sustainability

MDPI

Review

Potentials of Biomass Waste Valorization: Case of South America

Sofía Sampaolesi [1], Laura Estefanía Briand [1], Mario Carlos Nazareno Saparrat [2] and María Victoria Toledo [1,*]

1 Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. Jorge J. Ronco" (CINDECA), CCT La Plata-CONICET, Universidad Nacional de La Plata, CICpBA, Calle 47 No 257, La Plata 1900, Argentina; sampaolesi@quimica.unlp.edu.ar (S.S.); briand@quimica.unlp.edu.ar (L.E.B.)

2 Instituto de Fisiología Vegetal INFIVE, CCT La Plata-CONICET, Universidad Nacional de La Plata, Diagonal 113 y 61 No 495, La Plata 1900, Argentina; masaparrat@fcnym.unlp.edu.ar

* Correspondence: victoriatoledo@quimica.unlp.edu.ar

Abstract: Various surveys carried out by the government and scientific projects on the availability of direct and indirect waste biomass in South America have reported that Brazil and Colombia produce 97% of the total waste biomass in the region, directly obtained from their extensive plantations of sugarcane. In addition, Argentina generates 45% of the total indirect biomass, followed by Brazil, Peru, Chile and Paraguay. The major source of those residues comprises sub-products of the wood (43%) and alimentary industries (20% from sugarcane and 11% from tea). Meaningful quantities of agricultural waste originate from soybean and corn, as the continent produces 50% and 11% of the global harvest of these crops. The higher content of cellulose in eucalyptus and willow waste (49%), among woody residues, along with their low lignin levels, makes them more suitable for delignification and exploitation as a biorefinery feedstock. Regarding the remains of agroindustrial activities, sugarcane bagasse (53%), corn cob (40%), wheat straw (49%) and banana hulls (38%) are the remarkable ones. In this context, the latest research concerning the use of commercial enzymatic cocktails for cellulose and hemicellulose deconstruction and the consequent feedstock hydrolysis is reviewed. In addition, we introduce the potential applications of cellulases isolated from native Latin American microbiota explored by South American research groups.

Keywords: plant waste biomass; South American biowaste; waste valorization; cellulase; saccharification

Citation: Sampaolesi, S.; Briand, L.E.; Saparrat, M.C.N.; Toledo, M.V. Potentials of Biomass Waste Valorization: Case of South America. *Sustainability* **2023**, *15*, 8343. https://doi.org/10.3390/su15108343

Academic Editors: Zakaria Solaiman, Shamim Mia and Md. Abdul Kader

Received: 21 April 2023
Revised: 8 May 2023
Accepted: 8 May 2023
Published: 21 May 2023

1. Introduction

The biorefinery concept accounts for the integrated processes (both chemical and biochemical) to convert biomass into bioproducts such as biofuels, biochemicals, animal feed and biopolymers [1]. In turn, biorefineries might use two types of biomasses as feedstock, depending on the availability. For instance, the direct use of biomass to produce a certain product, such as corn or sugarcane to obtain bioethanol, or the utilization of waste biomass generated as residues of agroindustrial activity [2]. The first option is characteristic of large countries, such as the United States, China, Brazil, Australia and Southeast Asia, that are capable of growing a volume of edible plants to use both in human nutrition and in biorefineries without competition. The choice of using waste biomass is typical of European countries and Japan, as it reduces waste and they can benefit from it by developing it into useful products. Furthermore, it reduces garbage landfills, which, in these countries, is essential to solving environmental problems with the advantage of saving space since they have limited land [2]. As will be presented in the following sections, South American countries generate large amounts of agroindustrial waste, which is mainly used in the co-generation of energy with other industrial products to supply the source mills within the loop of the circular economy. In this context, the development of novel strategies and technologies to valorize that biowaste into useful products is an ongoing challenge. Now, as the first step to obtaining valuable products from biomass, it is necessary to somehow pretreat it to obtain reducing sugars that would act as building blocks for more complex carbon-containing substances. Biomass saccharification is achieved through various methodologies, such as acid hydrolysis, soaking in ammonium hydroxide, pretreatment with ferric chloride, incubation in ethanol and sulfuric acid, organic solvents (typically called organosolv process), alkali treatment under microwave irradiation, mixture steam explosion, enzymatic hydrolysis and combinations of chemical and biochemical methods [3,4].

Following the deconstruction of pretreated plant biomass, hydrolysis of the obtained cellulose and hemicellulose is performed with endoglucanases, exoglucanases or cellobiohydrolases and β-glucosidase types of enzymes, such as those from fungal sources. The endoglucanases degrade the 1,4-glycosidic bonds within the internal amorphous cellulose, while the cellobiohydrolases act on the reducing or nonreducing ends of the chain; the disaccharide cellobiose and the trisaccharides, generated in the process to a lesser extent, are hydrolyzed by β-glucosidases, releasing glucose [4–6]. The suitable enzyme cocktail might be either commercial or produced from native fungal species, as will be discussed later in this review.

The present work reviews the large availability of waste biomass in many countries of South America, along with ongoing research devoted to obtaining valuable substances from it. In this sense, the potentiality of biomass valorization from the perspective of biorefineries is discussed. As a first step, open information about the amount, type and composition of waste biomass is discussed. Then, the scientific research regarding the development of biocatalysts and their applications is presented, focusing on those based on cellulases and other lignocellulolytic enzymes of commercial and native origin. Specifically, the investigations on cellulolytic enzymes isolated, characterized and/or applied by South American research groups are reviewed, as are the development and optimization of deconstruction processes for South American residual biomasses. The information exposed in this review evidences the potential of Latin America to develop sustainable technology within a circular economy.

2. Mapping Available Waste Biomass in South America: Distribution, Source and Composition

Recording the nature and origin of residual biomass suitable to be used as feedstock for different bioprocesses and its availability in certain regions constitutes the first strategic step in the evolution of countries towards more sustainable industrialization models. Table 1 gathers information concerning the amount and nature of various sources of waste plant biomass from countries found in the literature (Argentina, Chile, Paraguay, Colombia, Peru, Brazil and Uruguay). In addition, Figure 1 summarizes the amount and origin of the waste biomass available in those countries. The sources of waste biomass are classified as direct or indirect. The direct supply of biomass involves crops and native forests, while the indirect one is the waste resulting from the processing of raw materials. The information was obtained mainly from the surveys carried out by the local governments using the WISDOM method of the Food and Agriculture Organization of the United Nations, FAO-UN [7–11]. Those reports have the objective of establishing the availability of waste biomass to exclusively generate bioenergy. However, not all of the countries apply such a methodology. Therefore, alternative reports, either from scientific projects or scientific literature, have been taken as reliable data on disposable biomass when no official government data were available. For instance, Welfle (2017) and Forster-Carneiro and coworkers (2013) published updated investigations on agricultural wastes that are available for biorefinery-based processes and bioenergy in Brazil [12,13]. Moreover, those publications presented a forecast of the residues and wastes of the agroindustry, forestry and crop plantations from 2020 to 2030. As expected, Brazil (72%) and Colombia (25%), the largest within the studied countries, account for 97% of the total production of the waste biomass directly from their extensive plantations of sugarcane, in the first place, followed by soybeans and maize. In the particular case of Argentina, Chile and Uruguay, the direct residues are mainly composed of woody waste biomass generated from the native forest and forestry, each of them contributing about 1% of the total production of the region. In turn, Argentina produces 45% of the total indirect biomass, followed by Brazil (26%), Peru (14%), Chile (7%) and Paraguay (6%). The major source of those residues comprises sub-products of the wood (43%) and food industries (20% from sugarcane and 11% from tea) and fiber production, solid urban residues, products that have been recovered from seed processing (peanuts and sunflower mills) and fruits (such as banana, blueberry, citrus and pitted fruits) [7].

Table 1. Nature, percentage and quantity of direct and indirect waste biomass in various countries of Latin America.

Country	Amount (t/Year) and Source		Nature and Source (%)		Reference
	Direct	Indirect	Direct	Indirect	
Argentina	8,475,731	10,131,736	forestry (38%), sugarcane bagasse (23%), tea (12%), grapevine (7%), banana (6%), rice (5%), others	mills (55%), forestry industries (31%), peanut processing (3%), others such as tree pruning residue (11%)	[7]
Chile	4,999,477	1,531,710	native forest, forestry, vine and various pruning residues	forestry industries	[8]
Paraguay	2,568,562–3,186,132	1,369,990	forest plantations (36%), productive forestry (34%), native forestry (35%)	sugarcane bagasse of bioethanol production	[9]
Colombia	182,643,563	254,255	sugarcane bagasse (74%), rice (8.7%), fruits (9.9%), panela cane (5.6%)	tree pruning residue (52.7%)	[10]
Perú	7,083,496	3,164,174	corn (39%), sugarcane (27%), rice (24%)	bagasse (98%), wood chips (2%)	[11]
Brazil	518,390,000 (agriculture residues—crops) 9,420,000 (forestry residues)	5,810,000	sugarcane (28%), soybean (32%), maize (19%)	industrial residues (47.7%)	[12,13]
Uruguay	2222	17,967	Wood chips and wood waste	oil industry (19%), wineries (6.5%), breweries (74%)	[14–18]

In the case of Paraguay, sugarcane bagasse, a byproduct of bioethanol production, is the main source of indirect biomass [9]. The amount of sugarcane bagasse produced per year was calculated through information on the area and yield of cultivated sugarcane, with a production of 0.320 kg of bagasse per kg of sugarcane, provided by bioethanol manufacturers. The main direct source of biomass in this country is the forestry of *Eucalyptus* spp. and native species that are used as domestic biofuel, showing a range from 2,568,562 to 3,186,132 tons per year of total biomass production.

In Uruguay, the government started an ambitious project in November 2014 called Biovalor for the survey of various sources of agroindustrial wastes and their valorization for energy purposes [14,15]. This project reported the amounts of indirect waste generated in the most important industrial sectors of the country, such as olive and sunflower oil production, wineries, meat and dairy production, poultry, tanneries, pork farming and brewing, among others. Table 1 and Figure 1 show the amount of biomass residue corresponding to the oil industry, winery and brewery in Uruguay.

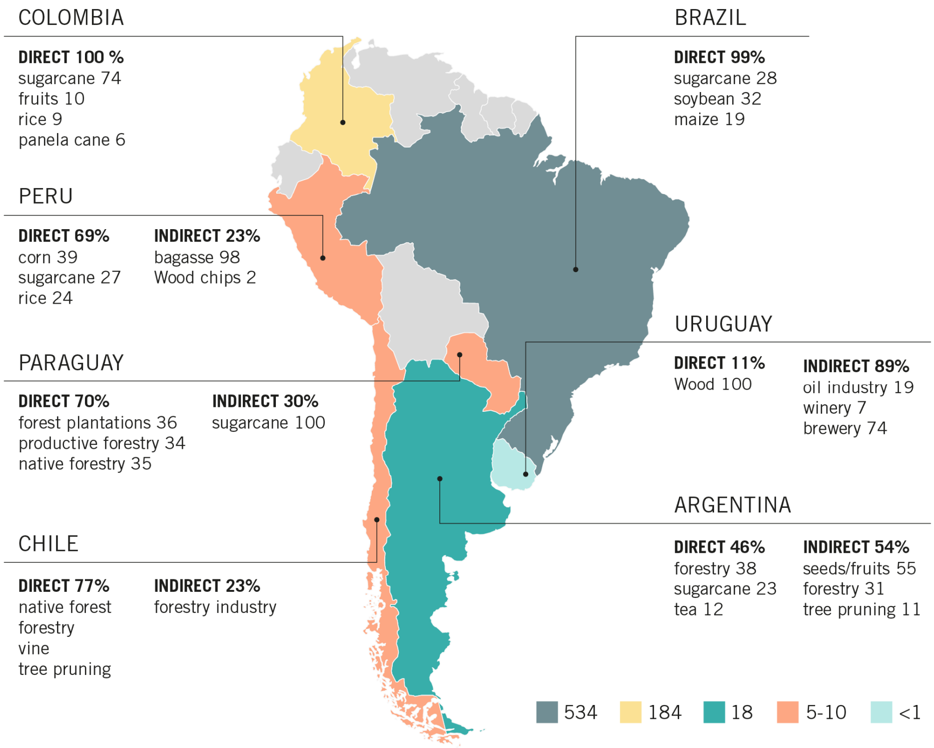

Figure 1. Millions of tons of waste biomass produced in various countries of South America shown in a colored code; percentage of direct and indirect and origin of the waste biomass produced in each country.

The forestry industry (composed mainly of pine and eucalyptus) in Uruguay provides the most abundant source of direct biomass waste. The report elaborated by the agency for the promotion of investment and export, Uruguay XXI, indicates that pulp-paper production is a major economic activity involved in Uruguayan forestry [16]. This activity generates untreated roundwood, chips, pulp, paper, cardboard, etc. In addition, the mechanical transformation of wood in sawmills produces treated roundwood, sawn timber, boards, joinery, packaging wood, furniture, moldings, etc. Moreover, the biomass byproducts of such economic activities are used in energy generation plants, providing 8% of the total consumption of electricity in the country. Del Pino and coworkers estimated that the direct biomass residue from forestry, such as non-commercial logs and branches (77%), needles (13%), twigs and floor litter, corresponds to 1140 tons per hectare, considering 200 pine trees per hectare, that is available after 22 years of growth [17,18]. Table 1 shows the amount of wood residue produced in Uruguay in the past year, according to the report of the Ministry of Livestock, Agriculture and Fisheries of Uruguay [18].

Composition of Waste Biomass: Key Information towards Biorefinery Strategies

Biorefineries integrate a variety of processes that use biomass, such as fuel and chemical product manufacturing, creating a new sustainable value chain from environmental and economic viewpoints, as discussed before. To accomplish these purposes, biorefineries use chemical, thermochemical and biological conversion strategies [19]. Knowing the lignocellulosic composition of the feedstocks is essential to defining suitable bioprocessing strategies. In this context, Table 2 gathers the reported data concerning the component fractions of common urban and agroindustrial wastes around the globe. Next, Table 3 focuses on the chemical composition of waste biomass most available in South America, as discussed in the previous section.

Of the three main biomass components, lignin is the most complex and recalcitrant to deconstruction, remaining the principal barrier for the access of enzymes such as cellulases to more digestible parts of the feedstock [20]. Moreover, enzymes can bind irreversibly to lignin through hydrophobic interactions, preventing the catalytic activity and increasing the quantity of expensive enzymes required for saccharification [21,22]. Lignin is composed of phenolic and non-phenolic structures, the latter being the more difficult to degrade. Non-phenolic is the main lignin fraction in most woods, meaning that feedstocks from woody species are usually more recalcitrant to delignification [23]. As has been deeply studied, pretreatments that eliminate lignin enhance the enzymatic digestibility of wastes and the sugar yield obtained by increasing the relative content of holocellulose (cellulose plus hemicellulose fraction) [22–24].

According to their biomass composition, eucalyptus and willow wastes are more suitable for delignification and exploitation as biorefinery feedstock, as is barley straw, which reveals the lowest lignin content. Among the pruning residues obtained from different tree species, olive tree pruning waste shows the highest potential for biomass deconstruction, followed by eucalyptus tree waste (see Table 2).

Table 2. Biomass composition of forestry, urban and agroindustrial wastes.

Biomass Source	% Dry wt [a]			Reference
	Cellulose	Hemicellulose	Lignin	
Willow sawdust	42.0	30.0	26.0	[25]
	42.5	26.1	23.0	[26]
	49.6 *	20.0 *	18.4	[27]
	29.7 *	16.4 *	24.1	[27]
Poplar wood chips	43.5 *	21.8 *	26.2	[28]
	43.7 *	21.5 *	23.9	[29]
	39.5	17.4 *	26.2	[30]
Pine wood chips	49.5 *	24.1 *	25.6 (AIL)	[31]
	42.5 *	20.8 *	27.9	[29]
	41.7 *	22.8 *	26.9	[29]
	45.0 *	21.8 *	28	[29]
	46.4 *	20.6 *	29.4	[28]
Eucalyptus wood chips			22.3 (AIL)	[32]
			20.6 (AIL) 4.8 (ASL)	[33]
	48.1 *	12.7 *	29.6	[29]
Eucalyptus pruning residue	46.1	26.0	25.1 (AIL + ASL)	[34]
Linden tree pruning residue	42.0	21.4	27.8 (AIL + ASL)	[34]
Plane tree pruning residue	34.0	24.2	38.8 (AIL + ASL)	[34]
Olive tree pruning residue	25.0	15.8	16.6 (AIL) 2.2 (ASL)	[35]
	28.6 *	13.6 *	21.4 (AIL) 2.3 (ASL)	[36]
Hazelnut tree pruning residue	37.2	20.45	28.5 (AIL) 2.5 (ASL)	[37]
Brewer's spent grain	13.1–25.4	28.4–29.96	11.9–27.8	[38]
	15.14	50.23	29.37	[39]
	14.47	4.38	29.57	[40]

Table 2. *Cont.*

Biomass Source	% Dry wt [a]			Reference
	Cellulose	Hemicellulose	Lignin	
Barley straw	33.1	24.9	16.1	[28]
	35.65 *	16.86 *	20.70 (AIL) 2.40 (ASL)	[41]
Fallen leaves pellets #	30.25	38.04	30.11	[42]

AIL: Acid-insoluble lignin. ASL: Acid-soluble lignin. [a] % dry wt: % mass fraction of dry material. * Estimated from the respective reference. # The mean value of three different pellets with different moisture content is reported.

Table 3. Type of biomass and composition of agricultural, agroindustrial and forestry wastes of South America.

Feedstock	Origin	% Dry wt [a]					Reference
		Cellulose	Hemicellulose	Lignin [b]	Extractives [c]	Ashes	
Sugarcane bagasse	Brazil	42.2	27.6	21.6	5.6	2.8	[43]
	Argentina	43.1 *	27.1 *	21.3	2.1	1.5	[44]
	Colombia	37.7	29.4	32.9	-	-	[45]
	Colombia	53.2	14.6	32.2	-	12.3	[46]
Panela cane	Colombia	43.6	33.0	21.8	-	-	[47]
	Colombia	36.1	24.2	33.3	-	-	
Corn	Perú	40.9	38.9	16.5	-	-	[48]
	Brazil	31.3	32.3	17.4	-	1.9	[49]
Soybean	Brazil	35.0 *	22.8 *	7.6	6.8	1.1	[50]
	Cuba	35.3	16.9	21.7	5.8	10.6	[51]
Wheat straw	Argentina	48.8 *	51.2	-	-	10.6	[52]
	-	39.7	30.6	17.7	-	7.7	[53]
Rice hulls	Brazil	36.2 *	19.8 *	23.9	2.32	12.5	[50]
	Argentina	34.1	15.8	19.0	8.2	15.0	[54]
Tea	China	17.5	16.4	19.5	-	-	[55]
Grapevine	Argentina	15.3	5.0	38.0	-	8.8	[56]
	Argentina	16.0	5.8	30.8	-	10.2	
Olive	Argentina	30.2	15.6	51.7	–	7.2	[57]
Banana	Brazil	36.3 *	9.2 *	8.4	25.2	8.0	[50]
	Brazil	26.8 *	12.7 *	10.7	22.9	8.0	
	Ecuador	38.0	8.7	8.9	24.1	17.6	[58]
	Ecuador	21.9	12.8	21.5	18.0	15.7	
Other fruits	Brazil	8.7 *	59.0 *	17.3	9.5	0.7	[50]
	Brazil	32.4 *	18.0 *	36.0	1.4	3.0	
Coffee	Brazil	35.3 *	27.2 *	24.5	4.2	2.0	[50]
	Colombia	35.4	18.2	23.2	-	1.4	[59]
Peanut	Argentina	81.2 *	18.8	-	-	1.47	[52]
	India	35.7	18.7	30.2	-	4.7	[60]
Forest industry residues	Chile	49.5 *	24.1 *	25.6	3.0	1.7	[31]
	Chile	50.5 *	21.9 *	20.1	3.1	1.1	
	Argentina	43.2	24.7	27.7	4.7	0.3	[61]
	Argentina	40.6	20.2	29.2	2.2	0.5	[62]
	Argentina	41.8	12.1	31.3	7.9	0.7	[63]
	Argentina	34.1	15.2	33.2	14.6	0.5	[64]
	Brazil	38.8 *	11.8 *	33.0	8.1	0.1	[50]

[a] % dry wt: % mass fraction of dry material. [b] Total lignin fraction. In some cases, it summarizes soluble and insoluble lignin fractions. [c] Organic extractives (acetone and other organic solvents). * Estimated from the respective reference.

Although brewer's spent grain and other agricultural wastes have a larger lignin content than certain woody feedstocks [39,40] (Table 2), the former could be more suitable for biomass conversion processes than pruning residues, depending on the phenolic and non-phenolic structure composition of lignin. Lobo Gomes et al. (2021) carried out the latest research on the enzymatic hydrolysis of brewer's spent grain in South America. They studied the enzymatic hydrolysis of two alkaline-pretreated barley bagasse samples and found that the higher the NaOH concentration, the greater the removal of lignin and hemicellulose, which in turn favors the enzymatic hydrolysis of cellulose [40].

Urban wastes from gardening and public thoroughfare pruning (foliage, plant residues, grass, etc.) were characterized by González et al. (2020). Pellets obtained from these residues, composed of 154 different species of trees, showed a high content of holocellulose with the potential to be used in biofuel manufacturing [42]. This alternative for reusing the gardening residue could prevent the burning of such biomass, a common practice that contributes to environmental pollution.

The most abundant lignocellulosic waste biomass originated as a by-product of agricultural and forestry activities. Crop processing implies the generation of important amounts of straw during the harvest through the threshing and removal of leaves, stalks and pods. The industrial processing of commodities requires further steps; then, additional disposals (the indirect waste biomass, as discussed before), such as bagasse and hulks, are produced.

Table 3 groups the main agricultural, agroindustrial and forestry wastes of South America in terms of quantities produced per year and their lignocellulosic composition. Sugarcane bagasse, a residue of the sugar, ethanol and first-generation biofuel industries, is mostly generated in Brazil, the world's largest producer of this crop, as discussed before [43], followed by Colombia and Argentina [65]. Its chemical composition was extensively studied by de Moraes Rocha et al. (2015) [43], who characterized 60 bagasse samples from the São Paulo state and from northeast Brazil, including five different varieties. The authors conclude that there was no significant variability in the lignocellulosic contents of the samples. The values reported by this group are in agreement with those published for Argentinian bagasse [44], but they have significant differences with the cellulose, lignin and ash content reported for Colombian industrial residue [45,46] (Table 3). Sugarcane bagasse and other wastes from panela processing are important recyclable biomass sources in Colombia, accounting for 2594.8 kWh/ton of potential energy through direct combustion strategies [47]. Despite intensive research efforts to obtain by-products from bagasse and other grains, only four operational biorefineries (demonstration plants) are installed in Brazil that are devoted to the production of second-generation biofuel from sugarcane bagasse [65].

Meaningful quantities of agricultural waste originate from soybean and corn, as the continent produces 50% and 11% of the global harvest of these crops, respectively [65]. South American countries are also major producers of wheat, especially Argentina and Brazil. Among these feedstocks, corn cob fiber is ideal for the obtention of reducing sugars due to its high content of cellulose [48] (Table 3); moreover, a mix of 1:1 stover and corn cob has been proven to be suitable as a feedstock for second-generation ethanol production [49]. Soybean hulls are the larger by-product of soybean processing, with the potential to generate acid hydrolysates for biofuel production [50].

The industrial processing of rice leads to the output of one ton of husks for every four tons of grain. This residue is suitable to be used as a substrate for biomass deconstruction, despite its relatively high percentage of ash (over 10%, see Table 3), which can impair the acid and enzymatic hydrolysis of the feedstock [50].

The cultivation of tea in Argentina has evolved in the last decades, reaching harvests above 85.4 thousand tons per year, while Brazil and other countries in the region have reduced their tea production. The manufacturing of tea-based beverages generates important quantities of tea leaf by-products that are usually disposed of by composting, incinerating or dumping in landfills. However, due to their low content of cellulose and hemicellulose [55] (Table 3), these wastes are not appropriate as biorefinery feedstock.

On the other side, coffee husks, obtained by dehulling the coffee grain, are an interesting residue from the cellulosic exploitation standpoint and are mainly produced by

Brazil, followed by Colombia [50]. For every ton of coffee produced, 0.18 tons of husks are generated, which are a waste type with high cellulose–hemicellulose and low ash content. Similar compositional characteristics of the peanut shell make both of these agroindustrial residues interesting as raw materials for biofuel production [52].

Fruit cropping constitutes another large source of lignocellulosic waste, especially in Brazil. Coconut fibers and açai seeds stand out for their richness in carbohydrates (cellulose plus hemicellulose) and very low content of ash [50]. Moreover, the remarkable amounts of banana residual biomass, which originated mainly in Ecuador, Brazil and Colombia, have drawn the attention of the research community to develop alternatives for its valorization. Annually, 20 million tons of stems and 1 million tons of stalks from banana production are discarded [50]. Guerrero et al. (2015) assessed the potential of banana residual biomass (starchy and lignocellulosic) from an Ecuadorian province by Geographic Information Systems [58]. The authors calculated that up to 19 million liters per year of first-generation bioethanol could be produced, leaving the lignocellulosic biomass to be exploited with an average energy potential of 12.9 MJ kg^{-1}.

The prominent development of viticulture in Argentina and Chile is coupled with the production of high amounts of agroindustrial waste, so its characterization as a potential renewable energy resource has gained interest. Rodríguez et al. (2018) determined low quantities of cellulose and hemicellulose in grapevine residues when compared with other lignocellulosic biomass [56] (see Table 3), meaning that this waste is not idoneous as a biofuel feedstock. However, its low percentage of ash, which positively affects its high heating value, and its high content of organic matter make it suitable for thermal treatment. Another important economic activity in the Cuyo region of Argentina is olive oil extraction by continuous two-phase centrifugation systems, whose main waste is the alperujo. Argentina is the biggest producer of olive oil in South America and the fifth-largest global exporting country. Giménez et al. (2020) studied alperujo and determined that the hydrocarbons obtained from the residue, with yields higher than 50%, have good properties to be used as an energy source [57].

In addition to the wastes associated with agricultural activities and crops, the forestry industry is also responsible for generating high amounts of lignocellulosic residual biomass, such as the sawdust produced in sawmills. Area and Vallejos (2012) extensively studied its suitability as a biorefinery feedstock [19]. In Chile, Muñoz et al. (2007) reported a maximum conversion to ethanol of 37% and 51% for pine and acacia forestry residues, respectively, using separate enzymatic hydrolysis and fermentation [31]. By applying a simultaneous processing strategy, the authors achieved a respective increase in the conversion yield of 44% and 65%. These results are in accordance with the reported potential of forestry wastes as a renewable energy resource related to their high cellulose content.

3. Enzymatic Saccharification towards Key Building Blocks for Waste Biomass Valorization

As was mentioned previously, regardless of the source of waste biomass, pretreatment is needed to enhance the availability of the substrate in the reaction catalyzed by enzymes. Physical, chemical, biological and mixed strategies, often classified into physicochemical or biochemical methods, are exploited to achieve biomass degradation and delignification in a process also called amorphogenesis, as reviewed elsewhere [66]. In the next stage of the bioprocessing of lignocellulosic materials, an enzymatic approach is applied to obtain the valuable reducing sugars from the holocellulose fraction.

Endoglucanases, cellobiohydrolases and β–glucosidases hydrolyze the cellulose into glucose units, the key building blocks for biofuel and bioproduct manufacturing. The cocktails containing those catalytic activities and auxiliary ones are produced by a few companies and commercialized worldwide, with basidiomycetes fungi as the main source of commercial cellulases. *Trichoderma viride*, *T. longibrachiatum* and *T. reesei* are considered the most productive and mutant strains of *T. resei* (*Hypocrea jecorina*) and are used to synthesize the enzymes at an industrial scale [67]. However, there is unexplored potential in making new enzyme cocktails from South America's native fungal species, as will be discussed in the following sections.

3.1. Saccharification through Commercial Enzymes: Applications in Biomass Waste Valorization in South America

Despite the amount and variety of waste biomass described in the previous sections, its enzymatic hydrolysis to generate value-added products is barely exploited. Most likely, the costs associated with using commercial enzyme cocktails and the need to optimize digestion conditions in terms of substrate specificity, temperature and pH of the pretreated biomass discourage the application of this technology. Table 4 summarizes the research available to date concerning the hydrolysis of biomass waste produced in South America employing commercial enzymes.

Brewer spent grain (BSG) has been thoroughly studied in Brazil and Colombia with different goals and purposes [40,68–72]. All the research groups performed an acid, alkali or acid–alkali pretreatment prior to hydrolysis.

In Brazil, Mussatto et al. (2007) carried out an exhaustive study of the use of BSG in lactic acid production [69]. They chemically hydrolyzed pretreated BSG with a commercial cellulase, producing 50 g L^{-1} glucose, which was then used as a fermentation medium for Lactobacillus delbrueckii to produce lactic acid. Later, the authors thoroughly studied the effect of different pretreatment methods on BSG raw material, concluding that higher efficiency on cellulose hydrolysis was achieved when the hemicellulose and lignin content was the lowest [70,71]. Regarding the research performed by Liguori et al. (2015), they saccharified the cellulose pulp obtained after pretreatment of BSG with a commercial cocktail of hydrolytic enzymes, achieving a glucose concentration of 75 g L^{-1}, which was then used as the substrate for ethanol production with a *Saccharomyces cerevisiae* selected strain [68]. Lobo Gomes et al. (2021) carried out the latest research on the enzymatic hydrolysis of BSG in South America. They evaluated the enzymatic hydrolysis of two alkaline-pretreated bagasse samples [40]. The authors found that the higher the NaOH concentration, the greater the removal of lignin and hemicellulose, which favors cellulose enzymatic hydrolysis. In Colombia, Dávila et al. (2016) simulated a biorefinery to produce ethanol, xylitol and polyhydroxybutyrate (PHB) [72]. They employed a commercial cellulase to produce glucose from BSG, which was then fermented to produce ethanol and PHB. Through the biorefinery approach, the authors achieved a reduction in the total production cost and the environmental impact of BSG treatment.

Regarding tree pruning residues as a source of fermentable sugars, it has been recently studied only by a research group in Argentina with the aim of producing second-generation bioethanol [73]. The authors optimized an alkaline pretreatment with calcium hydroxide over the raw sample, which induced morphological changes in the solid surface that favored the following hydrolysis step. For this purpose, a cocktail of commercial hydrolytic enzymes was employed to obtain higher amounts of glucose, which were then used to obtain promising amounts of bioethanol.

Another source of reducing sugars exploited in South America is pine sawdust. In the last five years, several works performed in Argentina have been published. Stoffel et al. (2017) and Rodriguez et al. (2017) optimized alkaline–acid pretreatment, achieving glucose yields much higher after hydrolysis with commercial enzymes than those obtained from untreated sawdust [74,75]. Kruyeniski's (2019) research group evaluated different pretreatments. Kraft–anthraquinone for lignin extraction allowed the highest enzymatic hydrolysis yield with commercial cocktails [76]. More recently, Mendieta et al. (2021) evaluated second-generation bioethanol production following different strategies. The pretreatment employed by the authors conditioned the enzymatic hydrolysis performance, obtaining the best accessibility of commercial enzymes to the substrate when the lignin content achieved was the lowest [73]. In addition, wood chips and bark were exploited from different varieties of pine in Chile and Colombia with the aim of producing bioethanol [78,79].

Table 4. Nature of the feedstock, country of origin, type of pretreatment, commercial biocatalyst used in the enzymatic hydrolysis, reaction conditions, yield of reducing sugars and objective of the investigation (pretreatment improvement and/or production of valuable substances) of biomass waste of South America.

Feedstock	Country of Origin	Pretreatment	Commercial Enzyme	Reaction Conditions	Yield	Objective	Reference
Brewer spent grain (BSG)	Brazil	Alkaline	Cellic®CTec3 (Novozymes, Bagsværd, Denmark)	50 °C, 200 rpm for 48 h in 0.1 M citrate buffer	>70% glucose	Pretreatment improvement	[40]
		Alkaline–acid	Cellulase and β-glucosidase from Novozymes	45 °C, 120 rpm, 72 h 8% (*w*/*v*) substrate with 2.2% (*v*/*v*) cellulase and 1% (*v*/*v*) β-glucosidase	75 g L^{-1} glucose	Ethanol production	[68]
		Acid–alkaline	*Trichoderma reesei* cellulase Celluclast 1.5 L (Novozymes)	45 °C, 100 rpm, 96 h 8% (*w*/*v*) substrate. Enzyme/substrate ratio of 45 FPU g^{-1}	57.8 g L^{-1} glucose	Lactic acid production	[69]
		Dilute acid and alkaline	*Trichoderma reesei* cellulase Celluclast 1.5 L (Novozymes)	45 °C, 100 rpm for 96 h in sodium citrate buffer (pH 4.8) with 0.02% (*w*/*v*) sodium azide. Enzyme/substrate ratio of 45 FPU g^{-1}	85.6% glucose	Pretreatment improvement	[70]
		Acid–alkaline	*Trichoderma reesei* cellulase Celluclast 1.5 L (Novozymes)	45 °C, 100 rpm, 96 h 8% (*w*/*v*) substrate in sodium citrate buffer (pH 4.8). Enzyme/substrate ratio of 45 FPU g^{-1}	57.8 g/L glucose, 7.5 g/L cellobiose	Lactic acid production	[71]
	Colombia	Acid	*Trichoderma reesei* cellulase Celluclast 1.5 L (Novozymes)	45 °C, 100 rpm for 96 h in citrate buffer solution (pH 4.8) at a solid-to-liquid ratio of 1-to-8. Enzyme/substrate ratio of 45 FPU g^{-1}	4.5% glucose	Xylitol, ethanol and polyhydroxybutyrate (PHB) production	[72]
Olive tree pruning	Argentina	Alkaline	Cellulase from *Trichoderma reesei* ATCC 26921 (≥700 units g^{-1}) (Sigma Aldrich, Søborg, Denmark) and hemicellulase from *Aspergillus niger* (0.3–3 units mg^{-1}) (Sigma Aldrich, St. Louis, MO, USA).	45 °C, 100 rpm for 24 h in 0.05 M sodium citrate buffer (pH 4.9). 4% (*w*/*v*) substrate concentration	220 mg sugars g^{-1} dry biomass	Bioethanol production	[73]

Table 4. *Cont.*

Feedstock	Country of Origin	Pretreatment	Commercial Enzyme	Reaction Conditions	Yield	Objective	Reference
Pine sawdust	Argentina	Alkaline–acid	*Trichoderma reesei* cellulases (51 FPU mL^{-1} of cellulose, Sigma Aldrich)	50 °C, stirring for 72 h in acetate buffer 50 mM (pH 4.8). 2% total solids	24.3% glucose	Study effect of pretreatment on substrate accessibility	[74]
		Alkaline–acid	Celluclast 1.5 L (Sigma)	50 °C, 150 rpm for 48 h in 0.05 M sodium acetate buffer (pH 4.8). Enzyme/substrate ratio of 20 U g^{-1}	1.81 g L-1 glucose	Pretreatment improvement	[75]
		Kraft–anthraquinone	Cellulase from *Trichoderma reesei* (Sigma Aldrich, Søborg, Denmark)	50 °C, 130 rpm for 72 h in 0.05 M sodium citrate buffer (pH 4.8). Enzyme/substrate ratio of 20 FPU g−1	EH% 100	Pretreatment improvement	[76]
		Soda–ethanol	Cellic®CTec2 (Novozymes)	37°C, 130 rpm for 48 h in 0.05 M sodium citrate buffer (pH 5), 1% hydrolysable cellulose (dry matter). Enzyme/substrate ratio of 30 FPU g^{-1}	≈100% EH; 11 g L^{-1} glucose	Bioethanol production	[77]
Pinus radiata wood chips	Chile	Acid–ethanol	Cellic®CTec3 (Novozymes)	50 °C, 150 rpm for 72 h in 0.05 M citrate buffer (pH 4.8). Enzyme/substrate ratio of 0.044 g g^{-1}	70 g L^{-1} glucose	Ethanol production	[78]
Pinus patula bark	Colombia	Alkaline	Celluclast 1.5 L and Viscozyme L	60 °C, 100 rpm for 72 h in 0.1 M citrate buffer solution (pH 4.8). Enzyme/substrate ratio 25 FPU g^{-1}	63 g L^{-1} hexose	Bioethanol and furfural production	[79]

Table 4. *Cont.*

Feedstock	Country of Origin	Pretreatment	Commercial Enzyme	Reaction Conditions	Yield	Objective	Reference
Sugarcane bagasse (SB)	Brazil	Acid	Cellulase from Trichoderma reesei (I) and mix of cellulase and β-glucosidase (II)(Genecor and Novozymes)	45 °C, 70 rpm for 24 h in 100 mM sodium citrate buffer (pH 4.8). Enzyme/substrate ratio of 30 FPU g^{-1}. Tween 20/substrate ratio of 0.08 g g^{-1}	I: 47.7% glucose II: 48.1% glucose	Study cellulose digestibility by modifying variables	[80]
		Acid–alkaline	Cellulase from *Trichoderma reesei* Multifect® (Genecor International Inc.)	48 °C, 200 rpm for 24 h in 0.05 M citrate buffer (pH 5.0). Enzyme/substrate ratio of 25 FPU g^{-1}	40.4 g L^{-1} glucose	Pretreatment improvement	[81]
		Acid	Cellic®Ctec2 (Novozymes)	50 °C, 200 rpm for 24 h in 0.1 M sodium citrate buffer (pH 5.0). Enzyme/substrate ratio of 30 FPU g^{-1}	Tops: 39.8 g L^{-1} Bagasse: 22.2 g L^{-1} Straw: 31.0 g LL^{-1}	Ethanol production	[82]
		Steam explosion	Cellic®Ctec2 (Novozymes)	50 °C, stirring for 96 h in 50 mM acetate buffer (pH 4.8). Enzyme/substrate ratio of 8.4 FPU g^{-1}	60–70 g L^{-1} glucose	Cellulosic ethanol production	[83]
		Hydrodynamic cavitation–alkaline pretreatment	Cellic C-Tec (Novozymes)	48 h in 50 mM sodium citrate buffer (pH 4.8). Enzyme/substrate ratio of 20 FPU g^{-1}	91% glucose	Pretreatment improvement	[84]
		Acid	P4 from *Trichoderma reesei* (AB enzymes)	40 °C, stirring, for 65 h in 0.05 M citrate buffer. Enzyme/substrate ratio 0.001 g L^{-1}	29.11 mg mL^{-1}	Selection of cellulolytic enzyme	[85]
		Acid–ultrasonic	Celluclast 1.5 L (I) and Cellic cTec2 (II) (Novozymes)	50 °C, 300 rpm for 24 h in 0.2 M sodium acetate buffer (pH 4.8). Enzyme/substrate ratio of 20 FPU g^{-1}	I: RS % 189, TCY % 45 II: RS % 192, TCY % 66	Study effect of ultrasound treatment	[86]
		Acid–SC-CO_2	Cellic cTec2 (Novozymes)	50 °C, 300 rpm for 24 h in 0.2 M sodium acetate buffer (pH 4.8). Enzyme/substrate ratio of 10 FPU g^{-1}	RS % 132, TCY % 32	Study effect of SC-CO_2 treatment	[87]

Table 4. *Cont.*

Feedstock	Country of Origin	Pretreatment	Commercial Enzyme	Reaction Conditions	Yield	Objective	Reference
Napiergrass	Uruguay	Acid–alkaline	Cellulase complex NS50013 and β-glucosidase NS50010 (Novozymes)	50 °C, 100 rpm, for 130 h in pH 4.8 buffered solution. Enzyme/substrate ratio of 5 FPU g^{-1} cellulase and 10 CBU g^{-1} β-glucosidase. PEG 6000/substrate ratio of 0.05 g g^{-1}	45% cellulose hydrolysis 27 g L^{-1} glucose	Fuel bioethanol production	[88]
King grass	Colombia	Alkaline	Acellerase 1500 (Genencor, New York, NY, USA)	50 °C, 180 rpm for 24 h in 0.05 M citrate buffer (pH 4.8). Enzyme/substrate ratio of 30 FPU g^{-1} cellulase and 10 CBU g^{-1} β-glucosidase.PEG 6000/substrate ratio of 0.05 g g^{-1}	78 g L^{-1} glucose	Fuel bioethanol production	[89]

EH = enzymatic hydrolysis; RS = Relative reducing sugar concentration; TCY = theoretical cellulose yield.

Sugarcane bagasse has been thoroughly studied in Brazil, employing different pretreatments and various commercial enzymes. Through different strategies, the acquisition of delignified samples is required to improve enzyme accessibility to cellulose. Araújo Barcelos et al. (2013) compared the effect of increasing the commercial enzyme loading over an untreated sample and raising the NaOH concentration [81]. The yield of enzymatic hydrolysis is much lower for the non-pretreated sample, regardless of the enzyme load. Instead, when alkaline pretreatment was performed, the higher cellulose content led to higher accessibility and enhanced enzymatic activity. Furthermore, it has been proven that the addition of a surfactant to the reaction mixture favors cellulose saccharification as it avoids the adsorption of the commercial enzymes to residual lignin [80]. Autohydrolysis (or steam explosion) as a pretreatment has also been performed, achieving high glucose recovery from native sugarcane bagasse [83]. Additionally, alkaline pretreatment combined with hydrodynamic cavitation improved the enzymatic digestibility of glucan, reaching 91% after 48 h [84]. Finally, de Carvalho Silvello et al. (2019, 2022) developed an acid pretreatment over sugarcane bagasse in combination with ultrasound (US) and supercritical carbon dioxide (SC-CO_2), considerably improving the enzymatic performance [86,87].

Promising results were found by Cerqueira et al. (2015), who analyzed the whole sugarcane biomass, including the bagasse, straw and tops [82]. The tops had the best performance for cellulose hydrolysis, achieving the highest glucose concentration in 24 h, followed by straw and, in last place, bagasse. These results enable more lignocellulosic biomass residues from sugarcane to be exploited for ethanol production.

Different varieties of grass have been studied as potential feedstock for alcohol production. Camesasca et al. (2015) employed napiergrass from Uruguay to generate ethanol, reaching the highest cellulose hydrolysis and glucose release after an acid–alkaline pretreatment in the presence of PEG 6000 as a surfactant [88]. Moreover, king grass was used in Colombia in order to produce butanol [89].

3.2. Native Fungal Enzymes Degrading Cellulosic Substrates and Their Potential Applications

Fungi are the main decomposers of lignocellulosic materials in terrestrial ecosystems, representing the most promising group for cellulolytic enzyme acquisition with the potential to be used in a variety of industrial processes. Cellulolytic fungi have evolved complex catalytic systems that activate under specific environmental conditions to adapt to their natural habitat. These extracellular enzymatic systems are mostly synthesized by aerobic fungi and are constituted by different enzymes that can be classified into two main categories: the classical hydrolytic enzyme group, including endoglucanases, exoglucanases, and β–glucosidases; and those proteins that catalyze oxidative processes, such as lytic polysaccharide monooxygenases (LPMOs) and cellobiose dehydrogenases (CDHs) [90]. Figure 2 depicts a model of the action of the various types of fungal enzymes degrading the cellulose fraction of lignocellulosic biomass.

These enzymatic activities act in a coordinated way through a specific extracellular protein assemblage, allowing fungi to decompose the surrounding biomass. However, additional fungal proteins or their sub-units, along with other cellulolytic and/or catalytic proteins synthesized by cellulolytic fungi, participate in the lignocellulose deconstruction through non-hydrolytic disruptive processes, such as adsorption. They include swollenins and other proteins with carbohydrate-binding modules (CBMs) involved in the first step of cellulolysis, amorphogenesis [91]. The non-catalytic mechanisms involved in amorphogenesis induce cell wall loosening and promote efficient cellulose utilization, leading to the disruption of a highly ordered cellulose matrix through its delamination, dispersion and swelling of cellulose chains into microfibrils (crystalline regions).

The previous cellulose deconstruction enhanced hydrolase access to its substrate [92]. In this sense, Ding et al. (2022) recently reported an expansion from *Talaromyces leycettanus* that binds to cellulose and breaks the hydrogen bonds within the polymer matrix through the action of specific amino acid residues [93]. The enzyme showed synergism with commercial cellulases in the pretreatment of corn straw and filter paper, proving to be a suitable tool for the efficient utilization of biomass. Therefore, since individual cellulolytic enzymes exhibit comparable activities on cellulose and/or its derivatives, synthetic cocktails composed of multi-enzyme mixtures are preferred as they display a stronger effect.

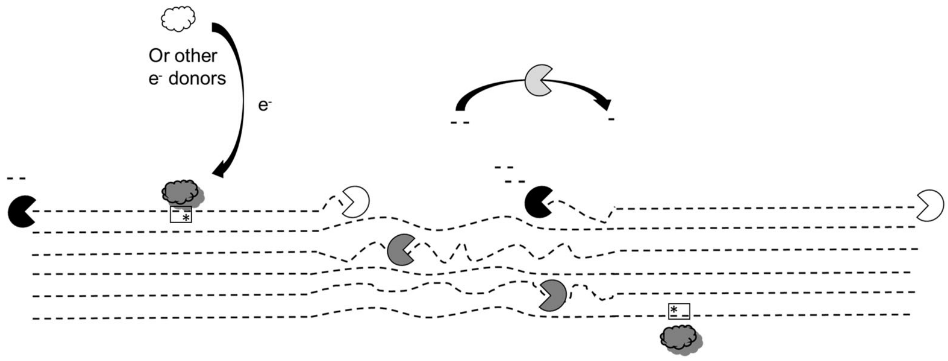

Figure 2. A model on enzymatic degradation of cellulose by aerobic fungi. The asterisk indicates oxidized monosaccharides by the enzyme activity. Pictures of Pacman correspond to hydrolytic enzymes: endoglucanases (dark gray), exoglucanases (white and black) and β-glucosidases (light gray). Cloud symbols correspond to oxidative enzymes: lytic polysaccharide monooxygenases (dark gray) and cellobiose dehydrogenases (white).

In addition to the several enzymes commercially available, such as the ones described in the previous section, some research groups in South America have investigated new fungal isolates with an outstanding ability to degrade cellulosic materials under extreme environmental conditions, leading to the characterization of enzymes capable of displaying these activities in those stressful contexts. Valencia and Chambergo (2013) reviewed the progress in Brazilian research focusing on the fungal potential for biomass degradation for bioenergy purposes [67]. Until that time, 136 isolates belonging to 23 genera and 45 species were reported, mainly represented by ascomycetes fungi of the genera *Trichoderma* (83 strains), *Aspergillus* (9 strains), *Penicillium* (4 strains), *Acremonium* (3 strains), *Thermoascus* (3 strains) and basidiomycetes belonging to *Agaricus* (1 strain), *Pycnoporus* (1 strain) and *Pleurotus* genera (2 strains). Cellulases, hemicellulases, ligninases and other auxiliary enzymes were identified and characterized in the collected fungi. A thorough review of the more recent scientific research developed in South America reporting cellulolytic enzymes from several native fungi, their taxonomic location and production systems is presented in Table 5.

Some authors suggest that each cellulolytic fungus has its own enzyme profile, which is relevant from an application point of view [95]. This premise advocates the development of enzymatic cocktails produced by native fungi isolated from biomass intended to be used as feedstock for biofuels and biorefineries. This would enhance the possibility of obtaining cocktails of substrate-specific and complementary enzymatic activities for the deconstruction of such lignocellulosic residues and of obtaining less expensive enzymatic cocktails that are tolerant to the rough conditions required for the amorphogenesis of biomass in the pretreatment stage, providing a key to the development of more profitable processes.

Early research from the group of Vega et al. (2012) aimed to find enzymes with a high tolerance for adverse conditions required for their application in industrial processes [100]. They carried out the bioprospection of plant-degrading fungi in soils from the undisturbed Macuya Forest near Pucallpa, Peru. The alkaline cellulase activity demanded by the modern textile industry was tested, and *Aspergillus* sp. LM-HP32, *Penicillium* sp. LM-HP33, and *Penicillium* sp. LM-HP37 were the best enzyme producers among the isolates. With analogous purposes, Picart et al. (2007) characterized *Penicillium* sp. CR-313 and CR-316 isolates from soil samples from the subtropical forest of Puerto Iguazú, Argentina, concluding that the thermostable cellulase secreted by CR-316, with a maximum activity registered at 65 °C, is a good candidate for industrial applications [98]. Further investigation of robust, well-adapted enzymes to rough conditions led Carrasco et al. (2016) from Chile to search for psychrotolerant yeasts capable of secreting cold-active amylases and cellulases [99]. They found *Rhodotorula glacialis* and *Mrakia blollopis* strains, which, respectively, displayed high amylase and cellulase activity under 22 °C and are therefore suitable for low-temperature industrial processes.

Table 5. Enzymes of cellulolytic systems from several aerobic fungi (of native origin), taxonomic location and production systems investigated by South American research groups.

Cellulolytic Enzyme Components and Other Ones Associated with Fungal Degradation of Plant Cell Wall	Fungal Sources	Production Systems	Reference
β-1,4 Endoglucanase, E.C. 3.2.1.4; cello-biohydrolase; E.C. 3.2.1.91; β-glucosidase, E.C. 3.2.1.21	*Ulocladium botrytis* LPSC 813 (Pleosporaceae)	Solid-state fermentation on Scutia buxifolia litter	[94]
Extracellular proteins showing cellobiohydrolase, β-glucosidase and endoglucanase activity	Fourteen white rot fungi isolated from the Misiones rainforest (Argentina) belonging to the genera *Pycnoporus* and *Trametes*	Agar and liquid cultures using specific inducers	[95]
β-1,4-endoglucanase, E.C. 3.2.1.4; β-glucosidase, EC 3.2.1.21; endo-1,4-β-xylanase, E.C. 3.2.1.8; pectin esterase, E.C. 3.1.1.11	Six compatible consortia of *Trichoderma* strains with *Aspergillus niger* or *Pleurotus ostreatus*	Solid-state fermentation on pineapple crown waste	[96]
C1-specific AA9 lytic polysaccharide monooxygenase	Recombinant protein from *Pycnoporus sanguineus* expressed in *Pichia pastoris*	Liquid cultures induced with methanol	[97]
Hydrolytic activity on different polysaccharides such as carboxy-methyl cellulose (CMC), Avicel, acid swollen cellulose, bacterial microcrystalline cellulose, laminarin, lichenan, starch, birchwood xylan and oat spelt xylan	*Penicillium* sp. CR-316 and *Penicillium* sp. CR-313 isolated from the subtropical soil of Puerto Iguazu' (Argentina)	Shaken liquid cultures on potato dextrose broth and mineral medium supplemented with CMC, Avicel or rice straw at 1%	[98]
CMCase	Yeasts isolated from the Antarctic region	Shaken liquid cultures and semi-solid ones supplemented with CMC	[99]
Alkaline cellulases	Fungi isolated from an undisturbed rainforest in Peru	Agar and liquid cultures using specific inducers	[100]

Other investigations have focused on the enzyme cocktails necessary for biomass deconstruction, using different mono- and multi-strain strategies to achieve them. Coniglio et al. (2017) studied 14 fungal isolates recovered from the rainforest of Misiones, Argentina [95]. They identified the *Trametes* sp. strain LBM033 as the best cellulase producer, with a 57 U L^{-1}, 226 U L^{-1} and 387 U L^{-1} yield of cellobiohydrolase, β-glucosidase and endoglucanase activities, respectively. Therefore, the authors concluded that this basidiomycete would be able to secrete a complete cellulolytic enzymatic complex suitable for biomass conversion. Using a novel approach, the Teixeira research group (2020) developed fungi-compatible consortia isolated from pineapple waste from Brazil [96]. Six consortia of *Trichoderma* strains with *Aspergillus niger* or *Pleurotus ostreatus* increased enzyme production compared to monoculture. The saccharification of pineapple crown waste with the consortia's enzyme cocktails produces 12.50% to 13.93% higher levels of reducing sugars. This multi-strain methodology has the potential to save costs in the manufacture of the cocktails by avoiding the step of blending the enzymes.

In recent years, the search and characterization of auxiliary enzymatic activities for biomass conversion have attracted the attention of the scientific community. In this context, Garrido and collaborators (2020) from Argentina cloned and characterized a recombinant secreted AA9 LPMO from the white-rot basidiomycete *Pycnoporus sanguineus* in the model yeast *Pichia pastoris* [97]. The synthesized enzyme boosted the activity of glycoside hydrolases from families GH1, GH5 and GH6, providing a clue to the versatility of LPMOs.

Most of the cited studies are derived from screening programs that analyze many fungal isolates belonging to different ecophysiological and taxonomic groups, such as those associated with litter, soil or wood from different habitats. Mainly, these studies used wild isolate cultures at the laboratory scale as enzyme sources, with only a few deepening their research into the specific iso-enzyme encoding sequences from selected hyperproducer strains to develop cloning strategies for their heterologous expression in biological models. Therefore, additional studies at the pilot scale in volumetric culture systems are still necessary for the identification of enzymes with enhanced stability to obtain suitable yields of cellulolytic cocktails under industrial conditions.

4. Conclusions and Future Directions

Throughout this review, the large amounts of direct and indirect residual biomass available in South America as biorefinery feedstocks were stated. Mainly, this biomass comprises the native forest sources, which are, in many cases, legally restricted or difficult to physically access; afforestation and crop exploitation, such as sugarcane, soybean and maize, constitute direct sources of biomass. The indirect sources remain more available as they are easy to locate at specific places (industries) and are free from legal restrictions. They are constituted by agroindustrial wastes, such as sugarcane bagasse and wheat straw obtained after commodity processing and highly valuable as raw materials for biofuel, and woody biomass waste, such as sawdust and wood chips. However, this potential for renewable energy generation is quite underutilized by South American countries since the major fraction of biomass waste is buried or burned. In the best cases, the combustion of residual biomass results in the thermochemical production of energy. In this context, the settlement of biorefineries in the region is still in its early stages.

The general picture retrieved from the analysis of each country report in regard to biomass availability is that a more in-depth survey of georeferenced, standardized and updated information, both on the demand and supply of biomass requirements, is needed to plan strategies and develop policies for improving biomass waste utilization. As an example, Argentina's estimations are around a surplus of 40 million annual tons of biomass suitable for energy generation, without considering the prospects of biogas generation from effluents produced in bovine and porcine feedlots and dairy farms. In conclusion, the integration of socioeconomic variables in the analysis is recommended to enable the understanding of the dynamics of bioenergy systems by studying the connection of biomass waste suppliers with plants consuming biomass for energy purposes and its strategic emplacement.

Funding: This research was funded by Consejo Nacional de Investigaciones Científicas y Técnicas CONICET of Argentina (projects PIP 11220200102016 CO, PIBAA 2872021010 0040CO and PIP 11220200100527 CO), Universidad Nacional de La Plata (project 11X-898) and Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT, PICT 2019-00207).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data was created.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ubando, A.T.; Del Rosario, A.J.R.; Chen, W.-H.; Culaba, A.B. A state-of-the-art review of biowaste biorefinery. *Environ. Pollut.* **2011**, *269*, 116149. [CrossRef]
2. Ohara, H. Biorefinery. *Appl. Microbiol. Biotechnol.* **2003**, *62*, 474–477. [CrossRef]

3. Ravindran, R.; Jaiswal, S.; Abu-Ghannam, N.; Jaiswal, A.K. A comparative analysis of pretreatment strategies on the properties and hydrolysis of brewers' spent grain. *Bioresour. Technol.* **2018**, *248*, 272–279. [CrossRef]
4. Zhang, Z.; Harrison, M.D.; Rackemann, D.W.; Doherty, W.O.S.; O'Hara, I.M. Organozolv pretreatment of plant biomass for enhanced enzymatic saccharification. *Green Chem.* **2016**, *18*, 360–381. [CrossRef]
5. Solier, Y.N.; Mocchiutti, P.; Cabrera, M.N.; Saparrat, C.M.N.; Zanuttini, M.A.; Inalbon, M.C. Alkali-peroxide treatment of sugar cane bagasse. Effect of chemical charges on the efficiency of xylan isolation and susceptibility of bagasse to saccharification. *Biomass Conv. Bioref.* **2022**, *12*, 567–576. [CrossRef]
6. Madadi, M.; Tu, Y.; Abbas, A. Recent status on enzymatic saccharification on lignocellulosic biomass for bioethanol production. *Electron. J. Biol.* **2017**, *13*, 135–143.
7. Alegre, M. *FAO Update of Biomass Balance for Energy Purposes in Argentina (In Spanish). Technical Documents Collection N° 19, Buenos Aires, Argentina*; FAO: Rome, Italy, 2020. [CrossRef]
8. Rojas Ponce, Y.; Meza Robayo, J.A. *Production and Consumption of Wood Fuels Spatial Analysis Using the Wisdom Method: Basis for a National Wood Energy Strategy*; Instituto Forestal INFOR: Santiago, Chile, 2010. (In Spanish) [CrossRef]
9. Pirelli, T.; Rossi, A. Sustainability of Forest Biomass for Energy and of Ethanol from Maize and Sugarcane in Paraguay. Results and Recommendations from the Implementation of the Global Bioenergy Partnership Indicators. Environmental and Natural Resources Management. Working Paper, No. 70, FAO. 2018. Available online: https://www.fao.org/publications (accessed on 10 April 2023). (In Spanish)
10. Biometrans. Biomethane Production for Transport Fuel from Waste Biomass. Diagnosis of Biomass Resources available in Latin America. CYTED Ciencia y Tecnología para el Desarrollo. 2018. Available online: http://cyted.org/sites/default/files/d1._diagnostico_de_los_recursos_de_biomasa_disponibles.pdf (accessed on 10 April 2023). (In Spanish)
11. Assureira Espinoza, E.G.; Assureira Espinoza, M.A. *Energy Potential of Waste Biomass in Peru*; Pontificia Universidad Católica del Perú: Lima, Perú, 2015. (In Spanish)
12. Welfle, A. Balancing growing global bioenergy resource demands—Brazil's biomass potential and the availability of resource for trade. *Biomass Bioenergy* **2017**, *105*, 83–95. [CrossRef]
13. Forster-Carneiro, T.; Berni, M.D.; Dorileo, I.L.; Rostagno, M.A. Biorefinery study of availability of agriculture residues and wastes for integrated biorefineries in Brazil. *Resour. Conserv. Recy.* **2013**, *77*, 78–88. [CrossRef]
14. Lorenzo, I. Circular Economy and Climate Change. Proyecto Biovalor, Ministerio de Industria, Energía y Minería, Uruguay. 2020. Available online: Biovalor.gov.uy (accessed on 10 April 2023). (In Spanish)
15. Quantification of Waste Generated in Agroindustrial Sectors Uruguay 2016. Technical Data Sheets. Available online: https://biovalor.gub.uy/materiales/ (accessed on 10 April 2023). (In Spanish)
16. Forestry Sector in Uruguay. Forestry Report. Uruguay XXI, Investment, Export and Country Brand Promotion Agency 2022. Available online: https://www.uruguayxxi.gub.uy/uploads/informacion/2ec25967b8d7bfd72de685fbe8d201e06b5507bd.pdf (accessed on 10 April 2023).
17. del Pino, A.; Hernández, J.; Arrarte, G. Nutrient export with logs, and release from residues, after harvest of a *Pinus taeda* plantation in Uruguay. *Open J. For.* **2020**, *10*, 360–376. [CrossRef]
18. Boragno, L.; Boscana, M. Forest Statistics 2022. Dirección General Forestal, Ministerio de Ganadería, Agricultura y Pesca, Uruguay. 2022. Available online: https://www.gub.uy/ministerio-ganaderia-agricultura-pesca/datos-yestadisticas/estadisticas/boletin-estadisticas-forestales-2022 (accessed on 10 April 2023). (In Spanish)
19. Area, M.C.; Vallejos, M.E. Biorrefinería a Partir de Residuos Lignocelulósicos: Conversión de Residuos a Productos de alto Valor. Editorial Académica Española, España. 2012. Available online: https://www.researchgate.net/publication/262933028_Biorrefineria_a_partir_de_residuos_lignocelulosicos_Conversion_de_residuos_a_productos_de_alto_valor (accessed on 15 April 2023).
20. Studer, M.H.; DeMartini, J.D.; Davis, M.F.; Sykes, R.W.; Davison, B.; Keller, M.; Tuskan, G.A.; Wyman, C.E. Lignin content in natural Populus variants affects sugar release. *Proc. Nat. Acad. Sci. USA* **2011**, *108*, 6300–6305. [CrossRef]
21. Rahikainen, J.; Mikander, S.; Marjamaa, K.; Tamminem, T.; Lappas, A.; Viikari, L.; Kruus, K. Inhibition of enzymatic hydrolysis by residual lignins from softwood-study of enzyme binding and inactivation on lignin-rich surface. *Biotechnol. Bioeng.* **2011**, *108*, 2823–2834. [CrossRef] [PubMed]
22. Hu, F.; Jung, S.; Ragauskas, A. Pseudo-lignin formation and its impact on enzymatic hydrolysis. *Bioresour. Technol.* **2012**, *117*, 7–12. [CrossRef] [PubMed]
23. García, A.; Alriols, M.G.; Labidi, J. Evaluation of different lignocellulosic raw materials as potential alternative feedstocks in biorefinery processes. *Ind. Crops Prod.* **2014**, *53*, 102–110. [CrossRef]
24. Bak, J.S.; Ko, J.K.; Choi, I.G.; Park, Y.-C.; Seo, J.-H.; Kim, K.H. Fungal pretreatment of lignocellulose by Phanerochaete chrysosporium to produce ethanol from rice straw. *Biotechnol. Bioeng.* **2009**, *104*, 471–482. [CrossRef] [PubMed]
25. Lempiäinen, H.; Lappalainen, K.; Haverinen, J.; Tuuttila, T.; Hu, T.; Jaakkola, M.; Lassi, U. The effect of mechanocatalytic pretreatment on the structure and depolymerization of willow. *Catalysts* **2020**, *10*, 255. [CrossRef]
26. Stolarski, M.J.; Szczukowski, S.; Tworkowski, J.; Wróblewska, H.; Krzyżaniak, M. Short rotation willow coppice biomass as an industrial and energy feedstock. *Ind. Crops Prod.* **2011**, *33*, 217–223. [CrossRef]
27. Han, S.-H.; Cho, D.H.; Kim, Y.H.; Shin, S.-J. Biobutanol production from 2-year-old willow biomass by acid hydrolysis and acetone–butanol–ethanol fermentation. *Energy* **2013**, *61*, 13–17. [CrossRef]

28. Tomás-Pejó, E.; Oliva, J.M.; Ballesteros, M. Realistic approach for full-scale bioethanol production from lignocellulose: A review. *J. Sci. Ind. Res.* **2008**, *67*, 874–884.
29. Álvarez, C.; Reyes-Sosa, F.M.; Díez, B. Enzymatic hydrolysis of biomass from wood. *Microb. Biotechnol.* **2016**, *9*, 149–156. [CrossRef]
30. Negro, M.J.; Manzanares, P.; Ballesteros, I.; Oliva, J.M.; Cabañas, A.; Ballesteros, M. Hydrothermal pretreatment conditions to enhance ethanol production from poplar biomass. *Appl. Biochem. Biotechnol.* **2003**, *105*, 87–100. [CrossRef]
31. Muñoz, C.; Mendonça, R.; Baeza, J.; Berlin, A.; Saddler, J.; Freer, J. Bioethanol production from bio-organosolv pulps of *Pinus radiata* and *Acacia dealbata*. *J. Chem. Technol. Biotechnol.* **2007**, *82*, 767–774. [CrossRef]
32. Gutiérrez, A.; Rencoret, J.; Cadena, E.M.; Rico, A.; Barth, D.; del Río, J.C.; Martínez, A.T. Demonstration of laccase-based removal of lignin from wood and non-wood plant feedstocks. *Bioresour. Technol.* **2012**, *119*, 114–122. [CrossRef] [PubMed]
33. Martín-Sampedro, R.; Eugenio, M.E.; García, J.C.; López, F.; Villar, J.C.; Díaz, M.J. Steam explosion and enzymatic pre-treatments as an approach to improve the enzymatic hydrolysis of Eucalyptus globulus. *Biomass Bioenergy* **2012**, *42*, 97–106. [CrossRef]
34. Gallina, G.; Cabeza, A.; Grénman, H.; Biasi, P.; García-Serna, J.; Salmi, T. Hemicellulose extraction by hot pressurized water pretreatment at 160 °C for 10 different woods: Yield and molecular weight. *J. Supercrit. Fluids* **2018**, *133*, 716–725. [CrossRef]
35. Cara, C.; Ruiz, E.; Ballesteros, M.; Manzanares, P.; Negro, M.J.; Castro, E. Production of fuel ethanol from steam-explosion pretreated olive tree pruning. *Fuel* **2008**, *87*, 692–700. [CrossRef]
36. Mateo, S.; Roberto, I.C.; Sánchez, S.; Moya, A.J. Detoxification of hemicellulosic hydrolyzate from olive tree pruning residue. *Ind. Crops Prod.* **2013**, *49*, 196–203. [CrossRef]
37. Sabanci, K.; Buyukkileci, A.O. Comparison of liquid hot water, very dilute acid and alkali treatments for enhancing enzymatic digestibility of hazelnut tree pruning residues. *Bioresour. Technol.* **2018**, *261*, 158–165. [CrossRef]
38. Kaur, S.; Dhillon, G.S.; Sarma, S.J.; Brar, S.K.; Misra, K.; Oberoi, H.S. Waste biomass: A prospective renewable resource for development of bio-based economy/processes. In *Biotransformation of Waste Biomass into High Value Biochemical*; Springer: New York, NY, USA, 2014; pp. 3–28. [CrossRef]
39. Borel, L.D.M.S.; Lira, T.S.; Ribeiro, J.A.; Ataíde, C.H.; Barrozo, M.A.S. Pyrolysis of brewer's spent grain: Kinetic study and products identification. *Ind. Crops Prod.* **2018**, *121*, 388–395. [CrossRef]
40. Lobo Gomes, C.; Gonçalves, E.; Galeano Suarez, C.A.; de Souza Rodrigues, D.; Cavalcanti Montano, I. Effect of reaction time and sodium hydroxide concentration on delignification and enzymatic hydrolysis of brewer's spent grain from two Brazilian brewers. *Cell Chem. Technol.* **2021**, *55*, 101–112. [CrossRef]
41. Han, M.; Kang, K.E.; Kim, Y.; Choi, G.-W. High efficiency bioethanol production from barley straw using a continuous pretreatment reactor. *Process Biochem.* **2013**, *48*, 488–495. [CrossRef]
42. González, W.A.; López, D.; Pérez, J.F. Biofuel quality analysis of fallen leaf Pellets: Effect of moisture and glycerol contents as binders. *Renew. Energy* **2020**, *147*, 1139–1150. [CrossRef]
43. de Moraes Rocha, G.J.; Marcos Nascimento, V.; Gonçalves, A.R.; Fernandes Nunes Silva, V.; Martín, C. Influence of mixed sugarcane bagasse samples evaluated by elemental and physical–chemical composition. *Ind. Crops Prod.* **2015**, *64*, 52–58. [CrossRef]
44. Area, M.; Felissia, F.; Vallejos, M. Ethanol-water fractionation of sugar cane bagasse catalyzed with acids. *Cell Chem. Technol.* **2009**, *43*, 271–279.
45. Larrahondo, J.E. Calidad de la Caña de Azucar. In *El Cultivo de la Caña en la Zona Azucarera de Colombia*; Cenicaña: Cali, Colombia, 1995; pp. 337–354.
46. Marrugo, G.; Valdés, C.F.; Chejne, F. Characterization of Colombian agroindustrial biomass residues as energy resources. *Energy Fuels* **2016**, *30*, 8386–8398. [CrossRef]
47. Sagastume Gutiérrez, A.; Eras, J.J.C.; Hens, L.; Vandecasteele, C. The energy potential of agriculture, agroindustrial, livestock, and slaughterhouse biomass wastes through direct combustion and anaerobic digestion. The case of Colombia. *J. Clean. Prod.* **2020**, *269*, 122317. [CrossRef]
48. Echeverría, C.; Bazán, G.; Sánchez-Gonzalez, J.; Lescano, L.; Pagador, S.; Linares, G. Pre-treatment by acidification and freezing on corncob polymers and its enzymatic hydrolysis. *Asian J. Sci. Res.* **2018**, *11*, 222–231. [CrossRef]
49. Correia Vieira, R.; Corrêa Antunes, D.P.; Rodrigues dos Santos-Rocha, M.S.; Lopes Barbosa, K.; Cabral dos Santos Silva, M.; Gomes, M.A.; Garcia Almeida, R.M.R. Enzymatic hydrolisis optimization from corn wastes by experimental design. *Int. J. Eng. Sci.* **2017**, *6*, 9–15.
50. Rambo, M.K.D.; Schmidt, F.L.; Ferreira, M.M.C. Analysis of the lignocellulosic components of biomass residues for biorefinery opportunities. *Talanta* **2015**, *144*, 696–703. [CrossRef] [PubMed]
51. Cabrera, E.; Muñoz, M.J.; Martín, R.; Caro, I.; Curbelo, C.; Díaz, A.B. Comparison of industrially viable pretreatments to enhance soybean straw biodegradability. *Bioresour. Technol.* **2015**, *194*, 1–6. [CrossRef]
52. Fermanelli, C.S.; Córdoba, A.; Pierella, L.B.; Saux, C. Pyrolysis and copyrolysis of three lignocellulosic biomass residues from the agro-food industry: A comparative study. *Waste Manag.* **2020**, *102*, 362–370. [CrossRef]
53. Espinosa, E.; Sánchez, R.; Otero, R.; Domínguez-Robles, J.; Rodríguez, A. A comparative study of the suitability of different cereal straws for lignocellulose nanofibers isolation. *Int. J. Biol. Macromol.* **2017**, *103*, 990–999. [CrossRef]
54. Dagnino, E.P.; Chamorro, R.E.; Romano, S.D.; Felissia, F.E.; Area, M.C. Optimization of rice hulls acid pretreatment and its characterization as a potential substrate for bioethanol production. *Ind. Crops Prod.* **2013**, *42*, 363–368. [CrossRef]

55. Zhao, T.; Chen, Z.; Lin, X.; Ren, Z.; Li, B.; Zhang, Y. Preparation and characterization of microcrystalline cellulose (MCC) from tea waste. *Carbohydr. Polym.* **2018**, *184*, 164–170. [CrossRef] [PubMed]
56. Rodríguez, R.; Mazza, G.; Fernández, A.; Saffe, A.; Echegaray, M. Prediction of the lignocellulosic winery wastes behavior during gasification process in fluidized bed: Experimental and theoretical study. *J. Environ. Chem. Eng.* **2018**, *6*, 5570–5579. [CrossRef]
57. Giménez, M.; Rodríguez, M.; Montoro, L.; Sardella, F.; Rodríguez-Gutierrez, G.; Monetta, P.; Deiana, C. Two phase olive mill waste valorization. Hydrochar production and phenols extraction by hydrothermal carbonization. *Biomass Bioenergy* **2020**, *143*, 105875. [CrossRef]
58. Guerrero, A.B.; Aguado, P.L.; Sánchez, J.; Curt, M.D. GIS Based assessment of banana residual biomass potential for ethanol production and power generation: A case ctudy. *Waste Biomass Valor.* **2015**, *7*, 405–415. [CrossRef]
59. Collazo-Bigliardi, S.; Ortega-Toro, R.; Chiralt Boix, A. Isolation and characterization of microcrystalline cellulose and cellulose nanocrystals from coffee husk and comparative study with rice husk. *Carbohydr. Polym.* **2018**, *191*, 205–215. [CrossRef] [PubMed]
60. Raju, G.U.; Kumarappa, S.; Gaitonde, V.N. Mechanical and physical characterization of agricultural waste reinforced polymer composites. *J. Mater. Environ. Sci.* **2012**, *3*, 907–916.
61. Stoffel, R.B.; Felissia, F.E.; Curvelo, A.A.S.; Gassa, L.M.; Area, M.C. Desresinación Alcalina y Tratamiento Ácido de Aserrín de Pino Destinado a Biorrefinería. In Proceedings of the 45° Congresso Internacional de Celulose e Papel da ABTCP/VII Congresso Ibero-Americano de Pesquisa de Celulose e Papel, Sao Paulo, Brasil, 9–11 October 2012. Available online: https://www.celso-foelkel.com.br/artigos/outros/2012_Desresinacao_serragem_pinus.pdf (accessed on 15 April 2023).
62. Stoffel, R.B.; Felissia, F.E.; Gassa, L.; Area, M.C. Biorrefinería a Partir de Residuos de la Industrialización Primaria de Pino: Caracterización de Materias Primas. In Proceedings of the VIII Jornadas Científico-Tecnológicas, FCEQYN, UNaM, Posadas, Argentina, 2–4 November 2011.
63. Hornus, M. *Optimización de la Extracción de Hemicelulosas de Aserrín de Eucalyptus Mediante Tratamiento Hidrotérmico*; Informe Beca de Estímulo a las Vocaciones Científicas: Posadas, Argentina, 2012.
64. Dagnino, E.P.; Chamorro, E.R.D.; Romano, S.; Felissia, F.E.; Area, M.C. Optimización de prehidrólisis de aserrín de Prosopis nigra para la producción de azúcares fermentables. In Proceedings of the 45° Congresso Internacional de Celulose e Papel da ABTCP/VII Congresso Ibero-Americano de Pesquisa de Celulose e Papel, Sao Paulo, Brasil, 9–11 October 2012.
65. Magalhães, A.I.; de Carvalho, J.C.; de Melo Pereira, G.V.; Karp, S.G.; Camara, M.C.; Coral Medina, J.D.; Soccol, C.R. Lignocellulosic biomass from agro-industrial residues in South America: Current developments and perspectives. *Biofuels Bioprod. Bioref.* **2019**, *13*, 1505–1519. [CrossRef]
66. Mankar, A.R.; Pandey, A.; Modak, A.; Pant, K. Pretreatment of lignocellulosic biomass: A review on recent advances. *Bioresour. Technol.* **2021**, *334*, 125235. [CrossRef]
67. Valencia, E.Y.; Chambergo, F.S. Mini-review: Brazilian fungi diversity for biomass degradation. *Fungal Genet. Biol.* **2013**, *60*, 9–18. [CrossRef] [PubMed]
68. Liguori, R.; Soccol, C.R.; de Souza Vandenberghe, L.; Woiciechowski, A.L.; Faraco, V. Second generation ethanol production from brewer's spent grain. *Energies* **2015**, *8*, 2575–2586. [CrossRef]
69. Mussatto, S.I.; Fernandes, M.; Dragone, G.; Mancilha, I.M.; Roberto, I.C. Brewer´s spent grain as raw material for lactic acid production by Lactobacillus delbrueckii. *Biotechnol. Lett.* **2007**, *29*, 1973–1976. [CrossRef] [PubMed]
70. Mussatto, S.I.; Fernandes, M.; Milagres, A.M.F.; Roberto, I.C. Effect of hemicellulose and lignin on enzymatic hydrolysis of cellulose from brewer´s spent grain. *Enz. Microb. Technol.* **2008**, *43*, 124–129. [CrossRef]
71. Mussatto, S.I.; Fernandes, M.; Mancilha, I.M.; Roberto, I.C. Effect of medium supplementation and pH control on lactic acid production from brewer´s spent grain. *Biochem. Eng. J.* **2008**, *40*, 437–444. [CrossRef]
72. Dávila, J.A.; Rosenberg, M.; Cardona, C.A. A biorefinery approach for the production of xylitol, ethanol and polyhydroxybutyrate from brewer's spent grain. *AIMS Agric. Food* **2016**, *1*, 52–66. [CrossRef]
73. Mamaní, A.M.; Maturano, Y.; Herrero, L.; Montoro, L.; Sardella, F. Increase in fermentable sugars of olive tree pruning biomass for bioethanol production: Application of an experimental design for optimization of alkaline pretreatment. *Period Polytech. Chem. Eng.* **2022**, *66*, 269–278. [CrossRef]
74. Stoffel, R.B.; Vinholi Neves, P.; Felissia, F.E.; Pereira Ramos, L.; Gassa, L.M.; Area, M.C. Hemicellulose extraction from slash pine sawdust by steam explosion with sulfuric acid. *Biomass Bioenergy* **2017**, *107*, 93–101. [CrossRef]
75. Rodriguez, M.D.; Castrillo, M.L.; Velázquez, J.E.; Kramer, G.R.; Sedler, C.I.; Zapata, P.D.; Villalba, L. Obtención de azúcares fermentables a partir de aserrín de pino pretratado secuencialmente con ácido-base. *Rev. Int. Contam. Ambie* **2017**, *33*, 317–324. [CrossRef]
76. Kruyeniski, J.; Ferreira, P.J.T.; Videira Sousa Carvalho, M.G.; Vallejos, M.E.; Felissia, F.E.; Area, M.C. Physical and chemical characteristics of pretreated slash pine sawdust influence its enzymatic hydrolysis. *Ind. Crops Prod.* **2019**, *130*, 528–536. [CrossRef]
77. Mendieta, C.M.; Felissia, F.E.; Arismendy, A.M.; Kruyeniski, J.; Area, M.C. Enzymatic hydrolysis and fermentation strategies for biorefining of pine sawdust. *Bioresources* **2021**, *16*, 7474–7491. [CrossRef]
78. Valenzuela, R.; Priebe, X.; Troncoso, E.; Ortega, I.; Parra, C.; Freer, J. Fiber modifications by organosolv catalyzed with H_2SO_4 improves the SSF of *Pinus radiata*. *Ind. Crops Prod.* **2016**, *86*, 79–86. [CrossRef]
79. Moncada, J.; Cardona, C.A.; Higuita, J.C.; Vélez, J.J.; López-Suarez, F.E. Wood residue (*Pinus patula* bark) as an alternative feedstock for producing ethanol and furfural in Colombia: Experimental, technoeconomic and environmental assessments. *Chem. Eng. Sci.* **2016**, *140*, 309–318. [CrossRef]

80. Santos, V.T.O.; Esteves, P.J.; Milagres, A.M.F.; Carvalho, W. Characterization of commercial cellulases and their usein the saccharification of a sugarcane bagasse sample pretreatedwith dilute sulfuric acid. *J. Ind. Microbiol. Biotechnol.* **2011**, *38*, 1089–1098. [CrossRef]
81. Araújo Barcelos, C.; Nobuyuki Maeda, R.; Vargas Betancur, G.J.; Pereira Jr, N. The essentialness of delignification on enzymatic hydrolysis of sugar cane bagasse cellulignin for second generation ethanol production. *Waste Biomass Valor.* **2013**, *4*, 341–346. [CrossRef]
82. Cerqueira Pereira, S.; Maehara, L.; Monteiro Machado, C.M.; Sanchez Farinas, C. 2G ethanol from the whole sugarcane lignocellulosic biomass. *Biotechnol. Biofuels* **2015**, *8*, 44. [CrossRef]
83. Neves, P.V.; Pitarelo, A.P.; Ramos, L.P. Production of cellulosic ethanol from sugarcane bagasse by steam explosion: Effect of extractives content, acid catalysis and different fermentation technologies. *Bioresour. Technol.* **2016**, *208*, 184–194. [CrossRef] [PubMed]
84. Terán Hilares, R.; dos Santos, J.C.; Ahmed, M.A.; Jeon, S.H.; da Silva, S.S.; Han, J.I. Hydrodynamic cavitation-assisted alkaline pretreatment as a new approach for sugarcane bagasse biorefineries. *Bioresour. Technol.* **2016**, *214*, 609–614. [CrossRef]
85. Aguiar, M.M.; Pietroboni, V.C.; Moura de Salles, M.; Pupo, M.; Hortense Torres, N.; Américo, J.H.P.; Richard Salazar-Banda, G.; Silva, D.P.; Rosim Monteiro, D.T.; Romanholo Ferreira, L.F. Evaluation of comercial cellulolytic enzymes for sugarcane bagasse hydrolysis. *Cellul. Chem. Technol.* **2018**, *52*, 695–699.
86. de Carvalho Silvello, M.A.; Martínez, J.; Goldbeck, R. Increase of reducing sugars release by enzymatic hydrolysis of sugarcane bagasse intensified by ultrasonic treatment. *Biomass Bioenergy* **2019**, *122*, 481–489. [CrossRef]
87. de Carvalho Silvello, M.A.; Martínez, J.; Goldbeck, R. Alternative technology for intensification of fermentable sugars released from enzymatic hydrolysis of sugarcane bagasse. *Biomass Conv. Bioref.* **2022**, *12*, 2399–2405. [CrossRef]
88. Camesasca, L.; Ramírez, M.B.; Guigou, M.; Ferrari, M.D.; Lareo, C. Evaluation of dilute acid and alkaline pretreatments, enzymatic hydrolysis and fermentation of napiergrass for fuel ethanol production. *Biomass Bioenergy* **2015**, *74*, 193–201. [CrossRef]
89. Gallego, L.J.; Escobar, A.; Peñuela, M.; Peña, J.D.; Rios, L.A. King Grass: A promising material for the production of second-generation butanol. *Fuel* **2015**, *143*, 399–403. [CrossRef]
90. Dimarogona, M.; Topakas, E.; Christakopoulos, P. Recalcitrant polysaccharide degradation by novel oxidative biocatalysts. *Appl. Microbiol. Biotechnol.* **2013**, *97*, 8455–8465. [CrossRef] [PubMed]
91. Gourlay, K.; Arantes, V.; Saddler, J.N. Use of substructure-specific carbohydrate binding modules to track changes in cellulose accessibility and surface morphology during the amorphogenesis step of enzymatic hydrolysis. *Biotechnol. Biofuels* **2012**, *5*, 51. [CrossRef]
92. Várnai, A.; Mäkelä, M.R.; Djajadi, D.T.; Rahikainen, J.; Hatakka, A.; Viikari, L. Carbohydrate-binding modules of fungal cellulases: Occurrence in nature, function, and relevance in industrial biomass conversion. *Adv. Appl. Microbiol.* **2014**, *88*, 103–165. [CrossRef] [PubMed]
93. Ding, S.; Liu, X.; Hakulinen, N.; Taherzadeh, M.J.; Wang, Y.; Wang, Y.; Qin, X.; Wang, X.; Yao, B.; Luo, H.; et al. Boosting enzymatic degradation of cellulose using a fungal expansin: Structural insight into the pretreatment mechanism. *Bioresour. Technol.* **2022**, *358*, 127434. [CrossRef]
94. Saparrat, M.C.N.; Arambarri, A.M.; Balatti, P.A. Growth response and extracellular enzyme activity of *Ulocladium botrytis* LPSC 813 cultured on carboxy-methylcellulose under a pH range. *Biol. Fertil. Soil* **2007**, *44*, 383–386. [CrossRef]
95. Coniglio, R.O.; Fonseca, M.I.; Villalba, L.L.; Zapata, P.D. Screening of new secretory cellulases from different supernatants of white rot fungi from Misiones, Argentina. *Mycology* **2017**, *8*, 1–10. [CrossRef]
96. Teixeira, W.F.A.; Batista, R.D.; do Amaral Santos, C.C.A.; Chagas Freitas Júnior, A.; Franchini Terrasan, C.R.; Pinheiro, R.; de Santana, M.W.; Gonçalves de Siqueira, F.; Coutinho de Paula-Elias, F.; de Almeida, A.F. Minimal enzymes cocktail development by filamentous fungi consortia in solid-state cultivation and valorization of pineapple crown waste by enzymatic saccharification. *Waste Biomass Valor.* **2021**, *12*, 2521–2539. [CrossRef]
97. Garrido, M.M.; Landoni, M.; Sabbadin, F.; Valacco, M.P.; Couto, A.; Bruce, N.C.; Wirth, S.A.; Campos, E. PsAA9A, a C1-specific AA9 lytic polysaccharide monooxygenase from the white-rot basidiomycete *Pycnoporus sanguineus*. *Appl. Microbiol. Biotechnol.* **2022**, *104*, 9631–9643. [CrossRef] [PubMed]
98. Picart, P.; Diaz, P.; Pastor, F.I. Cellulases from two *Penicillium* sp. strains isolated from subtropical forest soil: Production and characterization. *Lett. Appl. Microbiol.* **2007**, *45*, 108–113. [CrossRef] [PubMed]
99. Carrasco, M.; Villarreal, P.; Barahona, S.; Alcaíno, J.; Cifuentes, V.; Baeza, M. Screening and characterization of amylase and cellulase activities in psychrotolerant yeasts. *BMC Microbiol.* **2016**, *16*, 21. [CrossRef] [PubMed]
100. Vega, K.; Villena, G.K.; Sarmiento, V.H.; Ludueña, Y.; Vera, N.; Gutiérrez-Correa, M. Production of alkaline cellulase by fungi isolated from an undisturbed rain forest of Peru. *Biotechnol. Res. Int.* **2012**, *2012*, 934325. [CrossRef] [PubMed]