Feedstocks for Biofuels

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Abstract Considering the great interest of the countries around the world and the great number of research of many groups from Institutes, Universities, Companies, aiming to allow the use of biomass to produce biofuel, this chapter may give data and basic information about vegetable cultures and organic residues available to generate any kind of biofuel. Concerning to this a general view is given about crops where its main constituent component is sugar, starch, oil, with some principal examples. Besides, data, facilities and examples are given about lignocellulolytic cultures and residues, as far as solid and liquid residues generated in some industrial processes. The data available, includes, amount of each potential energetic source of raw material for biofuel, physic-chemical characteristics, production region, agronomic data, productivity, production, and other information useful for researchers works aiming the production of bioethanol, biodiesel, and biohydrogen.

Keywords Biomass, sugarcane · crop plants · lignocellulosic materials · organic waste

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1 Introduction

In recent decades, many countries have promoted actions for the development of renewable energy; the biofuel have had significant participation in their energy matrixes. The main motivation for the biofuel policies include, for example, reduce dependence on fossil fuels, greenhouse gases reducing and increasing agricultural commodities demand (Ziolkowska 2013). To achieve these goals, besides the economic, environmental, and social conditions, the availability of raw materials production and the potential to produce biofuels must be analyzed.

Considering the alternative technologies involved in renewable energy generation and those commercially viable, only the use of biomass as feedstocks in processes with high efficiency, has the flexibility to supply both the electricity generation sector and the biofuels for transport.

Different biomass has been used in the production of biofuels comprising crop plants, lignocellulosic materials and also organic waste, which include agricultural residues, municipal, and industrial (Table 1). Microalgae and algae is a considered a third-generation feedstocks for biofuels (Sinha and Pandey 2014) .

2 Sugar-Containing Plant Crops

2.1 Sugarcane

The sugarcane is a semi-perennial plant of family grasses originally from Southeast Asia that has long thin stem of the genus *Saccharum* L. The sugarcane cultivated is

Table 1 Different feedstocks used for biofuel production

Feedstocks	Biofuel	Country	Reference
Corn, soybean oil, sorghum	Ethanol, biodiesel	EUA	Koçar and Civas (2013)
Sugarcane, soybean, palm oil	Ethanol, biodiesel	Brazil	Koçar and Civas (2013)
Rapeseed, sunflower, wheatsugar beet, barley, sewage, manure, food wastes, landfill	Ethanol, biodiesel, biogas	EU	Koçar and Civas (2013)
Corn, cassava, sweet potato, rice, jatropha	Ethanol, biodiesel	China	Koçar and Civas (2013)
Corn, wheat	Ethanol	Canada	Koçar and Civas (2013)
Wheat, sugarcane, molasses, palm oil, cotton oil	Ethanol, biodiesel	Australia	Koçar and Civas (2013)
Vinasse wastewater	Biohydrogen	–	Fernandes et al. (2010)
Cheese whey wastewater	Biohydrogen	–	Azbar et al. (2009)

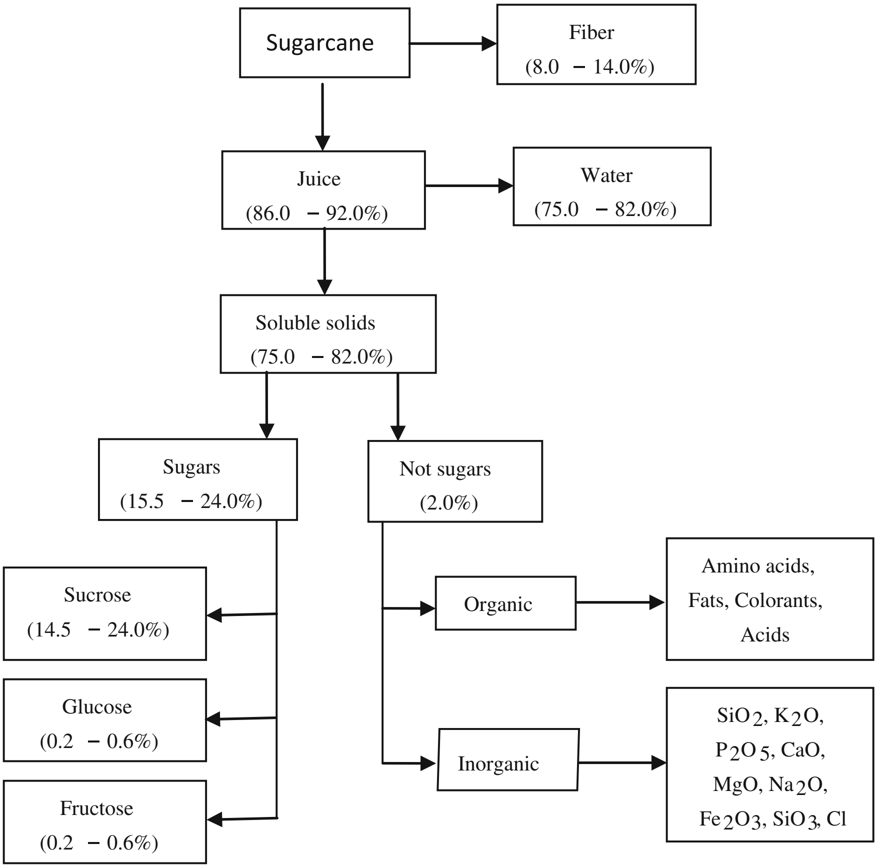

Fig. 1 Sugarcane mass balance (%). *Source* Adapted from Silva (2012)

a hybrid multispecies named *Saccharum* spp. It has a high concentration of sugar in the stalks, which makes up the aerial part of the plant while the sugarcane straw is at their tips and leaves (BNDES and CGEE 2008) is considered the main raw material for the manufacture of sugar and alcohol (ethanol).

The chemical composition of sugarcane varies widely, depending on weather conditions, the physical, chemical, and microbiological soil, variety, maturation stage, and others. In general the stalks are composed 65–75 % water, 8–14 % ashes and 10–17 % sugars (BNDES and CGEE 2008). A more detailed flowchart composition is shown in Fig. 1.

It fits easily in tropical climates, since it requires good amount of rainfall and sunlight. The tropics is privileged from the energy point of view, it presents better conditions for biomass production. In this sense, Brazil is the largest single producer of sugarcane with about 27 % of global production. As for the yield, Peru is first with 32 dry Mg/ha followed by Brazil with 18 dry Mg/ha (Kim and

Dale 2004). The Brazil should achieve average rate of increase in production of 3.25 % until 2018/19, and reap 47.34 million tons of sugarcane. For exports, the estimated volume for 2009 is 32.6 million tons (MAPA 2016).

Different by-products and residues are obtained by ethanol production and are used for energy, animal feed and as fertilizer. Sugarcane bagasse is the major subproduct and is obtained from juice extraction after the crushing of sugar cane. The production of ethanol from sugarcane is more energy efficient than others fonts (corn, sugarbeets, vegetable oils), mainly if sugarcane bagasse is used to produce power for the process and transport (IEA 2007; Lora and Nascimento 2004). Furthermore, using highly efficient boilers, up to 52 % of the bagasse would become available for other uses, such as biofuel production (Botha and Blottnitz 2006).

Sugarcane bagasse is composed essentially of cellulose, hemicellulose, lignin, and extractives. Several research groups studies technologies for sugarcane bagasse use with second-generation biofuels, for example, aiming the selection of sugarcane varieties or to down-regulate lignin biosynthesis in transgenic plants (Petersen et al. 2015). The process normally uses a pretreatment to biomass deconstruction to overcome recalcitrance and conversion to biofuels by enzymatic hydrolysis and subsequent fermentation (Jung et al. 2010).

2.2 Sugarbeet

The beets used in the ethanol production are sugar beet (*B. vulgaris*) also known as white beet originally from Europe. It is a plant whose tuber contains a high concentration of sucrose, and although these nonfood beets would not be efficient feedstock for the production of sugar for human consumption, it is one of the main raw materials for the production of biofuel.

Sugar beets are generally grown in the high-altitude region and in temperate climate but due to genetic enhancement, the crop has proven to adapt to various soil and climatic conditions (Içöz et al. 2009). It is recommended that these beets are grown in 3–5 year rotation with other crops to improve soil fertility and manage diseases and nematodes (Ali 2004).

Sugar beets are composed of about 75 % water, 18 % sugar, and 7 % insoluble and soluble materials. Because they have high sugar content beets, they are being considered for biofuels production. Most of the sugar beet is in the form of sucrose but other sugar as maltose, glucose, fructose are present, though these does not interfere with fermentation and distillation for the ethanol production (Haankuku et al. 2015).

Many countries have adopted bioethanol inclusion policies and sugar beet for its high content of sugars and not compete with food, it has been considered with potential for ethanol production. Theoretical ethanol yield gal/ton for sugar beet is 24.8–26.9 competing with other saccharide crops such as sugarcane (15.5–18.6) (Szulczyk et al. 2010). Besides, that could potentially double ethanol production per hectare compared to other feedstocks (corn, cellulose) (Shapouri and Salassi 2006; Panella and Kaffka 2010). Although the sugar beet area has decreased around 20 % between 2007 and 2010 in the EU (Eurostat 2011), USA Energy Independence and Security Act (EISA) of IEA (2007), was considered that sugar beets may be an eligible feedstock for advanced biofuel (NREL 2014).

2.3 Sweet Sorghum

Sweet sorghum is a perennial plant of Andropogoneae tribe and sub-family Panicoidae, Polaes order, *Poaceae* family, genereo *S.* *S*orghum species (Ratnavathi et al. 2010); is a native of tropical grass countries Africa, the Sudan, Ethiopia. *Sorghum* saccharine size is high, more than three meters, featured mainly due to its sweet and juicy stem as the sugarcane. The panicle (bunch) is open. It produces few grains (seeds).

Sorghum is a versatile crop, since their grain from the stalks and different products can be obtained, such as sugar, ethanol, paper, and other chemical compounds (Ratnavathi et al. 2010). The chemical composition of the juice obtained from stalks may result (Sipos et al. 2009) high ethanol productivity depending on the cultivar. Pereira Filho et al. (2013) noted that most of the characteristic value for the cultivar BR 506, reached 24. 895 L ha^{-1}, followed by BR 505, with 23.286 L ha^{-1}. However, in relation to the other cultivars (BR 505, 507, 501, and 601), the differences in relation to cultivate more productive were, respectively 1.609, 3.846, 4.609, and 8.194 L ha^{-1}.

Sweet sorghum cultivars are characterized by the accumulation of high levels of fermentable carbohydrates (15–23 %) within the stalk (Sarath et al. 2008; Smith et al. 1987). Total fermentable carbohydrates are comprised of three main sugars; sucrose (70 %), glucose (20 %), and fructose (10 %) variation in percentages depends on variety and environmental conditions (Prasad et al. 2007). Sweet sorghum requires less water and contains higher FC levels than corn, making it a favorable biofuel crop for semiarid temperate climate regions (Reddy et al. 2007). Sugar content in the juice increases with maturity, and is low prior to seed development. Sweet sorghum is typically seeded in widely spaced rows (30–40 inches). The ideal seeding rate for most sweet sorghum varieties is 3–4 seeds per linear foot of row with a final stand of 2–3 plants per linear foot of row. If plant populations are too high, the stalks will be spindly and contain less juice (Shoemaker and Bransby 2010).

Because of its agronomic flexibility and productivity, shorter growing cycle and percentage sugars of the same order of sugarcane,(Cunha and Severo Filho 2010) sweet sorghum is viewed as a viable feedstock option for ethanol production in some regions of the world (Davila-Gomez et al. 2011). In addition to industrial and agronomic characteristics, it can be used in the same system for the production of sugarcane, since it has the same physical characteristics (stalks), not requiring handling or to modify the facilities. In some countries (USA and Brazil), it is already being used in conjunction with sugarcane to increase the production of ethanol (Pereira Filho et al. 2013).

3 Starchy Crops

Among biofuels feedstocks, there are the starchy materials such as corn, cassava, wheat, and barley (Balat et al. 2008). However, corn is the most employed feedstock that is significantly used for bioethanol production. Starch materials must pass through an acid and or enzymatic pretreatment so as to produce a high sugar concentration for biofuel production. The following flowchart (Fig. 2) illustrates the main steps of the starchy materials till biofuel production.

3.1 Corn

In the 2013/2014, USA's corn production reached nearly 13.8 billion bushels (351.3 million metric tons) of corn. More than one-third of USA's corn crop is used to feed livestock, 13 % is exported and 40 % is used to produce ethanol. The remainder goes toward food and beverage production (Carter and Miller 2012; EIA 2013).

Corn stover, the residue left in the fields after harvesting corn, has been identified as a near- to mid-term agriculture residue feedstock for the lignocellulose-to-ethanol process. Corn stover has high carbohydrate content, can be collected in a sustainable fashion, and provides economic benefits to the farm community. Corn kernels have starch, which is an α-linked glucose polymer that can be easily broken down to glucose monomers and fermented to ethanol. It has fiber, which encases

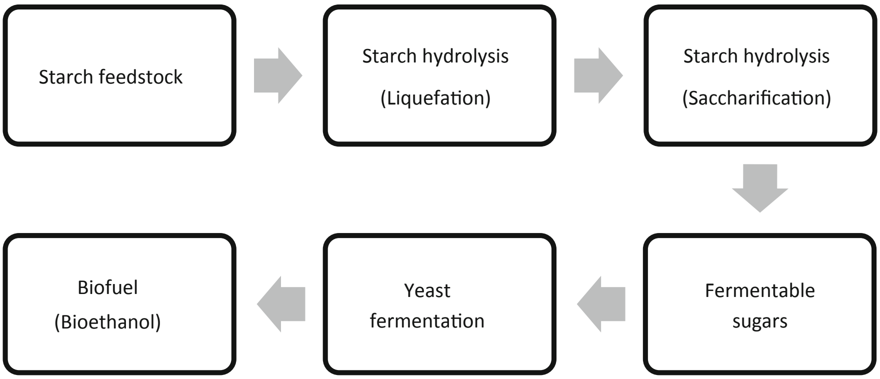

Fig. 2 Schematic diagram of bioethanol production by fermentation process of starch feedstock

Table 2 Corn kernel and corn stover compositions

Corn kernel	% Dry basis	Corn stover	% Dry basis
Starch	72	Cellulose	37.3
Hemicellulose/cellulose	10.5	Galactan/mannan	1.4
Protein	9.5	Xylan	20.6
Oil	4.5	Arabinan	2.1
Sugars	2.0	Lignin	17.5
Ash	1.5	Ash	6.1
		Acetate	2.0
		Extractives	13.0
% Humidity		% Humidity	

Source Watsom and Hamstad 1987

the starch, and about 15 % moisture. The comparative composition of corn kernel and corn stover is presented in Table 2 (Watsom and Hamstad 1987).

Currently, the maximum amount of pure ethanol that can be made from a bushel of corn is 2.74 gallons (98 gallons per ton at 15 % moisture or 115 gallons per dry ton). Yield is primarily dependent on the starch content, which may vary considerably.

Corn stover contains considerable quantities of cellulose, a beta-linked glucose polymer, which is more difficult to break down to glucose monomers than the α-linked polymer in starch. In addition, it contains hemicellulose, which is a more complex polymer of several sugars. The predominant sugars in hemicellulose are xylose and arabinose. These five-carbon sugars can also be fermented to ethanol with the proper microorganism. The maximum theoretical yield from corn stover with the composition is 107 gallons per dry ton (or 91 gallons per ton at 15 % moisture). Around the two sugar polymers is lignin. Lignin has an interesting by-product value and can be sold for different applications.

It is known that 1 acre yields about 130 bushels (3.65 tons at 15 % moisture) of corn, (USDA 2015) and about 1 ton of harvested corn yields 1 dry ton of stover. With an estimated 240 million dry tons of stover produced, the 80 million dry tons available for harvesting is equivalent to 6 billion gallons of ethanol (Glassner et al. 1998).

The U.S. Department of Agriculture (USDA) has a program devoted to the corn ethanol industry. Areas of scientific research address the establishment of new higher-value ethanol coproducts, the development of microbes capable of converting various biomass materials into ethanol, improved processes for the enzymatic saccharification of corn fibers into sugars, and various methods of improving corn ethanol process efficiencies (McLoom et al. 2000).

Fuel ethanol production from corn can be described as a five-stage process: raw material pretreatment, hydrolysis, fermentation, separation and dehydration, and wastewater treatment. The production of bioethanol from starch includes the breakdown of this polysaccharide to obtain an appropriate concentration of fermentable sugars, which are transformed into ethanol by yeasts. After washing, crushing, and milling the corn grains (dry milling process), the starchy material is gelatinized in order to suceptilize the amylose and amylopectin for enzymatic attack in the following liquefaction step. This step is considered as a pretreatment process because of the partial hydrolysis of the starch chains using thermostable α-amylase. The hydrolyzate obtained has reduced viscosity and contains starch oligomers called dextrins. Then, the fermentation process occurs where sugar is immediately assimilated by the yeast *Saccharomyces cerevisiae* in the same reactor and converted into ethanol. The culture broth containing 8–11 % (w/w) ethanol is recovered in a separation step consisting of two distillation columns (Quintero et al. 2008).

3.2 Cassava

Cassava is a shrub with tuberous roots. World production of cassava is around 281 million tones (Mt) a year. Africa contributes to more than half of global supply. Asia encourages the development of cassava crops for industrial and energy purposes. This continent contributes to around a third of world production, with 26 Mt produced by Thailand and 28 Mt by Indonesia. In Latin America, production is around 35 Mt where Brazil dominates with around 70 % of regional production and in third place in world production (Conab 2013).

Cassava is primarily grown for its roots but all of the plant can be used: the wood as a fuel, the leaves and peelings for animal feed and even the stem as dietary salt (UNCTAD 2015). Cassava is used in both human and animal food, in many industrial sectors, particularly in the form of starch, and more recently to produce ethanol. The current market price for fresh cassava roots is based on the food market price. Revenues are based on farm gate prices for fresh cassava roots that fluctuate due to seasonal influences and supply and demand (Van Eijck et al. 2014).

Cassava has starch 59–70 % of starch in its composition (Table 3), which is a polysaccharide comprising solely of glucose monomers that are linked together by glycosidic bonds. It is composed of two types of glucan namely amylose, a linear glucose polymer having only α-1,4 glycosidic linkage and amylopectin, a branched glucose polymer containing mainly α-1,4 glycosidic linkage in a linear part and a few α-1,6 at a branch structure (Sriroth et al. 2012).

Table 3 Cassava composition

Cassava	%
Moisture	59–70
Starch	77–94
Fiber/cell wall materials	1.5–3.7
Protein	1.7–3.8
Lipid	0.2–1.4
Ash	1.8–2.5

Source Breuninger et al. (2009)

Starch granules are less susceptible to enzyme hydrolysis. Upon cooking in excess water, the granular structure of starch is disrupted, making glucose polymers become solubilized and more susceptible to enzyme attacks. At the same time, the starch slurry becomes more viscous. This process is known as gelatinization and the temperature at which starch properties are changed is named as gelatinization temperatures. Different starches have different gelatinization temperatures that lead to different thermal treatment conditions (Swinkels 1998; Thirathumthavorn and Charoenrein 2005).

Cassava is still a small player on the biofuel scenario. In effect, with one ton of cassava, which has a starch content of 30 %, around 280 L can be produced of 96 % pure ethanol (Sriroth et al. 2012). The starch hydrolysis by enzymes is a two-stage process involving liquefaction and saccharification. Liquefaction is a step where starch is degraded by α-amylase, which hydrolyzes only α-1,4 and causes viscosity reduction of starch. Liquefying enzymes usually work at high temperatures (>85 °C) so that the enzyme can help reduce starch paste viscosity during cooking. Dextrins, which are obtained after liquefaction, are further hydrolzyed to glucose by glucoamylase enzyme. These enzymes can hydrolyze both α-1,4 and α-1,6 glycosidic linkage. Glucose is then converted to ethanol by yeast. After fermentation, approximately 10 % (v/v) ethanol are obtained and subjected to distillation and dehydration to remove water and other impurities, yielding anhydrous ethanol (Sriroth et al. 2012).

Nowadays, the production process of bioethanol from starch feedstock is developed to significantly reduce processing time and energy consumption by conducting saccharification and fermentation in a same step. This process is called "Simultaneous Saccharification Fermentation", or SSF process (Sriroth et al. 2012). In this SSF process, the liquefied slurry is cooled down to 32 °C, afterward glucoamylase and yeast are added together. While glucoamylase produces glucose, yeast can use glucose to produce ethanol immediately. No glucose is accumulated throughout the fermentation period (Rojanaridpiched et al. 2003).

4 Oil Seeds

Oilseeds are among the most important crops in international trade. Annually, world consumption of vegetable oils and fats exceeds 300 Mt (USDA 2015d). According to the FAO database (Faostat 2015), world production of vegetable oils increased more than 600 % in 40 years, jumping from 23.6 Mt in 1972/1973 crop season versus 180 Mt in the 2014/2015 crop season being produced mainly in United States (USA), China, Brazil, India, Argentina, and Indonesia. The oil produced is used mainly in nutrition, but also at industry application, fine chemistry, and energy.

There are hundreds of species with potential to provide oil for domestic use or as a raw material for oil chemistry or biodiesel industry. However, few of them have characteristics such as high oil content, well-structured supply chain and production

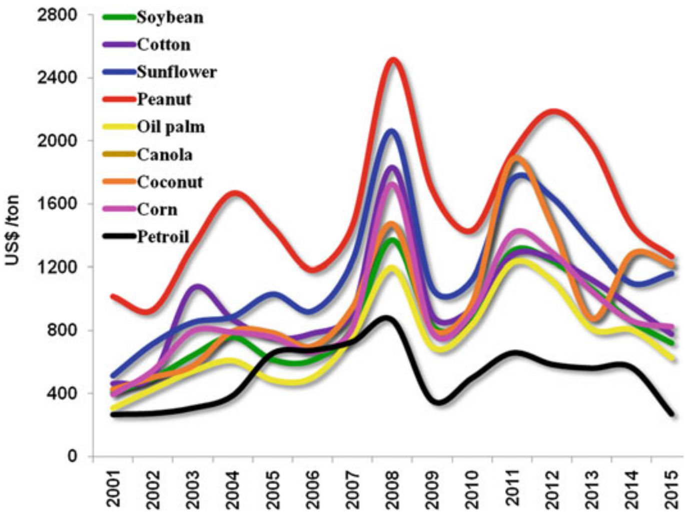

Fig. 3 Vegetable oil and petrol prices on the international market, adjusted to Sept, 2015

technology that justify their large-scale farming. About 80 % of vegetable oil produced worldwide comes from only four oil crops: palm (pulp + almond), soybean, rapeseed (canola), and sunflower. Four other crops account for the next 11 % share: peanut, cotton, coconut, and olive much suitable for nutrition application. Completing the world oil production dozens of other oil producing plants includes corn, castor, flaxseed, sesame, jatropha, jojoba, peanut among others.

As for biodiesel production, with a global production of about 35 billion liters (GL) (REN21 2015), and which demands annually over 30 Mt of vegetable oil and animal fat, four aspects are crucial for a given crop to be considered as a feedstock (Gazzoni et al. 2012): (a) large production; (b) well-organized value chain; (c) insertion as a commodity in the international market; and (d) competitive price, as compared to other oils, but specially against petrol, the fossil energy paradigm.

Figure 3 shows the evolution of market prices of the internationally traded vegetable oils, compared to international petrol prices. Each 1 % biodiesel added to mineral diesel results in the creation of 45,000 jobs, according to estimates of the Ministry of Agrarian Development of Brazil (Abreu et al. 2012).

4.1 *Feedstock for Biodiesel Production*

Depending on the oil content, yield and harvest of the seeds, the resulting oil volumes obtained from each hectare is variable according to the crop. Figure 4 presents the consolidated world oil production for the last 54 years, representing an eightfold increase.

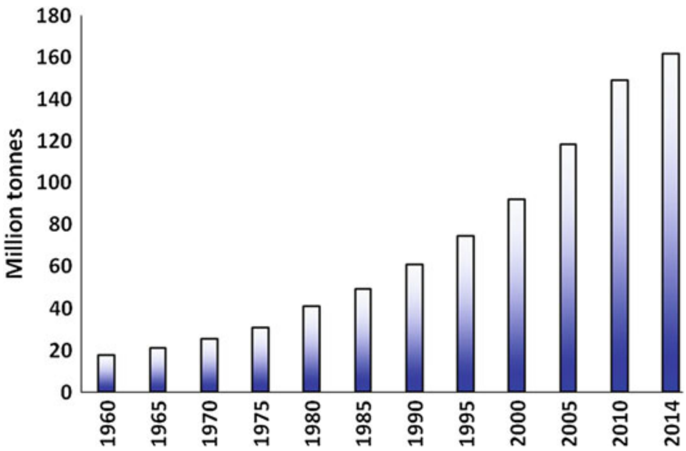

Fig. 4 World oil production from major oil crops

Oils have different characteristics, according to the crop. Oils are used for different purposes at industrial level (nutrition, oilchemistry, bioenergy, etc.). Its average composition included mainly saturated and unsaturated fatty acids. The four most important oil crops cultivated and traded in the international market, representing over 90 % of the global biodiesel feedstock are analyzed below.

4.1.1 Soybean (*Glycine Max* (L.) Merrill)

Soybean is one of the most important crops in the world, especially due to the high quality of its protein meal. Oil content (18–20 %) in the seed is lower than protein (36–40 %), but due to the large amount of soybean meal demanded to feed meat animals, the resulting oil volume is significant (EMBRAPA 1994).

In 2014, about 45 Mt of soybean oil was produced worldwide, being second only behind palm oil. In fact, soybean oil leads the vegetable oil production until last decade, and might be the leader again, in the near future. In 2013, Argentina cultivating 19.42 Mha with productivity of 2539 kg/ha produced 49.31 Mt, Brazil in 27.91 Mha, with a productivity of 2929 kg/ha produced 81.72 Mt and USA in 30.7 Mha, yielding 2915 kg/ha produced 89.48 Mt of soybeans. (FAOSTAT database).

Nowadays, in addition to the food market for humans and pets nutrition, new markets like bioenergy and oil chemistry, extend the horizons of soybean demand, increasing annual growing rates since 1990, when global production (108 Mt) was just one-third of the current (315 Mt) production. The mean annual growth during the last 20 years surpassed 8 Mt (Faostat 2015).

4.1.2 Oil Palm (*Elaeis Guineensis*)

Originally from the Gulf of Guinea, west central Africa, it is also known as African palm (dendê, in Brazil). Even known and used for millennia, its commercial cultivation started on the first decade of the twentieth century, in Malaysia. Palm is recognized as the oil crop that produces the largest amount of oil per hectare, and is responsible for 57 Mt of the global production of 170 Mt of vegetable oils (www.statista.com). Along with soybean oil, it accounts for over 60 % of the world vegetable oil production, but, considering the 2015 average oil yield of each crop, one hectare of palm oil yields the same amount of oil as 10 hectares of soybeans. (Corley and Tinker 2003)

The high oil yield allow palm oil to occupy only 8 % of the world area cultivated with oil crops, but providing almost a third of vegetable oil produced globally (Faostat 2015). Due to its tropical origin, palm oil is cultivated at humid tropics, as well as Southeastern Asian, Northwestern South America, and part of Central America. Presently, Asian countries account for nearly 90 % of its cultivated area. Indonesia, Malaysia, and Thailand are the major producers (FAOSTAT 2015). The largest importers are also located in Asia (China and India). In 2013, according to FAOSTAT database, Indonesia, Malaysia, Thailand, Nigeria, and Colombia produced, respectively, 26.9, 19.22, 1.97, 0.96, and 0.95 Mt of palm oil fruit.

The palm oil is used for bioenergy production, but the largest use is in the nutrition segment (industrial frying, chocolates, pasta, margarine, vegetable creams, cookies, ice cream), and in cosmetics industry (beauty products, shampoos, detergents, and soaps). The energetic balance (input/output) of biodiesel from palm oil is very favorable, sometimes reaching up to 1:8, according to Gazzoni et al. (2008).

The area presently used for palm oil cultivation in Southeastern Asia countries was formerly occupied by native forest, causing intense deforestation, collapsing the rainforest in countries like Indonesia within a decade.

In contrast, Brazil has the world largest reserve of suitable land for palm cultivation, estimated to be around 50 Mha (Müller 1980), but cultivates only 0.16 Mha (Faostat 2015), due to the restrictions imposed by the Brazilian environmental legislation for Amazonian lands, which restricts to 20 % the amount of area of a given farm, preserving 80 % of the biome (Müller and Furlan Junior 2001). So, Brazil is the nineth palm oil producer (0.37 Mt), resulting in continuous import of palm oil.

Palm oil is a perennial and huge oil production plant. However, its residues after oil extraction have only marginal or no commercial value. The main uses for palm oil residues are organic fertilizer or electricity generation by burning the waste. Palm oil fruits produce the palm oil itself, extracted from the pulp; and palm kernel oil, extracted from the fruit kernel. The oil fraction constitutes about 22 % of the weight of the palm bunch, and only 3 % is palm kernel oil. Lauric acid is almost absent in palm oil, the predominant component of palm kernel oil (Ramos et al. 2009). In 2013, Indonesia, Malaysia and Thailand produced 26.9, 19.22, and 1.97 Mt of oil palm, respectively, and 3.06, 2.27 and 0.18 Mt of Kernel oil. Then Nigeria and Colombia produced 0.96 and 0.95 Mt of palm oil and 0.51 and 0.08 Mt of kernel oil, respectively (FAOSTAT database).

4.1.3 Canola (Rapeseed) (*Brassica Napus* L.)

Rapeseed belongs to the Brasscicaceae family (formerly Cruciferae), the same family as mustard, broccoli, or cauliflower. The canola name results from a contraction of "CANadian Oil Low Acid", a variety of rapeseed modified in the 1970s by traditional breeding, by Canadian scientists from the University of Manitoba selected varieties, which oil has low erucic acid (toxic for humans and animals). The rapeseed differs from canola due to high levels of erucic acid and glucosinolate present in the grains.

Brassica oilseed varieties are among the oldest plants cultivated by humanity, with documentation of its use in India 4000 years ago, and in China and Japan 2000 years ago. Because of its lubricant properties, there was a high demand for rapeseed oil during World War I to supply the increasing number of steam engines in naval and merchant ships. After the war, the lubricant demand declined sharply, and other uses for the oil were developed (USDA 2015a).

Presently, canola is the leading group of varieties grown worldwide as rapeseed. The oil is the main product of canola, although its meal is also highly valued for the formulation of animal feed, because of the high protein content. According to De Mori et al. (2014), the oil content of canola seeds is high (38–45 %) and the volume of oil produced worldwide is surpassed only by palm and soybean oil.

Low amounts of unsaturated fatty acids are found in canola oil, being palmitic (16:0) the one with higher content (4 %). The major fatty acid found in canola is the mono-unsaturated oleic (18:1) (63 %), followed by polyunsaturated linoleic (18:2) (20 %) and linolenic (18:3) (9 %) (Ramos et al. 2009). High prices of canola oil make biodiesel from canola costly for the market and for supporting public policies. As for energy balance of biodiesel from canola oil, considering meal utilization, it was concluded that for each input energy unit along the life cycle 2.9 energy units are obtained; when considering only oil production (not computing energy on the meal) this relationship decreases to 1:1.4 (Gazzoni et al. 2009).

In 2014/15, world production of canola was 72 Mt of grains allowing the extraction of 26 Mt of oil, representing 16 % of global vegetable oil production (Faostat 2015). The leading production region is the European Union (24.0 Mt), followed by China (14.7 Mt), Canada (14.45 Mt), India (7.5 Mt) and Japan (2.0 Mt). Canola grain contains around 40 % of oil; Canola is more adapted to mild temperature regions, distant from the Equator (USDA 2015a). In 2013, according to FAOSTAT database, Europe, Canada, and China produced 9.91, 2.83 and 5.6 Mt of canola oil.

4.1.4 Sunflower (*Helianthus Annuus* L.)

The center of origin of sunflower is the region comprising Southwest USA and Northern Mexico, from where it disseminated to the rest of the continent. Its most likely domestication occurred in that region, where there is evidence of its cultivation by North American Indians over 3000 years ago (Lentz et al. 2001).

Russia was largely responsible for the spread of sunflower as a worldwide economically important crop. The importance of sunflower as edible oil source, only emerged by the 1920s. However, it was after World War II that sunflower aroused to the front line of oil crop production (USDA 2015b).

The global sunflower cultivated area in 2014 was, approximately, 18 Mha, with an overall production of 40 Mt of grain, 16 Mt of oil, and 17 Mt of meal (Faostat 2015), ranking fourth among the most important oils and meal production, globally. Sunflower vegetable oil is about 7.5 % of world production, behind palm (34 %), soybeans (30 %), and canola (16 %). The oil content of the seeds is about 45 %, consumed almost completely as edible oil for its excellent quality, while protein content situates on the range of 28–32 % (Leite et al. 2005; USDA 2015b).

According to Ungaro (2000), sunflower requires insensitive photoperiod and can be cultivated from the vicinity of the equator to latitudes above 40°. The optimum temperatures for proper plant growth are between 27 and 28 °C, but develops quite satisfactorily from 8 to 34 °C, being a good second summer crop (off-season) and an agronomic important option for rotation with soybeans, corn, and wheat.

The oil is rich in unsaturated fatty acids, like the monounsaturated oleic (18:1), with 16 % and the polyunsaturated linoleic, with 72 %; major saturated fatty acids are palmitic (16:0), with 6 % and stearic (18:0), with 4 % (Ramos et al. 2009).

Sunflower is used as ornament plant and its meals are used for feeding domestic bees, and sillage (animal fodder). The nutritional quality of sunflower oil is similar to the canola oil, being highly suitable for biodiesel production (Leite et al. 2005)

Regarding to energy efficiency of biodiesel production from sunflower oil, Gazzoni et al. (2005), using Life Cycle Analysis techniques, determined that with the whole grain destination (meal for nutrition, oil for biodiesel), 2.69 units energy were obtained from each energy unit input to the system. This relation was reduced when meal was not considered then each unit of input energy represented 1.61 units obtained from biodiesel use.

4.1.5 Minor and Potential Oil Crops

A series of species are used locally, even regionally, for oil production in small scale. Some are directed for self-consumption, either for human or animal nutrition, for soaps or energy production. Represents less than 5 % of the world oil production are restricted to commercial or purposes niches many of them based on native production and extractive systems but with median to high oil content, and a theoretical potential for oil production. Its commercial development depends on (a) possibility of production of over 500 kg/ha of oil, in order to compete with major oil crops; (b) domestication of the species; (c) establishment of production systems; (d) organization of the productive chain connecting growers, suppliers, processors, industry, and consumers. Among others, besides cotton and peanut, potential oil crops include, castor, oil radish, flaxseed, sesame, safflower, crambe, tucuman, oiticica, tung, pequi, jatropha, jojoba.

5 Lignocellulosic Wastes

Second-generation biofuels produced from (larger) feedstocks from lignocellulosic materials include cereal straw, forest residues, bagasse, and purpose-grown energy crops such as vegetative grasses and short rotation forests (Demirbas 2009). Among these sources for biofuel production, the percentage of sugar is variable, as well as the conversion processes used in the production of biofuel. A few companies in European Community (Gnansounou 2010) and USA have operated pilot plants to make cellulosic ethanol but no commercial amounts of the fuel are being made (Banerjee et al. 2010).

The main routes for obtaining bioethanol from lignocellulosic sources comprise several steps: pretreatment for delignification and release the cellulose and hemicellulose fractions; hydrolysis of cellulose and hemicellulose to fermentable sugars obtained (glucose, xylose, galactose, mannose, arabinose) (Sarkar et al. 2012). Furthermore, due to the high cost of enzyme, the current fuel grade ethanol produced from lignocellulosic material is still not able to compete with gasoline. In a contemporary process of lignocellulosic ethanol which is being worked out for more than 2–3 decades is not yet materialized into a viable technology. The permissible cost of enzymes is 15–30 cents/gallon of ethanol which is still not a reality (Menon and Rao 2012). Lignocellulosic materials could produce up to 442 billion liters per year of bioethanol (Balat 2011).

Among the main waste generated in the world and Brazil is sugarcane bagasse, rice hulls, oat hulls, straw and cob and corn husks, which have in their chemical pulp composition, hemicellulose, lignin, and other compounds (Sarkar et al. 2012).

5.1 Sugarcane Bagasse

The solid waste generated after processing the sugarcane is called bagasse. The chemical composition is 40 % cellulose, 25 % hemicellulose, 20 % lignin, and 10 % of other chemical compounds; it can be estimated that a ton of the pulp to produce approximately 300 L of ethanol (Halling and Simms-Boore 2008).

Sugarcane planted area in Brazil grew by 7.56 % per year during the last decade. The state of São Paulo was responsible for 55.3 % of all Brazilian sugarcane planted area in 2010, appreciating even more arable land values (Meyer et al. 2013).

The Brazilian Energy Plan scenarios estimate a mass sugarcane bagasse offering to be used only for second-generation ethanol around 7.0 × 106 tons year-1 for 2015, and 25.9 × 106 tons year-1 for 2030 (Hofsetz and Silva 2012).

Average productivity of sugarcane in Brazil is 85 tons per hectare; each ton of processed cane generated about 140 kg of straw and 140 kg of bagasse (dry basi), i.e., 12 tons of straw and 12 tons of bagasse. Assuming that the conversion of glucose to ethanol is complete, then full use of sugarcane (thatched, straw, and bagasse) can significantly increase ethanol production per hectare, from the current 7000 L to about 14,000 L. Sugarcane straw is 15 % of the weight of the stalks of sugar can ripe, or 12 % when seca. 13.29. In energy terms is the straw that is one-third of the potential energy of sugarcane that is currently underutilized (Santos et al. 2012)

Currently, 6000–7000 L of ethanol is produced from one hectare of sugarcane—not including the bagasse. When bagasse can be utilized for ethanol production, the output is likely to double to 12,000–15,000 L per hectare (Halling and Simms-Boore 2008).

5.2 Rice Husk

Rice (Oryza sativa) is a herbaceous plant included in the class Liliopsida (Monocotyledon), order Poales, Poaceae family, genus Oryza. It is one of the cereals produced and consumed in the world, characterized as staple food for over half the world's population. The annual rice production is approximately 606 Million tons. In this scenario, Brazil participates with 13.140.900t (2.17 % of world production)) (FAO 2015). Global production for 2015/16 is up from last month due to larger crops in China, the Philippines, and Mali, but remains at its lowest level in 4 years (FAO 2015).

Rice husk (RH), which is part of the rice paddy (rice grain), is a by-product of the rice milling process that involves the separation of the husk and bran (the outer layer of the rice grain) from the edible portion. Global production of RH is very significant and falls in the range of tens of millions of tons per annum. This presents an attractive opportunity to utilize such waste material for further processing particularly for the conversion into bioethanol. Typically about 50 % of the husk produced in a rice mill is burnt onsite to produce steam to drive the mechanical milling machinery (Abbas and Ansumali 2010)

Rice husk is composed mainly of cellulosic sugars. Being a lignocellulosic material, RH also contains lignin, which is present in up to 20 % of the husks. After gasification, RH ash is produced containing a useful secondary product—silica (SiO_2). Silica has been shown to be present in RH ash in high quantities varying from 15.30 to 24.60 % (Abbas and Ansumali 2010)

Rice straw is one of the abundant lignocellulosic waste materials in the world. It is annually produced about 731 million tons which is distributed in Africa (20.9 million tons), Asia (667.6 million tons), Europe (3.9 million tons), America (37.2 million tons), and Oceania (1.7 million tons). This amount of rice straw can potentially produce 205 billion liters bioethanol per year, which is the largest amount from a single biomass feedstock (FAO 2015).

5.3 Corn Stover

Corn (*Zea mays* L.) is a plant belonging to the family Gramineae/Poaceae. It is a monocotiledone slender stem, which can reach two meters in height (Thompson and Tyner 2014).

Corn stover consists in the different parts of the plant, which are the cobs, husks, stalks, leaves, and tassel (Thompson and Tyner 2014; Qureshi et al. 2010). Corn stover was reported as an average level of pulp (33–43 %), hemicellulose (20–34.5 %), lignin (8–14.1 %), protein (5 %), ash (4 %) (Aguiar and Ferraz 2011).

The potential amount of bioethanol derived from corn stover could replace 42:1 GL of gasoline used in a midsize passenger vehicle fueled by E85 (a mixture of 85 % ethanol/15 % of gasoline by volume), or about 3.8 % of world annual gasoline consumption (Kim and Dale 2004).

The United States is predominantly a producer of bioethanol derived from corn. Feedstock availability is not expected to be a constraint for bioethanol production over the next decade. Corn is expected to remain the predominant feedstock in the United States, although its share likely will decline modestly by 2015 (Balat 2011). In US, corn ethanol is currently the predominant biofuel, and is already using over 30 % of the corn produced (ERS 2010) though over 90 % of waste (corn stover) are left in the field (Kim and Dale 2004).

The current US stover yield (average from 2006 to 2010) was 7.3 Mg ha^{-1}. The annual total production was 237 Tg at present (2006–2010) and is projected to be 261 Tg in 2022 and 303 Tg in 2050 with an assumption of no changes in the total harvested area. Of the stover production, the cobs account for about 18 % (Tan et al. 2012).

5.4 Wheat Straw

Wheat (*T. aestivum*) is the world's most widely grown crop, cultivated in over 115 nations under a wide range of environmental conditions (Talebnia et al. 2010). Over the past 100 years, the yields of wheat have been increased and annual global production of dry wheat in 2008 was estimated to be over 650 Tg.

The overall chemical composition of wheat straws could slightly differ depending on wheat species, soil, and climate conditions. Cellulose, hemicellulose, and lignin content of wheat straw are in the range of 33–40, 20–25, and 15–20 (%w/w), respectively (Prasad et al. 2007).

The straw produced might be left on the field, plowed back into the soil, burned or even removed from the land depending on the decision made by landowner. Disposal of wheat straw by burning has been practiced for a long time. In recent years however, this practice has been challenged due to increased concern over the health effects of smoke from burning fields. Thus, finding an alternative way for disposal of surplus wheat straw is of high interest and an immediate necessity (Kerstetter and Lyons 2001).

6 Other Solid and Liquid Wastes

The organic waste from urban activity, rural, and mostly agricultural industry has been submitted to anaerobic digestion process. While reducing the pollution potential of waste, these processes provides end products as biogas or hydrogen. The production of biohydrogen and biogas from these sources is considered a promising solution for the energy demand (Lin et al. 2012).

Many studies have been conducted and projects have been developed at different scales to the development of the digestion process (Cortez et al. 2011). The kind of feedstocks is one of the factors related to the biodigester performance. The volatile solid content, the lignin content, and the C/N ratio of the waste influence the level of biological activity and consequently the production rates.

6.1 Wastewater

The wastewater from sewage or resulting from industrial processes is traditionally discarded by the industry as waste but can be used as feedstock to produce biohydrogen and biogas.

Many kinds of wastewaters are being studied in order to establish the process and performance parameters of fermentative biohydrogen production. Due to its low productivity and yield, the biohydrogen production on commercial scale is still developing and needs studies to become viable (Lin et al. 2012).

6.1.1 Vinasse

Vinasse is the main liquid stream from the first-generation ethanol production process. It is collected from the bottom of ethanol distillation columns. Due to its high level of organic compounds and nutrients, vinasse is a potential pollutant. In Brazil, sugarcane processing plants generally generate from 10 to 15 L of vinasse per liter of produced ethanol. More than 320 billion m^3 of vinasse were produced in 2014/2015 (UNICA 2015).

This residue has been tested as feedstock for biohydrogen and biogas. Fernandes et al. (2010) found vinasse as the highest potential feedstock for hydrogen production among other wastewater tested. The hydrogen yield was 25 mmol H_2/g COD.

The vinasse characteristics are dependent on the raw material. In the case of sugarcane vinasse, its composition also varies according to the fermentation feedstock. Bioethanol are mainly produced from sugarcane juice and/or molasses or corn (Moraes et al. 2015). The sugarcane vinasse characteristics are presented in Table 4.

Table 4 Physicochemical characteristics of sugarcane vinasse

Characteristic	
pH	3.8–5.0
Total solids (g/L)	21–85
Soluble solids (g/L)	4–31
Non-soluble solids (g/L)	3–13
COD (mg/L)	15,000–27,000
Water (%)	89–96
Organic matter in total solids (%)	70
Nitrogen (g/L)	1.0–3.5
Phosphorus (g/L)	0.4–4.0
Potassium (g/L)	9.0–13.0
Magnesium (g/L)	0.8–1.5

Adapted from Sydney (2013)

6.1.2 Glycerol

Glycerol is a feedstock for the industrial production of many products with commercial interests. However, when it comes from the production of biodiesel, the generated glycerin has a very low commercial value, primarily due to the impurities it contains.

Glycerol has become one of the most inexpensive and abundant carbon sources for microorganisms, since this is the main residue of the biodiesel production worldwide. Many workers have used crude glycerol from biodiesel process as a feedstock for biohydrogen production (Table 5). The conversion of glycerol to high energy fuels, such as the biohydrogen is an interesting and innovative alternative. It has been reported higher yields than those obtained with the conversion of sugars (Gonzalez et al. 2008).

Table 5 Biohydrogen production using crude glycerol as feedstock in different bioreactor systems

Bioreactor type	Hydrogen yield	Reference
120 mL serum bottles containing 40 mL media	2.73 ± 0.14 mol-H_2/mol glycerol	Ngo et al. (2011)
500 mL serum bottles with 250 mL of media	0.31 mol-H_2 mol/glycerol	Priscilla et al. (2009)
Packed-bed reactor of 60 mL working volume	63 mmol-H_2/L. h	Ito et al. (2005)
2 L glass flasks, with 1 L of liquid volume	200 ml-H_2/g COD	Bruna et al. (2010)
Bio-electrochemical two-compartment reactor	0.77 mol-H_2/mol glycerol	Sakai and Yagishita (2007)
Single-chamber membrane reactor	0.41 ± 0.1 m^3-H_2/m^3. d	Selembo et al. (2009)
125 mL serum bottles	4 mol-H_2/mol glycerol	Guillaume and Patrick (2009)

Adapted from: Sarma et al. (2012)

Table 6 Characteristics of palm oil mill effluent

Parameter	Values
pH	4–5
BOD (mg/L)	25,000
COD (mg/L)	55,000–60,000
Total Solids (mg/L)	40,500
Oils and grease (mg/L)	4000
Alkalinity ($CaCO_3$) (mg/L)	50–150

Source Ahmad et al. (2003)

6.1.3 Pome

POME (palm oil mill effluent) is the aqueous effluent from the production of biodiesel from palm oil and can be used for the production of biogas in anaerobic digester (Poh et al. 2010). The extraction process of oil from palm required 5–7.5 tons of water for each ton of oil. About 50 % of this water result as palm oil effluent (Ahmad et al. 2003). Due to its high content of phosphorous, carbon and nitrogen, this wastewater has highly negative environmental impact, and must be properly treated before disposal in water bodies (Poh et al. 2010).The anaerobic digestion of POME to produce biogas or biomethane has been studied (Table 6).

6.2 Urban Solid Wastes

The conversion of municipal solid waste to biofuel has become increasingly popular in recent years as a sustainable technology. In many industrialized countries around the world many facilities have operated in industrial-scale. In Edmonton, a Canadian city, 100,000 tons of municipal waste per year are converted into biofuels and chemicals. Also in San Francisco and Portland, in North America, 80–85 % of the residential organic waste is collected and composted (CleanTechnica 2014).

Different components of municipal solid waste determine the biogas and methane production potential. Getahun et al. (2014) found the highest biogas and methane yield with a mixed waste composed with fruit waste (15 %), food waste (12 %), yard waste (23 %), and paper waste (4 %). They attributed this due to its optimum C/N ratio (25:1) and good nutrient composition for the growth of methanogenic bacteria.

7 Conclusion and Perspectives

The diversity of renewable raw materials and residues used as feedstocks for biofuel production, combined with new technologies that have been developed, enable the future of this renewable energy source.

Biofuels include a very wide range of products, including bioethanol, biodiesel, biogas, biomethanol, biohydrogen, among others. The most common are bioethanol and biodiesel. Biodiesel is produced mainly from oil plants. For bioethanol production, the most interesting feedstocks are plants of rapid growth and annual collection, rich in simple sugars or easily hydrolysable. Sugar cane, beets, sweet *sorghum*, and cereals (corn, wheat, maize, cassava, etc.) are the most used.

Actually, microbial lipids, particularly single cell oils produced by oleaginous microorganisms have been used as potential raw material for biodiesel production due to their similar fatty acids compositions to vegetable oil. There is much interest in fuels produced from algae and a number of facilities are in the demonstration stage or commercial scale (Janssen et al. 2013). The process facility is generally colocated with a ethanol facility and utilizes carbon dioxide from the ethanol facility in its algae production process.

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