

Journal Pre-proof

High value-added lignin extracts from sugarcane by-products

Inês F. Mota, João da Silva Burgal, Filipa Antunes, Manuela E. Pintado, Patrícia S. Costa



PII: S0141-8130(23)00012-0

DOI: <https://doi.org/10.1016/j.ijbiomac.2023.123144>

Reference: BIOMAC 123144

To appear in: *International Journal of Biological Macromolecules*

Received date: 27 September 2022

Revised date: 21 November 2022

Accepted date: 1 January 2023

Please cite this article as: I.F. Mota, J. da Silva Burgal, F. Antunes, et al., High value-added lignin extracts from sugarcane by-products, *International Journal of Biological Macromolecules* (2023), <https://doi.org/10.1016/j.ijbiomac.2023.123144>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2023 Published by Elsevier B.V.

High value-added lignin extracts from sugarcane by-products

Inês F. Mota*, João da Silva Bural, Filipa Antunes, Manuela E. Pintado, Patrícia S. Costa

* Corresponding author email: imota@ucp.pt

Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Diogo Botelho 1327, 4169-005 Porto, Portugal

Abstract

This study evaluates the production of lignin bioactive extracts from sugarcane bagasse (SCB) and straw (SCS) alkaline black liquors using greener precipitating agents (methane sulfonic acid (MSA), formic acid (FA) and lactic acid (LA)) as replacers of sulfuric acid (SA), the most common one used in industry. Results showed that the highest precipitation yield was achieved by LA when applied to SCB (14.5 g extract/g SCB). Lignin SCB extracts were similar in composition in terms of total carbohydrates (61-70%), lignin (22-30%) and inorganics (1.6-2.6%). Regarding the SCS extracts, similar yields were obtained among all extracts, however; differences in composition were observed between SA and greener precipitating agents, particularly in terms of sugar content.

All extracts exhibited radical scavenging activity; overall the extracts were more effective in the scavenging of ABTS radical. FA was the most promising alternative to SA to recover lignin bioactive extracts. This work suggests organic acids as good candidates for obtaining valuable extracts from alkaline pulping of SCB and SCS instead of the conventional sulfuric acid, thus suggesting a green solution for this biomass valorization.

Keywords

Lignocellulosic biomass, alkaline extraction, precipitation, bioactive extracts, biorefinery

1. Introduction

The global Biorefinery using lignocellulosic biomass as feedstock for the development of sustainable processes to obtain products, chemicals, energy and fuels is growing considerably because of the decaying of fossil fuel reserves and to the need for a more efficient valorization of agro-industrial residues and industry byproducts [1].

Sugarcane (*Saccharum* s.p. hybrids) is a perennial monocotyledonous plant belonging to the *Gramineae* family originated from Asia. The sugarcane industry is a very important sector in Brazil in the production of sugar and first-generation ethanol from saccharose. This sector generates several by-products such as bagasse (SCB), straw (SCS), molasses, filter cake and residual wastes [2]. SCB and SCS (leaves and tops) are the main by-products of the alcohol industry accounting for about 140 kg each (dry basis) per ton of processed sugarcane [3,4]. Currently, SCB is used to suppress the energy demands of sugar and ethanol plants and SCS could either be maintained in the fields to make nutrients available or also burnt for energy [3,5]. The development of environmentally friendly processes for the valorization of these biomasses is still emergent and can be a significant economical advantaged for the sugarcane industry.

Usually, lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin interconnected and the inorganics and extractives represent a minority fraction. Cellulose is a linear homopolymer with monomeric units of anhydro-*D*-glucose linked through β -(1,4) glycosidic linkages

[6]. This arrangement confers rigidity and crystallinity to the molecule, being difficult to be hydrolyzed under mild acidic or enzymatic conditions. On the other hand, hemicellulose is a branched heteropolymer with a random and amorphous structure with little strength and thus, easily hydrolyzed by hydrothermal treatment and acid or enzymatic hydrolysis. Sugarcane hemicellulose contains both hexoses (glucose, manose and galactose) and pentoses (xylose and arabinose) being mainly composed of a backbone of xylose monomers with β -(1,4) linkages [7]. The molecule is also branched with uronic acids and *p*-hydroxycinnamic acids esterified with hemicellulose. Lignin is the reinforcing fraction conferring elasticity and mechanical strength to the plant. It is a complex aromatic macromolecule formed by the dehydrogenative polymerization of three phenylpropanoid monomers coniferyl, synapyl and *p*-coumaryl alcohols. In the specific case of sugarcane lignins, they are greatly acylated (*p*-coumaroylation) at their side chains, contain tricin flavonoid units and have ferulate residues cross-coupled between arabinoxylan and lignin [8].

SCB and SCS are lignocellulosic materials with similar compositions: SCB has about 39-45% cellulose, 23-27% hemicellulose, 19-32% lignin, 5-7% extractives and 1-3% inorganics; SCS has 33-45% cellulose, 18-30% hemicellulose, 17-41% lignin, 5-17% extractives and 2-12% inorganics [9–12]. The composition and availability of these biomasses offer a wide range of applications and valorization routes besides burning for energy, fuels and chemicals recovery. In this sense, there is extensive literature devoted to SCB and SCS reconstruction by hydrothermal, alkaline, acidic or organosolv pretreatments [13–15] and application of the respective fractions ranging from obtaining fuels (bioethanol), bioactive extractives (hydrophilic or phenolic-rich extracts), high added value molecules and biomaterials [16–20].

The biomass extraction with sodium hydroxide is one of the pretreatments extensively studied offering different advantages as this solvent is less caustic than acidic reagents, the applied mild conditions allow the solubilization of lignin and hemicellulose, and the equipment design is simple [21,22]. Most studies with SCB and SCS pretreated with sodium hydroxide are focused on the production of second-generation bioethanol or other liquid fuels, where the recalcitrant lignin polymer plays a limiting role for the necessary enzymatic saccharification of polysaccharides into monosaccharides and their subsequent fermentation [12,23–28]. These studies typically employ sodium hydroxide concentrations ranging from 0.18 to 15% w/v, temperatures of 98-175 °C, 0.75-1 h, a liquid to solid ratio, when mentioned, of 6-10, and with or without a milling/sieving stage. Some studies perform a primary hydrothermal pretreatment for a more efficient hemicellulose removal or biomass washing [12,15,25,26,29].

The pretreatments applied in SCB and SCS biomasses will result in different delignification levels and, thus, some studies are being conducted to understand the most appropriate pretreatment or its effect, particularly in the solid stream obtained, and correlate it with the intrinsic properties of SCB and SCS [8,30]. As for instance, Yu et al. 2013 [28] have removed from SCB about 21% cellulose, 24% xylans and 90% lignin employing 0.18% sodium hydroxide concentration, liquid solid ratio of 6

kg/kg at 110 °C for 1 h. In a study reported by Rezende et al. 2011 [26] a maximum of 88% of lignin was obtained from SCB pretreated with sodium hydroxide at a concentration above 2 %w/v, 120 °C for 0.75 h prior to a hydrothermal treatment employing an acid catalyst. With this combination of pretreatments, the authors managed to remove about 95% of hemicellulose, of which 80% were removed in the first hydrothermal stage. A maximum of cellulose removal of 35% was observed for treatments performed with sodium hydroxide concentrations above 2 %w/v.

Regarding the precipitation step, the acid precipitation is the most commonly method applied to obtain lignin fractions, being Lignoboost and Lignoforce two patented processes industrially applied [31,32]. Carbon dioxide (CO₂), hydrochloric acid and sulfuric acid are used to drop the pH and trigger the precipitation of the black liquor components (lignin and carbohydrates) [31–35]. However, precipitation with these mineral acids can raise environmental concerns, for example, the precipitation with hydrochloric acid leads to the formation of chlorinated compounds and with sulfuric acid, classified as carcinogenic agent to humans, releases foul gases such as H₂S and CO₂ which need to be handled (neutralized or recovered) from an industrial process point of view [34,36].

Recently, organic acids are being tested as a safer alternative to mineral acids because they are environmentally friendly, and they do not produce harmful reaction by-products. Additionally, the use of organic acids contribute to the circular economy since these acids can be obtained from biomass or as by-products of other processes. Studies revealed that some organic acids can improve the filtration process during lignin precipitation [33,35]. Moreover, precipitation with organic acids generates CO₂ that can be captured and used as precipitation agents as well [35]. In this sense, Da Silva et al. 2019 [33] evaluated the replacement of sulfuric acid by several organic acids (acetic, citric and lactic acid) in the precipitation of a kraft black liquor and observed that the organic acids gave higher lignin purity extracts with equivalent or better antioxidant activity.

Besides the raw material source, precipitation yields, and composition of the obtained extracts will depend on the process conditions such as ionic strength of black liquor, black liquor concentration in lignin and carbohydrates, final pH and temperature. Typical conditions applied are temperatures between 45-75 °C and pH drop up to 11-2 [32,34]. Lower temperature and final pH, along with higher ionic strength of the solution allow maximum precipitation yields. Most of the reported studies have shown complete precipitation at pH 4 [35]. Although some attempts have been made to overcome this problem, there is a demand for different green strategies.

Therefore, the present work proposes the alkaline extraction of sugarcane by-products using milder conditions and precipitation of the solubilized components (mostly lignin and hemicellulose) employing greener approaches (methane sulfonic acid, formic acid and lactic acid) for replacing traditional mineral acids, as well as for obtaining bioactive extracts. As far as we know, this is the first study comparing the impact of different greener solvents on the precipitation of SCB and SCS black liquors and antioxidant activity of the obtained extracts. All the precipitated extracts were characterized in terms of lignin, cellulose, hemicellulose, inorganics content, molecular weight

distribution, and glass transition temperature. The mineral sulfuric acid was also tested for comparison purposes. Because extracts from different biomasses, including sugarcane, have been reported as potential natural radical scavengers [37,38], the antioxidant activity of the studied extracts was assessed.

2. Material and methods

2.1. Raw material

Sugarcane bagasse (SCB) and straw (SCS) used in this work were kindly provided by Raízen (Brazil), air-dried overnight in an oven at 40 °C, milled (Retsch model SM100) and sieved to remove fines (fraction > 160 µm) (Retsch AS 200 basic).

2.2. Alkaline extractions and black liquor precipitation

Alkaline extractions of milled and sieved SCB and SCS were performed with 6%w/w sodium hydroxide in Schott bottles for 1 h at 90 °C (controlled by a water bath (Julabo SW22)), employing a liquid-solid ratio of 15. After the extraction, the solid phase was separated from the liquor, washed thoroughly with deionized water until neutral pH and dried at room temperature until equilibrium. The obtained black liquor was precipitated with mineral acids (sulfuric acid (SA) and methane sulfonic acid (MSA)) and organic acids (lactic acid (LA) and formic acid (FA)). For that, a solution of 6 M of the precipitating agent was prepared and the precipitation was conducted as described in literature [39] with minor changes, at 45 °C up to final pH of 4. The mixtures containing the precipitated extracts were separated by centrifugation (Thermo Scientific Heraeus Megafuge 16R) and washed firstly with acidified water (pH value of 3) and then with deionized water.

2.3. Characterization of raw and extracted biomasses

The water content and inorganics were gravimetrically determined at 105 °C (Venti-Line) and 550 °C (Nabertherm), respectively, until constant weight. The crucibles were previously calcined overnight at 550°C. All samples were analyzed at least in duplicate.

2.3.1. Quantification of total lignin and carbohydrates

Samples were submitted to acid hydrolysis for acid insoluble and soluble lignin and total carbohydrates content determination as described in literature [40]. Briefly, 3 mL of sulfuric acid 72%w/w was added to about 0.3 g of sample. The mixture was placed in water bath at 30 °C for 1 h and, afterwards, was incubated in an autoclave at 121 °C for 1 h after being diluted with deionized water up to 4%. The solution was cooled down and filtered through sintered glass filter crucibles previously calcined at 550 °C. The acid insoluble lignin was determined after drying the glass filter crucibles at 105°C. After dilution of the filtrate samples, the acid soluble lignin was quantified by spectrophotometry at 205 nm (Shimadzu UV Visible Spectrophotometer) employing the absorption

coefficient of $110 \text{ dm}^3 \text{ g}^{-1} \text{ cm}^{-1}$. The total carbohydrates content in the filtrate solution was quantified by high performance liquid chromatograph (HPLC) equipped with refractive index detector employing an Aminex HPX 87H column $300 \times 7.8 \text{ mm}$ (Bio-rad laboratories). The chromatograms were run in isocratic mode at 0.6 mL min^{-1} and $50 \text{ }^\circ\text{C}$. The mobile phase employed was 5 mM sulfuric acid solution and volume injection was $10 \text{ }\mu\text{L}$. All samples were analyzed at least in duplicate.

2.4. Characterization of black liquors

Total non-volatile solids and inorganics content were gravimetrically assessed at $105 \text{ }^\circ\text{C}$ and $550 \text{ }^\circ\text{C}$, respectively, until constant weight. Lignin concentration was spectrophotometrically determined at 280 nm (Shimadzu UV Visible Spectrophotometer) after adequate dilution employing a calibration curve obtained with a kraft standard lignin (Sigma-Aldrich, CAS 8002-05-1, purity $>95\%$) dissolved in 0.1 M sodium hydroxide solution. Apparent density was measured by weighting a known volume of liquor and pH value using a pH meter (Mettler Toledo).

2.5. Characterization of the lignin extracts

Extracts were characterized regarding total lignin, carbohydrates and inorganics, as previously described. The attenuated total reflectance - Fourier transform infrared spectroscopy, molecular weight distribution and glass transition temperature were assessed as described below.

2.5.1. Attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR (Perkin Elmer Frontier) by direct transmittance in a single-reflection ATR System was performed for the extracts to analyze main functional groups of lignin. Spectra were recorded between 550 and 4000 cm^{-1} with 16 scans and resolution of 4 cm^{-1} .

2.5.2. Molecular weight determination by Gel Permeation Chromatography (GPC)

Molecular weight determination was performed on an Agilent 1260 Infinity II system equipped with UV detector and quaternary pump. It was used two Agilent gel columns placed in series: Oligopore column $300 \times 7.5 \text{ mm}$ with nominal particle size of $6 \text{ }\mu\text{m}$ and Mesopore column $300 \times 7.5 \text{ mm}$ with nominal particle size of $3 \text{ }\mu\text{m}$ that measure molecular weights up to $4\,500 \text{ g mol}^{-1}$ and $25\,000 \text{ g mol}^{-1}$, respectively. A guard column Oligopore $50 \times 7.5 \text{ mm}$ was placed prior to the columns. Detection was performed at 268 nm and the volume of injection was $20 \text{ }\mu\text{L}$. GPC analysis were performed in isocratic mode employing dimethylformamide with $0.5\% \text{ w/v}$ of lithium chloride [41]. Chromatograms were run at $70 \text{ }^\circ\text{C}$ and flowrate of 0.8 mL min^{-1} . About 5 mg/mL of each standard or sample was dissolved in mobile phase solvent, stirred until complete dissolution and filtered through $0.45 \text{ }\mu\text{m}$ syringe filter before injection. Calibration curve was performed with 10 polystyrene molecular weight standards (Agilent) ranging from 162 and 9570 g mol^{-1} .

2.5.3. Differential scanning calorimetry (DSC)

DSC (Netzsch-Gerätebau GmbH DSC 204 F1 Phoenix®) was employed to determine the glass transition temperature (T_g). About 5 mg of sample was hermitically sealed in aluminum pans with pierced lids and analyzed under nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from $30\text{ }^\circ\text{C}$ to $550\text{ }^\circ\text{C}$. Inert atmosphere was maintained by purging nitrogen gas at a flow rate of 40 mL min^{-1} .

2.5.4. Antioxidant activity

2.5.4.1. 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) assay

The antioxidant activity was assessed according to the method described in literature [42] with some modifications. The concentration of ABTS radical was adjusted with methanol to an initial absorbance of $0.700 (\pm 0.020)$ at 734 nm . To $200\text{ }\mu\text{L}$ of this solution of ABTS was added $15\text{ }\mu\text{L}$ of sample or Trolox (positive control) or solvent (blank) in a 96-well plate. The mixture was incubated for 5 min at room temperature in the dark, and the absorbance at 734 nm was measured in a microplate reader. The radical stock solution was freshly prepared, and all the analyses were performed in triplicate. Samples were prepared by dissolving 10 mg of each extract in 1 mL of methanol, sonicated for 30 min, centrifuged at 15000 rpm for 5 min and the soluble fraction was gravimetrically determined. The percentage results of scavenging activity were calculated as % inhibition using the following equation (1):

$$\% \text{ Inhibition} = \frac{(A_c - A_s)}{A_c} \times 100 \quad (1)$$

where, A_c is the absorbance of control and A_s is the absorbance of the sample. The results were expressed as IC_{50} (i.e. the concentration of the sample required to inhibit 50% of the ABTS radical).

2.5.4.2. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) assay

The ability of the extracts to scavenge the DPPH radical was determined by the method described in literature [43] with minor modifications. For the DPPH assay, $175\text{ }\mu\text{L}$ of DPPH methanolic solution ($600\text{ }\mu\text{M}$) were added to $25\text{ }\mu\text{L}$ of each extract or butylated hydroxytoluene (BHT) or solvent (blank). Samples preparation was performed as previously described for the ABTS assay. After 30 min in the dark at room temperature, the inhibition of the DPPH radical was measured at an absorbance of 515 nm . The antioxidant activity was expressed as a percentage DPPH inhibition following Equation (1). All experiments were performed in triplicate. The results were expressed as IC_{50} (i.e. the concentration of the sample required to inhibit 50% of the DPPH radical).

3. Results and discussion

3.1. Alkaline extraction

The physical and chemical characterization of the raw material - sugarcane bagasse (SCB) and straw (SCS) - was performed and the results are shown in Table 1. The SCB showed a higher content of cellulose and lower contents of hemicellulose and total lignin than SCS (Table 1), being in line with the compositions reported in literature [9–12,44]. The raw materials were submitted to the same alkaline treatment and the respective extracted biomass obtained were characterized (Table 1). It was observed a low solubilization of cellulose (<1%), and high solubilizations of hemicellulose and total lignin (above 65%). In the case of the SCS, the extraction of hemicellulose and total lignin were higher than for SCB (Table 1).

Table 1. Chemical composition of raw SCB and SCS and respective extracted biomass obtained after alkaline pretreatment.

	(%wt, oven dried basis)				Cellulose removal (%)	Hemicellulose removal (%)	Lignin removal (%)	Solubilization Yields (%)
	Cellulose	Hemicellulose	% Total Lignin	% Inorganics				
Raw SCB	37.9 ± 0.4	32.7 ± 0.6 (Xylans 28.2 ± 0.7)	25.5 ± 0.7 (KL 22.9 ± 0.4)	3.8 ± 0.9	-	-	-	-
Raw SCS	34.9 ± 0.6	33.7 ± 0.3 (Xylans 28.30 ± 0.3)	26.5 ± 0.2 (KL 23.5 ± 0.1)	3.6 ± 0.2	-	-	-	-
Extracted SCB ^a	69.5 ± 3.6	19.4 ± 1.5 (Xylans 17.6 ± 1.7)	12.4 ± 0.8 (KL 11.20 ± 0.4)	2.7 ± 0.1	b)	65.5 ± 0.2	72.8 ± 0.2	44.0 ± 0.4
Extracted SCS ^a	74.8 ± 3.2	18.1 ± 1.4 (Xylans 15.4 ± 1.4)	11.03 ± 1.4 (KL 8.9 ± 1.2)	2.7 ± 0.4	0.8 ± 1.9	73.8 ± 0.5	80.7 ± 0.4	53.1 ± 0.9

SCB – sugarcane bagasse; SCS – Sugarcane straw, KL – Klason lignin (insoluble lignin); a) Expressed in w/w pretreated biomass; b) residual removal.

In this work, SCB solubilization yield (44.0%) was within the range of values found in the literature for different soda extraction conditions (23-49%) [23,24,26,27,45]. Herein, lignin is the major compound removed (72.8%) agreeing with other studies using sodium hydroxide concentrations above 1% (67-90%) [23,24,26–28,46]. Hemicellulose removal (65.5%) is slightly higher than others reported in the literature for sodium hydroxide concentrations above 1% (19-58%) [23,24,26–28,46]. The solubilization and delignification yields achieved for SCS were 53% and 81% were achieved, respectively (Table 1). The hemicellulose removal was slightly higher than that of SCB (73%), whereas the cellulose removal was similar (below 1%). Regarding the results obtained for cellulose, they were lower than expected considering those reported in similar studies for SCB (19-36%) and SCS (0.8 and 35%) [15,26–28]. This can be explained, at least in part, to the prior hydrothermal pretreatment employed that can disrupt the fibrous matrix and induce a boosting effect in the carbohydrates removal during the alkaline pretreatment.

3.2. Composition of black liquors

The composition of both black liquors was similar in terms of total non-volatile solids, inorganics content, and lignin and carbohydrates concentrations (Table 2). Although more compounds were

solubilized in the SCS (23%) as compared to the SCB (15%) (Table 1), the composition of both black liquors are similar suggesting the occurrence of material losses during the liquid-solid separation stage of SCS process. Density ($1.01 \pm 0.02 - 1.03 \pm 0.02 \text{ g mL}^{-1}$) and pH values (12.86 – 13.97) were similar for both liquors (Table 2).

Table 2. Sugarcane bagasse (SCB) and straw (SCS) black liquors composition in terms of non-volatile solids (C_{TS}), inorganics content (C_{ashes}), soluble lignin concentration (C_{Lignin}) and carbohydrates (C_{sugars})

	SCB	SCS
$C_{TS} \text{ (g L}^{-1}\text{)}$	98.4 ± 4.6	101.7 ± 3.8
$C_{ashes} \text{ (g L}^{-1}\text{)}$	66.9 ± 1.9	68.5 ± 2.9
$C_{Lignin} \text{ (g L}^{-1}\text{)}$	11.6 ± 1.2	11.7 ± 0.2
$C_{Sugars}^* \text{ (g L}^{-1}\text{)}$	17.6 ± 2.6	20.0 ± 3.6
Density (g mL^{-1})	1.03 ± 0.02	1.01 ± 0.02
pH value	13.07-13.97	12.86-13.10

* About 90-93% are xylan and arabinan

3.3. Alkaline black liquor precipitation with different solvents

3.3.1. Yields and composition of the sugarcane extracts

Different acid precipitation agents (mineral and organic) at a concentration of 6 M were employed to evaluate their influence in the precipitation yield, and extract composition. Precipitation yields and extracts compositions vary among both biomasses (Figure 1) and the precipitating agent employed. The precipitation yields for SCB ranged from 0 to 15%; LA allowed the highest value, followed by FA, SA and MSA. For SCS, lower precipitation yields were obtained ($<1.1 \text{ \% w/w}_{\text{raw biomass}}$) with FA showing the best result followed by LA, MSA and SA. To the best of our knowledge, no precipitation yields are reported in literature for sugarcane SCS. For both SCB and SCS, slightly higher precipitation yields were obtained employing the organic acids.

In the extraction step, the solubilization yield was higher for SCS (53%) than for SCB (44%) along with higher hemicellulose and lignin removals, whereas in the precipitation step, with an aqueous acid solution, the efficiency of the precipitation stage was much lower for SCS. Different results were also observed by da Silva *et al.* 2010 [10] after applying the same milling procedure and enzymatic hydrolysis conditions to SCB and SCS. The different performance behaviors during the extraction and precipitation step can be explained by the physical-chemical structural differences of biomasses [8,24] as, for instance, the different guaiacyl and syringyl unit proportions and different abundance of the interunit linkages reported [8]. In this regard, the introduction of a prior pre-treatment (e.g. hydrothermal) or using other precipitation methodologies (e.g. acid concentration, temperature, final pH value or adjustment of the ionic strength) must be found for SCS in order to obtain an economical feasible process [32,34].

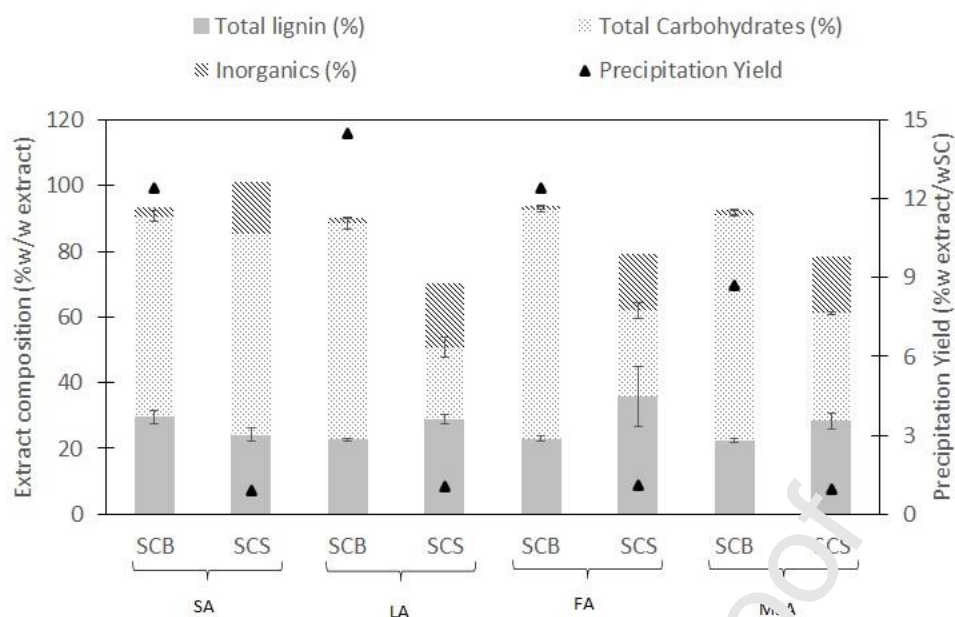


Figure 1. Composition of the lignin bioactive extracts obtained with different precipitating agents for sugarcane bagasse (SCB) and straw (SCS) expressed as % weight per extract weight and respective precipitation yields expressed as % weight of extract per weight of sugarcane (SC). SA-Sulfuric acid; LA-Lactic acid, FA-Formic acid and MSA-Methane sulfonic acid.

Overall, SCB lignin extracts were similar in composition and are mainly composed of total carbohydrates (61-70%, with xylan as the major component), lignin (22-30%) and inorganics (1.6-2.6%). In contrast, the composition of the SCS extracts was influenced by the applied acid. Comparing both biomasses, the performance of SA 6 M solution in terms of precipitation capacity of total carbohydrates, lignin and inorganics is similar. Regarding the remaining extracts from SCS, the total carbohydrates (22-26%), lignin (28-36%) and inorganics (16-17%) content are similar among the precipitating agents LA, FA and MSA, but different compared with SA.

3.3.2. FTIR-ATR spectra

Figure 2 and Figure 3 display the FTIR spectra of the different SCB and SCS lignin extracts. For extracts from SCB liquor, similar FTIR spectra were observed and no differences in chemical structure were identified according to the precipitating agent employed. All samples showed a broad band between 3650 cm^{-1} and 3050 cm^{-1} attributed to hydroxyl groups in phenolic and aliphatic structures. The region between 3000 cm^{-1} and 2830 cm^{-1} corresponds to C-H stretch in methyl and methylene groups and methoxyl groups, being similar for all samples. Aromatic skeletal vibrations are assigned to bands 1594 cm^{-1} (characteristic of condensed G-units), 1504 cm^{-1} , 1459 cm^{-1} and 1423 cm^{-1} . The presence of lignin is found in the bands 1594 cm^{-1} attributed to aromatic skeletal vibration characteristic of condensed G-units, 1324 cm^{-1} related to aryl ring breathing with C-O stretch characteristic for syringyl ring plus guaiacyl ring condensed and 1216 cm^{-1} attributed to guaiacyl units (condensed > etherified guaiacyl units, not relevant band). The presence of *p*-coumaric esters (typical

for GSH lignins) is shown by the presence of the shoulder at 1163 cm^{-1} (not relevant) and 975 cm^{-1} . These bands are very similar for all samples. The band 833 cm^{-1} is assigned to C-H out of plane in positions 2, 5 and 6 of S-units and all positions of H-units. In all samples, the polysaccharides presence is well noticed due to high intensity bands between 1200 cm^{-1} and 1000 cm^{-1} associated to hemicellulosic moiety [7]. High intensity peak in 1035 cm^{-1} is attributed to stretching and bending vibrations of C-O, C-C, C-OH and C-O-C. The presence of arabinosyl sidechains is identified by two low intensity shoulders in 1078 cm^{-1} and 975 cm^{-1} , and 896 cm^{-1} is characteristic of β -glycosidic linkages between the sugar units.

SCS extracts have a typical lignin-carbohydrate complex with the presence of the main functional groups identified in the region $1600 - 900\text{ cm}^{-1}$, being also noticeable the large amount of carbohydrates assigned to the bands 1030 cm^{-1} and $890-910\text{ cm}^{-1}$. This last observation agrees with the obtained physico-chemical composition.

The SCS sulfuric acid 6M extract had a similar FTIR spectra with the same functional groups and intensity to SCB extracts. On the contrary, the other SCS extracts have the same functional groups in the region $1600 - 900\text{ cm}^{-1}$ but with differences in band intensities. It was observed a reduction of hydroxyl groups (region $3600 - 3050\text{ cm}^{-1}$) and higher intensity of bands in region $3000-2860\text{ cm}^{-1}$ related to CH groups. The intensity of peaks in this region increased in the order $\text{MSA} < \text{LA} < \text{FA}$.

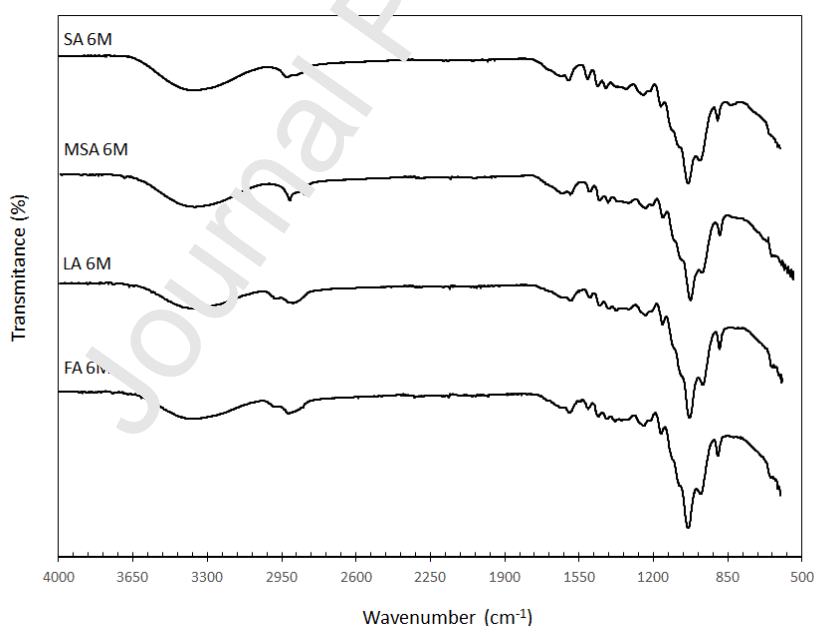


Figure 2. FTIR spectra of sugarcane bagasse lignin extracts. Precipitating agents: Sulfuric acid (SA), Lactic acid (LA), Formic acid (FA) and Methane sulfonic acid (MSA).

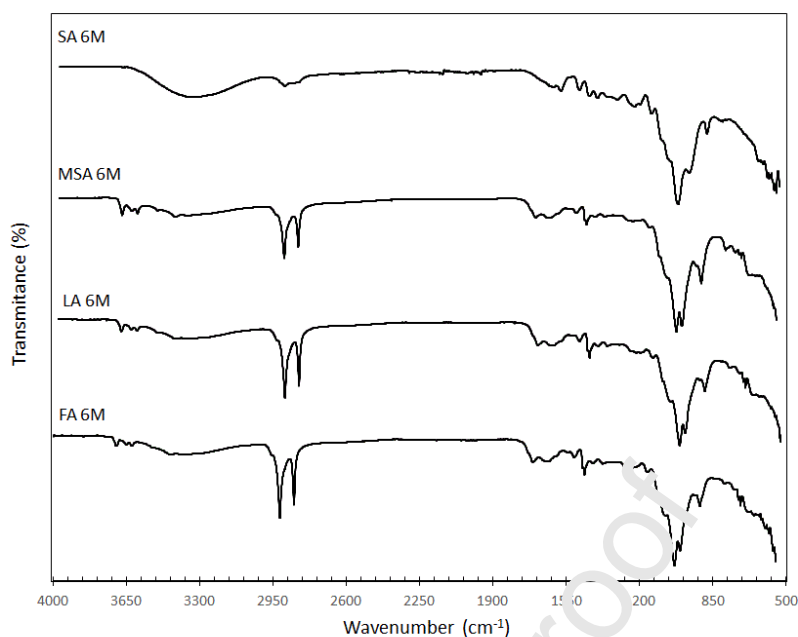


Figure 3. FTIR spectra of sugarcane straw lignin extracts. Precipitating agents: Sulfuric acid (SA), Lactic acid (LA), Formic acid (FA) and Methanesulfonic acid (MSA).

3.3.3. Molecular weight and glass transition temperature

Table 3 shows the molecular weights and polydispersity of the extracts employing different acid agents and the corresponding glass transition temperatures (T_g). In general, higher molecular weights were obtained for SCB extracts, regardless of the precipitating agent. In both biomasses, SA was the precipitating agent generating lower molecular weight extracts (17737 ± 1811 - 19870 ± 1990 , for SCS and SCB extracts, respectively). T_g is a property defining the transition between a glassy and rigid state from a flexible and rubbery state, important on the development of composite materials and varies according to biomass source, pretreatment and purification methodologies, molecular weight, hydroxyl groups content, lignin content and G/S unit contents. T_g will be higher the higher molecular weight, guaiacyl units (more reactive than syringyl units) and hydroxyl group contents [47,48].

In this work, it was not possible to determine the T_g for extracts obtained from SCS with MSA and FA since no inflection point was detected. The obtained T_g values ranged from 161 to 175 °C, being in line with those reported in the literature after kraft process and acid precipitation (alkaline pretreatment) [47]. It is stated that the T_g value of native lignins is between 65-105 °C and after kraft pretreatment and precipitation it increases to 124-174 °C [47]. Moreover, the high content of carbohydrates also contributes to the increase of the T_g value of the sample [47,49]. The present study allowed to confirm that, SCB extracts with higher molecular weights and carbohydrates showed higher T_g as well.

Table 3. Sugarcane bagasse (SCB) and straw (SCS) lignin extracts: weight-average molecular weight (Mw), number-average molecular weight (Mn), polydispersity (PD) and glass transition temperature (T_g).

Biomass	Precipitating agent	MW (g mol ⁻¹)	Mn (g mol ⁻¹)	PD	Tg (°C)
SCB	Sulfuric acid	19870 ± 1990	14483 ± 1478	1.37 ± 0.02	171 ± 8
	Lactic acid	26003 ± 400	18949 ± 444	1.37 ± 0.01	175 ± 2
	Formic acid	23007 ± 2442	16465 ± 1977	1.40 ± 0.02	168 ± 1
	Methane sulfonic acid	23638 ± 1016	17147 ± 703	1.30 ± 0.02	161 ± 1
SCS	Sulfuric acid	17737 ± 1811	12171 ± 1592	1.46 ± 0.04	165 ± 6
	Lactic acid	19375 ± 1070	13636 ± 926	1.42 ± 0.02	165 ± 6
	Formic acid	19261 ± 446	13466 ± 275	1.43 ± 0.02	a)
	Methane sulfonic acid	19805 ± 1071	13815 ± 852	1.43 ± 0.02	a)

a) Not possible to determine

3.3.4. Antioxidant activity

The antioxidant activity of SCB and SCS lignin extracts was evaluated using the ABTS and DPPH methods and the results are presented in Table 4. Data showed that, depending on the precipitating agent, different inhibitions are achieved demonstrating its relevance for the bioactivity of the sugarcane extracts. FA extracts from SCB showed the highest inhibition of both radicals (IC₅₀= 1.601±0.018 mg mL⁻¹ and 2.631±0.031 mg mL⁻¹, for ABTS and DPPH radicals, respectively). In the case of SCS, the highest inhibitions were also achieved by the FA extracts (IC₅₀=2.752±0.331 mg mL⁻¹ and 3.534±0.159 mg mL⁻¹) followed by MSA extracts (IC₅₀=2.248±0.029 mg mL⁻¹ and 5.356±2.259 mg mL⁻¹).

Table 4. Antioxidant activities of soluble fractions of sugarcane bagasse (SCB) and straw (SCS) lignin extracts, and reference antioxidants butylated hydroxytoluene (BHT) and Trolox assessed by the TEAC and DPPH assays.

Biomass	Precipitating agent	IC ₅₀ (mg mL ⁻¹)	
		ABTS	DPPH
SCB	Sulfuric acid	7.128 ± 0.212	>10
	Lactic acid	>10	>10
	Formic acid	1.601 ± 0.018	2.631±0.031
	Methane sulfonic acid	>10	>10
SCS	Sulfuric acid	3.348 ± 0.066	4.394 ± 0.159
	Lactic acid	4.458 ± 0.060	6.137 ± 0.259
	Formic acid	2.752 ± 0.331	3.534 ± 0.159
	Methane sulfonic acid	2.248 ± 0.029	5.356 ± 2.259

BHT IC₅₀ (mg mL⁻¹) = 0.288 ± 0.004 and 0.297 ± 0.004, for ABTS and DPPH radicals, respectively.

4. Conclusions

Different organic solvents were applied as greener alternatives to replace the mineral acid traditionally applied (sulfuric acid) in the recovery of lignin bioactive extracts from SCB and SCS.

Formic (FA), lactic (LA) and methane sulfonic acids (MSA) generated SCB and SCS extracts with similar lignin, carbohydrates and inorganic contents to their respective sulfuric fraction, except for SCS extract obtained with SA, which had higher carbohydrates content (61%) than the remaining SCS

extracts (22-33%). Overall, FA was the most auspicious organic precipitating agent for obtaining bioactive extracts from sugarcane bagasse and straw. This study proved the influence of the precipitation agent not only on the composition of SCS and SCB extracts as well as on their antioxidant potential for food and cosmetic applications.

Acknowledgments

Work funded by the European Regional Development Fund (ERDF), through the Operational Program for Competitiveness and Internationalization (COMPETE 2020) and Portugal 2020 to the project Alchemy (POCI-01-0247-FEDER-027578).

References

- [1] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W.J. Frederick, J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, The path forward for biofuels and biomaterials. *Science* (80-.). 311 (2006) 484–489. <https://doi.org/10.1126/science.1114736>.
- [2] G.C. Quintana, G.J.M. Rocha, A.R. Gonçalves, J.A. Velásquez, Evaluation of heavy metal removal by oxidised lignins in acid media from various sources, *3* (2008) 1092–1102.
- [3] G.A.A. Labat, A.R. Gonçalves, Oxidation in acidic medium of lignins from agricultural residues, *Appl. Biochem. Biotechnol.* 148 (2008) 151–161. <https://doi.org/10.1007/s12010-007-8120-0>.
- [4] A.V. da Rosa, ed., *Fundamentals of Renewable Energy Processes*, 3th ed., Academic Press, 2013. <https://doi.org/10.1016/C2011-0-06913-2>.
- [5] L.M.S. Menandro, H. Cantarella, H.C.J. Franco, O.T. Kölln, M.T.B. Pimenta, G.M. Sanches, S.C. Rabelo, J.L.N. Carvalho, Comprehensive assessment of sugarcane straw: implications for biomass and bioenergy production, *Biofuels, Bioprod. Biorefining.* 11 (2017) 488–504. <https://doi.org/10.1002/bbb.1760>.
- [6] C. Chatterjee, F. Pong, A. Sen, Chemical conversion pathways for carbohydrates, *Green Chem.* 17 (2015) 40–71. <https://doi.org/10.1039/c4gc01062k>.
- [7] J.X. Sun, X.F. Sun, R.C. Sun, Y.Q. Su, Fractional extraction and structural characterization of sugarcane bagasse hemicelluloses, *Carbohydr. Polym.* 56 (2004) 195–204. <https://doi.org/10.1016/j.carbpol.2004.02.002>.
- [8] J.C. del Río, A.G. Lino, J.L. Colodette, C.F. Lima, A. Gutiérrez, Á.T. Martínez, F. Lu, J.

- Ralph, J. Rencoret, Differences in the chemical structure of the lignins from sugarcane bagasse and straw, *Biomass and Bioenergy*. 81 (2015) 322–338. <https://doi.org/10.1016/j.biombioe.2015.07.006>.
- [9] L. Canilha, V.T.O. Santos, G.J.M. Rocha, J.B. Almeida e Silva, M. Giuliatti, S.S. Silva, M.G.A. Felipe, A. Ferraz, A.M.F. Milagres, W. Carvalho, A study on the pretreatment of a sugarcane bagasse sample with dilute sulfuric acid, *J. Ind. Microbiol. Biotechnol.* 38 (2011) 1467–1475. <https://doi.org/10.1007/s10295-010-0931-2>.
- [10] A.S. da Silva, H. Inoue, T. Endo, S. Yano, E.P.S. Bon, Milling pretreatment of sugarcane bagasse and straw for enzymatic hydrolysis and ethanol fermentation, *Bioresour. Technol.* 101 (2010) 7402–7409. <https://doi.org/10.1016/j.biortech.2010.05.008>.
- [11] S.C. Rabelo, H. Carrere, R. Maciel Filho, A.C. Costa, Production of bioethanol, methane and heat from sugarcane bagasse in a biorefinery concept, *Bioresour. Technol.* 102 (2011) 7887–7895. <https://doi.org/10.1016/j.biortech.2011.05.081>.
- [12] G.J.M. Rocha, A.R. Gonçalves, B.R. Oliveira, E.G. Olivares, C.E.V. Rossell, Steam explosion pretreatment reproduction and alkaline delignification reactions performed on a pilot scale with sugarcane bagasse for bioethanol production, *Ind. Crops Prod.* 35 (2012) 274–279. <https://doi.org/10.1016/J.INDCROP.2011.07.010>.
- [13] S. Al Arni, Extraction and isolation methods for lignin separation from sugarcane bagasse: A review, *Ind. Crops Prod.* 115 (2018) 330–339. <https://doi.org/10.1016/J.INDCROP.2018.02.012>.
- [14] L. Mesa, E. González, C. Cara, M. González, E. Castro, S.I. Mussatto, The effect of organosolv pretreatment variables on enzymatic hydrolysis of sugarcane bagasse, *Chem. Eng. J.* 168 (2011) 1157–1162. <https://doi.org/10.1016/j.cej.2011.02.003>.
- [15] A. Moubarik, N. Grimi, N. Boussetta, A. Pizzi, Isolation and characterization of lignin from Moroccan sugar cane bagasse : Production of lignin – phenol-formaldehyde wood adhesive, *Ind. Crop. Prod.* 45 (2013) 296–302. <https://doi.org/10.1016/j.indcrop.2012.12.040>.
- [16] M.R.V. Bertolo, L.B. Brenelli de Paiva, V.M. Nascimento, C.A. Gandin, M.O. Neto, C.E. Driemeier, S.C. Rabelo, Lignins from sugarcane bagasse: Renewable source of nanoparticles

- as Pickering emulsions stabilizers for bioactive compounds encapsulation, *Ind. Crops Prod.* 140 (2019) 111591. <https://doi.org/10.1016/J.INDCROP.2019.111591>.
- [17] M.A. Khan, S.M. Ashraf, V.P. Malhotra, Development and characterization of a wood adhesive using bagasse lignin, *Int. J. Adhes. Adhes.* 24 (2004) 485–493. <https://doi.org/https://doi.org/10.1016/j.ijadhadh.2004.01.003>.
- [18] Y. Park, W.O.S. Doherty, P.J. Halley, Developing lignin-based resin coatings and composites, *Ind. Crops Prod.* 27 (2008) 163–167. <https://doi.org/https://doi.org/10.1016/j.indcrop.2007.07.021>.
- [19] N. Ratanasumarn, P. Chitprasert, Cosmetic potential of lignin extracts from alkaline-treated sugarcane bagasse: Optimization of extraction conditions using response surface methodology, *Int. J. Biol. Macromol.* 153 (2020) 138–145. <https://doi.org/10.1016/J.IJBIOMAC.2020.02.328>
- [20] R. Zheng, S. Su, J. Li, Z. Zhao, J. Wei, X. Gu, R.H. Liu, Recovery of phenolics from the ethanolic extract of sugarcane (*Saccharum officinarum* L.) bagasse and evaluation of the antioxidant and antiproliferative activities, *Ind. Crops Prod.* 107 (2017) 360–369. <https://doi.org/10.1016/J.INDCROP.2017.05.050>.
- [21] A.K. Kumar, S. Sharma, Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review, *Bioresour. Bioprocess.* (2017). <https://doi.org/10.186/s40643-017-0137-9>.
- [22] A.A. Modenbach, Effects of sodium hydroxide pretreatment on structural components of biomass, *Biosyst. Agric. Eng. Fac. Publ.* 57 (2014) 1187–1198. https://doi.org/https://uknowledge.uky.edu/bae_facpub/84.
- [23] D.M. de Carvalho, J.H. de Queiroz, J.L. Colodette, Assessment of alkaline pretreatment for the production of bioethanol from eucalyptus, sugarcane bagasse and sugarcane straw, *Ind. Crops Prod.* 94 (2016) 932–941. <https://doi.org/10.1016/J.INDCROP.2016.09.069>.
- [24] D.M. de Carvalho, O. Sevastyanova, L.S. Penna, B.P. da Silva, M.E. Lindström, J.L. Colodette, Assessment of chemical transformations in eucalyptus, sugarcane bagasse and straw during hydrothermal, dilute acid, and alkaline pretreatments, *Ind. Crops Prod.* 73 (2015) 118–

126. <https://doi.org/10.1016/J.INDCROP.2015.04.021>.
- [25] F.M.V. Oliveira, I.O. Pinheiro, A.M. Souto-Maior, C. Martin, A.R. Gonçalves, G.J.M. Rocha, Industrial-scale steam explosion pretreatment of sugarcane straw for enzymatic hydrolysis of cellulose for production of second generation ethanol and value-added products, *Bioresour. Technol.* 130 (2013) 168–173. <https://doi.org/10.1016/j.biortech.2012.12.030>.
- [26] C.A. Rezende, M.A. de Lima, P. Maziero, E.R. DeAzevedo, W. Garcia, I. Polikarpov, Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility, *Biotechnol. Biofuels.* 4 (2011) 54. <https://doi.org/10.1186/1754-6834-4-54>.
- [27] C. Xu, J. Zhang, Y. Zhang, Y. Guo, H. Xu, C. Liang, Lignin prepared from different alkaline pretreated sugarcane bagasse and its effect on enzymatic hydrolysis, *Int. J. Biol. Macromol.* 141 (2019) 484–492. <https://doi.org/10.1016/j.ijbiomac.2019.08.263>.
- [28] Q. Yu, X. Zhuang, S. Lv, M. He, Y. Zhang, Z. Yuan, W. Qi, Q. Wang, W. Wang, X. Tan, Liquid hot water pretreatment of sugarcane bagasse and its comparison with chemical pretreatment methods for the sugar recovery and structural changes, *Bioresour. Technol.* 129 (2013) 592–598. <https://doi.org/10.1016/J.BIORTECH.2012.11.099>.
- [29] S.M.R. Wahba, A.S. Darwish, I.H. Shehata, S.S. Abd Elhalem, Sugarcane bagasse lignin, and silica gel and magneto-silica as drug vehicles for development of innocuous methotrexate drug against rheumatoid arthritis disease in albino rats, *Mater. Sci. Eng. C.* 48 (2015) 599–610. <https://doi.org/10.1016/J.MSEC.2014.12.054>.
- [30] J.-X. Sun, X.-F. Sun, R.-C. Sun, P. Fowler, M.S. Baird, Inhomogeneities in the Chemical Structure of Sugarcane, *J. Wood Chem. Technol.* 51 (2003) 6719–6725. <https://doi.org/10.1021/jf034633j>.
- [31] L. Kouisni, A. Gagné, K. Maki, P. Holt-Hindle, M. Paleologou, LignoForce system for the recovery of lignin from black liquor: Feedstock options, odor profile, and product characterization, *ACS Sustain. Chem. Eng.* 4 (2016) 5152–5159. <https://doi.org/10.1021/acssuschemeng.6b00907>.
- [32] W. Zhu, G. Westman, H. Theliander, Investigation and characterization of lignin precipitation in the lignoboost process, *J. Wood Chem. Technol.* 34 (2014) 77–97.

- <https://doi.org/10.1080/02773813.2013.838267>.
- [33] S.H.F. da Silva, O. Gordobil, J. Labidi, Organic acids as a greener alternative for the precipitation of hardwood kraft lignins from the industrial black liquor, *Int. J. Biol. Macromol.* 142 (2020) 583–591. <https://doi.org/10.1016/j.ijbiomac.2019.09.133>.
- [34] M. Helander, H. Theliander, M. Lawoko, G. Henriksson, L. Zhang, M.E. Lindström, Fractionation of technical lignin: Molecular mass and pH effects, *BioResources.* 8 (2013) 2270–2282. <https://doi.org/10.15376/biores.8.2.2270-2282>.
- [35] M. Namane, F. José García-Mateos, B. Sithole, D. Ramjugernath, J. Rodríguez-Mirasol, T. Cordero, Characteristics of Lignin Precipitated With Organic Acids As a Source for Valorisation of Carbon Products, *Cellul. Chem. Technol.* 50 (2016) 355–360.
- [36] N. Paidimarri, U. Virendra, S. Vedantam, Simultaneous recovery of hydrogen and chlorine from industrial waste dilute hydrochloric acid, *Int. J. Chem. Eng.* 2016 (2016) 1–13. <https://doi.org/10.1155/2016/8194674>.
- [37] R. Kaur, S.K. Uppal, Structural characterization and antioxidant activity of lignin from sugarcane bagasse, *Colloid Polym. Sci.* 293 (2015) 2585–2592. <https://doi.org/10.1007/s00396-015-0653-1>.
- [38] Z. Li, Y. Ge, Antioxidant activities of lignin extracted from sugarcane bagasse via different chemical procedures, *Int. J. Biol. Macromol.* 51 (2012) 1116–1120. <https://doi.org/10.1016/j.ijbiomac.2012.09.004>.
- [39] M. Namane, B.B. Sithole, D. Ramjugernath, Centrifugal washing and recovery as an improved method for obtaining lignin precipitated from South African kraft mill black liquor, 74 (2015) 1–6.
- [40] O. Ajao, J. Jeaidi, M. Benali, A.M. Restrepo, N. El Mehdi, Y. Boumghar, Quantification and variability analysis of lignin optical properties for colour-dependent industrial applications, *Molecules.* 23 (2018) 1–21. <https://doi.org/10.3390/molecules23020377>.
- [41] I.F. Mota, P.R. Pinto, J.M. Loureiro, A.E. Rodrigues, Purification of syringaldehyde and vanillin from an oxidized industrial kraft liquor by chromatographic processes, *Sep. Purif. Technol.* 234 (2020) 116083. <https://doi.org/10.1016/j.seppur.2019.116083>.

- [42] B. Gonçalves, V. Falco, J. Moutinho-Pereira, E. Bacelar, F. Peixoto, C. Correia, Effects of elevated CO₂ on grapevine (*Vitis vinifera* L.): Volatile composition, phenolic content, and in vitro antioxidant activity of red wine, *J. Agric. Food Chem.* 57 (2009) 265–273. <https://doi.org/10.1021/jf8020199>.
- [43] V. Bondet, W. Brand-Williams, C. Berset, Kinetics and mechanisms of antioxidant activity using the DPPH.Free Radical Method, *LWT - Food Sci. Technol.* 30 (1997) 609–615. <https://doi.org/https://doi.org/10.1006/fstl.1997.0240>.
- [44] G. Jackson de Moraes Rocha, C. Martin, I.B. Soares, A.M. Souto Maior, H.M. Baudel, C.A. Moraes de Abreu, Dilute mixed-acid pretreatment of sugarcane bagasse for ethanol production, *Biomass and Bioenergy.* 35 (2011) 663–670. <https://doi.org/https://doi.org/10.1016/j.biombioe.2010.10.018>.
- [45] Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu, J. Xu, Lignin depolymerization (LDP) in alcohol over nickel-based catalysts via a fragmentation-hydrogenolysis process, *Energy Environ. Sci.* 6 (2013) 994–1007. <https://doi.org/10.1039/c2ee23741e>.
- [46] F.F. De Menezes, J. Rencoret, S.C. Nakanishi, V.M. Nascimento, V.F.N. Silva, A. Gutierrez, J. Carlos, D. Rio, G. Jackson, M. Rocha, Alkaline pretreatment severity leads to different lignin applications in sugarcane biorefineries, *ACS Sustain. Chem. Eng.* 5, (2017) 5702–5712. <https://doi.org/https://doi.org/10.1021/acssuschemeng.7b00265>.
- [47] W.G. Glasser, Classification of lignin according to chemical and molecular Structure, in: *Lignin Hist. Biol. Mater. Perspect.*, American Chemical Society, 1999: pp. 216–238. <https://doi.org/doi:10.1021/bk-2000-0742.ch009>.
- [48] Q. Sun, R. Khunsupat, K. Akato, J. Tao, N. Labbé, N.C. Gallego, J.J. Bozell, T.G. Rials, G.A. Tuskan, T.J. Tschaplinski, A.K. Naskar, Y. Pu, A.J. Ragauskas, A study of poplar organosolv lignin after melt rheology treatment as carbon fiber precursors, *Green Chem.* 18 (2016) 5015–5024. <https://doi.org/10.1039/c6gc00977h>.
- [49] P. Mousavioun, W.O.S. Doherty, Chemical and thermal properties of fractionated bagasse soda lignin, *Ind. Crops Prod.* 31 (2010) 52–58. <https://doi.org/https://doi.org/10.1016/j.indcrop.2009.09.001>.

Author statement

Inês F. Mota: Conceptualization, Methodology, Investigation, Writing- Original draft preparation.

João da Silva Bural: Conceptualization, Methodology, Investigation, Writing - Review & Editing.

Filipa Antunes: Conceptualization, Methodology, Investigation, Writing - Review & Editing.

Manuela E. Pintado: Supervision.

Patrícia S. Costa: Conceptualization, Writing - Review & Editing and Supervision.

Journal Pre-proof

Declaration of interests

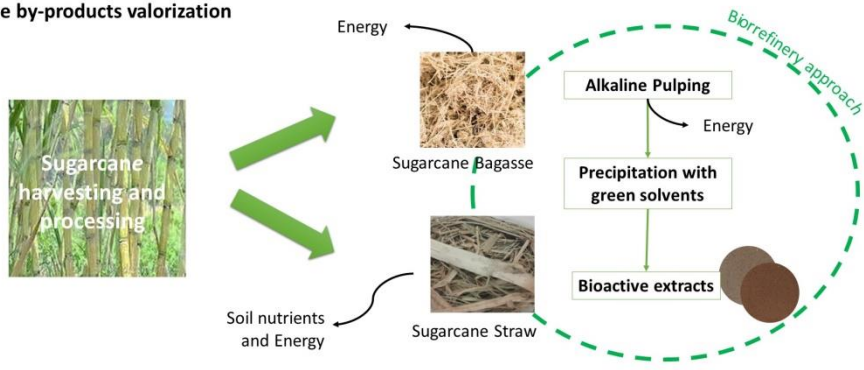
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof

Graphical abstract

Sugarcane by-products valorization



Journal Pre-proof

Highlights

Green processing of sugarcane industry side streams into value-added products

Sugarcane bagasse (SCB) and straw (SCS) were submitted to alkaline pretreatment

Organic acids generated lignin extracts with similar properties to the mineral acids

SCB extracts revealed different physicochemical properties than SCS extracts

Formic acid is a good alternative to sulfuric acid in obtaining antioxidant lignin extracts

Journal Pre-proof