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REVIEW: MAIN RAW MATERIALS USED FOR PRODUCTION OF 1^{ST} AND 2^{ND} GENERATION BIOETHANOL

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Abstract: *In recent years, many countries have adopted a strategy to replace conventional fuels which are obtained from petroleum refining with biofuels. This has happened due to rising oil prices, unpredictable depletion of oil reserves, increased greenhouse gas emissions and the negative impact on the environment. Bioethanol producţion 1stG has caused competition between fuels and food, because the main raw materials used for are sugar and starch raw materials. The United States is the world's largest producer of bioethanol from corn, followed by Brazil which uses sugarcane. In the Europe Union, the main raw materials for bioethanol production are wheat and sugar beet. Therefore, the second generation energy (including bioethanol producţion 2ndG) obtained from lignocellulosic materials (LCM) is gradually attracting global attention. Lignocellulosic biomass (LCB) is the most abundant natural organic source, in huge quantities, at low costs and not part of the human food chain.*

Keywords: sugar, starch, celullose, bioethanol, biofuel

1. Introduction

Biomass is considered a renewable energy, an important source of energy and chemical substances for future generations. Currently, reports show that worldwide biofuels production from lignocellulosic biomass (LCB) is 30 - 140 EJ, but it could increase to 130 - 400 EJ by 2070. [1]. The International Energy Agency (2011) estimates by 2050 biofuels will represent 27% of the total fuels used for transport [2].

Research is currently underway to convert lignocellulosic biomass (LCB) as efficiently as possible to obtain biofuels [3] and chemical substances [4]. Biomass has a low economic value, but it can be capitalized by different treatments: chemical [5], thermal [6] and biological [7].

In the current context of intensive search for energy sources which are environmentally friendly, woody biomass and especially woody wastes which result from forestry activities are of particular interest. A superior valorization of these wastes is that of their conversion into bioethanol. Subsequently, there is the possibility that hydrogen and / or synthetic gas can be obtained from bioethanol [8].

Bioethanol can be synthesized from various materials that can be classified into three categories [9]:

- simple sugars;
- starch;
- lignocellulose.

Bioethanol can be obtained from animal feed, corn grains (starch) and sugarcane (sucrose). An efficient source of energy available in huge quantities is lignocellulose. This can be used for bioethanol production, thus becoming more competitive in the future over fossil fuels [10 - 12].

2. Biofuels

Biofuels resulting from renewable biomass are becoming more and more affordable as a result and are therefore an important source of renewable energy to replace fossil fuels [13].

According to the legislation in force of the European Union, biofuels or other renewable fuels used in the transports sector are intended to replace diesel or gasoline. Thus, some objectives could be achieved such as:

• fulfilling the commitments on climate change;

• security of supply, thus leading to the protection of the environment;

• promotion of renewable energy sources.

Article 2, paragraph (1) lit. (a,b) within the framework of Directive 2003/30/EC of the European Parliament and of the Council of the European Union of 8 May 2003, defines [14]:

(a) 'biofuels' means liquid or gaseous fuel for transport produced from biomass;

(b) 'biomass' means the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal materials), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste;

According to art. 2, paragraph (2), lits (a-j) under the same Directive, classifies biofuels as follows [14]:

(a) 'bioethanol': ethanol produced from biomass and/or the biodegradable fraction of waste, to be used as biofuel;

(b) 'biodiesel': a methyl-ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel;

(c) 'biogas': a fuel gas produced from biomass and/or from the biodegradable fraction of waste, that can be purified to natural gas quality, to be used as biofuel, or woodgas;

(d) 'biomethanol': methanol produced from biomass, to be used as biofuel;

(e) 'biodimethylether': dimethylether produced from biomass, to be used as biofuel;

(f) 'bio-ETBE (ethyl-tertio-butyl-ether)': ETBE produced on the basis of bioethanol. The percentage by volume of bio-ETBE that is calculated as biofuel is 47 %;

(g) 'bio-MTBE (methyl-tertio-butyl-ether)': a fuel produced on the basis of biomethanol. The percentage by volume of bio-MTBE that is calculated as biofuel is 36 %;

(h) 'synthetic biofuels': synthetic hydrocarbons or mixtures of synthetic hydrocarbons, which have been produced from biomass;

(i) 'biohydrogen': hydrogen produced from biomass, and/or from the biodegradable fraction of waste, to be used as biofuel;

(j) 'pure vegetable oil': oil produced from oil plants through pressing, extraction or comparable procedures, crude or refined but chemically unmodified, when compatible with the type of engines involved and the corresponding emission requirements.

Liquid biofuels obtained from lignocellulosic materials (LCM), agricultural residues and other types of residues are produced in low quantities, approximately 1 billion liters in 2014, which means less than 1% of total liquid biofuel production [15]. Estimates showed that production will triple, but recently there has been a decrease of investments.

Currently, the costs of producing biofuels from lignocellulosic biomass (LCB) are much higher than those of conventional liquid biofuels and conventional fuels, but they are expected to become more competitive by 2030 and 2045. Recently, progress has been made by obtaining ethanol from a number of cellulose materials (mainly corn stover, corn cobs, straw, and leaves) can allow the development of this process through practice. Because the bioethanol production from these residues is still reduced, the development of the process of obtaining ethanol from cellulosic materials would require a rapid acceleration for the results to be the desired ones. Therefore, International Renewable Energy Agency (2016) states that programs for financing, research and development of demonstration projects are needed, as well as financial support for the development of the supply chain with raw materials [16].

For biofuels production can be used different types of raw materials and technologies, therefore they are classified as follows [17, 18]:

• first generation biofuels (1stG),
• second generation biofuels (2ndG)
• third generation biofuels (3rdG)

3. The main raw materials used in the production of first generation bioethanol (1stG)

Worldwide, the production of first generation bioethanol (1stG) is mainly made from two raw materials, such as corn and sugarcane.

Bioethanol 1stG is a biofuel produced from agricultural raw materials (figure 1) which contain sugar (sugar, molasses, sugar beet and fruit) or starch (corn, wheat, potatoes, etc.). Yeasts have the ability to directly ferment raw materials which contain simple carbohydrates and convert them into 1stG bioethanol. Therefore, molasses or sugarcane syrup can be fermented without the need for treatments such as milling, pretreatment, hydrolysis and detoxification (removing of inhibitors which affect the fermentation process). In the case of starchy raw materials, in order to obtain a high yield in bioethanol, it is recommended to apply a series of treatments such as milling, liquefaction and saccharification [19].

Figure 1 shows schematically the raw materials used for bioethanol production.

The main constituent which is present in cereals is starch (for example, starch content from corn is between 60 - 70%). This carbohydrate contains 15 - 25% amylose and 75 - 85% amylopectin [20].

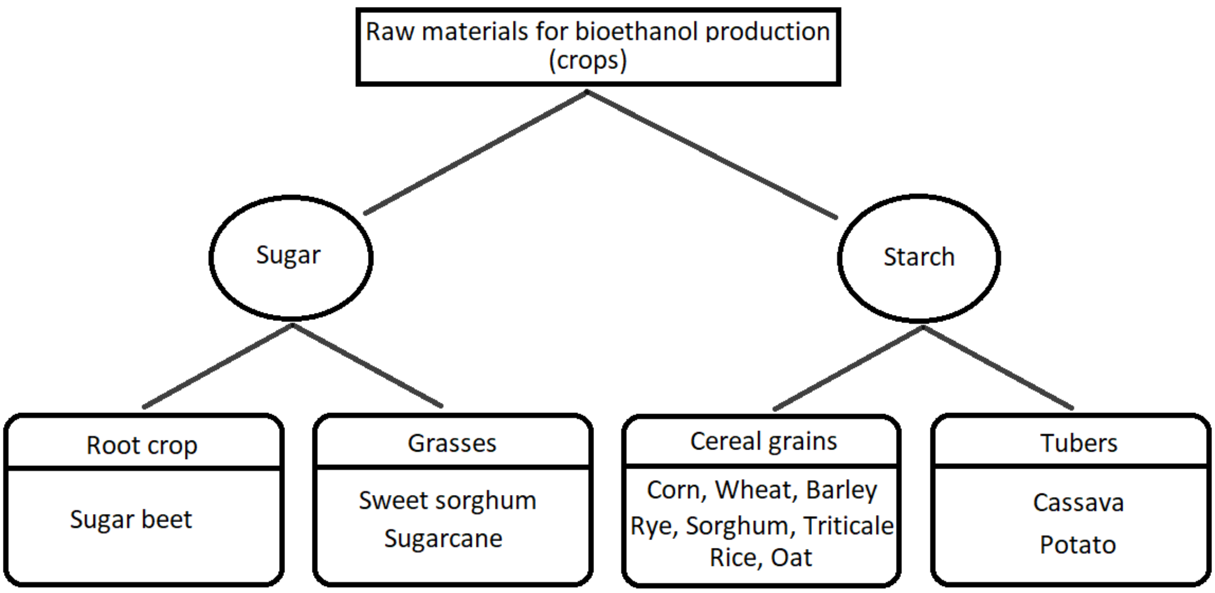

Figure 1. Raw materials for bioethanol production (crops)

The main constituent which is present in cereals is starch (for example, starch content from corn is between 60 - 70%). This carbohydrate contains 15 - 25% amylose and 75 - 85% amylopectin [20]. Amylose is a polysaccharide which has a linear structure and D-glucose molecules linked to each other by α-1,4 glycosidic bonds. Amylopectin is a macromolecule (DP 105 - 106) which has a branched structure, formed of D-glucose molecules linked by α- 1,4 and α- 1,6 glycosidic bonds [21 - 22].
The starch stored in cereal grains is derived from long chains of glucose molecules, which contain less or more than 1000 glucose molecules/amylose structure and between 1000 – 6000 glucose molecules/ amylopectin structure [23].
Table 1 contains the percentage of amylose and amylopectin in different types of starchy raw material.

In order to obtain bioethanol, the starch must be converted into glucose syrup. The step of converting the starch into glucose syrup is called enzymatic hydrolysis and is made with the help of α-amylases. The enzymatic hydrolysis of the starch is dependent on its physico-chemical structure and is known as easily hydrolysable starch and difficult hydrolyzable starch (due to the crystalline structure of the granules and requiring a gelatinization process) [27 - 28]. Starchy raw materials are most commonly used for ethanol production in North America and Europe. In tropical countries, tubers (e.g. cassava) are used as starch source for bioethanol production [27]. After this step, the mash will be fermented, distilled followed by dehydration to produce anhydrous ethanol [29]. Figure 2 shows the chemical structure of starch which is present in different starch raw materials.

Table 1

Amylose and amylopectin content in starchy raw materials [24 – 26, 98, 100]

Source	**Granule size (μm)**	**Amylose (%)**	**DP_n AM**	**β-LV (%)[a]**	**Amylopectin (%)**	**DP_n AP**
Common wheat	1 - 10 / 15 - 40	17 - 29	830 - 1570	79 - 85	75-80	13000 - 18000
Durum wheat	n.r.	26 - 28	n.r.	n.r.	n.r.	n.r.
Rye	1 - 10 / 10 - 50	22 - 26	n.r.	n.r.	n.r.	n.r.
Triticale	n.r.	23 - 27	n.r.	n.r.	n.r.	n.r.
Barley	n.r.	22 - 27	1220 - 1680	76 - 82	72.5	n.r.
Oat	n.r.	18 - 29	n.r.	n.r.	n.r.	n.r.
Rice	3 - 10	17 - 29	920 - 1110	73 - 87	65-85	2700 - 12900
Corn	5 - 30	25 - 28	320 - 1015	81 - 84	75-83	9600 - 15900
Sorghum	n.r.	22 - 30	n.r.	n.r.	75	n.r.
Sweet potato	n.r.	19 - 20	3280	76	81.1	n.r.
Potato	10 - 100	25 - 31	4920	68 - 80	76-83	11200
DP- average of polymerization degree; AM- amylose; AP- amylopectin; β- amylolysis limit value; n.r.- data not reported.						

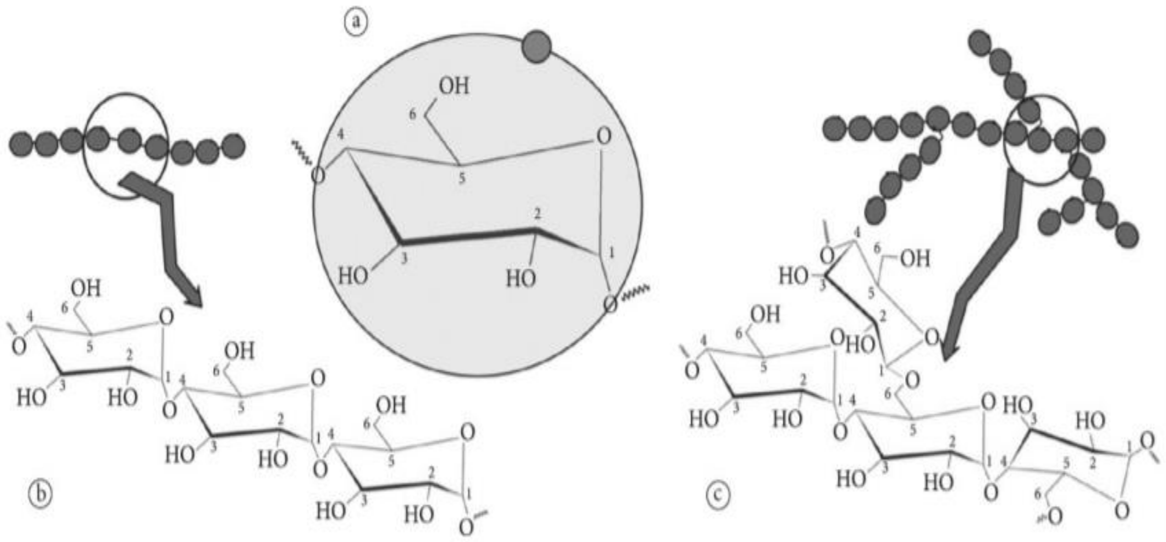

Figure 2. Chemical structure of starch - (a) glucose unit, (b) amylose and (c) amylopectin [30, 31]

Table 2

Ethanol production of the main raw materials [32 – 34, 38, 106]

Type of raw material	Global Yield t/ha	Specific conversion rate to ethanol, L/t	Annual ethanol yield, L/ha	Output/ input ratio	Cost, US$/kg	Cost of production of anhydrous ethanol US$/L
Corn	5.62 – 5.86[a]	350 - 460	6600	1.34 - 1.53	0.076	0.2325
Sorghum	1.47 – 1.49[a]	340	340 - 2040	n.r.	0.149	0.386
Sweet sorghum	25 - 35	68 - 86	1700 - 9030	n.r.	n.r.	n.r.
Wheat	3.39 - 3.49[a]	340 - 370	1020 - 3214	2.24 - 2.84	0.188	0.402
Barley	n.r.	345	1825	n.r.	n.r.	n.r.
Oat	n.r.	264	1413	n.r.	n.r.	n.r.
Triticale	n.r.	368	1757	n.r.	n.r.	n.r.
Sugarcane	70 - 122	68 - 70	5345 - 9381	2.5 - 10.2	0.0100	0.1980
Sugar beet	66 - 78	80 - 100	5000 - 6600	1.9	0.170	0.4910
Potato	17 - 20	100	1700 - 2000	n.r.	0.020	1.330
Cassava	20	180	3600	n.r.	n.r.	n.r.
Straw	1.93 - 3.86	170 - 261	n.r.	n.r.	n.r.	0.651
n.r.- data not reported; [a] - global yield t/ha (2017 - 2019)- [38];						

Table 2 presents a series of information about the production of ethyl alcohol from different raw materials.
Table 3 presents the chemical composition of different types of raw materials used for bioethanol production.
Calculation equations to determine glucose (a), xylose (c) and ethanol yields from these carbohydrates (b, d) [35]:

$$\text{Glucose (kg)} = \text{Glucan (kg)} \times \frac{180}{162} \quad \text{(a)}$$

$$\text{EtOH (kg)} = \text{Glucose (kg)} \times 0.511 \quad \text{(b)}$$

$$\text{Xylose (kg)} = \text{Xylan (kg)} \times \frac{150}{132} \quad \text{(c)}$$

$$\text{EtOH (kg)} = \text{Xylose (kg)} \times 0.511 \quad \text{(d)}$$

Table 3

Chemical composition of raw materials used to obtain bioethanol (% dry matter)

Type of raw material	Starch (%)	β-Glucan (%)	Protein (%)	Raw fat (%)	Fiber (%)	References
Corn	71.88± 1.5	0	8.84± 0.35	4.57 ±0.12	2.15± 0.18	[41]
Corn, waxy	65.3 – 72.9	n.r.	8.8 – 13.7	4.5 – 6.3	1.1 – 1.19[a]	[99]
Sorghum	78.18	0	7.29	2.49	3.64[a]	[42]
Sorghum, waxy	68.4 – 72.4	n.r.	9.7 – 12.2	3.3 – 6.8	1 – 1.7	[99]
Wheat	69.5	0	13.90	3.6	4.5	[42]
Wheat, hard	68	n.r.	12.1	0.8	0.21	[43]
Wheat, soft	68.5	n.r.	12.9	0.6	0.19	
Wheat, waxy	61.9 – 66.5	n.r.	9.4 – 14.2	0.9 – 1.2	0.2 – 0.3	
Barley, Hulled	56.38	4.26	7.92	n.r.	n.r.	[44]
Barley Hull-less	63.48	4.42	8.41	n.r.	n.r.	
Barley, various	50-65	1.9 - 10.7	8.1 - 21.2	0.9 - 3.3	n.r.	[45]
Barley nonwaxy	67.6	6.21	13.6	2.60	n.r.	[46]
Barley high-amylose	65.2	5.5	12.5	2.16	n.r.	
Barley waxy	65.6	6.60	15.5	2.65	n.r.	
Oats, whole	48.2	n.r.	11.3	4.4	13.2[a]	[47]
Oats Groats	57.1 -61.8	4.3-5.8	14.6 - 19.6	4.6 - 7.8	2.0[a]	[47, 48]
Oats, hulled	48.08±0.29	3.15±0.19	10.58±0.67	5.15±0.19	17.63±1.52	[49]
Oats, hull-less	31.55±3.72	3.29±0.26	15.71±1.10	9.66±1.17	22.97±1.89	
Rye	55 -65	2 - 3	10 – 15	2 - 3	1–3	[50]
Triticale	67.87	n.r.	10.33	n.r.	n.r.	[51]
Rice, brown, long-grain	77.24	n.r.	7.94	2.92	3.5[a]	[52]
Rice, white, short-grain	79.15	n.r.	6.50	0.52	2.8[a]	
Rice, white, glutinous	81.68	n.r.	6.81	0.55	2.8	
Pearl Millet	55.36 - 59.36	n.r.	10.14 - 11.82	3.62 – 4.46	0.77 – 1.21	[53]
Cassava	83.42 -87.35	n.r.	1.17 - 3.48	0.74 – 1.49	3 – 4[a]	[54]
Sweet Potato	68.95±1.75	n.r.	10.25±0.12	1.48±0.08	1.92±0.02	[55]
[a]- crude fiber; n.a.- data not reported.						

3.1. Corn *(Zea mays)*

Corn is a grain belongs to the family Grimanaceae [36], subfamily Panicoideae Maydeae, genus Zea and species Zea mays [37].

The distribution of the main components of corn grain varies, so most of the starch content is found in the endosperm and is bound to protein (gluten). The oil is present in the germ. The fiber contents are distributed in the endosperm, germ and at the tip of the grain. Also, the outer shell of the corn grain (pericarp) has a fiber content made of arabinoxilane and is covered by wax [101]. Figure 3 shows the anatomical structure of the corn grain.

Corn is the most cultivated cereal and ranks 1st in the world. In 2019, about 1.123 billion tons of corn were produced worldwide. Of this amount of corn, USA produced 364 million tons, followed by China 257 million tons, Brazil 101 million tons and Europe 64 million tons [38].

The amount of water required for maize to reach maturity is approximately 560 mm [116]. Annually, the maximum concentrations of potassium, phosphate and nitrogen required for optimal corn development are 160 lbs / acre, 70 lbs /

acre and 140 lbs / acre. Therefore, the dosage of these nutrients / acre depends on the concentrations of natural nutrients already existing in the soil. Compared to sugar beet, maize requires a double amount of potassium, whereas other nutrients needed are in smaller quantities. However, based on the amount of water needed for irrigation and the nutrients used on an acre surface, sugar beet will result nearly twice as much ethanol / acre. Therefore, to produce one liter of ethanol the energy consumed for irrigation and nutrient dosing is much lower for sugar beet compared to corn [117].

The chemical composition of corn grains is an important source for the production of biofuels, especially bioethanol. Following the cultivation of corn also results in a series of residues (corn stover, corn cobs, corn roots, leaves) which have various advantages over other energy raw materials [39]. These residues contain cellulose and hemicellulose can be recovered if they are pretreated by hydrolysis techniques. Most of the corn is used for animal feed, and the rest is used for population feeding and for other activities [40].

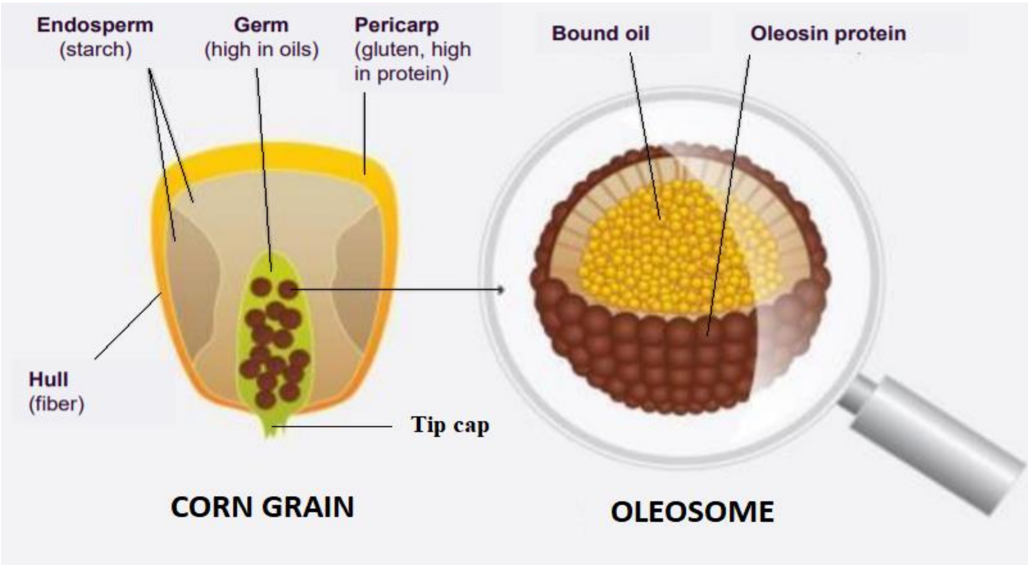

Figure 3. Anatomical structure of the corn grain [107]

3.2. Wheat *(Triticum spp.)*

World wheat production ranks 3rd, after corn and rice. Overall, wheat production in 2019 was 763 million tons, with 30.9 million tons higher than the 2018 production and only slightly lower than the record production in 2016 (765 million tons) [56].

In Canada, Europe and Australia several varieties of wheat are used as feedstock for ethanol production as fuel. In the United States, there are ethanol factories that ferment wheat starch. In Europe and Australia, wheat is considered the raw material to expand the fuel ethanol industry. Zhao et. al. (2009) [57] analysed 3 different types of wheat (waxy, soft and hard) to see if the chemical composition influences the yield of ethanol. From the obtained data, it was found that the yield is dependent on both total starch and protein content. However, the highest yield in ethanol was obtained from wheat with the highest total starch level. Most wheat raw materials have a higher content of starch and protein than corn or sorghum and have a lower fiber content [58 -59]. Figure 4 shows the anatomical structure of the wheat grain.

The technological scheme for obtaining bioethanol from wheat is similar to other cereals. The main steps are milling, enzymatic hydrolysis (transformation of starch into C6 sugars) and fermentation [60]. Then, at a temperature of 32 - 35° C and a pH of 5.2, the C6 sugars are converted by the yeasts into ethanol. After fermentation, the fermented mash will have an ethanol concentration of 10 - 15%. The yield in ethanol is about 0.53 GJ ethanol / GJ wheat (349 liters of ethanol / t wheat) [61], with the possibility to grow to 0.59 GJ ethanol / GJ wheat in 2020 [62].

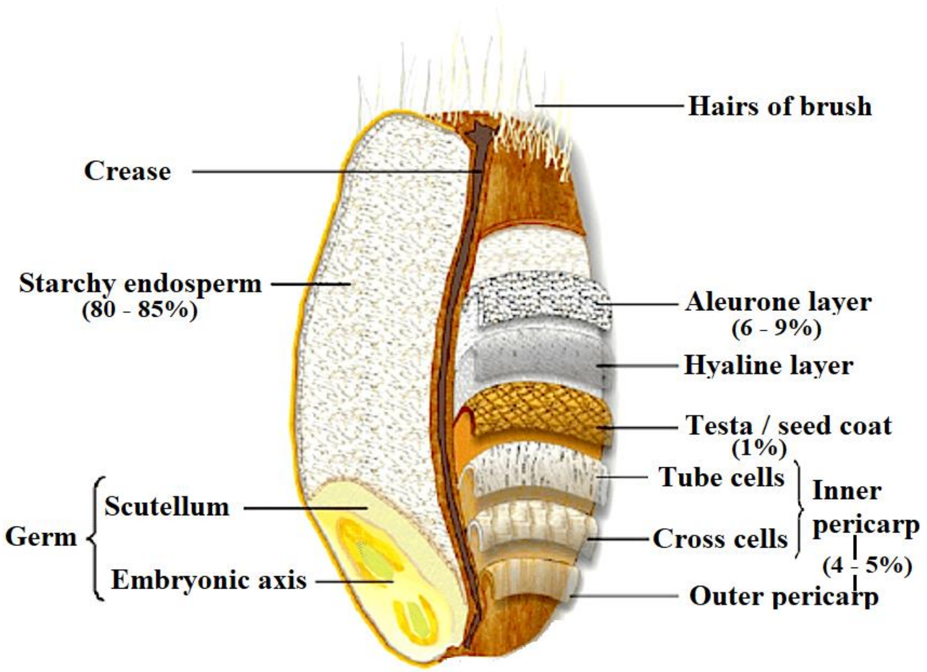

Figure 4. Anatomical structure of the wheat grain [108 - 109]

3.3. Sorghum *(Sorghum)*

Sorghum is a plant of Africa origin which belongs to the Poaceae family and is extremely efficient to use of water, carbon dioxide, nutrients and sunlight. In terms of global production, sorghum ranks the 5th after corn, wheat, rice, and barley [63]. In countries such as Africa, China and India, sorghum is considered a staple food, whereas in the United States, Australia and South America it is primarily used for animal feed [64]**.** Sorghum is cultivated because of its capacity to grow in areas with low precipitation and high temperatures are recorded, such as the semi-arid tropical and subtropical regions of the world, where it is difficult to grow other types of cereals. Also, during the dry season in some areas of Brazil sorghum is cultivated [65].

In 2019, about 59 million tons of sorghum were produced worldwide. From this amount of sorghum the United States of America produced 9 million tons, followed by Nigeria 6.8 million tons, Ethiopia and Sudan about 5 million tons each, Mexico 4.7 million tons and South America 4.5 million tons [38].

Sorghum has a relatively low economic value if it is sold directly as fodder cereals [66]. Sorghum grains are an important source of carbohydrates and fiber, about 72%. The main constituent is starch, which has properties similar to corn starch. There are hundreds of sorghum hybrids available on the market which can be used for bioethanol production. However, these sorghum hybrids have a different chemical composition and can certainly influence the hydrolysis and fermentation **[67].** In order to obtain the high yields of ethanol, it is important to know exactly the sorghum hybrid for the ethanol industry, but also the sorghum producers **[**43].

3.4. Barley *(Hordeum vulgare)*

Regarding barley production, it is ranked 4th worldwide and cultivated in relatively dry areas [68 - 70]. In 2019, around 138 million tons of barley were produced worldwide Approximately 56 million tons is produced by the European Union, followed by Russia with 16.7 million tons, Canada and Australia approximately 8.3 million tons each [38].

Barley has not been used for bioethanol production for a long time, because the chemical composition of barley is slightly different from other cereals and bioethanol production is more expensive compared to corn. The first negative factor is the presence of silicates from the hulls of the grain (it represents 2 - 6% of hull), which is abrasive and causes damage of the equipments for handling and processing of barley grains. For this reason, two strategies were used to change the abrasiveness of barley grains. The first strategy refers to the removal of the hull by abrasive techniques, such as hulling or peeling [72]. This process works well, but some of the starch can be removed, and the ethanol yield is reduced. Another strategy was to cultivate other barley hulled varieties.

Another aspect relates to the fact that most of the barley previously used for bioethanol production had low starch content and low yields of ethanol were obtained. Most of the barley used in the past was for food consumption and therefore had low starch content. Therefore, new varieties with higher starch content have been created recently for both barley varieties hulled and hull-less [44]. Many of these new varieties of barley, especially those hulls-less, have lower fiber content and higher starch content, which are more beneficial for bioethanol production.

Also, the presence of β-glucans in barley hinders bioethanol production, which is present throughout the grain mass, but especially in the endosperm. β-glucans are water soluble and have β-1.3 and β-1.4 glycosidic bonds. β-glucans in barley or oats have a high nutritional value in human diets, as it has been found that they can reduce LDL levels by 10 - 15%. The presence of β-glucans in bioethanol production is undesirable because it creates an extremely high viscosity, creating difficulties in mixing, pumping, saccharification and fermentation process [59].

3.5. Oat (*Avena sativa)*

Oat is a cereal used mainly for animal feed and less used for human nutrition. Oat losses are about 2%, but even if it were recovered, about 225 million liters of bioethanol could be obtained, which could replace 161 million liters of gasoline. Also, oat straws contain lignin, but especially cellulose and other polysaccharides that can be used for bioethanol production [40].

In 2019, about 21.9 million tons of oat were produced worldwide. From this quantity of oat, European Union produced 7.7 million tons, followed by Russia 4.7 million tons, North America and Oceania about 0.8 million tons each [38].

Like barley, oat grains have a similar content of β-glucans (4 - 6%). However, oats are different from other cereals in their high fat content (4 - 9%). Also, the hull-less oat has higher starch content than the hull varieties, thus obtaining a higher percentage of bioethanol [59].

3.6. Rice *(Oryza sativa)*

Rice is still an important food raw material and ranks 3rd in world grain production. Asia is the largest rice producer in the world. In 2019, about 499 million tons of rice were produced worldwide. From this quantity of rice China produced 148 million tons, followed by India 116 million tons, Indonesia 36 million tons, Thailand 20 million tons, and the USA and Brazil each 7 million tons [38].

It is known that the tribes of eastern India and the region of Tibet produce an alcoholic drink which is known as "sake". Even rice straw, like other agricultural by-products, can be used as an efficient means of producing alcohol as a fuel [40].

The rice has a high starch level (~75%), has no β-glucans and has a low fiber content. Although, barley has been shown to be a cost-effective raw material from which bioethanol can be obtained, however, it was more important to be used it for food consumption. Residues from rice fermented mash contain starch (32.6%), protein (55.8%), fat (8.2%) and raw fiber (2.1%) [59].

3.7. Rye *(Secale cereale)*

Over the last 20 years, there has been a decline in rye production. Last year (2019) about 10 million tons of rye were produced worldwide. From this amount of rye, EU produced 6.2 million tons, followed by Russia 1.9 million tons, Belarus 0.5 million tons, Ukraine 0.4 million tons, and Turkey 0.3 million tons [38].

Traditionally, rye has been used mainly for beer and food consumption. The rye was also used for bioethanol production. However, the use of rye for bioethanol production is modest compared to other raw materials, such as corn and sugarcane. Lately, rye has been used as a raw material for bioethanol production, due to the new requirements for the production of renewable fuels. Rye and triticale can be considered wheat substitutes for bioethanol production, because the starch content is about the same. [72, 73].

A disadvantage of using rye as a raw material for obtaining bioethanol is the relatively high content of pentosanes and β-glucans. Their presence causes a very high viscosity of the mash. Compared with barley and oats, the content of β-glucans in rye is approximately 2% [59]. Due to the high content of pentosanes and β-glucans, the viscosity is modified with the help of enzymes [74, 75]. The enzymes used to reduce the viscosity are pullulanase, cellulase, xylanase, β-glucosidase, pectinase and proteinase. Adding xylanase and pullulanase will increase the concentration of fermentable sugars, improve the fermentation efficiency, and increase the yield of ethanol [74].

3.8. Triticale *(Triticosecale)*

Triticale is a hybrid between wheat (Triticum) and rye (Secale) and was created for the fist time in laboratories at the end of the 19th century. This hybrid has some of the rye specific genes and can adapt to environmental conditions which are not favorable to wheat. Unlike barley and rye, the triticale mash does not have a high viscosity and therefore does not require an enzyme addition to reduce the viscosity. In Sweden, has been study of bioethanol production and it has been concluded that 1 L ethanol, 0.8 kg carbon dioxide and 0.8 kg DDGS result from 2.65 kg of triticale grains [76]. Also, several researchers have observed that triticale used for ethanol production have a higher endogenous α-amylase content, thus reducing the amount of enzymes used and thus reducing production costs [51, 77]. Also, triticale contains endogenous glucoamylase or other enzymes [78].

3.9. Pearl millet *(Pennisetum glaucum)*

Unlike sorghum and corn, pearl millet can grow in semi-arid conditions and is considered as a potential biofuel raw material for these regions. Wu *et al*. analysed four varieties of Pearl Millet (Pennisetum glaucum) to determine of bioethanol yield. In this study it was determined that millet varieties have a starch content between 65.3 - 70.39% of the dry matter. Compared to the dry matter, the protein and fat content is significantly higher than that of corn and ranges from 9.72 to 13.68%, respectively 6.80%. Therefore, in the 5 L vessel of a bioreactor were introduced millet mash successively with a raw material concentration of between 20 - 35% (a total volume of about 4 L), and during the fermentation a series of parameters were monitored. After processing the data was established that bioethanol yield from millet is similar to that of corn [79].

3.10. Sugarcane *(Saccharum officinarum)*

Sugarcane is a semi-perennial plant and belongs to the Poaceae family (grass family) and is specific to tropical and subtropical areas [80]. Compared to biomass that is high in starch, bioethanol production from sucrose as raw material does not require a saccharification step, because sugars are easily fermentable and the process of obtaining bioethanol is simple [81].

There are six recognized varieties of sugarcane. S. officinarum is the most common species, has the highest sugar content and is the most suitable in terms of industrial processing. Hybrids of S. officinarum were created and selected to be resistant to pests and dryness, to have a high sugar content and to give high biomass yield per hectare [82]. in 2012, worldwide sugarcane production was 1.96 billion tons, out of 26 million hectares of harvested area, and the main producing countries were Brazil, India and China, representing 39%, 19 % and 7% respectively [83]. It has been established that 4.8 Mha of land suitable for sugarcane cultivation are available in Eswatini, Malawi, Mozambique, South Africa, Tanzania, Zambia and Zimbabwe. This area is similar to sugarcane cultivation for ethanol production in Brazil. It is equivalent to 2.0% of agricultural land or 2.5% of pasture in these countries [84, 85].

Once harvested, the sugarcane should be processed between 24 – 72 hours. The process of sugar extraction consists of several stages. The first step is to crush the stems with specialized rolls to release the juice, followed by the step in which calcium hydroxide ($Ca(OH)_2$) is added to precipitate the fiber and the sludge. The solution is filtered and evaporated to concentrate and crystallize the sugar, and then it is removed by centrifugation. The non-crystallized sugar and the salts are concentrated to form the syrup called "black molasses - (BSM)" which can subsequently be used as a starting material for ethanol production [86].

Comparative studies have been carried out between the mechanized harvesting and the traditional process of manual combustion and cutting with regard to the mineral content of the sugarcane (potassium, calcium, silica, iron and copper). The data obtained showed that following the mechanized harvest the calcium, magnesium and silica content of the sugarcane juice increased by 13%, 32% and 7.6%, respectively, [110, 112]. The presence of these mineral substances can positively or negatively influence the fermentation process. Therefore, the presence of magnesium contributes to the increase of ethanol yield, whereas a high content of copper reduces the yield [111 - 112].

Annually, the sugar industry produces significant quantities of molasses. Molasses is the main by-product of sugar and is used mainly as a substrate for yeasts, for the production of bioethanol, biochemicals, but also for animal feed. The molasses has a total residual sugar content between 50 - 60% (m/V), and its main constituent is sucrose (60%). The largest quantities of molasses are obtained from the processing of sugarcane and sugar beet, which have a total residual sugars content (m/V) of 46% and 48% respectively. Following the process of obtaining dried fruit pulps from citrus fruit, molasses has about 45% (m/V) of residual sugars. Also, molasses with a concentration of about 43% (m/V) reducing sugars and 73% (m/V) solids results from the process of obtaining glucose from starch. The raw material used to produce glucose from starch is corn and sorghum (starch hirolysis is done with enzymes or acids) [113]. Therefore, molasses are a suitable source for bioethanol production.

3.11. Sugar beet *(Beta vulgaris)*

Sugar beet is an important source of sugar in Europe and North America. The largest producer of sugar beet is Russia, which in 2019 produced about 6.08 billion tons, followed by the US 4.47 billion tons, Turkey 2.7 billion tons, Ukraine 1.84 billion tons and China 1.32 billion tons [87].

Sugar beet has a good yield (25 – 50 tons / acre), grows in the temperate climate area and requires humidity lower than the sugarcane. On average, the yield of ethanol is 25 gallons of ethanol / t of sugar beet. From an economical point of view, bioethanol production from sugar beet is more expensive (applying chemical treatments and higher energy consumption) as opposed to sugarcane.

In order to grow to maturity, sugar beet needs about 560 mm of water (Efetha, 2008) but also different nutrients such as potassium, phosphate and nitrogen. The maximum concentrations of potassium, phosphate and nitrogen required for optimal development of sugar beet are 80 lbs / acre, 100 lbs / acre and 200 lbs / acre respectively [118]. Depending on the type of soil these nutrients are naturally found in different concentrations. Therefore, the dosage of these nutrients varies depending on the type of soil [119].

Recent studies have shown that the fermentation process can be influenced by both the sugar beet content of sugar beet and the other components in the dry substance. Therefore, the yield in bioethanol can be affected by the presence of impurities (potassium, nitrogen and sodium). These impurities can have a negative (inhibitory) effect on Saccharomyces cerevisiae and can cause reduced yeast cell growth, reduced glucose consumption and low bioethanol yield. Irrational use of fertilizers can result in NPK uptake that favors the presence of K, N and Na in high root concentration [104].

The chemical composition of beet root consists of 75% water and 25% dry matter. Of the total dry matter 75% is carbohydrates and about 5% pulp. The pulp is insoluble in water and consists of cellulose, hemicellulose, lignin and pectin. Sugar beet has a sucrose content between 12 - 20% [105].

Several authors have reported that sugar beet is one of the most efficient sources of ethanol / ha. It was determined that the fermentation process of sugar beet can be obtained between 100 and 120 L / t of ethanol (110 L / t, 103.5 L / t [88], 117 L / t respectively [89]. The energy supplied by one tonne of dehydrated sugar beet is approximately 3.89 GJ [90]. Ethanol has an energy content of 21.2 MJ / L [91], which means that 115 L / t of ethanol obtained from one tonne of sugar beet generates an energy value of 2.44 GJ / t sugar beet. According to FAO (2008), bioethanol production from sugar beet is of 5,060 L / ha, corn is 1,960 L / ha, wheat is 952 L / ha respectively, considering that on a surface of 1 ha the sugar beet production is 46 t / ha, corn 4.9 t / ha, wheat 2.8 t / ha respectively [92].

3.12. Cassava *(Manihot esculenta)*

Cassava is an important tropical plant called manioc, sagu, yucca or tapioca. Depending on the variety, the cassava root contains approximately 66.72 - 84.42% starch, 0.74 - 1.52% protein, 1.08 - 1.18% fiber, lipids 0.39 - 0.63%, mineral substances 1.05 - 2.39%, humidity 5.43 - 10.87% [93].
Compared to potato, rice or corn starches, the properties of cassava starch are different. The cassava starch has a high purity, has a neutral aroma, slight swelling, solubility, high viscosity development and a low tendency to downgrade [102].
It is estimated that in 2018 about world cassava production would be about 277 million tons (equivalent to fresh root), about half a percentage point higher than in 2017. Therefore, for 2018 the top 3 most important continents estimates to produce cassava are Africa with 160 million tons, in Asia at 85.5 30.5 million tons Latin America. Also, the top 5 most important countries estimated to produce cassava are Nigeria 56 million tons, Thailand 27 million tons, Indonesia 21 million tons, Brazil 20.9 million tons and Ghana 19.4 million tons [85]. Therefore, due to the large quantities produced by cassava yearly, as well as the high carbohydrate composition, this can be an important source for obtaining bioethanol.

3.13. Potato (*Solanum tuberosum*)

Potato (Solanum tuberosum) is an annual herbaceous plant that can reach a height of 100 cm. It produces a tuber known as potato and has a high starch content. The potato belongs to the Solanaceae family, the genus Solanum and includes at least 1000 species, including tomatoes and eggplants. The most cultivated species globally are S. tuberosum Andigenum (which is adapted to short-day conditions and is cultivated mainly in the Andes) and S. tuberosum Chilotanum (potato now cultivated worldwide).Throughout the growing period, the potato leaves produce starch that is transported to the ends of its underground stems (or stolons) and can form up to 20 tubers near the soil surface. The potato's chemical composition is 72 - 75%, starch 16 - 20%, protein 2 - 2.5%, fiber 1 - 1.8%, fatty acids 0.15% [132].
Due to the relatively low price, the potato is one of the most consumed foods and is in 3rd place after wheat and rice [133]. This food is easily prepared and has a high nutritional value [134].
In 2017, 388.19 million tonnes were cultivated worldwide. The largest potato producers are China 99.2 million tons, India 48.6 million tons, Russia 29.59 million tons, Ukraine 22.2 million tons, the United States 20 million tons [135].
European Union, in 2018 the cultivation of potatoes was realized on an area of 1.7 million hectares and the production was 51.9 million tonnes. The main potato-producing countries are: Germany (8.9 million tonnes, representing 17.2% of the EU total), France (15.2%), Poland (14.3%) and the Netherlands (11.6%) [136].

3.14. Sweet potato *(Ipomoea batatas)*

Sweet potatoes (Ipomoea batatas) are the second raw material which has a high content in starch and can be used for bioethanol production. In 2017, the global production of sweet potatoes was 113 million tons.

China produces 64% of global sweet potatoes, followed by Malawi and Nigeria [94, 95]. Chemical composition of Sweet potatoes is 60.1 – 71.4% starch, 4.86 - 6.53% proteins, 0.56 – 0.76% fats and 1.85 – 2.35% fibers [96].

As compared with cereals, the starch content of potatoes changes during its storage period. It was found that after a storage period of about 6 months and 8 months the potato starch content decreases by 8%, respectively 16.5% [103].

Putri *et al.* managed to obtain ethanol from sweet potato. A yield of 14% was obtained after the end of the 72-hour fermentation period. After 24 hours and 48 hours of fermentation, the yield of ethanol obtained was up to 3.66%, 3.33% respectively [97].

3.15. Agave (*Agavoideae*)

In Mexico, the juice extracted from the agave stem is used for the production of spirits, due to its high fruit content. This alcoholic beverage is known as Tequila and is produced only from *Agave tequilana weber*. Another assortment of agave alcoholic beverages is Mezcal, which is produced from different agave species (*A. angustifolia, A. americana, A. salmiana*, etc.). Stems from A. salmiana are about two times heavier than A. tequilana. Also, the leaves of A. salmiana are more succulent and thicker than those of A. tequilana. Once harvested, the agave strains are transported to the factories, where they will be subjected to thermal hydrolysis-assisted and juice extraction (mechanical and / or water-diffused) [120].

Following the extraction process, high fructose agave juices are fermented by yeasts, and then the mash is distilled. The solid residues (known as bagasse) as a result of juice extraction have a low sugar content, but they can also be used [120].

Agave species have the ability to use water efficiently due to specialized photosynthetic pathways known as crassulacean acid metabolism (CAM). This allows them to adapt and growth even when the quantities of water are low. Because the temperature is high during the day and the relative humidity is low, the agaves fix CO_2 at night, thus reducing losses through evapotranspiration [121]. Agave is xerophytic perennial plants and can be grown on semi-arid lands on which cannot be cultivated various crops that are used for human or animal feeding. [122]. Several researchers found that agave can produce 1stG bioethanol, and production costs, greenhouse gas (GHG) and yields in ethanol are comparable to those of corn, switchgrass and sugarcane [123].

Of the species of *Agave Spp.* cultivated in the Abu Dhabi area was obtain an ethanol yield of 6,750 L / ha [124], comparable to palm (3,000 L / ha) [125] or willow (900 L / ha) [126]. Agave Spp. it is resistant in periods of drought and unlike other plants does not require high nutrient concentrations [127]. However, Agave Spp. it needs water, and water is a problem in the Abu Dhabi area because it needs to be desalinated and this process is expensive [128]. In order to solve the problem related to the need of water, consideration was given to growing halophilic plants. For this reason, Salicornia [129] is widespread on the Abu Dhabi coast, and its ethanol yield is about 935 L / ha [130 - 131].

4. Advantages and disadvantages of bioethanol production

4.1. Advantages [114 - 115]

• For the production of bioethanol 1stG, any type of crop (corn, sugar cane, sugar beet, wheat, sorghum, etc.) containing sugar and starch can be used.

• Compared to fossil fuels, bioethanol reduces CO_2 emissions released into the atmosphere following the combustion process.
• In contrast to the pollutants emitted from the process of combustion of gasoline, the pollutants resulting from the combustion process of bioethanol are much lower. Therefore, the use of ethanol as a biofuel is beneficial for the conservation of the environment because it reduces the destruction of the ozone layer.
• Mixing bioethanol with gasoline contributes to the reduction of greenhouse gases.
• If certain bioethanol accidents or discharges occur, it is biodegradable or may be diluted to non-toxic concentrations.
• The raw materials used in the production of bioethanol are considered renewable sources.
• The production of bioethanol 2ndG from different types of lignocellulosic materials (LCM) could solve the competition between "biofuel vs food".

4.2. Disadvantages [114 - 115]
• The production of bioethanol from cereal crops or irrigable resources requires large areas of agricultural land, which is why natural habitats such as tropical forests can be destroyed.
• From the economic point of view of the bioethanol production, significant profits can be registered, and this can cause the farmers to give up the cereal crops destined to feed the population. By using agricultural land to obtain bioethanol, it can determine the price of food, thus creating a food crisis.
• Building a bioethanol plant requires large investments.
• To obtain high yields of ethanol, specific technical knowledge is required and involves many researches in this field (especially for bioethanol 2ndG).
• Waste management resulting from the bioethanol production process.

5. Conclusion

It is very important for biofuel production to get increased in order to replace fossil fuels, which contribute largely to global warming and climate change. Worldwide 1stG bioethanol is obtained from raw materials which contain simple sugars or starch which causes competition between "food vs fuel". In food industry, significant quantities of non-food lignocellulosic biomass can be used to produce 2ndG bioethanol.
Currently, the production of 2ndG bioethanol may not be as advanced as the 1stG, but great progress has been made. Every year, huge quantities of lignocellulosic materials (LCM) are generated from agriculture, which instead of being wasted can be converted into 2ndG bioethanol.

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