Research paper

Extraction and characterization of lignins from cashew apple bagasse obtained by different treatments

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A B S T R A C T

Lignins were extracted from different hydrolysates from the cashew apple bagasse (CAB). The hydrolysates, in turn, were obtained by pretreating the CAB with diluted acid (DA), acid/alkali (AA) and alkaline hydrogen peroxide (AHP). Lignin removal levels with AA and AHP were of 98.0% and 96.9%, resulting in high extraction yields and highly thermostable lignins. The lowest lignin yield was observed with the acid-only pretreatment. The FT-IR results showed that there was no significant difference between the main structures of the lignin isolated from the DA and AHP pretreatments, when compared to sugarcane lignin (SCL), the only exception being the lignin from AA. An ^{1}H–^{13}C HSQC NMR analysis demonstrated that AA pretreatment reduced the syringyl (S) and hydroxyphenyl (H) units, but increased the condensed guaiacyl (G) units, which may contribute to the higher thermal stability of the isolated lignins and to the absence of attached residues of carbohydrates. The detailed structural properties of the lignins extracted from CAB will enable the efficient utilization of these macromolecules within the biorefinery concept, with a positive impact on the economy.

1. Introduction

The current global economic model is based on sustainability. Therefore, there is a strong drive to encourage the recovery and reuse of natural resources, with a parallel deterrence towards the use of their non-renewable counterparts [1]. In this context, lignocellulosic biomasses stand out as potential feedstocks for the production of energy, fuels and chemicals [2], as they are widely available, renewable and not employed for feeding purposes [3]. Many raw materials, especially agro-industrial wastes such as the cashew apple bagasse, have been evaluated for their potential of reuse and value addition [4,5].

The cashew apple is a pseudo-fruit ubiquitous in the Northeast region of Brazil, South-Eastern Asia and Africa, exhibiting an outstanding social and economic role due to the exportation of cashew nuts. The cashew apple juice industry produces 15% (w/w) of the bagasse, which results in the generation of huge amounts of waste [6–8]. However, the composition of cashew apple bagasse (CAB) is a potential raw material that can be used as an alternative and inexpensive lignocellulosic material on the production of fuel and chemicals, such as ethanol and xylitol. CAB is reported to have a high lignin content (33–35.5%) [4,5, 9]. One drawback, however, is the fact that the CAB structure is highly recalcitrant to microbial and enzymatic biotransformation, limiting its use and deeming its direct conversion into value-added products economically unfeasible. Therefore, pretreatments steps are needed to disrupt the resistant structures of the lignocellulosic material to increase the digestibility of the matrix prior to conversion. Among various pretreatments, studies have focused on the employment of diluted sulfuric acid [9], acid-alkali [10], alkaline hydrogen peroxide [11,12] and protic ionic liquids [7]. Subsequent to this, enzymatic hydrolysis is usually performed aiming at depolymerizing the biomasses into fermentable sugars for conversion to fuels and chemicals [10].

During the pretreatment of CAB, lignin is discarded and classified as

a by-product. However, it can be a potential raw material for the production of different products, and understanding the structural characteristics of lignin from CAB is of great interest to the development of an efficient and economical process inside the biorefinery concept.

Lignin is the second most abundant natural polymer on earth, accounting for 17–32% of the lignocellulosic biomasses [13]. In spite of that, it has been vastly underutilized [13]. Lignin is insoluble in water and stable in nature, and acts as a 'glue' binding cellulose to hemicellulose. It had a three-dimensional structure and consists of three phenol groups: *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) [14].

The effective employment of lignin in the production of value-added products is only about 2% [15], with its major percentage still being used as fuel in thermal energy generation. However, the molecule can potentially contribute to the production of a wide range of value-added products such as foams, carbon materials, membranes, bio-based composites, engineered plastics, commodity chemicals and liquid fuels [16]. Currently, a wide variety of chemicals can be produced sustainably from the aromatic structures of lignin [3]. In addition to those, lignin presents a high antioxidant activity owing to the presence of phenolic groups and benzylic hydrogens [17,18].

The use of lignin in fuels and value-added chemicals enables the setting up of sustainable and economic biorefineries, since one of the major hurdles in these areas is the high recalcitrance and heterogeneity of lignin, which needs to be addressed [15,19,20].

Since lignin is obtained using relatively cheap waste materials, it is advantageous from an economic perspective regarding the processes that involve its usage [21]. There are different types of lignins, with their structures varying depending on the original feedstock and the isolation protocol [21,22].

For the past few decades, many researchers have studied lignin extraction from a variety of biomass matrices using different methods, such as soda pulping [23], kraft pulping [24], organosolv pulping [25], dilute and concentrated acid hydrolysis [26,27], alkaline hydrolysis [28] and combined pretreatment methods [29,30].

The kraft, soda pulping and organosolv processes provide high yields of lignin, but results in a highly modified structure [31]. The acid hydrolysis method has the advantage of enabling carbohydrate hydrolysis (mainly hemicellulose into soluble sugars), while simultaneously degrading and repolymerizing the lignin [32]. In this extraction method, lignin can be removed in the form of soluble fragments that are usually highly reactive under the hydrolysis conditions, causing undesired condensation reactions. Another disadvantage to this method is the corrosiveness and toxicity of most of the acids used [27].

The lignin obtained by the alkali extraction method, on the other hand, has moderate reaction severity. The separated macromolecule usually presents only slightly condensed structures. The method using ionic liquids is advantageous in which the solvent can be designed according to the required use, but their synthesis and purification are complex [1]. Therefore, recent research efforts tend to be pushed towards the combined use of these methods to effectively fractionate all biomass components (cellulose, hemicellulose, and lignin) with high quality, aiming at subsequent conversions [3].

Therefore, the effective extraction or separation of lignin from lignocellulose with high purity and a less condensed structure are crucial for an improved industrial use of lignin [1]. Its conversion to higher-value fuels and chemicals will significantly enhance overall biorefinery competitiveness.

In this context, the aim of the present study was to investigate the impact of different pretreatments on the structural characteristics and physicochemical properties of lignin from the cashew apple bagasse, as well as propose possible applications for the obtained lignins. The innovative aspect of this research can be attested by the inexistence of reports in the literature concerning the topic of lignins from CAB.

2. Material and methods

2.1. Materials

The raw cashew apple bagasse (*Anacardium occidentale* L.) used in this study was kindly donated by Jandaia Juice Industries (Ceará, Brazil). The cashew apple bagasse was washed with water, dried at 60 °C for 24 h and milled. Final particle sizes of 0.25–0.84 mm were obtained. The solid mass was named CAB and stored at 30 °C. Other reagents and chemicals used in the pretreatments were of analytical grade and are commercially available. The lignin extracted from steam-exploded sugarcane bagasse obtained with 0.25 mol dm^{-3} NaOH was used for comparison purposes. This lignin was provided by the Engineering School of Lorena (EEL-USP-Brazil) and the process is described by Rocha et al. [33]. Hereafter, the material is referred to as SCL (sugarcane lignin).

2.2. CAB pretreatments

2.2.1. Dilute acid (DA)

The pretreatment with dilute acid (DA) was conducted in an autoclave using 0.6 mol dm^{-3} H$_2$SO$_4$ solution and 30% (w/v) CAB at 121 °C for 15 min [34]. The solid and liquid fractions were separated by filtration. The recovered biomass solids (treated CAB, named CAB-H) were washed with water for the removal of any residual sugars and excess H$_2$SO$_4$, and put aside until further analysis. This pretreatment has already been reported in the literature to the same end and it was applied to CAB to obtain a liquid fraction rich in xylose, which was further used for producing xylitol [4,35]. However, in the aforementioned study, lignin was not recovered, but this is a crucial stage in the concept of biorefinery.

2.2.2. Acid-alkali (AA)

CAB was also pretreated by acid-alkali (AA) according to the best conditions obtained by Rocha et al. [34]. The acid pretreatment was carried out at 121 °C in an autoclave for 15 min using 0.6 mol dm^{-3} H$_2$SO$_4$ and 30% (w/v) CAB. The insoluble solids obtained from the acid pretreatment were impregnated with 1 mol dm^{-3} NaOH and re-submitted to autoclaving at 121 °C for 30 min. Then, a separation between the liquors and the solid fraction was performed by filtration. The recovered biomass solids (treated CAB, named CAB-HOH) were then washed with water to remove any residual sugars and excess NaOH and, finally, put aside until further analysis.

This combined pretreatment was evaluated with the acid-alkali dual action in mind. The acid pretreatment efficiently removes hemicelluloses by breaking ether bonds in lignin/phenolics carbohydrates complexes [36]. With the subsequent action of the sodium hydroxide, a more carbohydrate-free lignin can be obtained [37]. Also, this pretreatment has already been reported in the literature in a simultaneous process of lignin recovery and ethanol production from CAB [35].

2.2.3. Alkaline hydrogen peroxide (AHP)

CAB was also pretreated by alkaline hydrogen peroxide (AHP), according to the best conditions employed by Correia et al. [11]. 5.0 g of CAB was suspended in 100 mL of a solution of 4.3% (v/v) hydrogen peroxide (H$_2$O$_2$) at pH 11.5, with a H$_2$O$_2$ solution to dry biomass mass ratio of 5% (w/v). The treatment was conducted in an orbital shaker at 35 °C for 6 h and 250 rpm. After the pretreatment step, the liquor was separated from the solid fraction by filtration. The recovered solids (treated CAB, named CAB-AHP) were washed with water, to remove residual sugars and excess H$_2$O$_2$. This treatment was investigated for being reported as an efficient lignin extraction method that results in high yields [38].

For each evaluated pretreatment, the procedure was performed in triplicate. The lignin obtained for each procedure was characterized and the results of the characterization presented as their averaged value.

low, they still represent a substantial portion of the biomass composition. It is worth noting that the even though the extractive percentages were low, about 18.4% of the content was not assigned to lignin or sugars. Those are likely to be pectins bonded to the cell wall.

Table 1 also summarizes the effect of the pretreatments on the biomass composition. The content of the main compounds (glucan, xylan and lignin) of CAB, CAB-H, CAB-HOH and CAB-AHP varied significantly across the matrices, with the exception of the xylan content in CAB and CAB-AHP. Compared to the raw CAB, the CAB-H had higher glucan (25.37%) and lignin (50.70%) contents, but lower xylan (3.71%); the CAB-HOH had a higher glucan content (71.95%) but lower xylan (8.46%) and lignin (7.39%) contents; as for CAB-AHP, it presented higher glucan (44.16%) and xylan (18.28%) contents, but lower lignin (2.90%) content. The lignin content increased in the solid fraction obtained from the acid pretreatment due to the hemicellulosic content, which decreased from 16.3% to 3% w/w. The dilute acid treatment can achieve high rates of hemicellulose removal, however it is not effective in dissolving lignin. The xylan content of CAB-AHP was not significantly different from that observed in CAB because this pretreatment does not affect the hemicellulose chains [11].

The AA and AHP pretreatments removed more soluble lignins than the DA pretreatment. Lignin removal rates for AA and AHP were 98.0% and 96.9%, respectively, which were significantly higher than that of the DA pretreatment (11.7%). However, the lignin yield from liquids fractions was higher for the AA pretreatment (47.4%) when compared with the A (7.8%) and AHP (36.0%) pretreatments.

The mass balances regarding the major components of the liquid and solid fractions obtained in each treatment and the total mass of lignin obtained are shown in Fig. 1.

Analyzing the dilute acid (DA) pretreatment, 61.38 g of treated solids were recovered based on 100 g of dry untreated CAB (Fig. 1a). The solid fraction was composed majorly by lignin (50.70%), glucan (25.37%) and xylan (3.71%). The liquid fraction (174 g) at pH 3.7 $\pm$ 0.2, contained 2.36% of lignin. Subsequently, on the same basis, 4.11 g of lignin (11.7% of total) with a large amount of xylan (hydrolyzed to xylose) and a small amount of glucan (hydrolyzed to glucose) were added to the liquid fractions after the pretreatment. The overall yield of precipitate lignin from the liquid fraction was 7.85%, or 2.77 g. This step intended to depolymerize hemicellulose and cellulose, and it also affected lignin. During acid hydrolysis, low amounts of lignin could be removed in forms of soluble molecules [3]. The soluble lignin obtained for this pretreatment was 1.34 g (3.8% of the total).

The acid-alkali (AA) pretreatment yielded 9.34 g of solids containing mainly glucan (71.95%), along with xylan (8.46%) and lignin (7.39%), see Fig. 1b. The liquid fraction (583 g), at pH 12.2 $\pm$ 0.4, contained 20.77 g of lignin (58.9% of total) with a small amount of xylan and glucan. After the acid precipitation, solid lignin (16.7 g) was recovered, and the overall yield of precipitate lignin from the liquid fraction was 47.36 (which did not include the liquid fraction obtained in the first stage of the pretreatment with dilute acid). Most of the lignin is solubilized under the alkali condition, extracting lignin monomers and oligomers with a low number of condensed structures (Fig. 1B).

Pretreatment with alkaline hydrogen peroxide (AHP) gave a solid fraction (37.3 g) of a higher yield than that obtained in the acid-alkali pretreatment, composed mostly of glucan (44.16%), xylan (18.28%) and some lignin (2.90%), see Fig. 1c. A mass of 1560 g of liquid fraction at pH 10.4 $\pm$ 0.2 was obtained and, on the same basis, 34.18 g of lignin (96.9% of total) with small amounts of xylan, glucan and formic acid were obtained in the liquid fraction after the pretreatment. Following the acid precipitation, solid lignin (12.69 g) could be recovered and the overall yield of the precipitate lignin from the liquid fractions was 36%, with analysis indicating a total of 9.14% of soluble lignin. Oxidative catalytic fractionation uses oxidizing reagents (for example, H_2O_2) to promote the cleavage of ether linkages and lignin-carbohydrate complex bonds [11], and this pretreatment promotes high depolymerization and deoxygenation of lignin.

Therefore, for each 100 g of CAB, the mass extracted from the liquids fraction of the DA, AA and AHP pretreatments were 2.77 g, 16.70 g, and 12.69 g, respectively.

The DA and AA pretreatments were conducted at 121 °C, while AHP was conducted at 35 °C. The temperature also influenced the lignin extraction: higher temperatures led to the preferential cleavage of hydroxyl groups in the monolignol side chains, causing a separation of these molecules from the other components of the biomass. The chemical agents used in the pretreatments also showed an influence, since higher delignification yields are observed in the AA and AHP pretreatments. The DA pretreatment showed better performance at the removal of hemicellulose.

The solid fractions obtained from the AA and AHP pretreatments contained high amounts of glucan and xylan, and low amounts of lignin, and this favors enzymatic hydrolysis, especially when aiming at the obtainment of glucose that can be applied in the production of fuels [5, 10,12] and chemicals, inside the biorefinery concept.

The next sections present the characteristics and physicochemical properties of the lignins obtained with the different pretreatments. For each evaluated pretreatment, the procedure was performed in triplicate. The lignin obtained for each procedure was characterized and the result of the characterization, presented as the averaged value, and there was no significant difference among the lignin samples obtained from the same pretreatment for the characterization performed, at a 95% significance level ($p < 0.05$).

3.2. Immediate and elemental analysis from extracted lignins

Table 2 shows the results of the immediate and elemental analyses of lignins extracted by the different pretreatments of CAB. Immediate analysis of moisture, fixed carbon, volatiles, and ash, returned, respectively, 6.65%, 9.44%, 61.19% and 22.73% for AL; 9.43%, 28.15%, 57.60% and 4.82%, for AAL; and 5.71%, 9.67%, 78.64% and 5.96%, for PL.

Results also show that the AAL pretreatment resulted in a lower H content (2.16%), higher C content (54.46%) and higher O content (32.29%), compared to the other lignins. The O content of PL (28.54%) was higher than that of AL (20.59%). The increase of the O content might be due to the oxidation of the lignin side chains, what reinforces that oxidation reactions are likely to have occurred during the AHP in the presence of hydrogen peroxide. Oxygen and water can result from decomposition of hydrogen peroxide to form intermediates, such as superoxide and hydroxyl radicals, under alkaline conditions [11], with part of the oxygen involved in lignin degradation reactions and being incorporated into oxidized lignin products [47].

The DA process produced lignins with higher ash content, probably due to the greater precipitation of salts that may have formed from the basic compounds present in the hydrolysate and the sulfuric acid used to isolate the lignin.

The estimated HHV values of extracted lignins reduced due to the increased amount of oxygen content compared to the AAL and PL (Table 2). This parameter is especially important for the employment of lignin as an energy source [48].

Finally, the amount of methoxyl groups calculated from the elemental composition of lignins ranged between 1.35% and 18.36% as shown in Table 2. The lowest value was observed in AAL, indicating a demethoxylation reaction during the alkaline pretreatment and also the action of the dilute acid on the CAB in the previous step.

3.3. Lignin structure

Lignin bears a variety of functional groups, such as aliphatic hydroxyls, carbonyls, phenolic hydroxyls, methoxyls, and benzyl alcohol groups, which determine the polarity and the quality of both the cashew apple and sugarcane lignins.

The FT-IR spectra of the three lignins obtained from CAB are shown
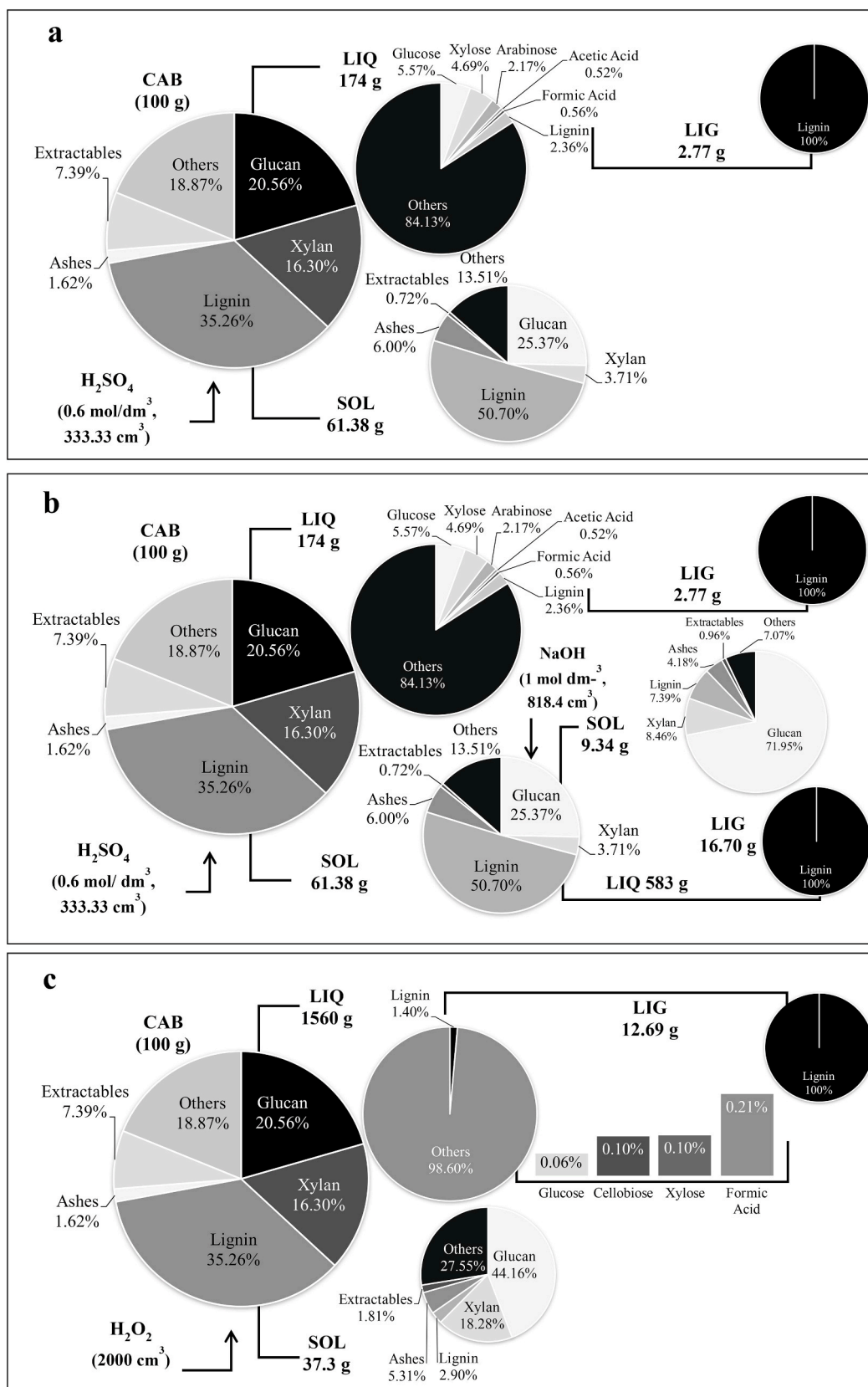
Fig. 1. Mass flow of the major components (glucan, xylan, and lignin) of the cashew apple bagasse pretreated by different methods, composition of the obtained liquid fractions and amount of extracted lignin. (a) Dilute acid pretreatment; (b) acid-alkali pretreatment; (c) alkaline hydrogen peroxide pretreatment. LIQ: liquid fraction; SOL: solid fraction; LIG: lignin.

Table 2
Immediate and elemental analysis of lignin from cashew apple bagasse extracted by pretreatment with dilute acid (AL), acid-alkali pretreatment (AAL) and pretreatment with alkaline hydrogen peroxide (PL).

Component (%)	Lignin		
	AL	AAL	PL
Moisture	6.65	9.43	5.71
Volatile matter	61.19	57.60	78.64
Fixed carbon	9.44	28.15	9.43
Ash	22.73	4.82	5.96
Carbon	48.15	54.46	51.5
Nitrogen	3.70	6.27	7.34
Hydrogen	4.83	2.16	6.66
Oxygen	20.59	32.29	28.54
Methoxyl groups (OCH$_3$)	8.17	1.36	18.36
Higher heating values (HVV), MJ/kg	19.49	15.75	21.82

in Fig. 2 along with that from the sugarcane lignin. All spectra exhibited absorption bands typical of lignin.

The band at 3421 cm^{-1}, which was present in all samples, was attributed to the stretching vibration of aromatic and aliphatic hydroxyl in the lignin and water absorbed by the sample [49,50]. The hydroxyl groups in lignins are likely derived from the cleavage of β–O–4 bonds among the phenylpropane units. Vibrations at 2924 cm^{-1} and 2844 cm^{-1} were assigned to asymmetric and symmetric C–H stretching of alkyl groups of the lignin structure [51,52].

AAL and PL samples showed a band at 1708 cm^{-1}, which was associated to the C=O stretching from the non-conjugated ketone, carbonyl and ester groups. The higher intensity of carbonyl groups in these lignins is due to the action of a high alkaline load combined with a high temperature, which could lead to excessive oxidations and possibly
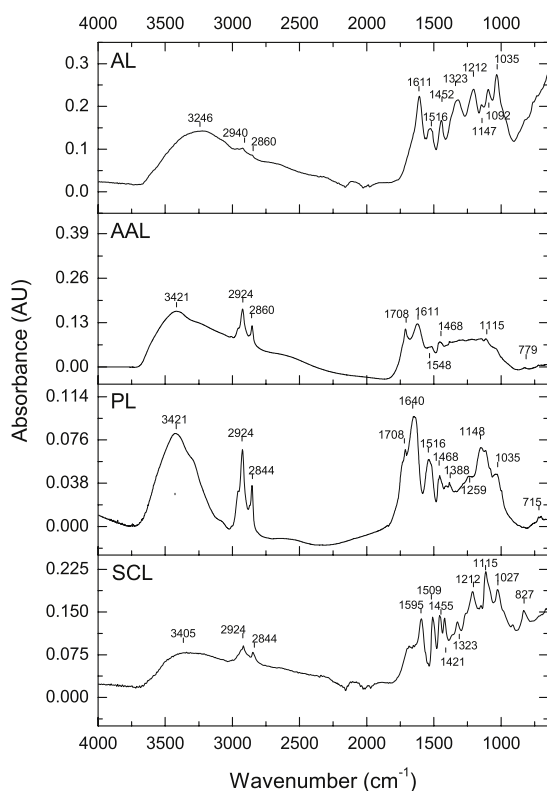

Fig. 2. FTIR spectra of lignin extracted from the cashew apple bagasse by different methods. (AL) lignin extracted from the cashew apple bagasse using acid pretreatment. (AAL) lignin extracted from the cashew apple bagasse using acid-alkali pretreatment (pH 13.5). (PL) lignin extracted from the cashew apple bagasse using alkaline hydrogen peroxidepretreatment (4.3% (v/v), pH 11.5, 5% (w/v) CAB, 35 °C, 250 rpm for 6 h). (SCL) Sugarcane lignin.

cause bond re-condensation in lignin during the alkaline pretreatment [53]. Also, the C=O stretching from conjugated *para*-substituted aryl ketones was characterized by the band observed at 1640 cm^{-1} [7,54]. The absorption bands spotted at around 1595 cm^{-1} (SCL) and 1611 cm^{-1} (AL) were attributed to aromatic skeletal vibrations (C=C).

The SCL presented a C=C stretching vibration in phenol rings located at 1516 cm^{-1} and 1420 cm^{-1}. The absorption band at 1420 cm^{-1} was due to symmetric bending vibrations of C–H bonds in methoxyl groups [7,51,55].

All CAB lignins exhibited bands at 1452 cm^{-1}, corresponding to C–H deformations (CH and CH$_2$) from phenol rings [51,55]. The band at 1212 cm^{-1} was assigned to the C–O group [49]. This band was more prominent in SCL and AL. Their FT-IR spectra also presented characteristics bands related to methoxyl groups of the syringyl unit (~1323 cm^{-1}) [54], being more intense in the spectra obtained from the AL and PL lignins.

Furthermore, the band at 1115 cm^{-1} was attributed to ether adsorption linkages (Fig. 2 SCL and PL), and the band at 1035 cm^{-1} was related to aromatic C–H in-plane deformations (guaiacyl > syringyl) plus C–O deformations in primary alcohols and non-conjugated C=O stretches (Fig. 2 AL).

According to Zhang et al. [56], the bands at 1604, 1515, 1462 and 1424 cm^{-1} indicated that the basic structure of lignin was not damaged during the fractionation process. Li et al. [19] studied five types of lignin treated with successive alkaline ethanol treatments, and the FT-IR spectra presented aromatic skeleton vibrations at 1594, 1507, and 1422 cm^{-1}, indicating a primary lignin structure. The FT-IR spectra of lignin extracted and analysed in this work suggested that the lignin fractions were similar and the primary structure of the lignin did not change significantly, except for AAL.

In order to characterize the extracted lignins using different treatments, ^{1}H–^{13}C HSQC-NMR was performed on the lignins extracted using dilute acid (Fig. 3a), and acid-alkali conditions (Fig. 3b), as well as on those extracted using alkaline hydrogen peroxide (Fig. 3c) and on the sugarcane lignin (Fig. 3d).

It is observed that the main compounds of lignin are syringyl (green contour) and guaiacyl (blue contour). Also, *p*-coumarate and oxidized syringyl are present in AAL (Fig. 3b), polysaccharides residues as aryl ether linkages (α–O–4 and β–O–4) are found in SCL (Fig. 3d), and other types of carbohydrate residues in PL, as highlighted by the square in Fig. 3c. Fatty acid residues were also observed in the HSQC-NMR spectrum (highlighted by the square in Fig. 3b), using the different extraction protocols (Fig. 3a to c). Fatty acids in lignin were previously observed in technical lignins from three main industrial pulping methods [31] and in crude lignin of perennial grass [57,58]. Chemical shifts are summarized in Table 3.

The use of different extraction protocols resulted in lignin with similar composition but with different signal intensity and even different chemical shifts to those observed for guaiacyl residues. The lignin obtained with AL presented more intense peaks and no carbohydrate residues. This occurs because the acid conditions induce cleavage of the lignin-carbohydrate crosslinks, mainly of hemicellulose chains [59]. In addition to that, the previous acid pretreatment was effectively utilized to remove hemicelluloses by breaking ether bonds in lignin/phenolics–carbohydrates complexes without dissolving the lignin [36,37]. The lignin obtained under the acid-alkali (AAL) conditions showed less intense peaks and an absence of carbohydrate residues attached. This fact can possibly occur due to a decrease in the S and H-units and inversely, to an increase in the condensed G-units. In the acid-alkaline pretreatment, a decrease in the S and H-units and an increase of condensed G units can be explained by the moderate reactivity towards condensation during pretreatment. The alkaline pretreatment disturbs the lignin structure and breaks linkages (such as aryl–ether, ester and C–C bonds) [3]. The lignin obtained by the pretreatment with alkaline hydrogen peroxide (PL) exhibited a spectrum with more intense peaks and low carbohydrate residues, showing that this condition results
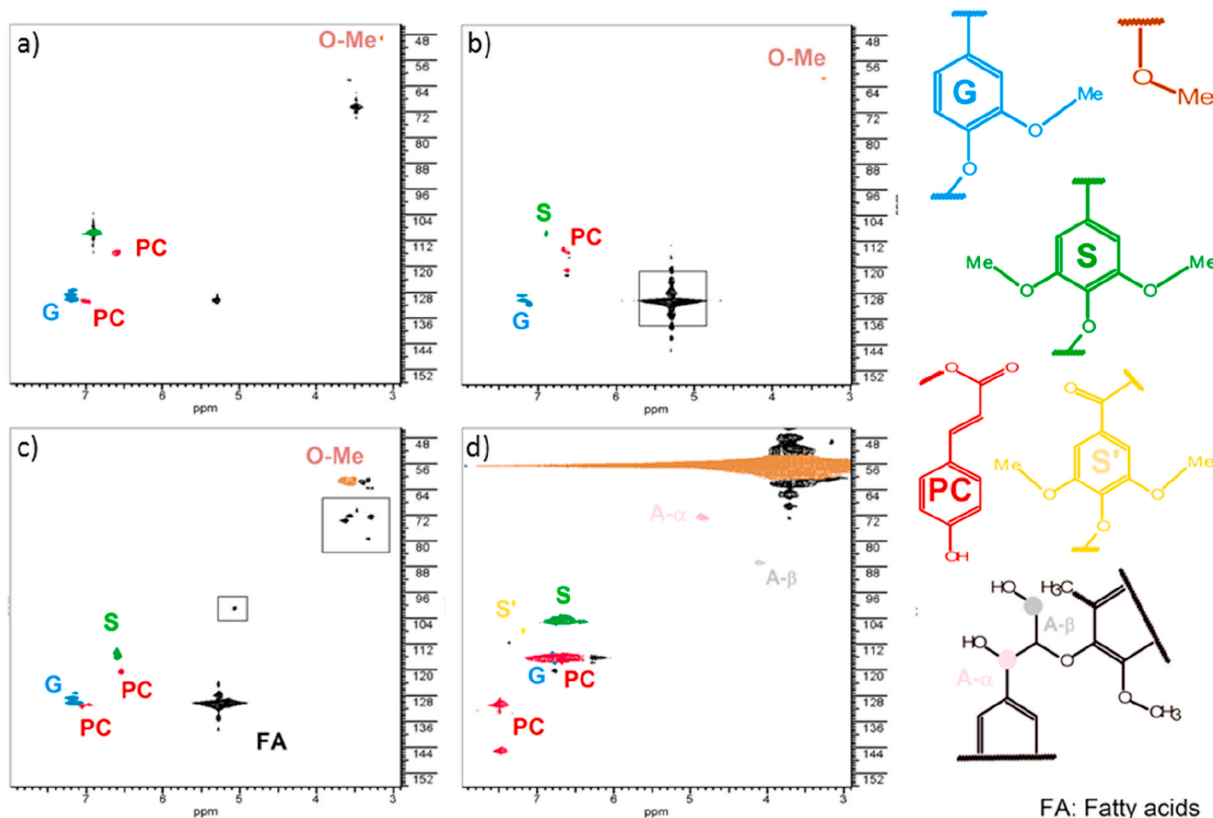
Fig. 3. ^1H–^{13}C HSQC NMR of lignin extracted from the hydrolysates of cashew apple bagasse obtained by (a) dilute acid pretreatment (AL); (b) acid-alkali pretreatment (AAL); (c) alkaline hydrogen peroxide (PL), and of the (d) sugarcane lignin.

Table 3

Nuclear magnetic resonance parameters for structural determination of lignin from cashew apple bagasse extracted by dilute acid pretreatment (AL), acid-alkali pretreatment (AAL), alkaline hydrogen peroxide pretreatment (PL); and sugarcane lignin (SCL).

Structures	Experimental signals (δ)^{13}C/^1H				Reference signals (δ)^{13}C/^1H
	AL	AAL	PL	SCL	Ref. 1 and 2
Oxidated Syringyl	no	no	no	107.5/ 7.19	106.3/7.3
Syringyl	109.3/ 6.9	109.4/ 6.90	113.9/ 6.60	104.9/ 6.65	104.3/6.7
p-coumarate	no	114.3/ 6.68	no	144.8/ 7.49	144.5/7.43
	130.6/ 7.00	130.7/ 7.00[a]	131.1/ 7.00	131.0/ 7.49	130.2/7.46
	115.7/ 6.60	119.6/ 6.64	120.5/ 6.55	115.5/ 6.79	115.4/6.76
	o	no	o	o	113.6/6.26
Guaiacyl	128.9/ 7.21	130.5/ 7.22	128.7/ 7.20	116.6/ 6.82	115.8/6.69
	130.4/ 7.20	131.5/ 7.13	130.5/ 7.18	119.8/ 6.79	119.1/6.79
	127.2/ 7.18	128.7/ 7.22	127.0/ 7.20	111.8/ 6.94	111.1/6.97
OCH3	62.1/ 3.56	60.3/ 3.34	61.3/ 3.56	56.9/ 3.73	56.4/3.07
A-α in β-*O*-4 linkages	no	no	no	72.4/ 4.84	71.8/4.86
A-β in β-*O*-4 linkages	no	no	no	86.8/ 4.10	83.4/4.38

Legend: no - not observed; o – overlapped.

[a] - not observed with the threshold used in Fig. 3.

in a more native-looking lignin.

The ratios between the intensity of syringyl and guaiacyl were determined, obtaining 0.999, 0.835, 1.080, and 9.141 for AL, AAL, PL and SCL, respectively. There was no significant difference in ratio among the lignins obtained from the cashew apple bagasse, but they were significantly different regarding the S/G ratio for SCL. This behavior occurs because, although the protocols are different, the biomass source is the same, differently from what occurred when comparing it to the lignin from the sugarcane bagasse.

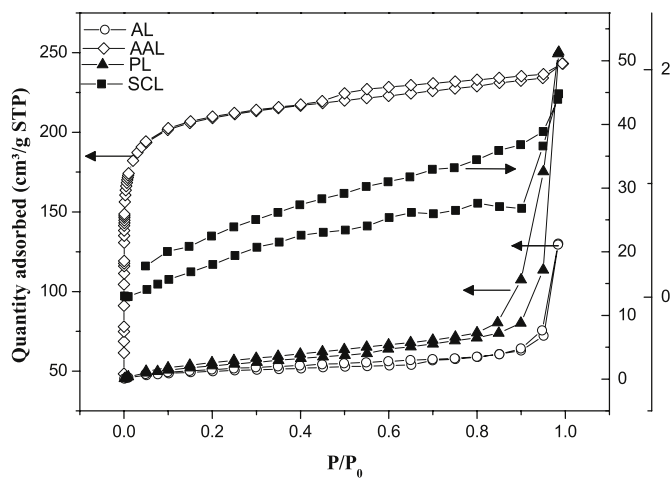N_2 adsorption-desorption isotherms of AL, AAL, PL and SCL samples

Fig. 4. N_2 adsorption/desorption isotherms at 77 K of lignins from cashew apple bagasse obtained by dilute acid pretreatment (AL, ○), acidic-alkali pretreatment (AAL, ◇), alkaline hydrogen peroxide pretreatment (PL, ▲) and sugarcane lignin (SCL, ■).

are shown in Fig. 4, while Table 4 reports the corresponding B.E.T. specific surface areas and the total pore volumes. The isotherms are quite different from each other, indicating that the pretreatments of CAB strongly affect the textural properties of the extracted lignin.

The AL and PL samples show a type III isotherm, which is typical of non-porous or macroporous materials with weak interactions. They have a surface area of 9.5 m^2 g^{-1} and 4.7 m^2 g^{-1}, respectively. The surface area of AL is similar to the lignin isolated from kenaf (*Hibiscus cannabinus*) by kraft treatment, with a surface area of 9.52 m^2 g^{-1} [60].

The AAL isotherm corresponds to a type I isotherm in the IUPAC classification, which is typical of microporous materials. As a consequence, AAL has a high value of the surface area, at about 814.2 m^2 g^{-1}. It can be noted that the curve also exhibits some hysteresis during the desorption phase, indicating the presence of mesoporous structures [61]. The specific surface area of AAL is close to the specific surface area of the Charbon 500 material (1025 m^2 g^{-1}) [62].

The SCL, in turn, shows an isotherm that is more representative of a type-II isotherm, according to the IUPAC classification, which is indicative of non-porous or macroporous materials. The reported surface area is 2.1 m^2 g^{-1}, the lowest among all the evaluated lignins.

3.4. Thermal stability

Thermal stability studies for the lignins extracted via the dilute acid, acid-alkali and alkaline hydrogen peroxide pretreatments were carried out by Differential Scanning Calorimetry (DSC). The DSC results show the variation of the curve in the degradation process (Fig. 5). For the extracted lignins, the DSC curves started with endothermic regions due to the heat required for the evaporation of moisture. After, the heat flow changed from endothermic to exothermic. In the second stage of heating, events were found up to 550 °C for AL, 450 °C for AAL, and up to 600 °C for PL.

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of lignin samples are shown in Fig. 6A e 6B, respectively. The behavior of the thermograms obtained for the lignins depends on the extraction protocol. Unlike AL, AAL, and PL, SCL demonstrated a different decomposition profile, with a more pronounced mass loss from 540 °C and up. At the end of the thermal degradation, the residual mass fraction was observed to have increased in the following order: SCL < AL < PL < AAL. The highest amount of residual fraction for AAL, compared to the residues obtained for AL and PL, may be attributed to the difficulty of decomposing this specific lignin due to condensation taking place during the AA pretreatment. Also, the thermal degradation behavior of lignin is related to its functional groups [63]. Lignins with a lower the content of functional groups, such as hydroxyl and methoxy groups, yields a higher amount of carbonized residues. Thus, lignins of higher functional groups content produced less carbon residues due to their lower thermal stability at 700 °C, as is the case with SCL (1.5%), compared to other lignins, while the AAL (lignin with lower content of methoxy groups) gave a higher percentage of residues (38.7%).

Overall, the lignins presented a small weight loss below 100 °C due to the gradual evaporation of water. The weight loss behavior of all lignins can be divided into stages relating to the different molecular weight fractions present in them.

The initial degradation temperature (100 °C) accounts for

Table 4
Specific surface area and total pore volume of lignins from cashew apple bagasse extracted by dilute acid pretreatment (AL), acid-alkali pretreatment (AAL), and alkaline hydrogen peroxide pretreatment (PL), and of sugarcane lignin (SCL).

Lignin	Surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})
AL	4.749	0.033
AAL	814.153	0.376
PL	9.495	0.080
SCL	2.079	0.003

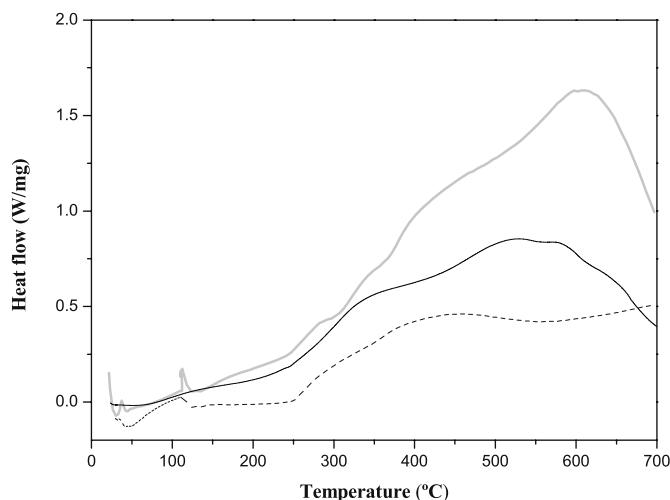**Fig. 5.** Differential scanning calorimetry (DSC) of lignins obtained by (—) dilute acid pretreatment, (—) acid-alkali pretreatment and (▪) alkaline hydrogen peroxide pretreatment.

approximately 10% of weight loss for all lignins. There is weight loss up to approximately 115 °C due to the evaporation of water and of low molecular weight substances, such as carbon monoxide and carbon dioxide. The thermal decomposition of lignin at 200 °C was due to the initiation of pyrolysis reactions, with the rupture of aliphatic compounds and linkages (e.g, ethers bonds, α-*O*-4 and β-*O*-4) [3].

The main degradation stage occurs in the temperature range of 300–500 °C, and it was associated with the interconnection fragmentation between units. Above 300 °C, ruptures of the bonds between units take place, resulting in the loss of lignin derivatives, including phenolics, alcohols, and aldehyde acids [22,64]. At 400 °C, degradation of the aromatic rings also occurs, along with the formation of coke [3]. Finally, a decomposition peak was possibly detected at very high temperatures (approximately 700 °C) in PL. The appearance of decomposition peaks at high temperature for PL can happened due to undergoes (re-)polymerization and cross-linking of lignin during the first stage of heating and a new degradation occurred at a higher temperature [65] or the peak refers to degradation of non-volatile inorganic residues [66].

3.5. Opportunities and prospects

Based on the characteristics of the extracted lignins, we propose the following possible applications:

The lignin obtained by acid pretreatment from CAB could possibly be used to produce gases of synthesis. The obtained gases can then be upgraded to fuels or chemicals using technologies developed for petroleum, including Fischer-Tropsch synthesis and methanol synthesis [3, 67]. In these processes, it is necessary to break these molecules, and the fact that lignins from this work show lower polymerization degrees may facilitate the process.

All lignins obtained (AL, AAL, and PL) may be used in the pyrolysis process for the production of oil and/or biogas. Pyrolysis is a thermochemical decomposition process that rapidly heats up the whole lignin to elevated temperatures in the absence of oxygen [68].

All the extracted lignins can also be possibly applied in the production of fuels. The conversion of lignin to fuels or well-defined chemicals involves two crucial processes (depolymerization and deoxygenation), and based on the characteristics obtained from PL (lignin extracted via oxidative fractionation), this seems to be the most appropriate pretreatment for this application [3,68].

The lignin obtained from the acid-alkali pretreatment (AAL) could be used in the production of fibers, carbon fibers and resins, since it presents higher thermal stability, and it may also be evaluated as a filler in
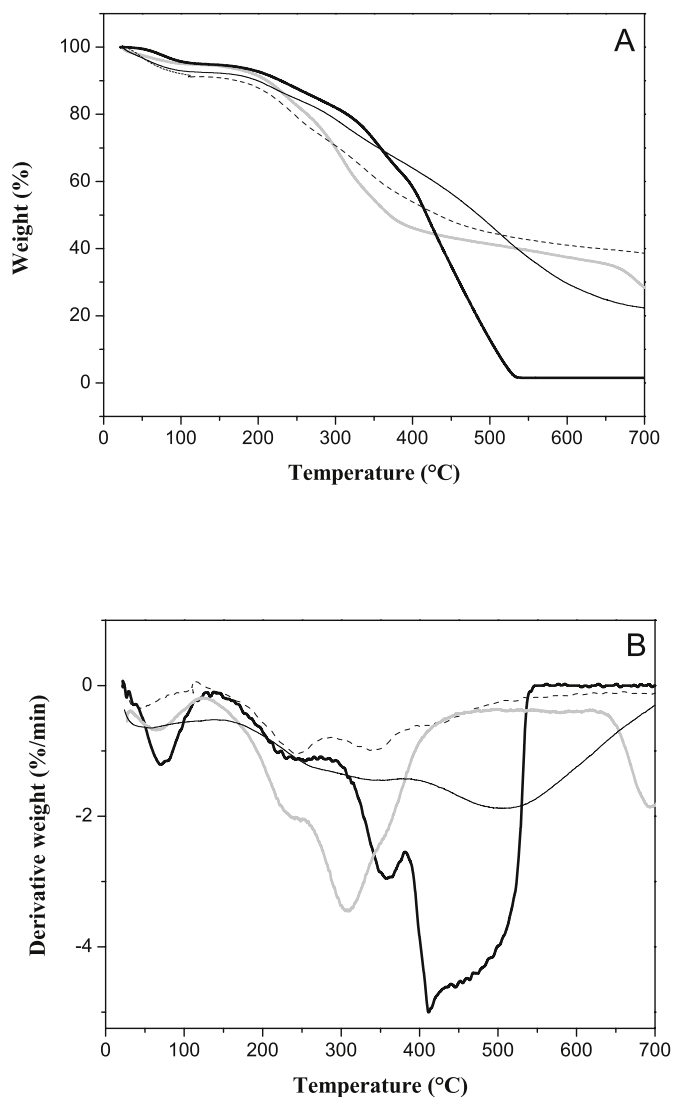
keeping its thermal stability. Compared to sugarcane lignin, the extracted lignins from the cashew apple bagasse exhibited better proprieties regarding thermal stability and superficial area. Finally, applications are emergent for these lignins in diverse areas, especially as sustainable alternatives to non-renewable products, as resins and/or as adsorbents.

Fig. 6. Thermal stability of the lignins obtained from different pretreatments of cashew apple bagasse represented by (A) weight loss and (B) derivative weight loss: (—) AL: lignin obtained from pretreatment with dilute acid; (—) AAL: lignin obtained from pretreatment with acid=alkali; (-) PL: lignin obtained from pretreatment with alkaline hydrogen peroxide; (-) SCL: sugarcane lignin.

bioplastic matrices [67], as an adsorbent, due to its superficial area, or as a support for enzyme immobilization. Also, the AAL showed a lower HHV, indicating that it can be used towards a plethora of applications aiming at adding value to kraft lignin, such as its use as an antioxidant, additive, polymer, among others.

Finally, the detailed structural properties of the obtained lignin fractions will benefit the efficient utilization of this natural biomolecule as a potential large-scale bio-based precursor for producing polymeric materials, adsorbents, biochemicals, functional carbon, biofuels, multifunctional polymer nanocomposites, and as supports for enzyme immobilization [3,15,37,67,69].

4. Conclusion

Cashew apple bagasse (CAB) has a high lignin content and the pretreatments with acid-alkali and alkaline hydrogen peroxide were effective in its fractionation to produce solids with high amounts of glucan and lignin. The characterization of the recovered lignin demonstrated that pretreatments utilizing acid-alkali and alkaline hydrogen peroxide are effective in depolymerizing the native lignin while, at the same time,

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