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# Microwave-assisted organosolv extraction of coconut shell lignin by Brønsted and Lewis acids catalysts



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Francisco Avelino <sup>a</sup>, Kássia Teixeira da Silva <sup>a</sup>, Men de Sá Moreira de Souza Filho <sup>b</sup>, Selma Elaine Mazzetto <sup>a</sup>, Diego Lomonaco <sup>a, \*</sup>

<sup>a</sup> Department of Organic and Inorganic Chemistry, Federal University of Ceara, 60440-900, Fortaleza CE, Brazil

<sup>b</sup> Embrapa Agroindustria Tropical, Rua Dra. Sara Mesquita, 2270, Planalto do Pici, 60511-110, Fortaleza CE, Brazil

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# ABSTRACT

The fractionation of renewable sources into their components has been extensively explored in order to replace the utilization of the petrochemical compounds. Among those, the obtainment of a high quality lignin for further applications stills a challenge, since its structure is severely affected by the extraction method. The aim of this work was to evaluate the physicochemical and structural effects on coconut shell lignin (CSL) caused by microwave-assisted organosolv delignification (MWAOD) under different acids catalysts. A screening of catalyst concentration and reaction time was employed to optimize the extraction condition for the MWAOD assays. Highest yields were obtained using aqueous solution of acetic acid (90%) combined with 2.0% of AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> or HCl under 110 °C for 20 min. Extractions using these catalysts were also performed under traditional heating in order to compare the efficacy of microwave irradiation in the yields and chemical structure of lignins. Under the same conditions, MWAOD produced lower molecular weight lignins with higher yields and purities. In terms of monolignol composition, both lignins were quite similar. It can be concluded that microwave-assisted organosolv process is an efficient and eco-friendly procedure for lignin extraction, in a matter of minutes, at high yields and purities, allowing their utilization for further technological applications.

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# 1. Introduction

In the recent years, the growing concern about the environment have made the scientific community explore alternative sources as raw material in detriment of the non-renewable fossil sources (Ali et al., 2017). Among the alternative renewable sources, biomass becomes an interesting and promising solution to generation of greener energy and chemicals, especially for Brazil, which has an

<sup>c</sup> Corresponding author.

E-mail address: lomonaco@ufc.br (D. Lomonaco).

enormous area destined for agriculture, as well as the greatest biodiversity on Earth.

Along with this great biodiversity, climate variety provides to tropical regions the appropriate conditions for the development of the agribusiness, which generates large amounts of low-cost residues coming from the processing of crops, and represent a potential form of environmental pollution (María and Millán, 2017). In Brazil, where the agricultural production accounts for 6.5% of the Gross Domestic Product (GDP), the agrowaste is a concerning problem, since this activity is one of the most important to the country's economy (Medina and Santos, 2017; Schlemper and Stürmer, 2014).

Among the main agrowastes generated in Brazil, coconut (*Cocos nucifera*) stands out since its economic relevance, where 285.000 ha are destined to its cultivation, yielding approximately 2 billion coconut fruits per year (Farias et al., 2017). After its industrial processing, the majority of solid parts are discarded or burned in industrial furnaces, both consisting in its underutilization and in an environmental pollution. Except the coconut edible part, there are the mesocarp, approximately 25% of the coconut weight, and the endocarp, or coconut shell (CS), representing 20% in mass of the



Abbreviations: GDP, gross domestic product; CS, coconut shell; CSP, coconut shell powder; H, *p*-hydroxyphenyl; PB, *p*-hydroxybenzoate; G, guaiacyl; S, syringyl; MWAE, microwave-assisted extraction; MWI, microwave irradiation; MWAOD, microwave-assisted organosolv delignification; CSALs, coconut shell acetosolv lignins; TH, traditional heating; FTIR, Fourier transform infrared spectroscopy; HSQC, heteronuclear single quantum coherence; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis; DTG, derivative thermogravimetric analysis; GPC, gel permeation chromatography; LCC, lignin-carbohydrate complexes; RPM, relative proportion of monomers; PDI, polydispersity index; CI-TMDP, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.

coconut (Bledzki et al., 2010; Rambo et al., 2015).

There are several works reporting the utilization of the coconut fibers as raw material for the generation of high value-added products, such as nanocellulose, while the utilization of CS is almost unexplored (Azeredo et al., 2015; Nascimento et al., 2014, 2016; Rosa et al., 2010; Uma Maheswari et al., 2012). Some papers report the use of CS in the production of char (Chen and Kuo, 2010), activated carbon (Arena et al., 2016; Prauchner and Rodríguez-Reinoso, 2012), fuels (Rout et al., 2016; Siengchum et al., 2013) and filler in composites and concretes (Bledzki et al., 2010; Gunasekaran et al., 2011; Jayaprithika and Sekar, 2016; Keerthika et al., 2016), applications that highlight its elevated lignin content, and turns it into a promising source for lignin extraction.

Lignin is the second abundant natural polymer after cellulose and the major natural source of phenolic compounds. It has structural function in the cell walls, conferring rigidity and protection from hydrolytic attack of pathogenic microorganisms (Bilal et al., 2017). Chemically, lignin is a hydrophobic amorphous polymer, formed by phenylpropanoid units: *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S), randomly linked.

The chemical structure of lignin has been extensively researched by different methods (Laurichesse and Avérous, 2014). The existence of several functional groups in its structure offers different possibilities to chemical modifications, in order to produce environmentally friendly products with technological applications, replacing petroleum-based materials.

However, lignin chemical structure depends on the raw material origin, as also on the extraction and isolation methods, which will influence its reactivity and, consequently, its applications. Traditionally, lignin is a byproduct of the pulp and paper industry, where the processes require the utilization of acid or alkali medium to promote the delignification of the raw material at elevated temperatures under high pressure.

These harsh conditions are achieved by using high-pressure reactors or autoclaves, which are based on conductive heating from an external source for several hours. These long reaction times are undesirable due high energy consumption, besides side reactions that can occur for lignin and the effects that pressure can cause in its structure (Li et al., 2012).

Recently, microwave-assisted extraction (MWAE) has been evaluated as an alternative method to promote the fragmentation of lignocellulosic biomass (Kurian et al., 2015; Li et al., 2012; Monteil-Rivera et al., 2012; Xie et al., 2015; Zhou et al., 2017, 2012). This method uses the microwave irradiation to heat, which is based on dipole rotation and ionic conduction, promoting faster chemical reactions with higher yields than traditional heating (Kappe, 2004). Therefore, this technique can be used as a sustainable methodology for lignin extraction, since it provides decrease in reaction times, as well as the utilization of low power ratings, reducing energy consumption and increasing efficiency.

Since in MWAE polar compounds must be used in order to absorb the radiation, the organosolv process is a suitable method for lignin extraction. In this process, organic solvents, such as alcohols and organic acids, are used to delignify lignocellulosic biomass, allowing their recovering and reutilization. Commonly, aqueous solutions of acetic acid and ethanol combined with low concentrations catalysts, such as H<sub>2</sub>SO<sub>4</sub> and HCl, are used to separate lignin and carbohydrates.

This process yields high purity and low molecular weight lignin than that obtained in industry, like Kraft and sulfite, which have high sulfur and ash contents limiting their technological applications. Despite the fact that Brønsted acids (HCl and H<sub>2</sub>SO<sub>4</sub>) catalyze lignin extraction in organosolv process, other works have used Lewis acids (MgCl<sub>2</sub>, FeCl<sub>2</sub>, CuCl<sub>2</sub>, FeCl<sub>3</sub>, ZrCl<sub>2</sub>, AlCl<sub>3</sub>) as catalysts, evaluating their effects in lignin structure (Constant et al., 2015; Huang et al., 2016; Schwiderski et al., 2014; Wang et al., 2016).

However, these works performed the lignin extraction at elevated temperatures and pressure, and it is necessary to consider the combined effects of these parameters. To the best of our knowledge, there are no reports on the use of microwave irradiation combined with Lewis acids as catalysts under mild conditions (atmospheric pressure) to promote delignification of biomass.

Therefore, the aim of this study was evaluate the physicochemical and structural effects on coconut shell acetosolv lignins (CSALs) caused by microwave-assisted organosolv delignification (MWAOD) using different Lewis (MgCl<sub>2</sub>, MnCl<sub>2</sub>, CoCl<sub>2</sub>, ZnCl<sub>2</sub> and AlCl<sub>3</sub>) and Brønsted acids (CH<sub>3</sub>COOH, H<sub>2</sub>SO<sub>4</sub> and HCl), and compare the results with those obtained by traditional heating (TH).

# 2. Experimental

#### 2.1. Materials

The following chemicals were used as received: glacial acetic acid (Synth), H<sub>2</sub>SO<sub>4</sub> (98%, Vetec), HCl (37%, Synth), ZnCl<sub>2</sub> (Cromoline), AlCl<sub>3</sub> (98%), DMSO-d6 (99.96%), MgCl<sub>2</sub> (98%), MnCl<sub>2</sub> (98%), CoCl<sub>2</sub> (97%), THF (HPLC-grade), chloroform-d (99.96%), pyridine (99%), chromium (III) acetylacetonate (99.99%), cyclohexanol (99%) and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%) were supplied Sigma-Aldrich.

#### 2.2. Raw material preparation

The CSs were supplied by Ducoco Produtos Saudáveis (Itapipoca, Brazil). They were milled in a knife mill (Fritsch pulverisette 19) using sieves with pores diameter of 0.5 mm. The coconut shell powder (CSP) was characterized based on TAPPI T203 cm-99, T204 cm-97, T211 om-02, T421 om-01 and TAPPI T222 om-2 for determination of alpha-cellulose, extractives/fat, ash, moisture and lignin, respectively. The holocelullose and hemicellulose contents were determined by the procedure described by Yokohama et al. (Yokoyama et al., 2002). The composition of CSs was cellulose ( $25.14 \pm 3.74\%$ ), hemicellulose ( $20.9 \pm 2.4\%$ ), lignin ( $33.7 \pm 1.84\%$ ), extractives ( $10.3 \pm 0.09\%$ ), fat ( $0.64 \pm 0.02\%$ ) and moisture ( $3.65 \pm 0.07\%$ ).

#### 2.3. Microwave-assisted extraction (MWAE)

The microwave-assisted extractions were performed in a Milestone (Sorisole, Italy) microwave reactor, model StartSYNTH, operating in an open-vessel configuration at a frequency of 2.45 GHz. The temperature was controlled by a contact-less infrared sensor, and the power applied was limited to a maximum of 500 W.

MWAE assays were divided in two stages. The first was a screening for the selection of ideal catalyst concentration and reaction time. In these experiments, CSP (10 g) was introduced in a round-bottom flask containing 100 mL of acetic acid/water solution (9/1, v/v) and the catalyst (H<sub>2</sub>SO<sub>4</sub> or HCl) in different concentrations (0.5, 1,0 or 2.0% v/v). The extractions were performed at 110 °C during defined reaction times (5, 10, 20 or 30 min), under atmospheric pressure. Extractions without any catalyst were carried out to evaluate the ability of acetic acid to catalyze lignin hydrolysis.

The second stage was the evaluation of the effects caused in lignin structure by using different Lewis acids as catalysts comparing them with the traditional Brønsted acids. In these experiments, the same amount of CSP was used and 2.0% w/v MgCl<sub>2</sub>, MnCl<sub>2</sub>, CoCl<sub>2</sub>, ZnCl<sub>2</sub> and AlCl<sub>3</sub> were added into the acetosolv

solution. These experiments were carried out at 110 °C during 20 min under atmospheric pressure. For both stages, the temperature program used consisted of a fast heating step (3 min) followed by a plateau during which power varied in a narrow range (100–200 W) to maintain temperature at the target value.

At the end of the reactions, samples were cooled down for 10 min. The black liquor was isolated from the solid residue by filtration (pore diameter of 28  $\mu$ m) and washed with acetic acid (60 °C). The resultant black liquor was concentrated and precipitated in deionized water at 60 °C, using a black liquor to water ratio of 1:10 (v/v) and allowing the mixture to rest at room temperature for 24 h.

After that time, lignin was vacuum-filtered (pore diameter of  $8 \,\mu$ m), washed with deionized water until pH 6.0 and dried at 105 °C. Lignin yield was calculated according to Equation (1):

$$\eta = \frac{m_{LigIsol}}{m_{LigCSP}} \tag{1}$$

where  $\eta$  is the lignin yield (%);  $m_{\text{LigIsol}}$  is the mass of lignin isolated in the MWAOD process (g) while  $m_{\text{LigCSP}}$  is the mass of lignin in CSP (g) as determined by TAPPI standards (Section 2.2).

# 2.4. Lignin extractions using traditional heating (TH)

In order to compare the effects that the heating source would cause on the properties of lignins, the same extracting conditions used for MWAOD assays were applied for TH. The catalysts that produced the highest yields were chosen to be used in TH experiments. CSP (10 g) was introduced in a round-bottom flask with 100 mL of acetic acid/water solution (9/1, v/v) containing 2.0% (w/v or v/v) AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl as catalysts. The reactions were performed in an oil-bath at 110 °C during 20 min under atmospheric pressure. The reaction time began to be counted when the solution temperature reached 110 °C. The treatments after the extractions were exactly the same used for those conducted using microwave irradiation. The TH-lignins were characterized by FTIR,  $^{1}$ H- $^{13}$ C HSQC, GPC and TGA techniques in order to assess differences in their structures in relation to those obtained by MWAOD.

#### 2.5. Characterization of lignins

The purity of lignin samples was calculated by TAPPI T222 om-2 method with modifications (Corners, 2002). About 1.0 g of lignin was treated with 17 mL of sulfuric acid (72 wt %) at room temperature for 24 h. The solution was diluted with deionized water to 4 wt % sulfuric acid and refluxed for 4 h. After the end of the reaction, the system was cooled for 30 min at room temperature. The acid-insoluble residue was isolated by vacuum filtration and washed with deionized water. After these washings, the residues were dried at 105 °C for 24 h.

The acid-soluble lignin was determined using the first filtrate obtained in the acid-insoluble lignins. The filtrate was diluted with  $4 \text{ wt } \% \text{ H}_2\text{SO}_4$  with 1:10 (v/v) ratio and the acid-soluble lignin was calculated from the UV absorbance at 215 and 280 nm. The sum of acid-insoluble and acid-soluble lignins was reported as the total lignin content (purity) of the samples.

Elemental analyses (carbon, hydrogen, nitrogen and sulfur) of the MWAOD-lignins were performed using a Perkin Elmer 2400 Series II CHN-S/O according standard procedures (CHNS results available in supplementary material in Table S2).

Fourier transform infrared spectroscopy (FT-IR) was performed in a Perkin Elmer FT-IR/NIR FRONTIER, using an attenuated total reflectance (ATR) accessory with ZnSe crystal surface. Spectra were acquired between 4000 and  $550 \text{ cm}^{-1}$  with resolution of  $4 \text{ cm}^{-1}$  using the arithmetic average of four scans. The relative content of functional groups was calculated based on the methodology described by Bykov (2008) (Bykov, 2008).

The heteronuclear single quantum coherence (HSQC) experiments were performed in a Bruker Avance DPX 300 operating at 300 and 75 MHz for <sup>1</sup>H and <sup>13</sup>C nuclei, respectively. Lignin (100 mg) was dissolved in 1.0 mL of DMSO-d6, and solvent peak was used as internal reference (DMSO  $\delta_{\rm H}/\delta_{\rm C}$  2.50/39.5).

<sup>31</sup>P NMR experiments were carried out after phosphytilation of lignins, according to Granata and Argyropoulos (1995) with modifications (Granata and Argyropoulos, 1995). Lignin (30 mg) was dissolved in 450 µL of a solvent mixture (C<sub>5</sub>H<sub>5</sub>N:CDCl<sub>3</sub>, 1.6/1 v/v ratio). To this solution were added 100 µL of chromium (III) acetylacetonate solution (5.0 mg mL<sup>-1</sup>) and 100  $\mu$ L of cyclohexanol solution (10.85 mg mL<sup>-1</sup>). Finally, 100 µL of 2-chloro-4,4,5,5tetramethyl-1,3,2-dioxaphospholane (Cl-TMDP) was added to the mixture, followed to the addition of solvent mixture until the mark of 1 mL. Experiments were performed on a Bruker Avance DPX500 spectrometer operating at 202.46 MHz for <sup>31</sup>P nucleus. Chemical shifts reported are related to the hydrolysis reaction of Cl-TMDP, which generates a signal at 132.2 ppm. Quantitative analysis using cyclohexanol as internal standard was carried out based on previous reports (Granata and Argyropoulos, 1995; Pu et al., 2011). In order to establish a pattern of integration, signals were integrated according to the following chemical shifts: internal standard (145.39–144.97 ppm), aliphatic-OH (150–145.50 ppm), C .-substituted-OH (144.5–141.2 ppm). guaiacvl-OH (141–138.50 ppm), *p*-hydroxyphenyl-OH (138.4–137.20 ppm) and COOH-OH (136.5-133.34 ppm).

Differential scanning calorimetry (DSC) analyses were performed in a Mettler-Toledo (Schwerzenbach, Switzerland) DSC 823e. Sample (10 mg) was placed in aluminum crucibles closed with a lid centrally punctured. Samples were heated from 25 to 90 °C, where temperature was kept constant for 10 min, then cooled from 90 to 0 °C, where temperature was kept constant for 3 min and heated from 0 to 250 °C, under a nitrogen atmosphere (50 mL min<sup>-1</sup>) at a scanning rate of 20 °C min<sup>-1</sup>.

Thermogravimetric (TGA) analyses were performed in a Mettler-Toledo (Schwerzenbach, Switzerland) TGA/SDTA851e. Sample (10 mg) was heated from 30 to 900 °C under nitrogen atmosphere (50 mL min<sup>-1</sup>) at a scanning rate of 10 °C min<sup>-1</sup>.

Gel permeation chromatography (GPC) analyses were performed in a Shimadzu LC-20AD (Kyoto, Japan) at 40 °C using a setup comprising two identical analytical GPC columns in series (Phenogel 5 Linear/Mixed columns, 7.38 mm × 300 mm, Phenomenex, Torrance, CA, USA), a flow rate of 1.0 mL min<sup>-1</sup> and HPLC-grade THF as eluent. The samples were monitored by UV–Vis detector (Shimadzu SPD-M20A) at 280 nm. Lignin (2 mg) was dissolved in 2 mL HPLC-grade THF and filtered using 0.22 µm PTFE filter. Then, 100 µL of this solution was injected into the GPC system. Standard calibration was performed with polystyrene standards Phenomenex ALO-2761 (Phenomenex, Torrance, CA, USA,  $M_w$  range  $362-2.52 \times 10^6$  g mol<sup>-1</sup>).

#### 3. Results and discussion

#### 3.1. Microwave-assisted organosolv delignification (MWAOD)

Initially, the effect of three parameters was evaluated in the MWAOD experiments: the catalyst (without catalyst,  $H_2SO_4$  and HCl), its concentration and the reaction time (Fig. 1 (A) and (B)).

Since the catalysts used were Brønsted acids, the most important feature that influenced on the lignin yield was their strength. This behavior can be seen by the increase on yield with the increase



Fig. 1. Effect of catalysts, their concentrations and reaction time on lignin yield.

in strength of the acids, as shown in Fig. 1(A) and (B).

The low yields obtained using  $CH_3COOH$  as catalyst shows its poor ability to produce  $H_3O^+$  ions, which are responsible for the protonation of ether groups present in lignin, catalyzing their hydrolysis and increasing the yield.

Fig. 1(A) and (B) also show that the increase in the catalyst concentration combined with the increase in the reaction time enhanced the extraction yield. This behavior occurs due to the increase in the concentration of  $H_3O^+$  ions, which enhances the amount of ether bonds that can be protonated and subsequently hydrolyzed. In addition, longer reaction times usually provide

higher probabilities to occur effective collisions between the reactants, which increase the rate of reaction in this case represented by the lignin yield.

However, when catalysts' concentration was 2.0% v/v there were no significant differences between yields using 20 and 30 min, as shown in Fig. 1(A) and (B). This can be attributed to kinetic factors, suggesting that from 20 min to higher reaction times the delignification process reaches a plateau and the amount of extracted lignin is practically constant. Therefore, condition of 2.0% v/v of catalyst combined with 20 min of reaction was chose for the next steps of this work.

 Table 1

 Influence of Brønsted and Lewis acids on the lignin yield, Klason and acid-soluble lignin and purity of lignins.

| Catalyst             | Cation hardness (eV) | Lignin yield (%) | Klason Lignin<br>(%) | Acid-soluble lignin<br>(%) | Purity (%) |
|----------------------|----------------------|------------------|----------------------|----------------------------|------------|
| CH <sub>3</sub> COOH | 6.4                  | $9.20 \pm 0.7$   | 76.7                 | 1.43                       | 78.1       |
| CoCl <sub>2</sub>    | 8.2                  | $14.8 \pm 1.2$   | 84.0                 | 2.52                       | 86.5       |
| MnCl <sub>2</sub>    | 9.3                  | $14.6 \pm 1.8$   | 78.9                 | 3.4                        | 82.3       |
| ZnCl <sub>2</sub>    | 10.8                 | $14.3 \pm 0.1$   | 82.8                 | 1.58                       | 84.4       |
| MgCl <sub>2</sub>    | 32.5                 | $17.0 \pm 1.7$   | 78.0                 | 2.92                       | 80.9       |
| AlCl <sub>3</sub>    | 45.8                 | $53.9 \pm 2.4$   | 80.0                 | 3.40                       | 83.4       |
| $H_2SO_4$            | $\infty$             | $56.6 \pm 5.2$   | 83.5                 | 2.26                       | 85.8       |
| HCI                  | ∞                    | $54.4 \pm 3.3$   | 81.9                 | 3.82                       | 85.8       |



Fig. 2. Proposed mechanisms for both types of catalysts during lignin hydrolysis.



Fig. 3. Fingerprint region of FTIR spectra of organosolv lignins.

Another parameter investigated was the nature of catalyst. Based on the optimized conditions for the Brønsted acids, other five Lewis acids, with variable cation hardness, were employed in lignin extraction. The hardness of each cation was estimated by Pearson model (Parr and Pearson, 1983; Pearson, 1988).

The values of cation hardness, lignin yield, acid-insoluble lignin and purity of the lignins obtained by Lewis and Brønsted acids catalysts are shown in Table 1.

In general, Table 1 shows that the increase of cation hardness enhanced the extraction yield. This fact probably occurs because Lewis acids with higher cation hardness coordinate more efficiently with the oxygen atoms present in the ether groups, since the majority of bonds between the monomers in lignin structure are ether type, such as  $\beta$ -O-4 type. The greater the coordination power of the catalyst more electrophilic these sites will be, making them more susceptible to hydrolysis.

Comparing the results, the only Lewis acid that presented similar yield to Brønsted acids was AlCl<sub>3</sub>, suggesting that they have similar acidic power despite the mechanism of the former be based on coordination and the latter based on protonation of oxygen atoms. Therefore, these results showed that the acidic power has a significant influence on yield, but not so much in the lignin purity.

Fig. 2 shows a schematic representation of the proposed mechanisms for both types of catalysts during the lignin hydrolysis. Thus, there were proposed pathways considering a fragment of lignin formed by H, G and S units linked by  $\beta$ -O-4 linkage, due to its abundance in lignin structure. Therefore, it is important to highlight that there are two possible mechanisms for the Lewis acids. The first would be based on the coordination of water molecules

from the acetosolv solution, which will make their hydrogen more acidic to protonate the ether bonds while in the second would be based on the direct coordination of the metal to the oxygen atom of the ether groups (Fig. 2).

It is worth mentioning that the major published papers about microwave-assisted delignification were performed under high pressure, which is a limiting factor since the amount of raw material used is too low (0.2–2 g) (Li et al., 2012; Monteil-Rivera et al., 2012; Xie et al., 2015; Zhou et al., 2017). This is unfavorable from an industrial perspective, since the scale-up of this process would be very difficult. Moreover, there are high-volume microwave reactors for pilot plant purposes (atmospheric pressure), which would simulate a scale up of certain process (Microwave Chemical Co., 2018).

Some of the aforementioned works reported low lignin yield (10–25%) even with the use of high temperatures and pressures, as reported by Monteil-Rivera et al. (2012), Li et al. (2012) and Xie et al. (2015).

Recently, Zhou et al. (2017) performed a delignification assays using softwood pellets and diluted sulfuric acid at 190 °C during 10 min, obtaining a lignin yield of 82.31% with purity of 80.64%. Comparing this result with those presented in the present study, it is observed that we obtained lignins with comparable and higher purity under milder conditions and lower pressure (atmospheric).

Xie et al. (2015) performed delignification of different biomasses using a mixture of glycerol/methanol as solvent and sulfuric acid as catalyst at 120 °C during 30 min under high pressure and obtained low lignin yields (17.62–23.04%) and low purity (75–77%). Again, in this work under conditions much milder we report higher lignin yields and purities.

It is also necessary to consider that delignification experiments performed in reactors under traditional heating, combining high pressure with elevated temperatures and long reaction times, result in excessive energy consumption (Avelino et al., 2018; Fernández-Rodríguez et al., 2017; Løhre et al., 2017; Maniet et al., 2017; Pinheiro et al., 2017).

The results presented in this work show the energy efficiency of the microwave heating, producing lignins with higher yields and purities compared to those reported in the literature for MWAOD and TH experiments. It is worth mention that during the MWAOD the power applied was monitored during the whole experiments and the average value for all experiments was around 135 W, representing an extremely low energy consumption during the extractions, confirming that MWAOD represents an sustainable alternative to delignification of biomass under mild conditions.

# 3.2. Structural characterization

#### 3.2.1. Fourier transform infrared spectroscopy (FTIR)

The main functional groups in the organosolv lignins, as well as any structural modification resultant from the extractions, were investigated by FTIR (Fig. 3). The main bands in the fingerprint region were compared by the ratio between their areas and that of the band at  $1510 \text{ cm}^{-1}$  (Table S1).

The peak assignments were conducted based on a previous report (Faix, 1991). Fig. 3 shows the fingerprint region of lignin spectra, where the characteristic bands of chemical bonds are found. Among these, some are related to the lignin backbone (region I), such as C=C stretching of the aromatic ring skeleton at 1593 and 1510 cm<sup>-1</sup>; C-H deformations at 1459 cm<sup>-1</sup> and aromatic skeletal vibrations coupled with C-H in plane deformation at 1420 cm<sup>-1</sup>.

The absorption bands at 1708, 1268, 1163 and 1123 cm<sup>-1</sup> were assigned to C=O stretchings (region II), which is commonly



Fig. 4. Aromatic regions in <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectra of CSALs obtained: (A) CH<sub>3</sub>COOH; (B) CoCl<sub>2</sub>; (C) MnCl<sub>2</sub>; (D) ZnCl<sub>2</sub>; (E) MgCl<sub>2</sub>; (F) AlCl<sub>3</sub>; (G) H<sub>2</sub>SO<sub>4</sub> and (H) HCl. Main structures present in the CSALs: (S) syringyl; (G) guaiacyl; (H) *p*-hydroxyphenyl and (PB) *p*-hydroxybenzoates.

attributed to lignin-carbohydrate complexes (LCC). These bands can be used to estimate the efficiency of the delignification process, since their decrease indicates the cleavage of benzyl ester bonds (Liu et al., 2017). There were also residual carbohydrates in all organosolv lignins, although the intensities of these bands varied with the type of catalyst, which were evaluated by their relative contents (Table S1).

In Fig. 3, the absorption bands at 1330 and  $1123 \text{ cm}^{-1}$  are characteristic of syringyl units (region II), while those at 1510, 1268

#### Table 2

| Assignments of the light | n <sup>1</sup> H- <sup>13</sup> C correlation | signals in the | HSQC NMR | spectra of |
|--------------------------|---|----------------|----------|------------|
| CSALs.                   |   |                |          |            |

| Label             | $\delta_{C}/\delta_{H}$ (ppm) | Assignment   |
|-------------------|-------------------------------|--|
| S <sub>2,6</sub>  | 6.67/104                      | C <sub>2</sub> -H <sub>2</sub> and C <sub>6</sub> -H <sub>6</sub> in S |
| G <sub>2</sub>    | 6.98/111.6                    | C <sub>2</sub> -H <sub>2</sub> in G                                    |
| G <sub>5</sub>    | 6.69/115.2                    | C <sub>5</sub> -H <sub>5</sub> in G                                    |
| G <sub>6</sub>    | 6.78/119                      | C <sub>6</sub> -H <sub>6</sub> in G                                    |
| H <sub>2,6</sub>  | 7.03/130.5                    | C <sub>2,6</sub> -H <sub>2,6</sub> in H                                |
| PB <sub>2,6</sub> | 7.68/131.2                    | C <sub>2,6</sub> -H <sub>2,6</sub> in PB                               |
| PB <sub>3,5</sub> | 6.61/114.3                    | C <sub>3,5</sub> -H <sub>3,5</sub> in PB                               |

 Table 3

 Relative proportion of monomers for CSALs obtained by using different catalysts.

| _ |                   |       |       |       |           |           |
|---|-------------------|-------|-------|-------|-----------|-----------|
|   | Lignin            | S (%) | G (%) | H (%) | S/G ratio | H/G ratio |
|   | CH₃COOH           | 14.6  | 85.3  | 0     | 0.17      | 0         |
|   | CoCl <sub>2</sub> | 18.5  | 68.6  | 12.9  | 0.27      | 0.19      |
|   | MnCl <sub>2</sub> | 16.4  | 76.7  | 6.9   | 0.21      | 0.09      |
|   | ZnCl <sub>2</sub> | 15.6  | 75.2  | 9.2   | 0.21      | 0.12      |
|   | MgCl <sub>2</sub> | 19.9  | 67.9  | 12.1  | 0.29      | 0.18      |
|   | AlCl <sub>3</sub> | 28.9  | 51.0  | 20.0  | 0.57      | 0.39      |
|   | $H_2SO_4$         | 20.7  | 57.3  | 22.0  | 0.36      | 0.38      |
|   | HCl               | 21.5  | 53.6  | 24.9  | 0.40      | 0.46      |
|   |                   |       |       |       |           |           |

and  $1031 \text{ cm}^{-1}$  with relatively high intensity (Table S1) are related to guaiacyl units (regions I and II) (Constant et al., 2016). The band at 853 cm<sup>-1</sup> was assigned to C-H out-of-plane in positions 2, 5 and 6 of guaiacyl units (region III).

It is possible to identify in all lignin spectra the presence of a bands at  $1163 \text{ cm}^{-1}$ , assigned to C=O vibration of conjugated esters

(region II), and at 831 cm<sup>-1</sup>, assigned to the aromatic C-H out-ofplane vibrations in H units (region III), important spectral features of HGS lignins, although their intensities suggest that the amount of this monomer is very low.

# 3.2.2. <sup>1</sup>H-<sup>13</sup>C HSQC NMR

In order to obtain more detailed information on the structure of

# Table 4

Quantification data of hydroxyl groups present in MWAOD lignins.

| Index/Lignin                                     | AlCl <sub>3</sub> | $H_2SO_4$ | HCl  |
|--|-------------------|-----------|------|
| OH aliphatic content (mmol g <sup>-1</sup> )     | 0.49              | 0.28      | 0.63 |
| C <sub>5</sub> -substituted-OH                   | 0.65              | 0.84      | 0.80 |
| Guaiacyl-OH                                      | 0.56              | 0.53      | 0.69 |
| p-Hydroxyphenyl-OH                               | 0.51              | 0.39      | 0.60 |
| OH phenolic content (mmol g <sup>-1</sup> )      | 1.72              | 1.76      | 2.09 |
| COOH content (mmol $g^{-1}$ )                    | 0.12              | 0.10      | 0.15 |
| Total OH groups' content (mmol g <sup>-1</sup> ) | 2.33              | 2.14      | 2.87 |
| OH <sub>phen.</sub> /OH <sub>total</sub>         | 0.74              | 0.82      | 0.73 |



Fig. 5. <sup>31</sup>P NMR spectra of MWAOD lignins and their main substructures.

CSALs, samples were analyzed by  ${}^{1}\text{H}{-}^{13}\text{C}$  HSQC NMR. Fig. 4 shows the aromatic regions ( $\delta_{C}/\delta_{H}$  100–140 ppm/6.0–8.0 ppm) of CSALs, where the main cross-peaks were assigned according to Rencoret et al. (2013) and are listed in Table 2. In addition, the aliphatic region spectra ( $\delta_{C}/\delta_{H}$  50–90 ppm/3.0–5.5 ppm) of CSALs are available in supplementary material (Figure S1).

The obtained lignins presented similar composition, in which the monomeric units S, G, H and p-hydroxybenzoate (PB) were their main constituents.

Except for CH<sub>3</sub>COOH, all the other catalysts generated lignins with significant amounts of PB units, originated from oxidized H units, which is in accordance with the results described by Constant et al. (2016).

Furthermore, the spectral features showed in the <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectra corroborate with those in FTIR spectra. The latter showed the presence of bands attributed to C=O vibration of conjugated esters, considered a typical band for HGS lignins, probably due to the presence of PB units, which has an ester group conjugated with the aromatic ring, as shown in Fig. 4. This was confirmed by the presence of cross-peaks related to C<sub>2,6</sub>-H<sub>2,6</sub> ( $\delta_C/\delta_H$  131.2/7.68) and C<sub>3,5</sub>-H<sub>3,5</sub> ( $\delta_C/\delta_H$  114.3/6.61) correlations for PB units in the HSQC spectra.

It is also evident that in all  ${}^{1}$ H- ${}^{13}$ C HSQC NMR spectra the crosspeaks related to G and S units had higher intensities, which is in accordance to the FTIR, since the bands at 1330 and 1123 cm<sup>-1</sup> (S unit) and 1510, 1268 and 1031 cm<sup>-1</sup> (G unit) stood out.

The relative proportion of monomers (RPM) was calculated as the ratio between the cross-peak area of the individual monomers and the sum of the cross-peaks areas of all monomers (Table 3).

Table 3 shows that the nature of the catalysts influenced in the RPM, suggesting that hardness and acidic power favored specific cleavages, as indicated by S/G and H/G ratios. This behavior can be seen in Fig. 4, where the cross-peak related to PB<sub>3,5</sub> only appeared when CoCl<sub>2</sub> and AlCl<sub>3</sub> were used. This indicates a preferential cleavage of 5-5' and  $\beta$ -5 linkages, generating PB units with carbon 5 available to correlate with its respective hydrogen.

It is also suggested that CSALs samples that presented only cross-peak related to  $PB_{2,6}$  had a different cleavage pattern than those which presented only  $PB_{3,5}$ . This means that the other catalysts may be acted in different type of linkages, such as the 5-O-4. This cleavage generates two fragments with hydroxyl groups in the carbons 5 and 4, which explains the absence of  $PB_{3,5}$  units in those spectra.

In a general way, the relative proportion of guaiacyl units decreased in lignins obtained with  $AlCl_3$ ,  $H_2SO_4$  and HCl. These catalysts can possibly be favoring the occurrence of recondensation reactions, in which the position 5 of the G ring was involved.

# 3.2.3. <sup>31</sup> P NMR

Quantitative <sup>31</sup>P NMR spectra were obtained to assess the amount of aliphatic, phenolic (5-substituted-OH, guaiacyl-OH and *p*-hydroxyphenyl-OH) and carboxylic acids hydroxyl groups present in MWAOD-lignins (AlCl<sub>3</sub>,  $H_2SO_4$  and HCl). The <sup>31</sup>P NMR spectra for these lignins and the identified substructures are shown in Fig. 5. The data obtained from quantification are summarized in Table 4.

Fig. 5 shows that the main hydroxyl groups are part of syringyl/ G-condensed, guaiacyl and *p*-hydroxyphenyl units. These corroborates with <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectra, in which were observed the presence of cross-peaks related to S<sub>2,6</sub>, G<sub>2</sub>, G<sub>5</sub>, G<sub>6</sub>, H<sub>2,6</sub>, PB<sub>3,5</sub> and PB<sub>2,6</sub> substructures. In addition, the FTIR spectra of these lignins showed the presence of characteristic absorption bands related to S and G units, as also a characteristic band (1163 cm<sup>-1</sup>), typical for HGS lignins.

The distribution of hydroxyl groups shown in Table 4 are in good

agreement with the literature (Constant et al., 2016; Pang et al., 2017).

Another observation from Table 4 is the total OH phenolic content, which has its highest value for MWAOD-HCl lignin, reinforcing the hypothesis that this catalyst had the best performance in promoting cleavage of aryl alkyl ether bonds.

# 3.2.4. Molecular weight distribution

The differential molecular weight distributions of CSALs are shown in Fig. 6 and their weight-average  $(M_w)$  and number-average  $(M_n)$  molecular weights and polydispersity index (PDI) are given in Table 5.

The molecular weight distribution,  $M_w$ ,  $M_n$  and PDI values of a lignin sample indicate the severity of the extraction process (combination of temperature and reaction time) used to the delignification of the biomass (Constant et al., 2016). It is also possible to evaluate the effect of the catalyst on this process, since the temperature and reaction time was kept constant.

Table 5 shows that the  $M_w$  and  $M_n$  varied randomly by using different catalysts. In addition, the PDI values showed that CSALs had narrow molecular weight distributions, which means that these lignins were composed of fragments with low heterogeneity. In a general way, it was observed a trend in the  $M_w$  values, in which lignins with higher  $M_w$  values ( $M_w > 1900 \text{ g mol}^{-1}$ ) were obtained using less acidic catalysts (soft acids, from CH<sub>3</sub>COOH to MgCl<sub>2</sub>), while catalysts with high acidic power (AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl) generated lower molecular weight lignins ( $M_w < 1900 \text{ g mol}^{-1}$ ). All the  $M_w$  values are in good agreement with previous studies. (Constant et al., 2016).



Fig. 6. Differential molecular weight distribution of CSALs obtained by GPC.

# Table 5

Weight-average  $(M_w)$  and number-average  $(M_n)$  molecular weights and polydispersity  $(M_w/M_n)$  of CSALs.

| Catalyst          | $M_w$ (g mol <sup>-1</sup> ) | $M_n$ (g mol <sup>-1</sup> ) | PDI  |
|-------------------|------------------------------|------------------------------|------|
| CH₃COOH           | 1902                         | 1027                         | 1.85 |
| CoCl <sub>2</sub> | 2328                         | 1225                         | 1.90 |
| MnCl <sub>2</sub> | 2351                         | 1053                         | 2.23 |
| ZnCl <sub>2</sub> | 2103                         | 1056                         | 1.99 |
| MgCl <sub>2</sub> | 2169                         | 1082                         | 2.01 |
| AlCl <sub>3</sub> | 1845                         | 960                          | 1.92 |
| $H_2SO_4$         | 1753                         | 906                          | 1.93 |
| HCl               | 1780                         | 944                          | 1.89 |



Fig. 7. (A) TG and (B) DTG curves of CSP and CSALs.

These results corroborates with those obtained by Constant et al. (2016), in which the authors studied the influence of several Lewis acid catalysts on the structural and chemical properties of lignins extracted from wheat straw. They reported that the use of harder Lewis acids, such as Ga(OTf)<sub>3</sub>, ZrOCl<sub>2</sub> and Sc(OTf)<sub>3</sub> generated low molecular weight lignins and with lower amounts of  $\beta$ -aryl ether linkages.

The tendency observed in  $M_w$  values can be correlated to the RPM values obtained in  ${}^{1}H{}^{-13}C$  HSQC NMR experiments (Table 3), in which the increase in the cation hardness generated lignins with lower amounts of G unit. This can be due to the extensive cleavage of the 5-O-4 linkages, in which new phenolic hydroxyl groups were formed in the position 5 of G ring, decreasing the intensity of the cross-peak of  $C_5 - H_5$  correlation and, consequently, the proportion of G unit present in those lignins.

# 3.2.5. Thermogravimetric analysis (TGA)

The thermal stability of lignin is a property that strongly depends on its molecular weight, its carbohydrates content and the identity of chemical bonds in its structure. Therefore, it is possible to establish a link between the thermal stability of lignin and its macromolecular structure. Fig. 7 shows the TGA and DTG curves for the CSP and CSALs. Onset and maximum degradation temperatures (T<sub>onset</sub> and T<sub>max</sub>) and char yield values are summarized in Table 6.

Among CSALs samples, it was observed a dependence between purity of CSALs and  $T_{\text{onset}}$  values, which were also dependent on the catalyst used. This shows the great ability of the catalysts employed in cleaving the linkages between lignin and carbohydrates (LCC), yielding lignins with elevated purity and with higher thermal stabilities.

The weight loss in the range of 310-500 °C is mainly attributed to the cleavage of ether and carbon-carbon bonds, so called interunit linkages, between different lignin monomers (Pang et al., 2017). It was observed that more acidic catalysts (AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl) yielded lignins with higher  $T_{max}$ , indicating that these

| Table 6                   |                    |                  |
|---------------------------|--------------------|------------------|
| Thermal properties of CSP | and CSALs obtained | by TGA analysis. |

| Catalyst             | T <sub>onset</sub> (°C) | T <sub>max</sub> (°C) | Char yield (%) |
|----------------------|-------------------------|-----------------------|----------------|
| CSP                  | 252                     | 334                   | 3.45           |
| CH <sub>3</sub> COOH | 168                     | 223                   | 10.6           |
| CoCl <sub>2</sub>    | 212                     | 351                   | 21.7           |
| MnCl <sub>2</sub>    | 204                     | 265                   | 16.8           |
| ZnCl <sub>2</sub>    | 211                     | 267                   | 16.7           |
| MgCl <sub>2</sub>    | 207                     | 263                   | 22.2           |
| AlCl <sub>3</sub>    | 214                     | 340                   | 15.1           |
| $H_2SO_4$            | 235                     | 360                   | 23.3           |
| HCl                  | 205                     | 348                   | 11.7           |



Fig. 8. DSC curves indicating the  $T_g$  of CSALs obtained.

| Table /   |      |
|---|------|
| $T_{\alpha}$ values obtained for CSALs by DSC analy | ses. |

| Catalyst                       | $T_{\rm g}(^{\circ}{\rm C})$ |
|--------------------------------|------------------------------|
| CH₃COOH                        | 142                          |
| CoCl <sub>2</sub>              | 131                          |
| MnCl <sub>2</sub>              | 139                          |
| ZnCl <sub>2</sub>              | 139                          |
| MgCl <sub>2</sub>              | 131                          |
| AlCl <sub>3</sub>              | 135                          |
| H <sub>2</sub> SO <sub>4</sub> | 140                          |
| HCI                            | 133                          |

# Table 8

| i ilysicochenicai and structurai data obtained for infigini | Physicochemical and | l structural data | obtained for | TH-lignins |
|---|---------------------|-------------------|--------------|------------|
|---|---------------------|-------------------|--------------|------------|

| Catalyst          | Lignin yield (%) | Purity<br>(%) | T <sub>onset</sub> (°C) | $T_{max}$ (°C) | Char yield (%) | $M_w$ (g mol <sup>-1</sup> ) | $M_n$ (g mol <sup>-1</sup> ) | PDI  |
|-------------------|------------------|---------------|-------------------------|----------------|----------------|------------------------------|------------------------------|------|
| AlCl <sub>3</sub> | 37               | 72.5          | 187                     | 331            | 0              | 2380                         | 1053                         | 2.26 |
| $H_2SO_4$         | 41               | 72.5          | 194                     | 352            | 2.7            | 2709                         | 1205                         | 2.25 |
| HCl               | 66               | 75.7          | 179                     | 344            | 19             | 3018                         | 1183                         | 2.55 |

samples present significant amounts of carbon-carbon bonds, such as 5,5',  $\beta$ - $\beta$  and  $\beta$ -1, which could also justify their elevated  $T_{max}$  values.

At temperatures higher than 500 °C there is the occurrence of condensation reactions between the aromatic rings of high molecular weight fragments, leading to the formation of a highly stable carbonaceous structures (Costes et al., 2017), which justify the high char yield values shown in Table 6.

# 3.2.6. Differential scanning calorimetry (DSC)

DSC measurements were performed to determine the glass transition temperature ( $T_g$ ) of CSALs. The  $T_g$  of lignin is affected by several factors, such as the molecular weight, crosslinking degree and thermal history stored in the glassy state of the samples (Lange et al., 2016). Considering the polyphenolic structure of CSALs, different electronic interactions can occur, such as the classical hydrogen bonding, hydrogen bonding to aromatics, and  $\pi$ -stacking between aromatic units (Hu, 2002).

In Fig. 8 are indicated the  $T_g$  of CSALs and the obtained values are summarized in Table 7.

Table 7 shows that the  $T_g$  values of CSALs varied from 131 to 142 °C, in which the higher value was obtained for lignin extracted without addition of catalyst. Since CH<sub>3</sub>COOH-lignin had the lowest purity, the significant amount of residual carbohydrates in its structure could contribute for  $T_g$  observed due the increased number of hydrogen bonding between the polymeric chains, reducing their mobility.

#### 3.3. Comparison with TH-lignins

Traditional heating (TH) experiments were performed in order to compare the properties of TH-lignins with those obtained in MWAOD, evaluating if microwave irradiation (MWI) favored the occurrence of selective reactions. In these comparisons, there were evaluated the lignin yield, purity, thermal stability, molecular mass distribution and monomeric constituents, which are shown in Table 8.

In Table 8, it is observed that lower yields were obtained in TH experiments when the catalysts used were  $AlCl_3$  and  $H_2SO_4$ . This shows that the MWAOD promoted a faster fractionation of the CSP due to the faster temperature increase and to a more extensively cleavage of aryl alkyl ether bonds, yielding fragments with high solubility in acetic acid.

The FTIR spectra of TH-lignins presented a similar pattern to those of MWAOD-lignins (Fig. 3), as shown in Figure S2. This shows that the heating source did not affected the functional groups present in both type of lignins. However, there are some particularities in TH-lignins spectra, such as the relative content of some functional groups, as shown in Table S3.

In terms of composition,  ${}^{1}H^{-13}C$  HSQC spectra of TH-lignins showed that the RPM values of TH-lignins were significant different than those of MWAOD-lignins (Figure S3 and Table 9). It is observed that for H<sub>2</sub>SO<sub>4</sub> and HCl-TH-lignins there was a decrease in the relative amounts of G units.

Comparing the data presented in Table 8 with those in Table 5, is observed that the TH-lignins had higher values of  $M_w$  and  $M_n$  than

| Table 9  |                                      |
|----------|--------------------------------------|
| Relative | proportion of monomers of TH-lignins |

| Catalyst                       | S (%) | G (%) | H (%) | S/G ratio | H/G ratio |
|--------------------------------|-------|-------|-------|-----------|-----------|
| AlCl <sub>3</sub>              | 16.1  | 65.9  | 18.0  | 0.24      | 0.27      |
| H <sub>2</sub> SO <sub>4</sub> | 15.0  | 54.3  | 30.7  | 0.28      | 0.57      |
| HCl                            | 26.2  | 49.4  | 24.4  | 0.53      | 0.49      |

that of MWAOD-lignins, as shown in Figure S4. These higher values can be attributed to the existence of higher amount of carbohydrates (Lan et al., 2011), which corroborate with the results observed in FTIR, as well as by their purities.

In addition, the lower PDI's indicate that the MWAOD-lignins were composed of more homogeneous fragments and suggest that MWI provided a better control of the molecular weight distributions of the lignins.

The data presented in Table 8 also showed a lower thermal stability of TH-lignins in relation to MWAOD-lignins. This can be seen by their  $T_{\text{onset}}$  and  $T_{\text{max}}$  values, indicating higher amounts of residual carbohydrates and lower purities (Figures S5 and S6).

# 4. Conclusions

The use of Lewis acids as catalysts in the microwave-assisted organosolv delignification (MWAOD) experiments showed that these compounds yielded lignins with structural and thermal properties comparable to those obtained by using traditional Brønsted acids. Among the Lewis acids, AlCl<sub>3</sub> generated a lignin with similar properties to those obtained by H<sub>2</sub>SO<sub>4</sub> and HCl, which indicates this Lewis acid as an alternative catalyst.

Despite these interesting and promising results, further investigations are been conducted in order to assess the scaling-up of this protocol along with the optimization of reaction conditions for the utilization of other biomass residues as feedstock.

Thus, it can be concluded that microwave irradiation combined with the organosolv process promoted the delignification of coconut shell under mild conditions with higher efficiency and lower energy consumption than traditional heating, representing a great combination of green methods for extraction of lignin from biomass waste, with elevated yield, purity, and remarkable structural and thermal properties, making them suitable for further technological applications.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/i.jclepro.2018.04.126.

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