ORIGINAL RESEARCH

Structural and chemical characterization of lignin and hemicellulose isolated from corn fibers toward agroindustrial residue valorization

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Abstract Corn fiber (CF) is an agroindustrial residue obtained from starch or corn syrup. Currently, there has been increasing research interest in lignocellulosic materials from these residual materials. Consequently, this paper is a novel approach that complements the structural and chemical characterizations already published in the literature for CF. In this study, isolation, chemical composition and characterization was conducted of hemicellulose by means of ^{1}H NMR and FTIR-ATR and Klason lignin by means of acid soluble lignin (ASL) and acid insoluble lignin (AIL) determination using UV spectrophotometry and Py–GC−MS. Hemicellulose was obtained after aqueous extraction, lipid removal, delignification and alkaline extraction. The isolated hemicellulose from CF confirmed the presence of arabinoxylan, which was similar to the results reported in the literature. The CF contained 8.0% and 4.0% ASL and AIL, respectively. Regarding lignin, the study identified more than 47 primary pyrolysis products for ASL, with 17%, 20% and 59% relative molar abundance for lignin, carbohydrates, and other products, respectively, and 39 primary pyrolysis products with 44% and 7% relative molar abundance for lignin and carbohydrates, respectively. The main products derived from lignin were phenol, 4-methylphenol, guaiacol, 4-vinilguaiacol, syringol and syringylaldehyde. The peaks of lignin derivatives indicated that the Klason method is effective for lignin isolation, and the Py–GC−MS technique allowed for the identification of the presence of residual lignin in AIL and ASL from CF. In this context, lignocellulosic components of CF are chemically suitable for use as raw materials to transform biomass into high value-added products.

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Graphical abstract
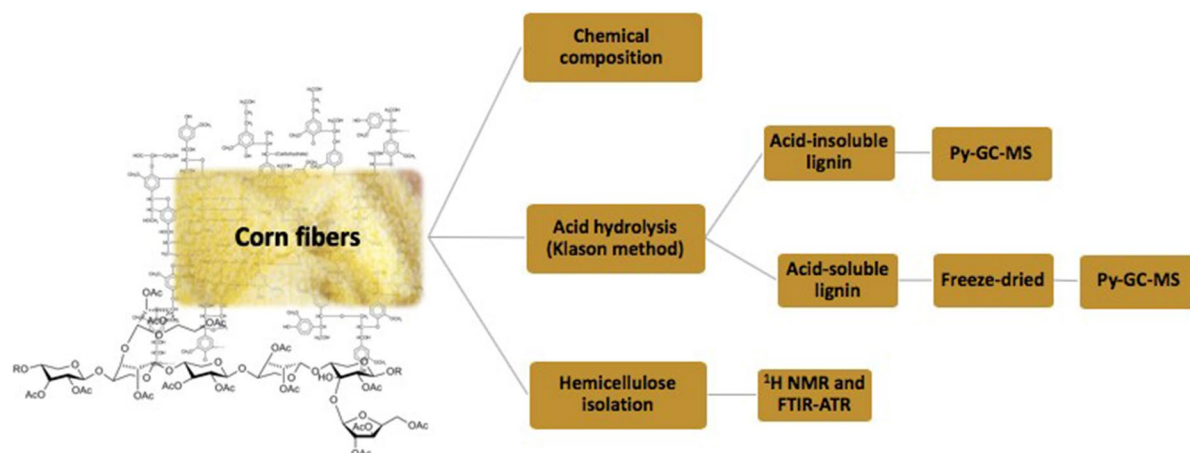
Introduction

Corn is an important industrial crop for the production of foods, but its industrial application is wider, for example, in the production of thickener, and binds oils and ethanol (Leathers 1998; Sindimilho 2005; Deutschmann and Dekker 2012). In the 2021/22 marketing year, the amount of corn produced worldwide amounted to over 1.2 billion metric tons. In that year, the United States was the largest producer of corn. This was closely followed by China and Brazil (United States Department of Agriculture 2022).

Corn grain is a fruit, called caryopsis, with a dry basis composition of starch (61–78%), proteins (6–12%), fiber (2–4%), oil (3–6%) and minerals (1–4%), distributed in a heterogeneous way on the four main physical structures of the grain: The endosperm, germ, pericarp (husk) and tip. The pericarp represents, on average, 5% of the total mass of the grain, with cell layers composed of cellulose and hemicellulose, although some content of lignin is also found on it (Paes 2007).

Corn fiber (CF) is an agroindustrial residue obtained from starch or corn syrup production and is commonly used for livestock feed. CF has a low market value and is a mixture of coarse fibers (from kernel pericarps or hulls) and fine fibers (from endosperm cellular material). Variable levels (11–23%) of adherent starch are also present in CF (Leathers 1998). CFs are constituted mainly by three structural components or fractions—lignin, cellulose and hemicellulose—and each component has specific properties destined for different uses in biorefineries.

Searches for uses of CF more highly valued than animal feed have long focused on the hemicellulose fraction, which accounts for over 50% of dry, starch-free fiber (Watson 1987; Kálmán et al. 2006; Álvarez et al. 2017; Barbosa et al. 2018; de Mattos et al. 2019). In the specific case of CF, the xylans usually present a chemical structure formed by 4-O-methyl-D-glucuronic acid, L-arabinose and D-xylose joined by intermolecular hydrogen bonds in the ratio 2:7:19 (Silva et al. 1998). Nuclear magnetic resonance (NMR) spectroscopy is a spectroscopic technique used to identify the molecular structure of lignocellulosic materials. ^{1}H NMR is applied to study alkali-extracted hemicellulose from plants, in addition to the degree of substitution of xylan and the efficiency of reactions (Peng et al. 2012; Silva et al. 2015). In previous papers, xylan isolated from CF has been shown to be applicable as an additive in papermaking (Barbosa et al. 2016, 2018), textile printing (Bartos et al. 1990; Song et al. 2016), the production of chemicals such as furfural (Barbosa et al. 2014; Cornelius and

Ta 2021) and the pharmaceutical industry (Lichnerova´ et al. 1991; Khaire et al. 2022). In this context, corn fibers are an example of an alternative source and contain a considerable reservoir of hemicellulose and lignin.

Lignin is a macromolecule that constitutes part of the chemical composition of CF; furthermore, lignin permits expansion of the bioproduct possibilities to monomers, polymers and chemicals of high-value added (Boerjan et al. 2003; Beramendi-Orosco et al. 2004; Gillet et al. 2017; Boschetti et al. 2019; Barbosa et al. 2022). Lignin is currently quantified via the Klason method, in which the extractive-free carbohydrate fraction of biomass is hydrolyzed with acid and the remaining material is determined gravimetrically as lignin. This lignin is called acid-insoluble lignin (AIL), according to the Technical Association of the Pulp and Paper Industry (TAPPI; T222 om-98). However, hardwoods (HWDs), corn fibers, sugarcane bagasse and other biomass contain a certain amount of lignin that is purportedly solubilized under the acidic conditions of the Klason method and that must be quantified by some other procedure to assess the total amount of lignin. This acid-soluble lignin (ASL) has been measured by ultraviolet (UV) spectroscopy in the filtrate of the biomass acid hydrolysate derived from the Klason method (Swan 1965; Goldschmid 1971; Yasuda and Murase 1995; Yasuda et al. 2001).

The resulting large values for ASL content (2–6% by biomass wt), especially for certain eucalyptus wood types, have triggered suspicions about the accuracy of these ASL measurement approaches. Some compounds derived from degraded sugars may absorb UV light more intensely than predicted in the known methods, leading to overestimations of ASL content.

The quantitative determination of lignin content with the Klason method is considered good, but for high ASL content values, it is necessary to study the structural composition of lignin. An alternative analysis used for the structural characterization of lignin is pyrolysis coupled with gas chromatography–mass spectrometry (Py–GC−MS) (Silvério et al. 2008; Vaz Jr 2016; Brumano et al. 2020). This analysis requires very small samples, without any preparation, over short times and based on thermal degradation of lignin, producing components that can be analyzed by gas chromatography–mass spectrometry; with the application of this analytical technique, we can obtain information about the chemical constitution of macromolecular species, e.g., precursor constituents, for lignin.

The chemical composition is a paramount factor for the development of processes for the production of renewable chemicals from lignocellulosic material, and this paper reports a structural and chemical characterization of CF using advanced analytical techniques. Indeed, it is relevant to obtain a proper analytical characterization of regional biomass to apply the best conversion processes for the economic approach for biomass valorization, i.e., chemical, biochemical and physical processes. Therefore, this study aimed to determine the chemical composition, isolation and characterization of hemicellulose by means of ^{1}H NMR and FTIR-ATR, and Klason lignin by ASL and AIL using UV spectrophotometry and Py–GC−MS. Consequently, this paper complements the characterizations published for CF, involving the quantification of lignin derivatives obtained via the Klason method, in addition to hemicellulose isolation.
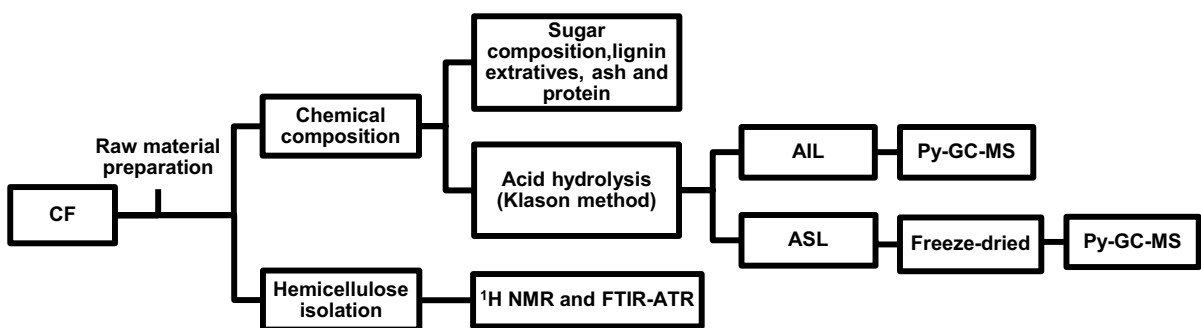

Fig. 1 A diagram of the whole analytical workflow of structural and chemical characterizations for CF

Materials and methods

Raw material preparation

CF was kindly provided by Cargill of Uberlândia, Brazilian state of Minas Gerais (southeastern region). CF was ground in a Wiley-type mill to produce sawdust and sieved to ensure particle size uniformity according to TAPP standard T257 cm-85. The sawdust that passed through the 40-mesh screen and was retained in the 60-mesh screen was selected for chemical analysis. Subsequently, the sample was air-dried and conditioned in a temperature- and humidity-controlled room (23 ± 1 °C, $50 \pm 2\%$ RH) until equilibrium moisture content was achieved ($\sim 10\%$). All samples were extracted with acetone and subjected to moisture determination in accordance with TAPPI standard T204 cm-07 (Technical Association of the Pulp and Paper Industry 1997). The whole analytical workflow of structural and chemical characterizations for CF is shown in the diagram in Fig. 1.

Reagents

All reagents, solvents and analytical standards were acquired from commercial sources. NaOH, 3,5-dimethylphenol, nitrobenzene, chloroform, acetone, 5-formyl-2-furoic acid, 3,5-dimethylphenol, H_3PO_4, formamide, pyridine, acetic anhydride, hydrochloric acid, diethyl ether, $CDCl_3$, and TMS (99.9 wt%) were purchased from Sigma−Aldrich, USA. H_2SO_4, oxalic acid, hydrogen peroxide, glacial acetic acid, ethanol, methanol, and acetonitrile (98% wt%) were acquired from Merck, Germany.

Chemical composition

The carbohydrate composition of CF was evaluated by high-performance anion exchange chromatography with a pulse amperometric detector (HPAEC-PAD). HPAEC-PAD was carried out in a Dionex ICS-3000 (Dionex, USA) system equipped with a CarboPac PA1 (250 mm $\times$ 4 mm) analytical column and was performed after sample pretreatment (30 °C, 1 h) with aqueous 72% (w/v) H_2SO_4 followed by hydrolysis with 3% (w/v) H_2SO_4 in an autoclave (AB 25 A 60 L, Phoenix Luferco, Brazil) at 1 kgf/cm^2 and 120 °C for 3 h. The monosaccharides were separated isocratically with 0.001 mol L^{-1} NaOH for 45 min at a flow

rate of 1 mL min^{-1} according to Wallis et al (1996). The solid residue after hydrolysis was considered AIL according to TAPPI standard T222 cm-11 (Technical Association of the Pulp and Paper Industry 2011a) and was determined gravimetrically. ASL was determined by measuring the UV absorbance of the filtrate and analyzed by a UV technique (Cary 50 Probe, Varian, USA) and was determined according to TAPPI standard UM 250 (Technical Association of the Pulp and Paper Industry 2011b), where 215 nm was the absorbance value of the lignin filtrate and 280 nm was used for correction of the potential interference from furfural and 5-hydroxymethylfurfural formation from carbohydrates during acid hydrolysis (Goldschmid 1971).

The composition of lignin, particularly the syringyl/guaiacyl ratio (S/G ratio), was obtained by extractive-free sawdust together with NaOH aqueous solution and nitrobenzene into a stainless-steel reactor and heating to 170 °C for 2.5 h. After the oxidized material was extracted with chloroform and analyzed by high-performance liquid chromatography (HPLC) (Shimadzu with SCL-10A system controller, Japan) with UV detection and the following conditions: column, LC-18; mobile phase, acetonitrile/water (1:6 v/v), pH 2.6 with TFA; detection, UV, 280 nm; column temperature, 40 °C; and flow rate, 1.5 mL/min. The chromatographic standards were vanillin for guaiacol and syringaldehyde for syringyl according to Lin and Dence (1992). Ashes was determined by calcination according to TAPPI standard T211 om-12 (Technical Association of the Pulp and Paper Industry 2011c). Extractives in acetone were analyzed according TAPPI standard T204 cm-07 (Technical Association of the Pulp and Paper Industry 2007). Total uronic acids were measured after hydrolysis with H_2SO_4 to 5-formyl-2-furoic acid, which was calorimetrically determined after reaction with 3,5-dimethylphenol by UV spectroscopy (Cary 50 Probe, Varian, USA) at 450 nm (Scott 1979). The acetyl group contents were determined in the extractive-free sawdust after hydrolysis with oxalic acid at 120 °C for 80 min using HPLC (Shimadzu with SCL-10A system controller, Japan) with UV detection, according to Solár et al. (1987). The HPLC instrument used was from Shimadzu with an SCL-10A system controller and an LC-18.5 mm column, 25 cm (18.5 mm $\times$ 25 cm) (Shimadzu LC Shim-pack CLC-ODS, octadecyl, Japan). The temperature was 40 °C, the injection volume

was 20 μL, and the flow rate was 0.6 mL min^{-1}. The mobile phase was H_3PO_4, 37 mmol L^{-1} (pH 2.2) adjusted with NaOH. The protein content was determined by the Kjeldahl method (IDF 1993). All results were calculated from duplicate determinations.

Hemicellulose isolation and spectroscopic characterization

Hemicellulose was obtained following the methodology described by Silva et al. (1998). The CF sawdust was subjected to aqueous extraction at a ratio of 30 g of CF to 1000 mL of distilled water with constant stirring for 12 h. The mixture was centrifuged, and the solid phase was dried in a climatic room at 23 °C and 50% humidity for 24 h. After drying, the material obtained was subjected to the delignification process at a 1:10 ratio (w/v) using hydrogen peroxide 2% (w/v) at pH values of 11 and 70 °C for 2 h. The delignified raw material was washed with distilled water with three times the volume of suspension.

Solubilization of hemicellulose was performed by alkaline treatment, when the material was then subjected to 10% NaOH (w/w) at 25 °C for 24 h under slow agitation at a ratio of 1:10 (w/v). Then, the solution was neutralized by adding glacial acetic acid (pH value of 7.0). Hemicellulose was precipitated by the addition of ethanol in the proportion of three volumes of ethanol to 1 volume of the solution. The obtained product was centrifuged for 10 min at 4000 rpm, resulting in a consistency of 20% viscosity.

The acetylation process was used to increase the hydrophilicity, and structural analysis was performed by ^1H NMR. The esterification of arabinoxylan was carried out using the experimental conditions described in Stepan et al. (2012). Arabinoxylan (1.00 g) was dispersed in formamide (25 mL). Pyridine (40 mL) was added, followed by acetic anhydride (6.6 mL). After stirring at room temperature for 3 h, another portion of acetic anhydride (6.6 mL) was added, followed by the same amount after another 3 h. After 30 h, the viscous dark solution was poured (under vigorous stirring) into 1.3 L of 2% ice-cold hydrochloric acid. The white fluffy precipitate was filtered on a Buchner funnel with filter paper and washed with excess (0.5 L) deionized water, then with 0.5 L methanol and finally with 0.5 L diethyl ether. Then, the samples were dried in a fume hood overnight.

Nuclear magnetic resonance analysis

^1H NMR measurements were carried out on the isolated hemicellulose. Acetylated hemicellulose (~ 10 mg) was dissolved in 0.4 mL of CDCl$_3$ containing 0.03% (v/v) TMS. One-dimensional ^1H NMR spectra were acquired with a Mercury-300/Varian, USA spectrometer at 300.069 MHz (32 k data points, 30 excitation pulse duration of 2.2 ls, spectral width of 6 kHz, acquisition time of 3.3 s and relaxation delay of 10 ms) in 5 mm probes with direct detection, using TMS as internal standard (δ = 0.00).

Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR)

A Varian 660-IR spectrometer (Varian, USA) equipped with a liquid nitrogen-cooled mercury cadmium telluride detector and an attenuated total reflectance (ATR) probe was used in this work. The sample was placed on the ATR probe to collect the FTIR spectrum. During the experiment, 60 scans were coadded to achieve an acceptable signal-to-noise ratio, with wavenumbers ranging from 4000 to 500 cm^{-1}. All the spectra were recorded at a resolution of 4 cm^{-1}.

Structural investigation of acid hydrolysis (Klason method) by Py–GC−MS

For the structural investigation of lignin obtained by the Klason method, ASL was freeze-dried. AIL and lyophilized ASL were pyrolyzed at 550 °C for 10 s using a Pyr A-4 furnace pyrolizer (Shimadzu, Japan) coupled to a GC−MS apparatus (Shimadzu, Japan, model PQ5050A) using a fused silica capillary column (DB-5, 30 m × 0.25 mm ID, 0.25 μm film thickness). A finely powdered sample (100 μg) was deposited in a small platinum cup that was then inserted into a quartz tube (2 mm × 40 mm) placed in the pyrolysis chamber. The pyrolysis chamber was kept at 250 °C and purged with helium to transfer the pyrolysis products as quickly as possible to the GC column. The chromatograph oven was ramped from 40 °C (4 min) to 300 °C at a rate of 4 °C min^{-1}. The final temperature was held for 40 min. The injector and GC−MS interface were kept at 200 °C. The mass spectrometer was operated in the electron impact ionization mode at 70 eV with a mass scan range of

Table 1 Chemical composition, % (w/w) results CF (percentage on oven-dry weight basis) and reported by other authors

Component, %(w/w)	Results	de Mattos et al. (2019)	Barbosa et al. (2014)	Lili et al. (2011)
Glucose	32.9	33.5	47.1	34.6
Xylose	16.9	17.4	28.0	27.0
Arabinose	11.3	11.7	5.4	3.6
Galactose	3.1	3.3	2.2	–
Mannose	0.7	0.8	0.2	–
Acetyl groups	1.9	1.7	2.9	0.3
Uronic acids	1.0	0.9	2.2	–
ASL	8.0	–	–	–
AIL	4.0	–	–	9.4
Total lignin[a]	12.0	8.4	17.8	–
S/G	0.1	–	–	–
Ash	0.9	0.7	1.2	2.5
Extractives	14.0	20.8	–	–
Proteins	11.5	–	–	–

All sugars expressed as anhydrounits in polymers;

[a]Total lignin (including AIL and ASL)

40–600 Da. The temperatures of the detector and the GC−MS interface were 250 and 290 °C, respectively. Compounds were identified by comparing their mass spectra with the GC−MS spectral library (Wiley 333 000), and the results were interpreted according to del Río et al. (2005), Silvério et al. (2008), and Ralph and Hatfield (1991).

Results and discussion

Chemical composition of CF

The chemical compositions of CF (percentage on an oven-dry weight basis) are shown in Table 1, as well as the data based on two replicate determinations. The raw materials are defined by their sugar composition (glucose, xylose, arabinose, galactose, mannose, acetyl groups, uronic acids), lignin (ASL, AIL, S/G ratio and total lignin), extractives, ash, and protein. Due to the presence of ash, AIL analysis gave an overestimation of the lignin content; therefore, the lignin content was corrected by the ash content (Anglès et al. 1997).

The CF presented a total sugar content of 67.8%. When compared to the literature data, this content is lower than that observed in CF, such as 69.3% (de Mattos et al. 2019) and 88.0% in corn cob (Barbosa et al. 2014), but higher than other values found in corn cob (65.2%) (Lili et al. 2011). The structural

carbohydrates (glucose and xylose), which are the major substrates for furan production, accounted for approximately 49.8% of the CF (Table 1). These values are in the range found by other researchers for this kind of material (Van Dongen et al. 2011; Silva et al. 2015; Barbosa et al. 2018). It is known that pentoses and hexoses, respectively, are the precursors for furfural and HMF formed during the conversion of lignocellulosic biomass (Sánchez et al. 2013; Barbosa et al. 2014; Guo et al. 2019). Determination of the initial quantity of the main constituents available in biomass allows for the calculation of the yields and theoretical conversion rates of furfural from raw material by the calculation of furfural-production efficiency.

Additionally, the data showed that the pentose content (xylose + arabinose) was associated with the presence of uronic acids and acetyl groups, suggesting that corn fiber hemicellulose could be classified as 4-O-methyl-glucuronoarabino-xylan acetate (GAX), similar to those proposed, for example, for corn stover hemicellulose (Silva et al. 1998) and corn cob in Silva et al. (2015), which constitutes an adequate content comparable to that found in wheat hulls, cotton seeds, and nut shells commonly used for furfural production (Mansilla et al. 1998; Liu et al. 2018; Sun et al. 2020). In papermaking, some studies have pointed out that the xylans added onto pulp can also improve paper strength properties such as the

tensile index (Sihtola and Blomberg 1975; Sjöberg et al. 2002; Barbosa et al. 2018).

The chemical composition of CF showed that total lignin was 12.0%. Because of the current importance of lignin as a raw material for the production of bioproducts and biofuels (Egüés et al. 2014; Vaz Jr 2018), samples were also analyzed for their AIL and ASL contents. The lignin contents in the ASL and AIL fractions were 8.0 and 4.0%, respectively. These values are acceptable for chemical production. However, its low S/G ratio, that the is, low number of syringyl units, will condense more during the acid hydrolysis procedure and produce low ASL in the filtrate (Gomes et al. 2015). The S/G ratio of CF reflects the content of lignin ASL and AIL.

Another unique characteristic of CF is its high content of extractives (14.0%) and proteins (11.5%), probably caused by contamination during the processing of corn kernels. These may include starch, proteins and oils that are susceptible to extraction by the eluotropic solvent series procedure applied.

Hemicellulose isolation and spectroscopic characterization

The process used to isolate hemicellulose can be considered efficient for CF, with a total concentration of xylose and arabinose (Table 1) of 28.2%; hemicellulose was obtained after the isolation of xylose and arabinose at a concentration of 44.7% from a process with a yield of 60%. Therefore, the final xylose and arabinose yield was 26.8%. The arabinoxylan content is 88% of the sum content of xylose and arabinose (de Mattos et al. 2019), i.e., 23.6% arabinoxylan, 21.2% xylan and 2.4% arabinan.

The isolated hemicellulose was analyzed through FTIR-ATR and ^{1}H NMR. An FTIR-ATR spectrum of unmodified hemicellulose and acetylated hemicellulose from CF is shown in Fig. 2 A and B, respectively. The bands found at 3340 and 2979–2899 cm^{-1} indicate the OH stretching and CH bond deformation of CH_2 and CH_3 groups, respectively (Egüés et al. 2014). The prominent band at approximately 3340 cm^{-1} represents the hydroxyl stretching vibrations of the hemicellulose and water involved in hydrogen bonding (Sun et al. 2004; Morais et al. 2017).

According to Sun et al. (2004), bands between 1175 and 1000 cm^{-1} are typical of xylans. At 1042 cm^{-1}, stretching and bending vibrations of C–O, C–C, C–OH, and C–O–C were observed (Fig. 2). It was possible to see two low-intensity shoulders at the 1042 cm^{-1} peak (at 1162 and 979 cm^{-1}), which have been reported to be attached only at positions of the xylopyranosyl constituents (Sun et al. 2004; Morais et al. 2017). The intensity changes in these two bands indicate the contribution of arabinosyl substituents.

Fig. 2 FT-IR spectra. **A** CF unmodified hemicellulose, and **B** acetylated hemicellulose
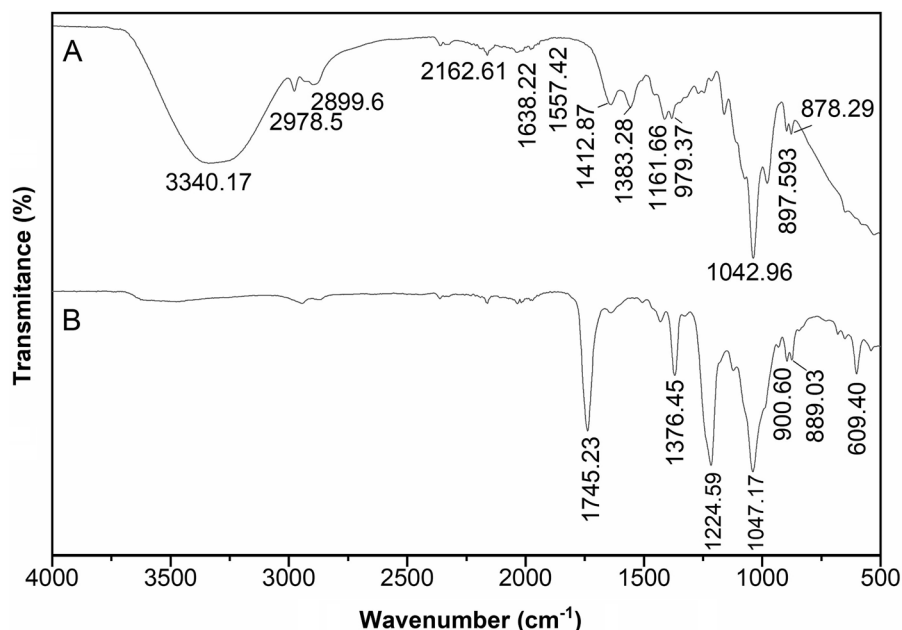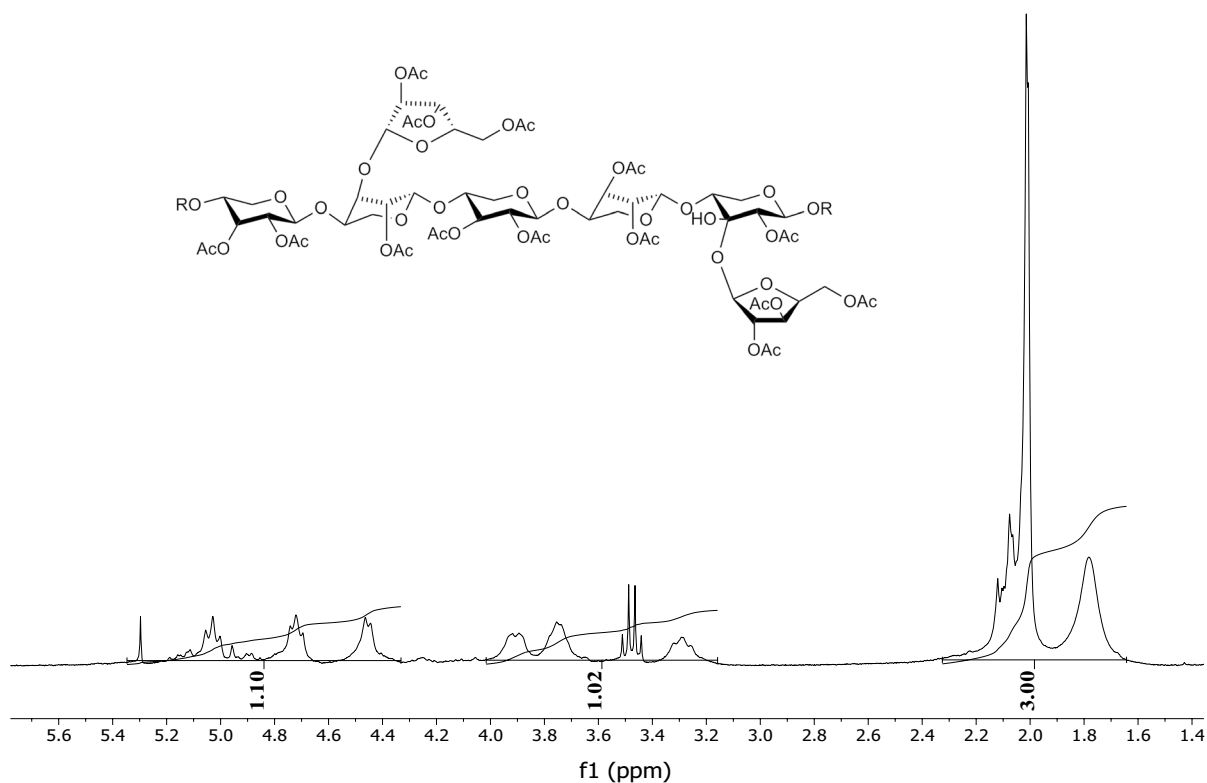
Fig. 3 ^{1}H NMR spectrum of acetylated hemicellulose (dissolved in CDCl$_3$) and the structure of acetylated 4-*O*-methyl-(glucurono) arabinoxylans
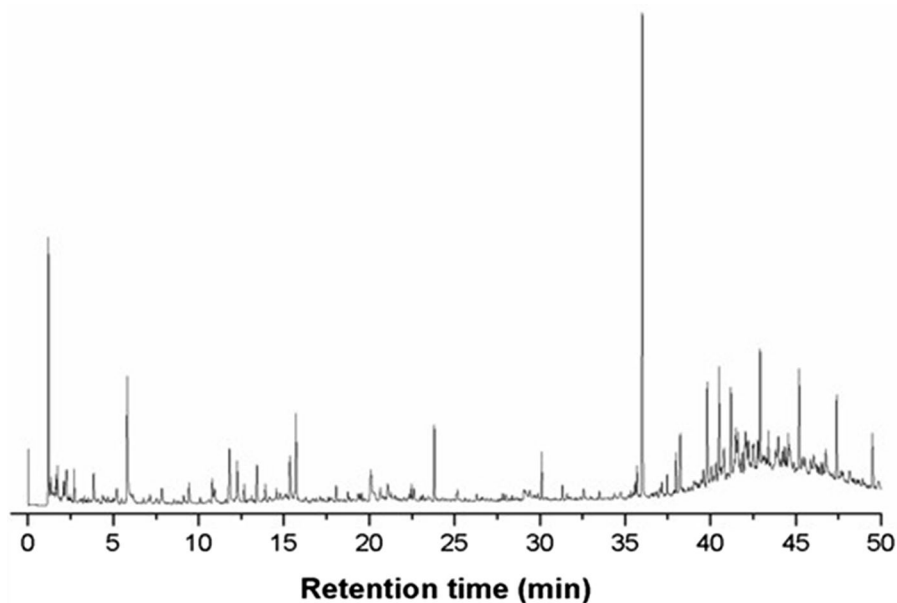
Therefore, it was used for the identification of arabinoxylan structures.

FT-IR spectroscopy was mainly carried out to ensure that the acetylation process truly occurred. The prominent band at approximately 3340 cm^{-1} (Fig. 2A) represents the hydroxyl stretching vibrations of the hemicellulose and water involved in hydrogen bonding (Sun et al. 2004). The decrease in the band at 3340 cm^{-1} (Fig. 2B) indicates that hydroxyl groups and adsorbed water were almost completely substituted during the acetylation process. Two other peaks at 1552 and 1412 cm^{-1} (Fig. 2A) were observed and correspond to CH and OH bending, respectively (Sun and Tomkinson, 2002; Egüés et al. 2014). Acetylation could be clearly verified by the presence of three important ester bands at 1745 cm^{-1}, C=O ester, 1376 cm^{-1}, –C–CH$_3$, and 1224 cm^{-1}, –C–O-stretching band. The lack of peaks at 1840–1760 cm^{-1} (Fig. 2 B) suggests that the product is free from unreacted acetic anhydride (Sun et al. 2004; Morais et al. 2017; Lu et al. 2021).

The efficiency of the acetylation reaction was also verified by ^{1}H NMR, as shown in Fig. 3. Important peaks appeared in the spectrum at 1.9–2.0, 4.5 and 5.0 ppm, indicating methyl protons of ester chains, anomeric protons of xylan and anomeric protons of D-arabinofuranosyl, respectively (Egüés et al. 2014; Morais et al. 2017).

The degree of arabinose substitution of xylan is the key factor that positively affects the maximum degree of substitution, and the ratio obtained xylose and arabinose was approximately 9 units of xylose per unit of arabinose, as shown in Fig. 3. Then, the maximum degree of substitution of this material is obtained through the sum of available OH groups per sugar multiplied by the sugar concentration. Other authors found different degrees of substitution values by ^{1}H NMR for acetylated hemicellulose between 0.49 and 1.53 due to variation in the conditions of the reaction, such as reaction temperature, reaction time, dosage of catalyst and amount of acetic anhydride (Sun et al.

Fig. 4 A typical pyrogram
of ASL of CF. For the list
of components, see Table 2

Identification of fragments of ASL analyzed by Py–GC−MS

The analytical pyrolysis method is based on the degradation of lignin into monomeric fragments induced by thermal energy under an inert atmosphere, producing a mixture of relatively simple aromatic compounds. These compounds can be directly separated by gas chromatography and identified by mass spectrometry (Ralph et al. 1991; Zier et al. 1997; Silvério et al. 2008). Then, lignin can be chemically characterized on the basis of the pyrolysis products.

The samples from CF were pyrolyzed, and the pyrolysis products were separated and characterized by Py–GC−MS. A typical pyrogram of CF is shown in Fig. 4. It was possible to identify a total of 47 compounds for CF (Table 2). These compounds were broadly classified as carbohydrate derivative products, lignin derivatives and others (extractives and proteins derived).

Approximately 20% of the compounds identified for CF are products derived from carbohydrate pyrolysis. Acetic acid, 5-methylfuran, furfural, furfuryl alcohol, 3-furaldehyde, cyclopentanone, 5-methylfuran, 5-hydroxymethylfurfural, and 2,3-dihydrobenzofuran were some of the observed carbohydrate derivatives. This implies that acid hydrolysis occurred efficiently and that carbohydrate degradation resulted in furanic compounds.

The main products derived from lignin are phenol, 2-cresol, 4-cresol, guaiacol, 4-ethylphenol, 5-methylguaiacol, catechol, 2-*tert*-butylphenol, 4-ethylguaiacol, 2-methyl-5-isopropylphenol, 4-vinylguaiacol, syringol, 2-methyl-6-*tert*-butylphenol and 2,6-di-*tert*-butylphenol. These substances were identified in previous works involving lignin degradation by analytical pyrolysis [40]. Other compounds also detected included dimethylnitrosamine, ethylene glycol, methylbenzene, 1-chloro-2-ethylhexane, 2,4-dimethyl-1-decene, phenylacetaldehyde, acetone anil, dimethyl phthalate, 4-methyl-2,6-di-*tert*-butylphenol, 2-butyl-5-isobutylthiophene, lauric acid diethanolamide, ethylhexyl benzoate, ethylphenoxy benzene, 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 1,3-diphenyl-1-butene, octadecane, nonadecane, diisobutyl phthalate, henicosane, and methyl palmitate. These may be generated by the degradation of extractives and proteins. It was observed that the content of compounds from other sources in the CF was greater than that of carbohydrate and lignin.

Although not commonly investigated, the amount of ASL seems to be related to the lignin S/G ratio. The amount of syringyl monomers will condense less during the strong acid hydrolysis treatment, since the C5 position in the aromatic ring is blocked in the

**Table 2** Main compounds identified by Py–GC−MS in ASL of CF

Retention time (min)	Compound	Molecular formula	Molecular weight (g mol^{-1})	Relative area (%)	Origin
1.195	Chloroacetic acid	$C_2H_3O_2Cl$	94.50	8.58	C,L
1.340	UI	–	–	0.56	–
1.653	Ethylene glycol	$C_2H_6O_2$	62.07	0.73	O
1.734	5-Methylfuran	C_5H_6O	82.10	0.64	C
2.257	Acetic acid	$C_2H_4O_2$	60.05	1.95	C,L
2.737	Dimethylnitrosamine	$C_2H_6N_2O$	74.08	–	O
3.834	Methylbenzene	C_7H_8	92.14	0.75	O
5.811	Furfural	$C_5H_4O_2$	96.09	4.96	C
6.740	Furfuryl alcohol	$C_5H_6O_2$	98.10	–	C
9.435	1,2-Cyclopentanedione	$C_6H_8O_2$	112.13	0.67	C
10.791	5-Methylfurfural	$C_6H_6O_2$	110.11	0.95	C
11.803	Phenol	C_6H_6O	94.11	3.65	L
12.258	UI	–	–	1.28	–
12.673	1-Chloro-2-ethylhexane	$C_8H_{17}Cl$	148.67	0.7	O
13.420	2,4-Dimethyl-1-decene	$C_{12}H_{24}$	168.32	2.02	O
13.914	Phenylacetaldehyde	C_8H_8O	120.15	0.64	O
14.561	2-Cresol	C_7H_8O	108.14	0.38	L
15.359	4-Cresol	C_7H_8O	108.14	1.81	L
15.713	Guaiacol	$C_7H_8O_2$	124.14	3.4	L
18.067	UI	–	–	0.76	–
18.753	4-Ethylphenol	$C_8H_{10}O$	122.16	0.31	L
19.582	5-Methylguaiacol	$C_8H_{10}O_2$	138.17	0.25	L
20.094	Catechol	$C_6H_6O_2$	110.10	1.48	L
20.651	2,3-Dihydrobenzofuran	C_8H_8O	120.15	0.54	C
21.074	5-Hydroxymethylfurfural	$C_6H_6O_3$	126.11	0.63	C
22.472	2-*tert*-Butylphenol	$C_{10}H_{14}O$	150.22	0.61	L
22.616	4-Ethylguaiacol	$C_9H_{12}O_2$	152.18	0.55	L
23.137	2-Methyl-5-isopropylphenol	$C_{10}H_{14}O$	150.22	0.2	L
23.810	4-Vinylguaiacol	$C_9H_{10}O_2$	150.18	3.55	L
25.104	Syringol	$C_8H_{10}O_3$	154.16	0.11	L
25.165	2-Methyl-6-*tert*-butylphenol	$C_{11}H_{16}O$	164.25	0.17	L
27.822	2,6-Di-*tert*-butylphenol	$C_{14}H_{22}O$	206.33	0.28	L
27.992	Acetone anil	$C_{12}H_{15}N$	173.26	0.31	O
28.381	Dimethyl phthalate	$C_{10}H_{10}O_4$	194.18	0.13	O
29.076	UI			0.32	–
30.109	4-Methyl-2,6-di-*tert*- butylphenol	$C_{14}H_{22}O$	220.35	2.23	O
31.323	2-Butyl-5-isobutylthiophene	$C_{12}H_{20}0S$	196.35	0.7	O
31.601	Lauric acid diethanolamide	$C_{16}H_{33}NO_3$	287.44	0.21	O
35.700	Ethylhexyl benzoate	$C_{15}H_{22}O_2$	234.34	1.37	O
36.013	Ethylphenoxy benzene	$C_{14}H_{14}O$	198.27	26.34	O
37.162	3,5-di-*tert*-Butyl-4-hydroxybenzaldehyde	$C_{15}H_{22}O_2$	234.34	0.48	O
37.465	1,3-Diphenyl-1-butene	$C_{16}H_{16}$	208.30	0.98	O
37.986	Octadecane	$C_{18}H_{38}$	254.50	1.89	O
38.239	Nonadecane	$C_{19}H_{40}$	268.52	4.01	O
39.806	Diisobutyl phthalate	$C_{16}H_{22}O_4$	278.35	5.72	O

Table 2 (continued)

Retention time (min)	Compound	Molecular formula	Molecular weight (g mol^{-1})	Relative area (%)	Origin
40.503	Henicosane	$C_{21}H_{44}$	296.57	5.34	O
41.189	Methyl palmitate	$C_{17}H_{34}O_2$	270.46	4.46	O

C Carbohydrates*; L* Lignin*; O* Other*, UI* Unidentified

Fig. 5 Typical pyrogram of AIL of CF. For the list of components, see Table 3
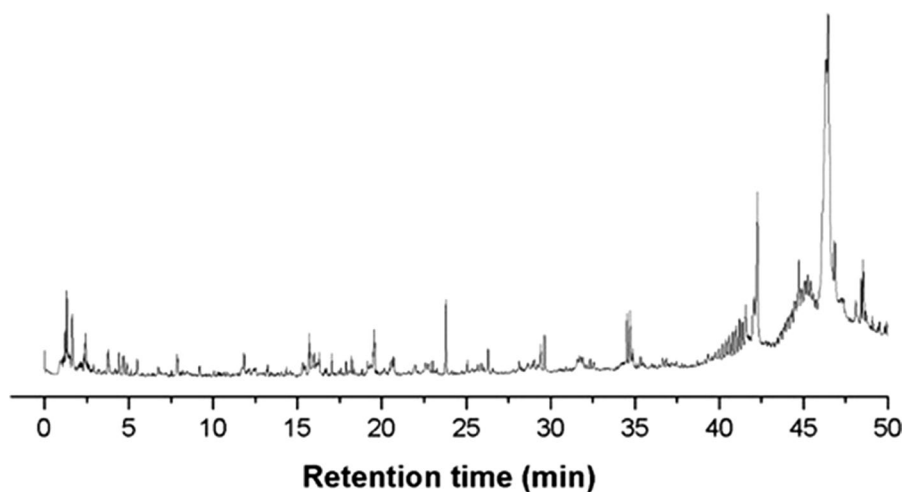
syringyl units. These blocked C5 positions prevent C5 condensation. Therefore, lignin containing a high S/G ratio, that is, a high number of syringyl units, will condense less during the acid hydrolysis procedure and produce more soluble lignin in the filtrate (Gomes et al. 2015; Brumano et al. 2020). However, when looking at the S/G ratio (0.09) in Table 1, the CF presented a low value, despite the ASL content (8%) being high. In general, the ASL content correlates positively with its lignin S/G ratio. This demonstrates that the quantification of ASL by the UV-spectrophotometric method is not consistent. Despite the existing correction for compounds derived from carbohydrates for the method, it is evident that there are other components that affect the result of the ASL content (Swan 1965; Goldschmid 1971; Yasuda and Murase 1995; Yasuda et al. 2001).

Identification of fragments of AIL analyzed by Py–GC−MS

As mentioned, the principle of the pyrolysis technique is the fragmentation of lignin into monomeric compounds (Lima et al. 2008; Brumano et al. 2020). The pyrogram (Fig. 5) for the AIL samples of CF showed the prevalence of lignin derivatives. Thirty-nine compounds were identified for CF (Table 3).

Lignin extracted from grass is composed of monomeric phenylpropanoid units known as *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) in different ratios, with H-units still comparatively minor proportions (Ralph and Hatfield 1991; Kawamoto 2017). Moreover, grass has a considerable amount of typified *p*-hydroxycinnamates (e.g., *p*-coumarates and ferulates) linked to lignin or polysaccharides (del Río et al. 2015). Pyrogram analysis showed the presence of lignin and *p*-hydroxycinnamate derivatives. The 4-vinylphenol came from *p*-hydroxycinnamate. The main pyrolysis products derived from lignin were phenol, 4-cresol, 2-methyl-3-buten-1-ol, guaiacol, syringol, 4-vinyl-2-methoxy-phenol, and syringylaldehyde. A more condensed structure for the AIL is expected, and this trend was demonstrated by Gomes et al. (2015) and Brumano et al. (2020).

By pyrogram analysis, it is possible to realize that the AIL for CF is composed mainly of derivates from

Table 3 Main compounds identified by Py–GC–MS in the AIL fraction of CF

Retention time (min)	Compound	Molecular formula	Molecular weight (g mol^{-1})	% Relative area	Origin
1.231	Chloracetic acid	$C_2H_3O_2Cl$	94.5	2.85	C,L
1.378	2-Methyl-3-buten-1-ol	$C_5H_{10}O$	86.13	6.07	L
1.584	Ethylene glycol diformate	$C_4H_6O_4$	118.09	5.15	O
1.785	Acetic acid	$C_2H_4O_2$	60.05	2.56	C,L
3.865	Methylbenzene	C_7H_8	92.14	1.60	O
4.725	Pyrrolidinoethanamine	$C_6H_{14}N$	114.19	1.05	O
5.828	Furfural	$C_5H_4O_2$	96.09	1.11	C
11.767	Phenol	C_6H_6O	94.11	1.32	L
14.550	2-Cresol	C_7H_8O	108.14	0.60	L
15.366	4-Cresol	C_7H_8O	108.14	1.85	L
15.741	Guaiacol	$C_7H_8O_2$	124.14	2.50	L
16.369	2,5-Dimethylphenol	$C_8H_{10}O$	122.17	1.12	L
17.693	2-Ethylphenol	$C_8H_{10}O$	122.16	0.97	L
18.033	3,6-Dimethylphenol	$C_8H_{10}O$	122.17	2.07	L
18.742	4-Ethylphenol	$C_8H_{10}O$	122.16	0.49	L
19.055	3-Methylguaiacol	$C_8H_{10}O_2$	138.17	0.84	L
19.607	5-Methylguaiacol	$C_8H_{10}O_2$	138.17	3.12	L
20.651	4-vinylphenol	C_8H_8O	120.15	0.75	L
21.262	4-Ethylanisole	$C_9H_{12}O$	136.19	1.21	O
22.634	4-Ethylguaiacol	$C_9H_{12}O_2$	152.18	0.68	L
23.106	2-Allylphenol	$C_9H_{10}O$	134.18	0.28	L
23.214	Homocatechol	$C_7H_8O_2$	124,14	0.32	L
23.842	4-Vinyl-2-methoxy-phenol	$C_9H_{10}O_2$	150.18	6.40	L
24.164	3-Methoxy-5-methylphenol	$C_8H_{10}O_2$	138.17	0.16	L
25.137	Syringol	$C_8H_{10}O_3$	154.16	0.98	L
25.228	Eugenol	$C_{10}H_{12}O_2$	164.20	0.60	L
25.584	4-Propylguaiacol	$C_{10}H_{14}$	166.22	0.81	L
26.902	Isoeugenol	$C_{10}H_{12}O_2$	164.204	1.84	L
28.200	Methylsyringol	$C_9H_{12}O_3$	168.19	1.17	L
29.387	Acetoguaiacone	$C_9H_{10}O_3$	166.18	1.58	L
31.944	UI	–	–	1.08	–
32.249	Methyl *p*-hydroxyhydrocinnamate	$C_{10}H_{12}O_3$	180.20	0.80	O
34.520	Syringylaldehyde	$C_9H_{10}O_4$	182.17	4.15	L
34.996	Vanillylacetone	$C_{11}H_{14}O_3$	194.23	1.00	L
36.523	Acetosyringone	$C_{10}H_{12}O_4$	196.19	0.73	L
36.907	Methyl *p*-coumarate	$C_{10}H_{10}O_3$	178.187	0.80	O
38.880	UI	–	–	0.69	–
39.138	4-hydroxy-3-methoxy-Cinnamic acid	$C_{10}H_{10}O_4$	194.19	1.19	L
42.081	Palmitinic acid	$C_{16}H_{32}O_2$	256.42	7.71	O
46.461	Linoleic acid	$C_{18}H_{32}O_2$	280.45	40.15	O

C: carbohydrates; L: lignin; O: other; UI: unidentified

guaiacyl lignin (guaiacol, 5-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, acetoguaiacone, vanillylacetone, isoeugenol, and eugenol) and syringyl lignin (syringol, methylsyringol, syringylaldehyde, acetosyringone). These substances were identified in previous works involving lignin degradation by analytical pyrolysis (del Río et al. 2007; Kawamoto 2017). The presence of 4-ethylphenol in the pyrograms of CF AIL was attributed to H-units (and not carbohydrates), so it is probable that phenol in this sample also comes from H-units (Lourenço et al. 2018).

Among the carbohydrate derivatives, the only compounds identified were furfural and acetic acid (Alen et al. 1996; Moldoveanu 2010), indicating lignin derived by acidic hydrolysis from the Klason method and its effectiveness for lignin isolation. The other compounds identified show relative areas above 50% of the total peak area, which is the estimate of the total relative area for other compounds, except for carbohydrates.

Conclusion

The present work constitutes, to our knowledge, the structural characterization of lignin formed by the Klason method of CF. Regarding this macromolecule, the study identified more forty-seven primary pyrolysis products for ASL, with 17%, 20% and 59% relative molar abundances of lignin, carbohydrates, and other products, respectively. Measurement of ASL is necessary for the accurate quantification of lignin in CF because lignin derivatives are present in the acid filtrate from the Klason lignin method. Analytical pyrolysis of ASL from CF showed a prevalence of peaks related to products derived from extractives and proteins. This quantification of ASL by UV spectrophotometry, despite existing correction for compounds derived from carbohydrates for the method, demonstrates that there are other components that affect the ASL content.

Thirty-nine primary pyrolysis products of AIL from CF with 44% and 7% relative molar abundance from lignin and carbohydrates, respectively. The main products derived from lignin were phenol, guaiacol, 3-methylguaiacol, syringol syringylaldehyde and acetoguaiacone. Only furfural and acetic acid were identified as carbohydrate derivatives during the pyrolysis of AIL. The peaks of lignin derivatives indicated that the Klason method is effective for lignin isolation, and the Py–GC−MS technique allowed the identification of the presence of residual lignin in AIL and ASL from CF.

Regarding hemicellulose, the results obtained in this study showed that the isolation process was efficient. The isolated hemicellulose from CF confirmed the presence of arabinoxylan and its importance as a source of xylose for the production of chemicals or additives in printing and writing paper.

From these results, we concluded that the chemical composition is a paramount factor for the development of processes for the production of renewable chemicals from lignocellulosic material. The lignocellulosic components of CF are chemically suitable for use as raw materials to transform biomass into higher value-added products.

Declarations

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