	Distiller dried grains, cassava pulp	Biogas	Kuiper et al. (2007)

carried out with two different technologies: dry-grind process and wet mill process. The main differences between the two processes are the feedstocks preparation steps and the number and type of by-products obtained. As in corn processing, once the starch has been recovered, the fermentation and distillation processes are similar in both dry-grind and wet mill facilities. Table 2.2 shows the main feedstock used for 1G ethanol production and their respective main co-products and some common destination.

Wet milling begins soaking the chips in acid to soften the material and separate the fibers. Then, starch and proteins are separated. On the other hand, dry grinding process starts grinding the chips. Then, water added to the ground material, and the mixture is cooked and mixed with enzymes. This process obtains distiller dried grains with soluble (DDGS) as only by-product after fermentation step. However, the use of this by-product is limited due to its high fiber content. Additionally, cassava pulp, also known as root cake, is the residue remaining after extraction of starch from the grinded root. This residue can be further employed for biogas production (Kuiper et al. 2007).

There is a consensus in the literature regarding the processes that use sugarcane to produce G1 bioethanol as being the best raw material in all aspects (energy balance, GHG emission savings and production cost).

Production of ethanol from sugarcane is in close competition with the sugar market, leading to a reduction in biofuel production in countries such as Brazil. Ethanol from corn is limited by a similar paradox with the increasing value of food on the world's market. Although very advantageous for the producers, increases in the sugar price are a problem for the bioethanol business.

2.5 Conclusion and Future Prospective

The fuels obtained from biomass have reached a crucial step in the substitution of petroleum derivatives by representing an alternative with low greenhouse gas emissions and an almost inexhaustible production capacity. The other great

advantage is associated with the processes, technologies used, and infrastructure already installed that allows it to be adapted to different raw materials (whether saccharinic ethanol, starch ethanol or cellulosic ethanol). A wide variety of renewable energy sources are being studied, leading to the belief that new biomasses or better cultivars using new fermentation strains can lead to more environmentally sustainable and economically balanced processes. Promising results, even at pilot scale, identify different feedstocks as promising sources for biorefineries. Ethanol made of sustainable cellulosic feedstock is standard fuel for future, because this biomass is the biggest and renewable in biosphere.

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Conflict of Interest The authors declare no conflict of interest.

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