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Analysis of the lignocellulosic components of biomass residues for biorefinery opportunities

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ABSTRACT

The present study aims to identify the renewable resources available in Brazil such as açai seed, coconut husks, coffee husks, rice husks, eucalyptus sawdust, grass, soy peel, bamboo, banana stems and banana stalks. To identify such renewable energy sources, samples were examined for their physical and chemical characteristics using X-ray diffraction (XRD), proximate and ultimate analyses, thermogravimetric analysis (TGA), calorific value determination, near-infrared (NIR) spectroscopy, UV spectroscopy, high-pH anion-exchange chromatography (HPAEC-PAD) and accelerated solvent extraction (ASE). Among the biomasses, açai and coffee exhibited higher total sugar content, 67.70% and 62.55%, respectively. Sawdust exhibited low ash, along with the highest calorific value and lignin content. The highest glucose contents were observed in bamboo (44.65%) and sawdust (38.80%). The maximum yield for the bioproducts levulinic acid (LA), formic acid (FA) and furfural were estimated; açai exhibited the highest yield of LA and FA, while coffee exhibited the best furfural yield. All of these properties indicate that the residues are potential candidates for bioenergy production.

1. Introduction

The levels of greenhouse gases in the atmosphere, the worldwide dependence on fossil fuel-based energy sources and the global energy consumption have drastically increased in the last few decades. As a result, an increasing number of attempts have been made to identify cost-effective renewable energy sources. Among the potential resources, lignocelluloses are the only biomasses presently available in the amounts required to displace fossil fuels, with a world production of approximately 220 billion oven-dry tons (ODTs) per year [1]. This level of biomass production has led to the concept of biorefining, a process that integrates biomass conversion processes and equipment to produce multiple fuels, power and chemicals from biomass [2].

Therefore, biorefining increases the possibilities of diversification and decentralization of energy supplies and encourages energy self-sufficiency at the local and national levels. Lignocellulosic biomass is a renewable raw feedstock for conversion into liquids, gases, fuels, chemicals and other thermochemical products relevant to industry, and in most cases, lignocellulosic biomass remains an untapped resource [3].

There is an ongoing debate regarding whether our food supply should be sacrificed for use as energy crops. The efficient utilization of forestry and agri-food industry residues that do not compete with food production is of great importance, not only for minimizing the environmental impact but also for obtaining higher profitability [4].

Latin America is estimated to have the highest biomass potential, after accounting for food production and resource constraints [5]. Brazil is one of the most prominent producers of biomass residues, with abundant and renewable energy sources [6]. Apart from sugarcane bagasse and straw, other biomass sources from agricultural residues should be considered to prevent overdependence on a single resource [1]. Some of these other biomass sources are rice husks, açai seed, eucalyptus sawdust, coconut husks, coffee husks, elephant grass, bamboo, soy peels, banana stems and banana stalks. Elephant grass and bamboo are not residues from any agricultural industries, but they are energy-producing crops by themselves and are very promising for use in biorefineries.

Rice husks (*Oryza sativa*) are abundant lignocellulosic waste, with an annual rice production in 2014/2015 of 481 million tons [7]. Brazil is the most important Latin American producer of rice husks, producing a total of 16.5 million tons [7]. Every 4 t of rice harvested is accompanied by the production of 1 t of husks [8]. The options for the disposition of rice residues are limited by the

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high silicon content, slow decomposition in the soil and high mineral content [9].

Soybean (*Glycine max*) is a major crop in the world, with an estimated 2014/2015 production of approximately 238 million tons [7]. With 85.7 million tons produced, Brazil is the second the largest soybean producer in the world. For every kilogram of soybean produced, 0.08 kg of husk is generated (8%) [10]. Part of this byproduct is used in the animal feed industry due to the high fiber content and low lignin content [11].

Brazil is known as the largest producer of coffee (*Coffea arabica* L.), producing 2.7 million tons of the 8.5 million total tons produced in the world in 2014 [12]. Of the several residues generated from harvesting, processing, and consumption, the husks are the main byproducts of the coffee industry. For every ton of coffee produced, 0.18 t of husks are produced [13]. The husks are used for various purposes because they are rich in carbohydrates and other nutrients [14]. However, considering the large amounts generated, there is still a need to find alternative uses for this solid residue.

Bananas (*Musa paradisiaca* L.) and their residual biomasses (stems and stalks) are a potential feedstock. Annually, approximately 95.6 million tons of bananas are produced, with a total production of 6.9 million tons in Brazil [7,15]. From this production, approximately 20 million tons of stems and 1 million tons of stalks are generated.

Brazil produces a substantial amount of lignocellulosic agricultural waste such as coconut biomass (*Cocos nucifera* L.), with approximately 1.8 billion coconuts produced annually, corresponding to 2.7 million tons [16]. The fibers are obtained from the mesocarp and represent approximately 25% of the coconut fruit mass [17]. Coconut fibers can easily be used for the biorefinery process because they consist mainly of carbohydrate.

Bamboo biomass (*Bambusa vulgaris*) receives the most attention due to the high growth rate, the short renovation period under various soil and climate conditions and the easy propagation [18].

Another potential biorefinery feedstock is eucalyptus sawdust (*Eucalyptus globulus*), which is produced in large quantities by sawmills and is not completely used by the wood industry [19]. Brazil has highly developed forest plantations dominated by eucalyptus species, with an estimated planted area that is over 4.8 million hectares [20].

Elephant grass (*Miscanthus gigantus*) is a lignocellulosic material that has attracted interest due to its high calorific value, abundance (over 40 t of dry biomass is produced per hectare/year) and short production cycle (6 months) [21].

The potential of the açai seed (*Euterpe oleracea* Mart.) was also evaluated. Brazil is the largest world producer of açai, producing 112.676 t/year of the fruit, of which 93.521 t/year is residue (seed). Interest in açai has recently risen due to its high content of carbohydrate compounds [22].

Some characterization studies on the use of waste nonfood biomass for chemical, physical, biological and thermal conversion processes have been reported. Examples include studies that investigated the utilization of rice husk [9]; bioethanol production from rice straw, bagasse, corn and wheat straw [23]; banana biomass as a potential renewable energy resource [15]; the hydrolysis of bamboo for the production of fuel ethanol [18]; the production of ethanol using soybean carbohydrates [10]; ethanol production from coffee industry waste hydrolysates [13]; grass (elephant and Bermuda grass) as a feedstock for biofuel production [21,24]; the acid hydrolysis of wood sawdust for xylose production [19]; and biorefining opportunities using different plant biomass [2].

Characterization of biomasses as a feedstock for chemical production requires a knowledge of the physicochemical characteristics of the biomass. These characteristics depend on the variability of different proportions of lignin, carbohydrates, moisture, ash, extractives, etc., in the feedstocks. For example, moisture and ash are important parameters if direct burning or pyrolysis is the goal [25]. A high nitrogen concentration reduces the hydrocarbon yield during thermochemical conversion. The calorific value of a biomass is an indication of the energy value of the fuel [26]. The lignin content is an important parameter in considering the application of fibers in pulping, pyrolysis and bio-oil production [27]. Finally, high extractive content can negatively interfere with the analytical results for lignin [28]. A high sugar content favors products with high economic value, such as organic acids, biofuels and other chemicals [29,30].

This study presents a detailed characterization of 10 different Brazilian biomasses that are abundant and discarded without proper disposal.

2. Material and methods

2.1. Samples

The rice husks and soy peels were harvested during May to August of 2011 in the south region (state of Rio Grande do Sul) where the largest producers in Brazil are located. The coffee husks, bamboo, elephant grass and sawdust samples were collected in 2011 (March and April), and all of this biomass originated from the southeast region of Brazil (state of São Paulo). The açai seed was obtained from the north (state of Pará), while the coconut fibers were obtained from the northeast regions (state of Bahia). The banana residues were collected across the country, from the south to the north. All of the samples were properly frozen during transportation to avoid the degradation of their properties.

Approximately 500 g of each biomass was cut into small pieces (1 cm × 1 cm × 0.5 cm), mixed, and dried at 105 °C using the primary oven-dry method as defined in ASTM D-3173-87 [31] until a constant weight was achieved. The samples were then ground with a Romer micromill (Romer Labs, São Paulo, Brazil) and sieved ($180 > \times > 850$ µm) for future chemical and physical analyses.

All of the analyses were performed in duplicate, and the standard deviations from the duplicates were less than 0.50% for the extractives, lignins, calorific value, ash, volatile matter, fixed carbon and moisture. For elemental and carbohydrate analyses, all of the results had a standard deviation of less than 1.00%.

2.2. Chemical analyses

2.2.1. Extraction

Approximately 10 g of each sample was extracted with 95% ethanol via the accelerated solvent extraction method using the Dionex ASE 200 system (Thermo Fisher Scientific, Waltham, MA, USA) at a pressure of 1500 psi, a temperature of 100 °C, a heating time of 5 min and a static cycle time of 7 min. Three static cycles were used for each sample. After extraction, the remaining solid was transferred to a Petri dish and left to air dry for 2 days; the extractive content was then determined.

2.2.2. Hydrolysis

The extracted sample (300 mg) was then subjected to a two-stage acid hydrolysis process using the procedure described by the national renewable energy laboratory (NREL) [32]. In the first step, the sample in 72% sulfuric acid (3 mL) was transferred to a water bath maintained at 30 °C for 1 h and stirred every 10 min. In the second stage, 84 mL of water was added to the sample, and the sample was transferred to an autoclave for 1 h at 120 °C. Pressure tubes containing a solution of a known sugar composition were placed in the same autoclave and used to determine the sugar losses associated with hydrolysis.

2.2.3. *Lignin content*

The lignin content was determined using the procedure established by NREL [32]. The acid-soluble lignin (ASL) content was determined in the hydrolysates by UV spectroscopy using a Shimadzu UV-1700 (Shimadzu, Kyoto, Japan) at a wavelength of 205 or 240 nm, depending on the biomass. The solid residue from filtration, which is called the acid-insoluble residue (AIR), was dried overnight at 105 °C and then ashed in a muffle furnace (575 °C) to determine the acid-insoluble ash (AIA). The Klason lignin (KL) was determined as AIR minus AIA. The total lignin (TL) content was determined as the sum of ASL and KL.

2.2.4. *Carbohydrate content*

The hydrolysate allowed for the analysis of the liberated monosaccharides (arabinose, galactose, rhamnose, glucose, xylose and mannose) by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) using an electrochemical detector (ED 40) equipped with a CarboPac-PA 10 column and a precolumn. The recovery solutions of the hydrolysates and the sugars were diluted with a solution containing a known concentration of fucose, which was used as the internal standard. All of the sugars were separated within 25 min with deionized water as the eluent.

2.2.5. *Visible-near-infrared spectra*

For the acquisition of the visible-near-infrared spectra of the samples, a FOSS XDS instrument (FOSS, Hillerød, Denmark) equipped with the associated rapid content analyzer (RCA) module and a diffuse reflectance detector was utilized. The spectra were collected over a spectral range of 400–2500 nm (full range) with 0.5-nm increments and were averaged over 32 scans. Each sample was analyzed in triplicate, and the average spectrum was used.

2.2.6. *Elemental analysis*

Common organic elements such as C, H, N and O were examined with a PerkinElmer Elemental CHNSO analyzer. The sample (1.0 mg) was inserted in a tin boat assortment to determine the composition percentages of C, H and N. The percentage of O was determined by difference as the remaining percentage after C, H and N determination.

2.2.7. *Thermogravimetric analysis (TGA)*

TGAs of the biomass samples were performed using the EXSTAR 6000 TG/DTA, a Thermo-Gravimetry/Differential Thermal Analyzer instrument. The devolatilization characteristics of a sample of 0.5 mg were investigated from 20 to 650 °C at a rate of 10 °C/min. The flow rate of the purge gas (nitrogen) was 60 mL/min.

2.2.8. *Bioproduct content*

The yield of the bioproducts of interest, such as levulinic acid (LA), formic acid (FA) and furfural, can be estimated as [30]:

$$\text{LA}\,(\%) = 0.\,5 \times \text{hexose}\,\% \tag{1}$$

$$\text{FA}\,(\%) = 0.\,2 \times \text{hexose}\,\% \tag{2}$$

$$\text{Furfural}\,(\%) = 0.\,5 \times \text{pentose}\,\% \tag{3}$$

2.3. *Physical analyses*

2.3.1. *Proximate analysis*

The proximate analyses were performed according to ASTM methods 3173-87, 3174-04 and 3175-07 [31,33,34]. The moisture content was determined as the loss of mass after drying at 105 °C in an oven overnight, and the ash content was determined as the residue after combustion in a muffle furnace at 575 °C for 3 h. The volatile matter was determined using a 1.0 g sample of known dry matter content in the muffle furnace maintained at 950 ± 10 °C for 7 min.

The percent of fixed carbon (FC) was calculated as the difference between the ash and volatile matter content for the dried biomass [35].

2.3.2. *Calorific value*

The calorific values were determined using a static bomb calorimeter (IKA C2000); a sealed Parr 1108 and sample pellets of 1.0 g were used for each analysis. A cotton thread was attached to the platinum ignition wire and placed in contact with the pellet. The bomb was filled with oxygen at 25 °C, and 1.0 cm^3 of water added to the bomb. The calorimeter jacket was maintained at a constant temperature using circulated water at 25 °C.

2.3.3. *X-ray diffraction analysis*

The XRD analysis was performed using a Shimadzu diffractometer XRD-7000 (Rigaku, Tokyo, Japan) using Cu Kα radiation at 40 kV and 30 mA over the scanning angle range of $5° < 2\theta > 50°$ at a scanning speed of $0.5°\ \text{min}^{-1}$.

To calculate the crystallinity index (CI) of cellulose from the diffractograms, two different methods were used. In the first method, the CI was calculated from the ratio of the height of the crystalline peak (I_c) ($22° < 2\theta < 23°$) and the height of the minimum intensity (I_{am}) at the amorphous peak ($18° < 2\theta < 19°$) according to Eq. (4) [36].

$$\text{CI} = \frac{I_c}{I_{am}} \times 100 \tag{4}$$

In the second method, individual peaks were adjusted from the diffraction intensity profiles using a curve-fitting process. To perform this curve-fitting process, a peak fitting program (PeakFit; www.systat.com) was used, assuming Gaussian functions for each peak. A broad peak at approximately 21.5° was assigned to the amorphous contribution (see Fig. 1). Iterations were repeated until the convergence of [1] χ^2 (14 significant digits) was obtained, which corresponds to an R^2 (coefficient of determination) value greater than 0.94 for the deconvolutions. The sum of the area under the crystalline (101; $1\bar{0}1$ and 002 peaks, Fig. 1) adjusted peaks (I_c) and the amorphous broad band (I_a) was used to calculate the CI according to the following equation [37]:

$$\text{CI} = \frac{I_c}{I_c + I_{am}} \times 100 \tag{5}$$

3. Results and discussion

The ideal biomass characteristics include the production of high yields of bioproducts while minimizing the chemical/energy requirements, low input energy, low cost and the use of the most abundant feedstocks [1,2].

The results in Table 1 indicate that grass and rice husks exhibited higher percentages of ash (over 10%) when compared with the ash percentages of other biomasses. This high percentage of ash is not promising because it affects the acid hydrolysis by increasing the acid consumption [25]. The enzymatic hydrolysis can be retarded because the ash cations can migrate into the solution and affect the cellulose activity [38].

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[1] $\chi^2 = \frac{(\nu_o - \nu_e)^2}{\nu_e}$

ν_o is the experimental value and ν_e is the adjusted value.

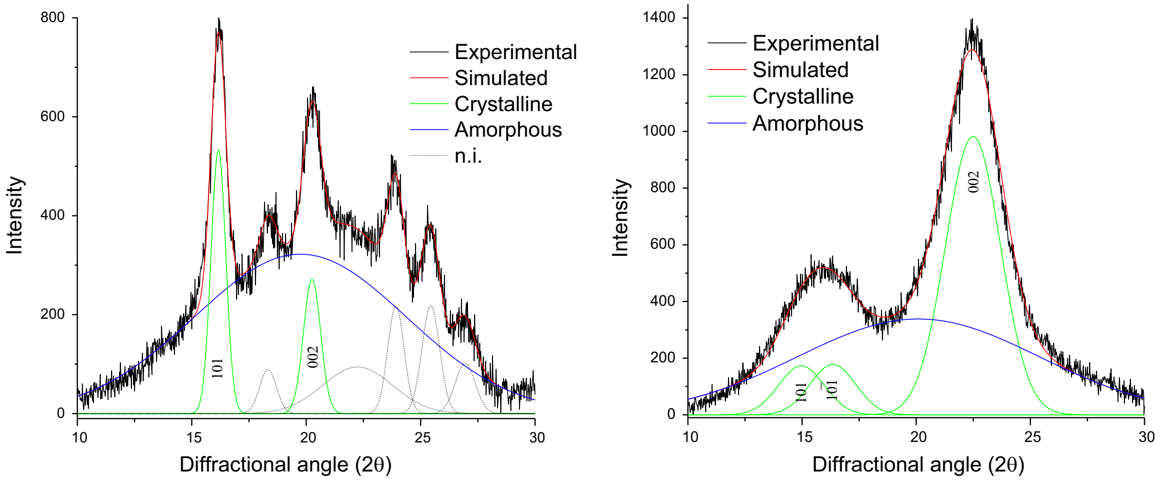

Fig. 1. X-ray diffraction analyses of açaí and sawdust biomass using the peak deconvolution method.

The moisture content absorbs heat that would otherwise be available. Additionally, the excess moisture in the biomass enhances the transport, hampers the storage and reduces the calorific value [2]. Banana and açaí seed residues had considerable moisture contents that may affect the cost of the process (Table 1). The proximate analyses of volatile matter and fixed carbon indicated that the highest result for the fixed carbon, 22.70%, was found in the coffee husks, and the lowest result, 7.23%, was found in soy peels, indicating that coffee husks may be better for use in charcoal production. The higher amount of volatile matter in the soy peels is an indication that they can be harnessed to produce energy by combustion.

The calorific value of biofuels is one of the critical properties of interest and is inherently influenced by the chemical composition of the biomass [39]. The sawdust, which had a higher lignin content compared to other biomasses, also exhibited a higher calorific value. Higher calorific values result in higher lignins and extractives because they contain less oxygen than the polysaccharides present in the holocellulose (cellulose and hemicellulose). This relationship was observed in the banana stems and stalks, which had lower lignin content and therefore a calorific value lower than the calorific value of the other biomasses (Table 1). A relationship with the extractive content was not as significant as that relationship for the lignin. Fig. 2 shows the positive and negative relationship (Pearson correlation) between the calorific value and the chemical composition. With respect to the moisture and ash content, which influence the decrease of the available energy from the biomass, only a negative relationship was found between the calorific value and the ash content, while the moisture did not seem to have an effect on the calorific value.

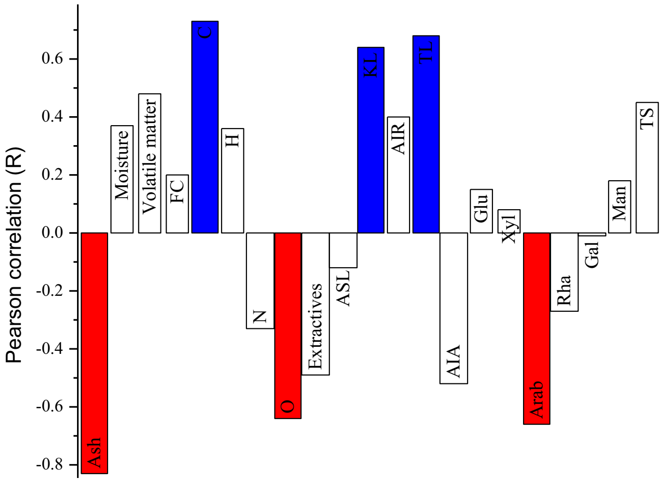

Fig. 2. The relationship between the chemical composition and the calorific value of the biomasses (ASL: acid soluble lignin; KL: Klason lignin; AIR: acid insoluble residue; TL: total lignin; AIA: acid insoluble ash; FC: fixed carbon; Glu: glucose; Xyl: xylose, Ara: arabinose; Rha: rhamnose; Gal: galactose; Man: mannose and TS: Total sugar).

In comparison to common biomasses available in Canada such as wheat straw, barley straw, flax straw, timothy grass and pinewood, the range of calorific value was approximately the same, with a slight superiority for the Brazilian biomasses [35]. The wheat straw from Canada exhibited the highest calorific value (20.3 MJ kg^{-1}), which was comparable to the calorific value of sawdust from Brazil (20.0 MJ kg^{-1}). The timothy and elephant

Table 1
Proximate, ultimate and calorific values of biomass.

Biomass	Proximate analysis (%)			Fixed carbon	Elemental analysis (%)				Calorific value (MJ kg^{-1})
	Ash	Moisture	Volatile matter		C	H	N	O	
Açaí seed	0.69 ± 0.04	13.27 ± 0.18	80.77 ± 0.20	18.50 ± 0.20	47.60 ± 0.84	6.40 ± 0.41	0.78 ± 0.03	45.12 ± 0.19	18.60 ± 0.30
Banana stems	8.00 ± 0.13	12.56 ± 0.03	80.27 ± 0.15	9.96 ± 0.19	39.00 ± 0.36	5.44 ± 0.05	0.82 ± 0.01	54.84 ± 0.21	16.13 ± 0.35
Banana stalk	8.00 ± 0.01	8.04 ± 0.20	73.25 ± 0.02	22.13 ± 0.02	37.95 ± 0.98	4.73 ± 0.44	1.46 ± 0.07	55.85 ± 0.89	15.73 ± 0.15
Bamboo	1.71 ± 0.01	9.01 ± 0.03	81.08 ± 0.05	17.20 ± 0.05	44.60 ± 0.09	5.55 ± 0.10	0.91 ± 0.08	48.93 ± 0.08	18.33 ± 0.20
Coconut	2.96 ± 0.25	9.87 ± 0.40	77.00 ± 0.10	20.05 ± 0.27	47.40 ± 0.20	5.41 ± 0.16	0.55 ± 0.01	46.64 ± 0.19	18.70 ± 0.20
Coffee	2.00 ± 0.15	10.00 ± 0.20	75.40 ± 0.20	22.70 ± 0.25	43.34 ± 0.55	5.55 ± 0.13	2.25 ± 0.07	48.86 ± 0.25	18.06 ± 0.30
Sawdust	0.11 ± 0.01	10.10 ± 0.08	83.88 ± 0.10	16.00 ± 0.10	50.30 ± 0.11	6.08 ± 0.08	0.15 ± 0.06	43.43 ± 0.09	20.00 ± 0.40
Grass	13.0 ± 0.05	8.10 ± 0.04	76.50 ± 0.05	10.81 ± 0.07	42.00 ± 0.99	5.21 ± 0.18	2.03 ± 0.12	50.95 ± 0.70	16.77 ± 0.13
Rice husks	12.5 ± 0.06	8.00 ± 0.10	71.24 ± 0.10	16.27 ± 0.10	35.86 ± 0.95	4.40 ± 0.50	0.28 ± 0.09	59.46 ± 0.86	16.35 ± 0.18
Soy peel	1.14 ± 0.01	9.10 ± 0.18	88.81 ± 0.20	7.23 ± 0.20	45.04 ± 0.65	6.70 ± 0.22	2.90 ± 0.68	45.35 ± 0.78	17.90 ± 0.20

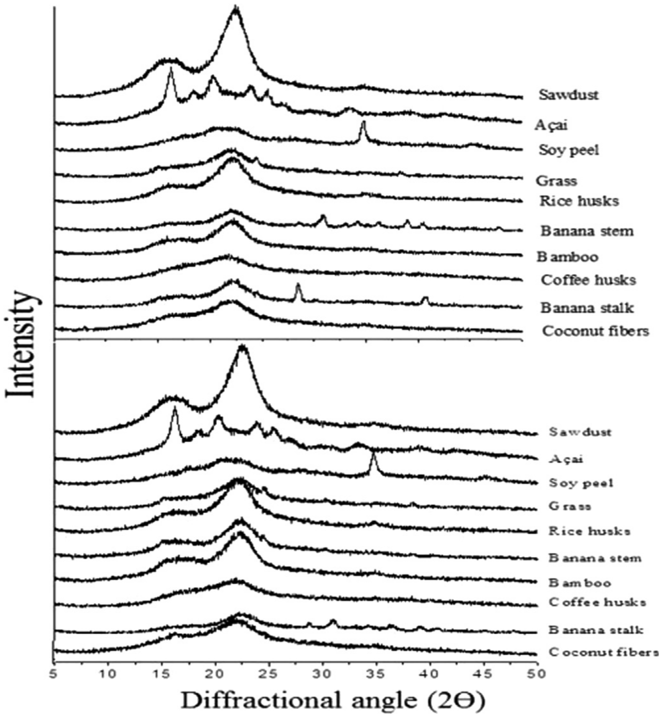

Fig. 3. X-ray diffraction analyses of the biomass samples before (above) and after (below) extractives removal.

grass biomasses from Canada and Brazil, respectively, exhibited the same gross calorific values (16.7 MJ kg^{-1}).

Currently, miscanthus from Europe and sugarcane bagasse and straw from Brazil are the main energy biomass residues available. The calorific values are 17.74 [40], 19.25 and 20.3 MJ kg^{-1} [29,41] for miscanthus, bagasse and straw, respectively. The values are close to the values obtained for the promising biomasses being proposed in this work.

For banana fibers, soy peels, elephant grass and coffee husks, the relative amounts of nitrogen were always higher than those in the other biomasses. The higher nitrogen content is the reason these materials can be used as a fertilizer [42].

The results from the XRD analysis are presented in Fig. 3. The crystallinity of the lignocellulosic materials is considered a major factor influencing the efficiency of the acid/enzymatic hydrolysis [43]. Thus, it is extremely important to determine the degree of crystallinity to assess the amount of reagents required for the subsequent steps.

Intense X-ray diffraction peaks, characteristic of cellulose, were detected at $2\theta=22^\circ/23^\circ$ and $15^\circ/17^\circ$ for all feedstocks, indicating the existence of crystalline regions [44]. The diffractogram for banana fibers also exhibits narrow diffraction peaks, probably from inorganic substances (ash) or other contamination [42]. Açaí seed, soy peels, sawdust and rice husks exhibit one peak in $2\theta=34.7^\circ/35^\circ$, which is also probably associated with cellulose.

The maximum crystallinity calculated by Method 1 (Eq. (4)) was observed for rice husks, with a CI of 57%, followed by elephant grass and sawdust, both with CIs of 55%. The literature indicates a CI of 46% for rice husks, which was calculated using the same method [45]. The calculated crystallinities of the banana residues, with CIs of 50% and 44% for stems and stalks, respectively, exhibited significant differences when compared with the result found in the literature for pseudostem with a CI of 39% [42]. The calculated CI values of bamboo and coconut were found to be 44% and 40%, respectively. The coconut results are in accordance with the results in the literature, which are in the range of 40% to 44% [46]. Açaí seed and coffee husks exhibited a CI of 30%, and the minimum crystallinity was obtained for soy peel (25%).

Fig. 1(A) and (B) shows the deconvolution of the XRD diffractograms from the açaí and the sawdust that were used to calculate CI using a deconvolution method. The crystallinity index calculated by Method 2 (area) was approximately 10% below the levels of intensity (Method 1). An important assumption for this analysis was that an increased amorphous contribution is the main contributor to peak broadening, decreasing the actual value of the crystallinity. However, in Method 1, a simple height comparison cannot be expected to provide a reasonable estimate of cellulose crystallinity, as it neglects the variation in the peak width, which can also be affected by the crystallite size. For these reasons, both Method 1 and Method 2 can only be taken as a rough approximation of the contribution of the amorphous cellulose to the crystalline cellulose diffraction spectrum [44].

Diffractograms of the samples after the removal of the extractives were also recorded and are shown in Fig. 3.

During the ethanol extraction, the extracted samples were observed to be similar to the raw feedstocks. Only the banana stem extract exhibited an appreciable difference, with a cleaner diffractogram, which is probably attributed to the removal of inorganic substances (ashes) or other contaminants.

The crystallinity of the biomasses is related mainly to the wax content [43]. This effect was confirmed after removal of the extractives by the increase in the crystallinity index (from 2–11%) of all biomasses except for the coconut sample (Fig. 3).

The average spectrum over the visible to NIR range of each biomass is shown in Fig. 4. The main bands in the visible region were located at approximately 460 nm and 670 nm. The latter band is associated with the conjugated π-bond system of the chromophores, in which the contributions from lignin and chlorophyll are important. The band centered in the region of 670 nm, which was more evident in the elephant grass, bamboo and coconut samples and appeared as just a shoulder in the coffee samples, is attributed to chlorophyll [47].

In the NIR region, the spectra were dominated by the water signals, with an intense combination band at 1940 nm and the first overtone bands of the O–H stretching at 1450 nm. However, other compounds with O–H bonds, such as carbohydrates and lignin, can contribute to spectral features in these regions. The signal of carbohydrates can be observed as a broad band near 2100 nm, but this region probably exhibits overlap with the alkyl (CH$_n$)

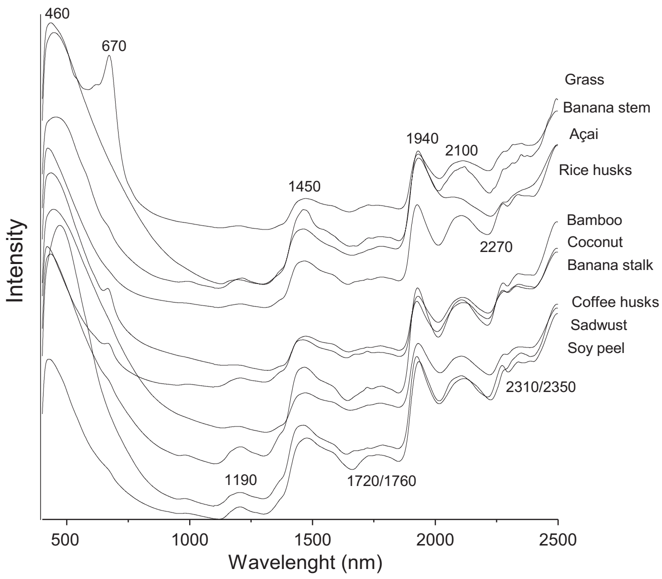

Fig. 4. Near-infrared spectral analysis of the biomass samples.

Table 2
Composition of sugars in the biomasses (values are given in %).

Biomass	Glucose	Xylose	Arabinose	Rhamnose	Galactose	Mannose	Total sugar
Açaí seed	8.66 ± 0.03	3.18 ± 0.40	0.69 ± 0.10	0.17 ± 0.03	1.43 ± 0.03	53.60 ± 0.05	67.71 ± 0.53
Banana stems	36.32 ± 0.13	5.36 ± 0.01	2.37 ± 0.01	3.16 ± 0.00	0.72 ± 0.02	0.61 ± 0.27	45.53 ± 0.44
Banana stalks	26.83 ± 0.05	6.94 ± 0.15	2.89 ± 0.05	0.27 ± 0.05	1.18 ± 0.00	1.46 ± 0.14	39.56 ± 0.35
Bamboo	44.65 ± 0.98	14.78 ± 0.43	0.81 ± 0.03	0.06 ± 0.07	0.32 ± 0.02	0.07 ± 0.01	61.57 ± 1.00
Coconut	32.41 ± 0.14	14.37 ± 0.26	1.79 ± 0.12	0.30 ± 0.03	0.71 ± 0.08	0.35 ± 0.07	50.00 ± 0.11
Coffee husks	35.33 ± 0.16	21.89 ± 0.09	1.62 ± 0.15	0.51 ± 0.08	1.54 ± 0.08	1.68 ± 0.01	62.55 ± 0.56
Sawdust	38.80 ± 0.20	9.72 ± 0.05	0.26 ± 0.27	0.25 ± 0.01	1.23 ± 0.00	0.35 ± 0.12	50.60 ± 0.11
Grass	27.52 ± 0.21	16.12 ± 0.24	3.56 ± 0.06	0.10 ± 0.10	1.22 ± 0.01	0.24 ± 0.27	48.84 ± 0.55
Rice husks	36.17 ± 0.15	16.65 ± 0.38	1.70 ± 0.04	0.13 ± 0.01	0.83 ± 0.02	0.49 ± 0.21	56.00 ± 0.66
Soy peel	35.05 ± 0.99	9.85 ± 0.01	4.64 ± 0.04	0.92 ± 0.00	3.13 ± 0.02	4.31 ± 0.02	57.90 ± 1.00

vibrational bands. These groups also exhibit a pair of bands at 2310/2350 nm along with a pair at 1720/1760 nm and a band at 1190 nm (first and second overtones of C–H stretching, respectively) [35]. For lignin, in the NIR region, specific bands (CH or OH aromatic) such as those at 950 nm, 1100 nm and 1670 nm [47] were not observed as clear peaks but appeared as an unresolved shoulder in the region near 2270 nm (Fig. 4).

Tables 2 and 3 present the chemical composition of the biomasses. The contents of alcohol extracts for different biomass samples indicated that banana residues exhibited the maximum (23–25%) and the coconut fibers exhibited the minimum (1.4%) extractive content, whereas the other biomasses exhibited reasonable amounts of extract materials. In this study, the extracts exhibited significant differences in the percentage of the total sugars due to the hemicellulose that can be removed during the ethanol extraction.

The sugar composition in coconut, grass and eucalyptus sawdust (approximately 50%) are comparable. Açaí seed, bamboo and coffee husks have a total sugar content above 60%. However, for açaí seed, the high percentage of the total carbohydrates is assigned to the mannose content, which is approximately 90% of the total composition, whereas the coffee husks presented a high percentage of xylose (22%). Bamboo and sawdust have a high percentage of glucose, indicating that they the most promising materials for obtaining ethanol. The results indicated that the main sugar is glucose in all biomasses, except in açaí seed. The results reported in this work are similar to the results previously reported in the literature [10,13,18,22,42,48].

Although lignins holds a great potential as a renewable source of fuels and aromatic chemicals, valorization technologies for lignins are substantially less developed than for polysaccharides. However, the economic viability of future lignocellulosic biorefineries depends upon conversion of both cellulose and lignin to value-added compounds. Thus, a high lignin content is important for utilizing these feedstocks in a sustainable biorefining industry [27]. Additionally, coconut and sawdust biomasses are promising feedstocks in this context.

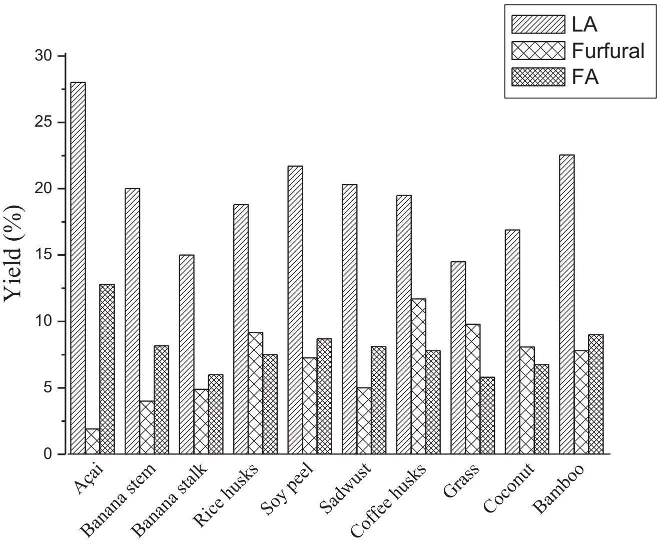

Fig. 5. Estimated yield of levulinic acid (LA), formic acid (FA) and furfural.

To demonstrate the potential of these biomasses, the LA, FA and furfural yields were estimated using Eqs. (1)–(3), and the results are shown in Fig. 5. The glucose units released by degradation of cellulose undergo acid-catalyzed intermolecular dehydration and are thus converted to 5-hydroxymethylfurfural (5-HMF). In a second step, due to the conditions of the reaction medium, 5-HMF is degraded, leading to the formation of LA (primary hydrolysis product) and FA [29]. The mannose and hexose found in greater amounts in açaí seed undergo the same process as glucose, thereby providing LA and FA in satisfactory amounts of 28.00% and 13.00%, respectively (Fig. 5).

Regarding the pentoses, the highest percentage was found in coffee husks (xylose content of 22%), favoring the furfural yield

Table 3
Composition of lignin types and ethanol extractives in the biomasses (values are given in %).

Biomass	Ethano extractives	ASL	KL	AIR	TL	AIA
Açaí seed	9.50 ± 0.04	1.63 ± 0.07	15.63 ± 0.26	15.80 ± 0.26	17.30 ± 0.33	0.16 ± 0.01
Banana stems	25.15 ± 0.06	1.32 ± 0.06	7.06 ± 0.23	7.58 ± 0.28	8.40 ± 0.29	0.52 ± 0.18
Banana stalks	22.85 ± 0.50	2.20 ± 0.00	8.50 ± 0.01	10.75 ± 0.09	10.68 ± 0.01	2.28 ± 0.08
Bamboo	12.60 ± 0.13	1.50 ± 0.02	16.20 ± 0.08	16.20 ± 0.16	17.60 ± 0.10	0.15 ± 0.08
Coconut	1.41 ± 0.44	1.30 ± 0.07	34.60 ± 0.37	30.50 ± 0.24	36.00 ± 0.44	0.35 ± 0.13
Coffee husks	4.20 ± 0.49	2.13 ± 0.06	22.33 ± 0.25	22.40 ± 0.25	24.50 ± 0.31	0.05 ± 0.03
Sawdust	8.12 ± 0.04	2.30 ± 0.00	30.55 ± 0.04	30.60 ± 0.02	33.00 ± 0.04	0.02 ± 0.03
Grass	11.54 ± 0.09	4.33 ± 0.03	11.30 ± 0.13	19.70 ± 0.19	15.61 ± 0.16	8.40 ± 0.07
Rice husks	2.32 ± 0.06	1.05 ± 0.01	22.85 ± 0.16	34.82 ± 0.21	23.90 ± 0.17	12.30 ± 0.04
Soy peel	6.80 ± 0.11	4.90 ± 0.40	2.70 ± 0.11	2.80 ± 0.03	7.60 ± 0.50	0.09 ± 0.08

ASL: acid soluble lignin; Kl: Klason lignin; AIR: acid insoluble residue; TL: total lignin; AIA: acid insoluble ash.

Table 4
The results from the literature for experimental yields (%) of levulinic acid (LA), formic acid (FA) and furfural.

Biomass (%)	Cellulose	Hemicellulose	AL	AF	Furfural	Sources
Sugarcane bagasse	43.3	25.7	63.0	–	–	[29]
Miscanthus	37.1	18.03	72.0	–	27.3	[49,50]
Rice husks	31.0	24.3	59.4			[51]
Grass	35.2	19.8	–	–	31.4	[52]
Pine wood	36.5	18.7	–	–	33.6	[52]
Corncob	30.2	31.7	–	–	19.1	[52]

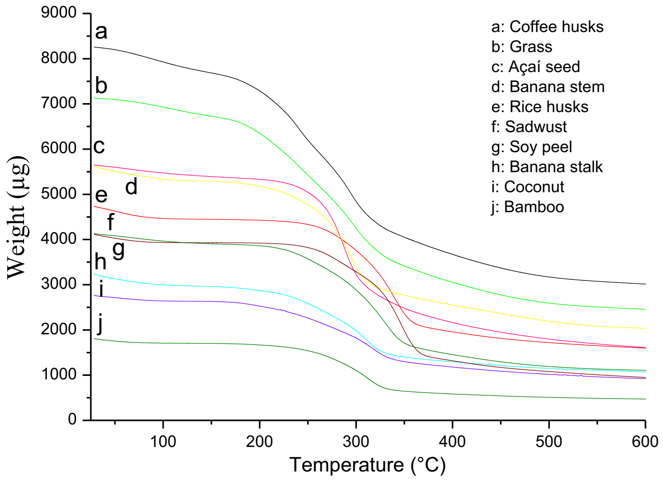

Fig. 6. Thermogravimetric analysis of the biomass samples.

(12%). Lower yields of LA and FA were observed in grass, whereas the lowest furfural yield was found for the açaí (2%).

Some results from the literature for LA, FA and furfural yields are presented in Table 4. These results indicate the potential of Brazilian biomasses for use in byproduct production.

The thermal analyses (TGAs), particularly the thermogravimetry (TG) and derivative thermogravimetry (DTG), enable the determination of the chemical constituents in a simple and rapid manner [17]. The results of thermogravimetric analysis are shown in Fig. 6.

The first stage of decomposition occurs at a temperature between 50 and 100 °C, attributed mainly to water loss [42]. Low molecular weight compounds and other volatile organic compounds (extractives) evaporate between 120 and 250 °C. In the range of 100 to 200 °C, the biomasses are thermally stable. The devolatilization temperature for the majority of samples initiates between 200 and 250 °C. In this stage, the weight loss is usually lower for species with high lignin content. Coconut, sawdust, coffee husk and rice husk samples had the highest percentage of total lignin (Table 3). Thus, this relationship is true only for rice husks, sawdust and coconut. Coffee husks were one of the biomasses with a larger weight loss in this range (200–250 °C), which was associated with an even higher concentration of lignin.

The main weight loss occurred between 250 and 350 °C for all biomasses and could be associated with the decomposition of the sugars. The first peak was attributed to the decomposition of hemicellulose (250–300 °C) and the second to cellulose (300–350 °C). Above 400 °C, the biomasses had a continuous and slow weight loss associated with lignin decomposition [42]. The ash is considered to be the material that remains at temperatures above 500 °C. Using the weight loss associated with those regions identified in Fig. 6, it was possible to obtain a rough approximation of the chemical composition of the raw materials under study. However, the results appeared to be somewhat inaccurate, with a higher lignin content and a lower hemicellulose content than normal when compared with the results in Tables 2 and 3. The problem with TGA is that the mass lost in a given temperature interval may not necessarily result from the perceived component in this region, and hence, the substance may be overestimated. Additionally, the same chemical composition in 10 different biomasses may not always be lost in the same temperature ranges. For these reasons, TGA provides a rough estimation of the feedstock composition; such estimations can be used in screening procedures.

4. Conclusions

The feedstocks analyzed in this study are abundant and promising for biorefining opportunities in Brazil. The physicochemical characterization indicated that in general, all of the feedstocks exhibit different important parameters for bioenergy production, such as high calorific value, high carbohydrate content, high lignin content and low extractive and ash content. Coffee husks and bamboo are potential candidates for bioenergy production due to their high cellulose and hemicellulose content, high calorific value and low ash content. However, banana residues (stalks and stems) are not suitable feedstocks for bioenergy production due to the high moisture content that prevents their transportation, in addition to the high extractive content and low calorific value.

In conclusion, the characterization of Brazilian residues ensures that these biomasses can be utilized for gasification and liquid fuel production, as well as for second generation biofuels. Therefore, the Brazilian biomass has the potential to favorably compete with other conventional biomass sources such as miscanthus and sugarcane bagasse/straw for use in biorefining technologies.

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