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Lignocellulosic biomass conversion into bioenergy: feedstock overview

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Public Interest Statement

While many of the advances in materials science have been driven by breakthroughs in material design and fabrication, understanding the changes that occur in a material during its utilization or operation in devices is of immense importance for its successful integration. Considering these aspects and the continued growth in materials research, there is a clear need for new topical journals which can serve researchers to understand the phase transitions and exploit the phenomena to current, state-of-the-art research in the field of materials science, moreover with full accessibility.

Abstract

One of the most felt current problems in the worldwide scientific community is replacing fossil fuels with renewable sources. Fossil fuels as a source of energy have produced numerous unfavourable effects over the years, such as the decrease in air quality and the increase in global temperature. Nowadays, the rapid depletion of these fuels is provoking fluctuations in global market prices with relative crises in non-energy-independent states. Lignocellulosic biomass represents a largely widespread bio-derived carbon source on earth and a potential feedstock for obtaining ethanol, syngas, and fuels. Till now, their potential for reducing impacts and oil dependence has never fully exploited industrially. However, the increasing demand for renewable fuels and chemicals has pushed research toward new processing methods to recover and use this valuable biomass source. The purpose of this review, divided into four parts, is to review this research field, highlighting the most recent industrial developments for converting lignocellulosic biomass to biofuels. In this first part, after a brief discussion of the current energy production scenario, biomass sources will be classified. The production, structure, and composition of lignocellulosic biomasses will be discussed, focusing on biomass production costs, land use, and requirements for its conversion to biofuels.

Keywords: phase change materials, chilling, thermal energy storage, oils, esters, glycerol.

1.Introduction

The increasing of oil price, as well as the increase of energy demand and carbon dioxide emissions responsible for the greenhouse effect, are driving the scientific and industrial research efforts towards a new kind of fuels with a low environmental impact, increasing the importance of renewable energy sources and thus the sustainability of energy and fuels production [1].

In 2018, about 80 % of the world's total energy supply was satisfied by fossil fuels, with a share for natural gas, oil, and coal equal to 22.8 %, 31.6 %, and 26.9 %, respectively. In the same year, about 14 % of world energy demand was covered by renewable energy sources (RES) as biofuels and waste (9.3 %), hydro (2.5 %), and others (2.0 %, including wind, solar, geothermal, and tides) [2].

The world's biofuel production (i.e., fuels produced from biomasses) increased by 10 billion litres in 2018 to reach an overall output of 154 billion litres. The United States and Brazil were the largest biofuel producers in 2018. Biofuel production is expected to increase 25 % during 2019-2024 to reach an overall output of 190 billion litres [3].

Biofuels can generally be defined by source, type, and generation and classified as primary and secondary ones. Primary biofuels are directly used as raw materials to generate heat and electricity (e.g., pellets, woodchips, forest and crop residues, landfill gases, etc.) or in industrial facilities. They can be exploited through devices from few kilowatts to hundreds of megawatts depending on the plant size [4]. Secondary biofuels are derived from processed raw materials and are mainly used in the transport sector (e.g., bioethanol, biodiesel, and biogas). The latter, depending on the raw materials from which they are derived, are generally processed by (i) thermochemical (combustion, gasification, and pyrolysis), (ii) chemical (biomass into liquid fuels), and (iii) biochemical conversion (fermentation) [4–6] (Figure 1).

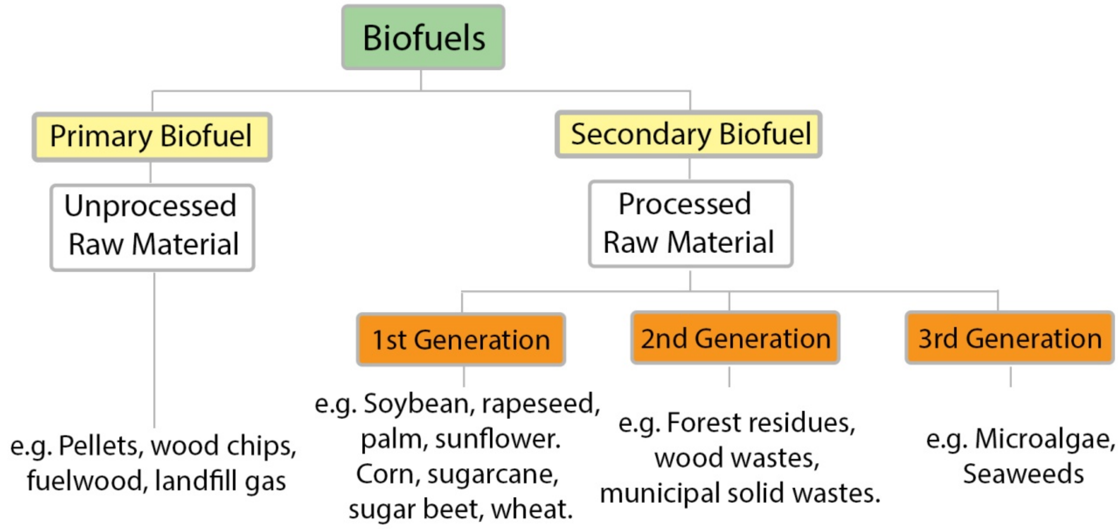

Figure 1. Biofuels classification.

Secondary biofuels, depending on the used feedstock for their production, can be further grouped into three families:

I. First-Generation Feedstocks (FGF) consist mainly of easily transformable products such as palm, rapeseed, soybean, and sunflower for bio-diesel production, and sugarcane, corn, sugar beet, and other plants having a high content of readily fermentable sugars for bioethanol production [7,8];

II. Second-Generation Feedstocks (SGF) consist mainly of lignocellulosic biomasses, also collected from natural wastes;

III. Third-Generation Feedstocks (TGF), currently under the industrial development stage, consist mainly of cellulose and lipids-rich algal biomasses [9,10].

Photosynthetic plants/algae are CO_2-sequestrators during their growth, and CO_2 is re-emitted into the environment during the subsequent conversion into energy [9,11,12]. This review aims to discuss the energy exploitation of second-generation biofuels, focusing on the feedstocks' main characteristics to produce biofuels.

2. Lignocellulosic biomasses

Lignocellulosic biomass mainly consists of cellulose (about 40-50%), hemicelluloses (about 25-35%), lignin (about 15-40%) (Figure2, pectin, and other components (1-15%), with concentrations depending on the starting biomass [13,14].

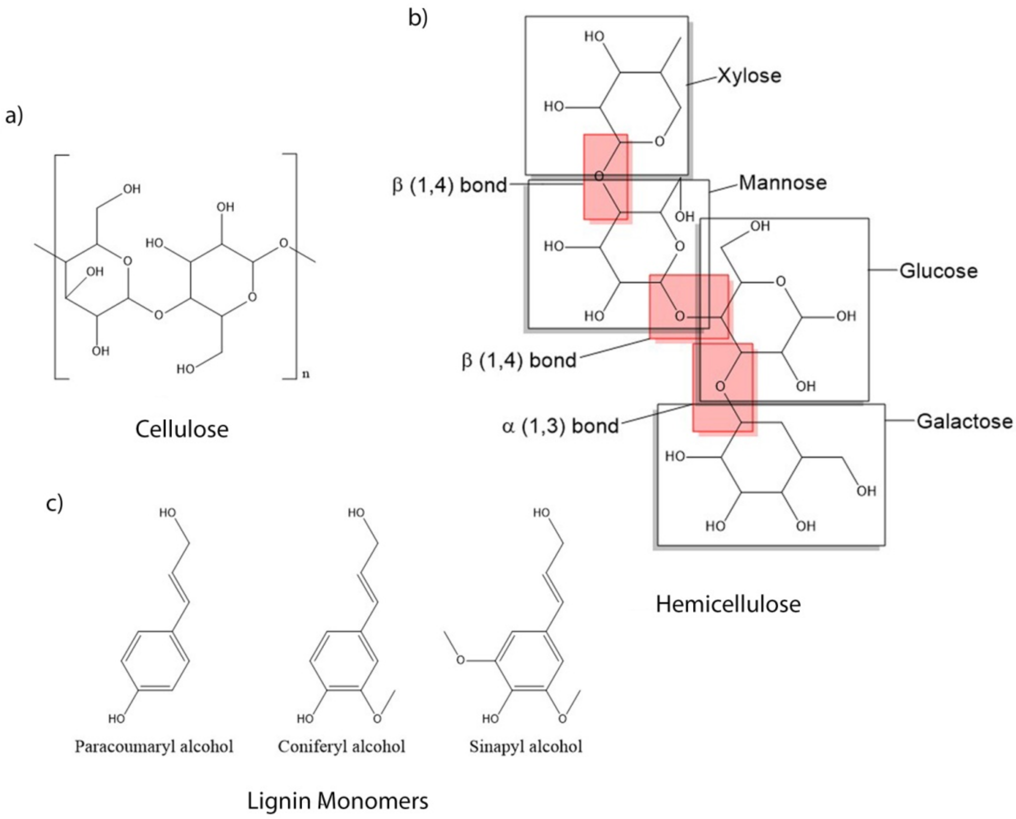

Figure 2. Chemical structure of the main biomass components: a) cellulose polymer structure, b) possible hemicellulose structure including Xylose-β-(1,4), Mannose-β-(1,4), Glucose-α-(1,3) and Galactose (other hemicellulose sugars are rhamnose and arabinose) c) Representation of the three subunits constituting the lignin polymer.

Generally, a lignocellulosic plant cell consists of primary and secondary walls (Figure 3a). A primary wall is made of rigid structures of cellulose microfibrils immersed in an amorphous matrix, mainly mposedof flexible polysaccharides of hemicelluloses and gel phase of pectin and small amounts of structural proteins (Figure 3b). Cellulose microfibrils consist of single polysaccharide chains, formed by linear β-D-glucose chains connected by 1,4-bonds (Figure 2) [15]. Moreover, toward the end of cellular expansion, some cells remain in their growth stage, synthesizing secondary walls constituted by cellulose, lignin, and other polysaccharides. These new walls are usually thick and work as mechanical support for the cell. When the secondary wall synthesis begins, the xylan (polysaccharide belonging to hemicelluloses) and lignin content increase, while the pectin synthesis drastically decreases [15].

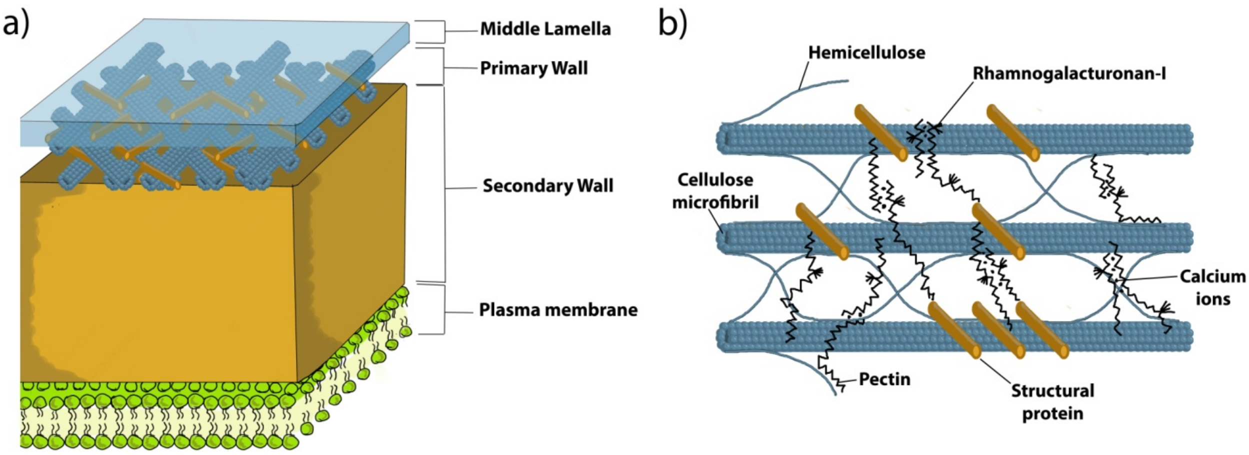

Figure 3. a) Schematization of the cell wall in plants, in which the middle lamella is a layer composed of pectin, able to wrap the cell walls of two adjoining plant cells, b) General structure of the primary wall.

Lignin is a phenolic polymer with a complex and irregular structure that gives impermeability, structural strength, and resistance against microbial attack and oxidative stress to the plant. It consists of three sub-units of aromatic alcohols: coumarin, coniferyl, and synapyl alcohol. These phenolic monomers are linked together by alkyl-aryl, alkyl-alkyl, and aryl-aryl bonds, making a three-dimensional network structure; this network, in turn, is connected by strong covalent bonds to cellulose and hemicellulose structures [16–18].

In addition to the mentioned components, vegetable biomasses are characterized by a lipids-rich membrane, protecting a plasma where starch, sugars, fatty acids, or other valuable compounds can be accumulated [19].

3. Lignocellulosic biomass composition for processing

The treatment/processing of the starting biomass is of paramount importance; it depends on its structure and is affected by the considered species, harvesting period, and type of cultivation [20]. Table 1 shows cellulose, hemicellulose, and lignin components in different living biomass types belonging to FGF, SGF, and TGF. The primary source of sugars derives from cellulose and hemicellulose, while removing lignin still represents the most energy-consuming pretreatment, thus increasing operating costs [21,22]. Nevertheless, lignin is composed of precious aromatics. Even though, at the moment, lignin is mainly used for energy recovery processes in the industrial production of ethanol from sugar cane, microorganisms-driven degradation processed to other precious products are currently under industrial development [8,23,24].

Table 1. Chemical composition of some biomass types[7].

Type of biomass	Fiber type	Chemical composition			Ref.
		Cellulose (%)	Hemicellulose (%)	Lignin (%)	

Bagasse	Sugarcane bagasse	42–48	19–25	20–42	[19]
	Sweet sorghum bagasse	34–45	18–27	14–21	
Straw	Rice straw	28–36	23–28	12–14	
	Wheat straw	33–38	26–32	17–19	
	Barley straw	31–45	27–38	14–19	
Seed	Cotton seed hairs	80–90	5–20	0	
Forestal wastes	Grass	25–40	25–50	10–30	
	Softwood	40-44	23-28	25-31	
	Hardwood	45-50	25-35	18-24	
Agricultural wastes	Nut shells	25–30	25–30	30–40	
	Bamboo	26–43	15–26	21–31	
	Banana waste	13.2	14.8	14	
	Coffee pulp	35	46.3	18.8	
Municipal wastes	General MSW	33–49	9–16	10–14	
Algal Biomass	Ulva lactuca	9.13	20.6	1.56	[25]
	Gelidium amansii	16.6	58.6	0	[26]

SGF and the TGF present very high and almost absent lignin content, respectively. Even though a high lignin content characterizes some FGF (e.g., sugar cane), the extractable sugars are easily fermentable by the yeasts. Therefore the final bioethanol yields are acceptable from an economic point of view. SGF accounts for a wide range of starting materials like woodchips, agricultural and forest residues, and municipal solid wastes, which are for a wide range of starting materials like woodchips, agricultural and forest residues, and municipal solid wastes. Ts for a wide range of starting materials like woodchips, agricultural and forest residues, and municipal solid wastes. Through longer and more expensive lignin removal pretreatments, they may be converted to other products for energy uses [27].

As previously mentioned, it is possible to identify three generations of feedstocks based on the biomass's primary structure [8,10]). The use of first-generation feedstocks such as sugarcane and corn presenting high concentrations of readily fermentable sugars for bioethanol production competes with sources for the human/animal diet [10]. However, taking advantage of some countries' climate and government subsidies, the production of first-generation biofuels showed rapid growth, mainly in Brazil and the U.S., which are now the largest sugarcane producers corn-derived bioethanol, respectively [8,28].

Second-generation biofuels can be exploited via thermochemical conversions, such as pyrolysis processes. The obtained syngas and bio-oils contain a series of interesting chemical molecules, including oils, that can be transesterified for biodiesel production [29]. Pyrolysis can be carried out in a circulating or bubbling fluidized bed reactor without oxygen and with temperatures of about 450-600 °C; unfortunately, the scale-up at the commercial size of these processes presents severe technical, logistical, and economic challenges [29]. On the other side, third-generation biofuels exploit microalgae and macroalgae biomass rich in cellulose, sugars, and lipids and deficient in lignin. Their pretreatment, thus, presents negligible economic impacts on their processing cost. Furthermore, microalgae offer a fast biomass growth rate, as a microalga can divide themselves several times per day, doubling the biomass growth speed during the exponential phase. On the other hand, the extreme and sophisticated conditions for the plant/process control confine the industrial project to a development stage (the main difficulty of this generation feedstock is upstream of the pretreatment process [30–32].

4. Costs associated with lignocellulosic biomass cultivation

Costs related to the cultivation, harvest, and transporting of the biomass raw materials (before its transformation) are often underestimated and overlooked. Since an FGF such as corn is an annual crop, it requires much more energy and expenses than a perennial crop (e.g., willow), requiring lower amounts of fertilizers, pesticides, and energy for the plant [33] . In terms of production and transport costs of the raw material, 1411 €/ha and 897 €/ha results for corn and willow, respectively, with transport costs accounting for about 70 % of total expenses [13,33]. Despite their high costs of production, FGF exploitation was made possible thanks to government programs and economic subsidies such as the case of Brazil where, since 1975, spent about 11.3 billion USD have been spent in the Pró-Alcohol national program, to favor the production of ethanol from sugar cane to get away from the oil dependence [34]. As a result, Brazil's sugarcane arable land has increased from around 2 million hectares in 1975 to 10 million in 2017, with an increase in ethanol production from 594000 m3, to about 27 million m3/y. Bioethanol was responsible for 32.3% of the total energy consumed in light vehicles in Brazil in 2014 (Figure 4) [35,36].

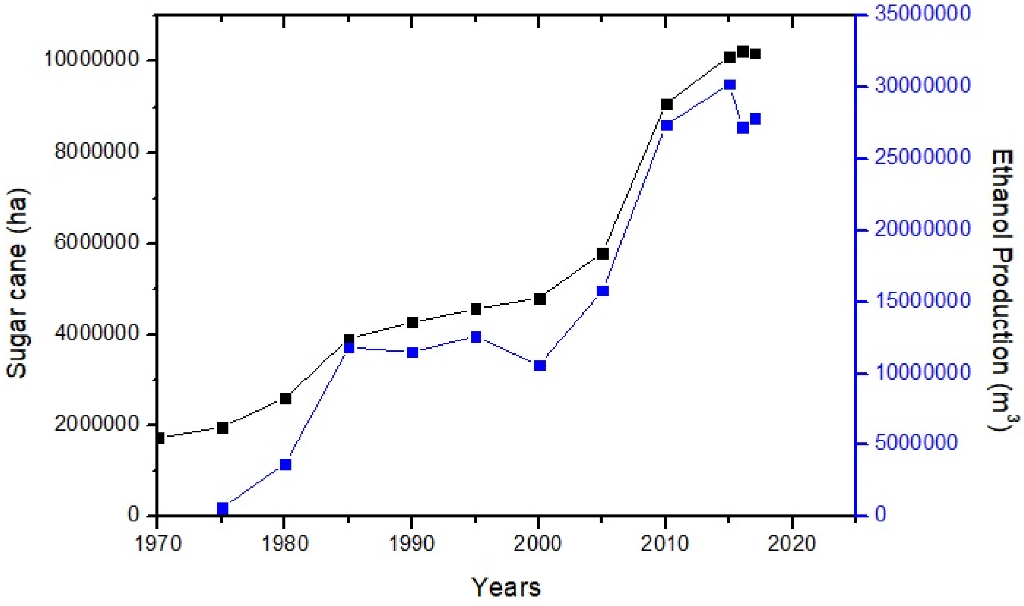

Figure 4. ha of arable land for sugar cane production and m3 of ethanol production in Brazil.

The advantage of SGF is the source of the raw biomass, which is mainly composed of waste material, where pretreatment becomes one the most critical phases of the whole process [10]. Compared to the FGF, whose raw material price is around 67% of the total costs, the share of feedstock in the SGF is about 30-50% of the total production costs [37]. TGF is the most expensive option for biofuel production.The technology available is still not able to compete with market prices since the ratio between the final yield of the product and its costs cannot satisfy a low-cost market. [38,39]. Biodiesel from microalgae is at least seven times more expensive than biodiesel from other crops.

Furthermore, the cheapest biodiesel is more costly than second-generation biomass-derived ethanol, costing two to three times more than gasoline's average cost [37]. The TGF mainly includes the cultivation of algae that aims to satisfy biofuels' global needs; this feedstock is primarily divided into seaweeds (or macroalgae) and microalgae. Industrial technology for the production of seaweed for feed and pharmaceutical production is already widely used worldwide, with Asia as the most significant producer that reaches about 80% of world production [40]. The main drawback of the development of technology suitable for large-scale microalgae cultivation is the effective unfeasibility from an economic point of view[41].

Seaweeds and macroalgae cultivation (e.g., Gelidium, Saccharina, Ulva, Kappaphycus etc.) at the industrial level comprise mainly two different techniques. The first one exploits species already existing in nature, improving their environment to favour their development but considering many parameters so that the favored species does not invade the whole ecosystem (only 6% of global production). The second one (aquaculture) aims to insert native or non-native cultures within an ecosystem, changing it if necessary [40,42]. Among the main production problems of seaweed at the industrial level, there are other species' epiphyte growth. [40]. Industrial microalgae (e.g. Chlorella sp., Nannochloropsis sp., Scenedesmus sp., Phaeodactylum sp., Tetraselmis sp., etc.) cultivation techniques include Open Pond (O.P.) systems and closed Photobioreactors (PBRs) for the cultivation of freshwater or brackish-to-saline water microalgae [43].

Despite trying to overcome the challenges of O.P. systems, which are less sophisticated in control and more subject to possible external contaminations, their cheapness and ease of installation and use make this technology one of the most exploited systems. On the other hand, PBRs, as more controlled systems with great potential in yield and quality, remain challenging to manage, and their costs are too expensive to be used in fuel production [43].

Conclusion

Lignocellulosic biomass represents a widespread potential feedstock for obtaining precious chemicals, first and second-generation fuels. In this review, constituting only the first of a more comprehensive one about converting lignocellulosic feedstocks for bioenergy production, biomass sources were classified according to their nature and composition. Moreover, the show, structure, and design of lignocellulosic biomass were discussed, focusing on production costs, land use, and biofuels processing. From what has emerged, land use and production costs represent still challenges for their widespread usage. As compared to first-generation biofuels, the recovery of precious chemicals and aromatics represents a highly desirable achievement, potentially decreasing the impact of the production of these chemicals compared to the corresponding fossil-derived ones. Compared to third-generation feedstocks, poor in lignin, second-generation lignocellulosic biomass production is cheaper and can be exploited shortly to its full potential. In the next parts of this review, they will be related to the optimization of industrial processes of first, second, and third-generation biomass for bioethanol production by the fermentation process, biofuels obtained by transesterification process, syngas obtained by gasification and gas, bio-oil and char from pyrolysis.

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