Adding value to lignins isolated from sugarcane bagasse and Miscanthus

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ABSTRACT

Attempt to depolymerize industrial organosolv lignin (from sugarcane bagasse) and lignins extracted from sugarcane bagasse and Miscanthus fibers (isolated by a soda/anthraquinone process) in presence of an anthraquinone acid catalyst (AQCOOH) was described. With the aim to substitute formaldehyde by glutaraldehyde, a dialdehyde that can be obtained from natural sources, lignins were reacted with glutaraldehyde and studied as phenolic-type resins for thermosets. The reactions were predominantly analyzed by SEC and 13C NMR spectrometry. The Organosolv lignin–glutaraldehyde resin was used to prepare a composite reinforced with sugarcane bagasse fibers. Control samples were also prepared; specifically, composites based on phenol-formaldehyde and organosolv lignin–formaldehyde matrices. The results of the impact and the flexural strength tests of these composites showed that the organosolv lignin and glutaraldehyde can successfully replace phenol and formaldehyde, respectively.

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1. Introduction

Lignocellulosic materials are particularly attractive as raw materials for biofuel production because of their relatively low cost, great abundance and sustainable supply (Bozell et al., 2011; Lacerda et al., 2012). They are constituted mostly of cellulose, hemicelluloses, lignin, which are interlaced in the hetero-matrix of the plant cell wall (Fengel and Wegener, 1989). The most profitable biorefineries that integrate low-value fuel for the production of high-value chemicals derived from each of the primary components of LC materials will require a significantly greater emphasis on the yields and purities of the resulting individual biorefinery process streams used for the production of the chemicals (Bozell et al., 2011).

The composition of sugarcane bagasse can vary according to, among other factors, climatic conditions and the soil properties where sugarcane was grown. The fibers used in previous studies, which were harvested from the same region of those grown for this study, showed cellulose, hemicellulose, lignin and ash contents of approximately 55%, 17%, 25% and 1%, respectively (Hoareau et al., 2004). Sugarcane bagasse is currently used as the main source of the energy required by sugar and ethanol mills as well as for generating electricity to be sold. However, a considerable amount of the produced bagasse is currently wasted. With future technological improvements of boilers and processes, it will be possible to supply the same quantity of energy with less bagasse and use the surplus for the biorefinery production of ethanol and other added value chemicals (Rocha et al., 2012). In previous studies, the lignin extracted from bagasse via the organosolv process was used for the preparation of phenolic-type resins. The aim of these studies was to use these resins for the preparation of a phenolic-type matrix in composites reinforced with lignocellulosic fibers, such as sugarcane bagasse (Hoareau et al., 2006), sisal (Paiva and Frollini, 2006; Ramires et al., 2010) and textile fibers (Silva et al., 2011). This lignin was also used to modify the surfaces of lignocellulosic fibers to further use the fibers as reinforcements in composites (Megiatto et al., 2007, 2008). In addition, in a previous study, the sugarcane bagasse organosolv lignin was carboxymethylated and then applied as a stabilizing agent in ceramic suspensions (Cerrutti et al., 2012).

Miscanthus plants display excellent productivities, in that they are fast growing and exhibit low sensitivities to illness (Villaverde et al., 2012). Among this family, Miscanthus giganteus was previously identified as a potential high-yielding bioenergy crop in Europe and the United States and as a source of biomass for the refinery process (Glowacka et al., 2010; Vanderghem et al., 2011, 2012).
Despite the fact that lignin is the main aromatic renewable bioresource, this polymer remains under-utilized. A wide variety of bulk and fine chemicals can be produced in a sustainable way from the aromatic structures of lignins (Vanderghem et al., 2011). High-molecular-weight lignins can be used to produce carbon fibers, polymer modifiers, adhesives and resins (Frollini and Castellan, 2012). Also, lignins possess antioxidant activity due to the presence of phenolic groups and benzylidene hydroxogens (García et al., 2010; Portes et al., 2007). Nevertheless, very few low-molecular-weight chemicals derived from lignins are commercially available despite the numerous studies that have been devoted to depolymerization methods (Torr et al., 2011). This is due to the complex structures of lignins that depend on their origin (e.g. hardwoods, softwoods, and grasses). Lignins extracted from annual plants have, in general, a greater number of active sites that are available to react because they contain a greater proportion of p-hydroxyphenyl-type aromatic rings (H) compared to the lignin extracted from wood (Fengel and Wegener, 1989).

The ortho positions of H units with respect to the phenol hydroxyls are free to attack electrophiles such as aldehydes, therefore favoring the reaction.

This paper describes attempts to valorize lignins extracted from sugarcane bagasse (Bg) and Miscanthus (Ms) fibers under soda/anthraquinone process as well as an industrial organosolv sugarcane bagasse lignin (Og). Trials to depolymerize lignin macromolecules into fragments of lower molecular mass using an anthraquinone catalyst (AQCOOH, Fig. 1), was presented. Anthraquinone was known to cleave β-O-4 inter-unit linkages through an electron transfer mechanism (Dimmel et al., 1987). The lignin materials were mainly characterized by size exclusion chromatography (SEC) and 31P NMR spectrometry. Additionally phenolic resins were prepared from an alkaline reaction (potassium hydroxide) of the lignins Bg, Ms and Og with glutaraldehyde, used as a model of dialdehydes that can be obtained from natural resources. The availability of such resins to be used as part of composites was assessed by the preparation and the study of a composite made with the organosolv lignin–glutaraldehyde resin reinforced by sugarcane bagasse fibers. Control samples were also prepared, specifically composites based on phenol–formaldehyde and organosolv lignin–formaldehyde matrices.

2. Materials and methods

2.1. General

All chemical reagents purchased from Sigma–Aldrich (Saint Quentin Fallavier, France) or Acros Organics (Geel, Belgium) were used without any purification. Sugarcane bagasse was kindly provided by Santa Lúcia (Araras, São Paulo, Brazil). Miscanthus giganteus fibers were from France and were kindly given by La Chambre d’Agriculture de la Gironde (Bordeaux, France). In addition, an industrial acid organosolv lignin, Og, which was extracted from sugarcane bagasse using ethanol/water as the solvent and sulfuric acid as a catalyst (Hilist, 1997, 2007), was kindly provided by Dedini Agro S/A (Piracicaba, São Paulo, Brazil) for use in these experiments.

Aiming to remove extractives such as waxes, terpenes, and fatty acids, the sugarcane bagasse fibers, used afterward to reinforce the composites, were extracted with cyclohexane/ethanol (1:1 (v/v), reflux, 10 h). The fibers were further washed with distilled water (room temperature) and dried in an oven (with air-circulated) at 105 °C until a constant weight was reached. The composition (20.9 ± 0.2 total Klason lignin, 0.75 ± 0.04 ash, 56.5 ± 0.3 α-cellulose, 21.8 ± 0.3 hemicellulose), the moisture (5.5 ± 0.2%), and the crystallinity (47%) of the sugarcane bagasse fibers were determined as described elsewhere (Hoareau et al., 2006; Ramires et al., 2010).

UV–vis spectra of lignin samples were recorded on a Perkin Elmer Lambda 18 spectrometer (Perkin Elmer, Courtaboeuf, France). The lignins were dissolved in a mixture of 9:1 dioxane/water (v/v). Infrared spectra of the lignin fractions were recorded on a Thermo-Nicolet-type Avatar 370 FTIR spectrometer (Thermo Fisher Scientific, Courtaboeuf, France) after mixing with dry KBr (concentration: 1%, w/w) and pressing under vacuum to form transparent pellets.

Nuclear magnetic resonance (NMR) spectra (1H) of acetylated lignins were recorded on a Bruker Avance spectrometer (Bruker SA, Wissembourg, France), operating at 300 MHz. The spectra were calibrated to the solvent peaks (CHCl3 at δ 7.26 ppm). Additionally, 31P NMR was used to quantify the hydroxy groups in the lignins according to Argyropoulos (Argyropoulos, 1994a; Granata and Argyropoulos, 1995). The 31P NMR spectra were recorded on a Bruker DPX-400 spectrometer operating at 162.06 MHz for 31P after derivatization of the lignin samples with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. Instead of using a mixture of CDCl3/pyridine (1:1.6, v/v) as the solvent (Argyropoulos, 1994a; Granata and Argyropoulos, 1995), a higher CDCl3/pyridine ratio of 1.6:1 (v/v) was chosen to precipitate and eliminate by filtration the residual sodium chloride, which was formed after the depolymerization of the lignins. The spectra were calibrated to the signal at 132.2 ppm due to the reaction of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane with residual water and to the signal of chloroform at 144.8 ppm (Wu and Argyropoulos, 2003).

Size exclusion chromatography (SEC) of the lignin samples was performed on acetylated samples that were solubilized in tetrahydrofuran (THF). The analyses were performed at 25 °C on a Thermo-Separation Scientific apparatus (Thermo Fisher Scientific, Courtaboeuf, France) that was equipped with an STP100 pump, an AS 3000 autosampler, a UV SP2000 detector set at 254 nm, and three Tosohas TSK columns (G 2000 HXL, G 3000 HXL, G 4000 HXL). Tetrahydrofuran (THF) was used as the eluent (1 mL min⁻¹), and the molecular masses were calibrated relative to polystyrene standards. An HPLC technique used for sugar analysis of residual hemicelluloses in lignin fractions was performed on the same equipment that was used for SEC; however, the detector was a Waters 410 refractometer, and the separation was performed with a Bio-Rad Aminex HPX87P300 (300 mm × 7.8 mm) column using water as the eluent at a flow rate of 1 mL min⁻¹.

For SEC and 1H NMR analyses, the lignin fractions were quantitatively acetylated according to a procedure described by Megiatto et al. (2009). Briefly, the lignin samples (750 mg) were reacted with 1:1 pyridine/acetic anhydride (v/v, 20 mL) under a nitrogen atmosphere at 60 °C for 18 h. The remaining acetic anhydride was eliminated by reacting the mixture with methanol (50 mL) for 3 h at 80 °C. The methyl acetate was eliminated by evaporation under vacuum, and the remaining pyridine was co-distilled under vacuum with toluene (2 × 10 mL). Finally, the mixture was evaporated to dryness, the residue was dissolved in CH2Cl2 (50 mL) and the minor insoluble impurities were filtered. Acetylated lignin samples were obtained after elimination of the solvent.

2.2. Isolation of lignins

Before pulping, bagasse fibers, cut at ~1.5 cm length, were placed in water for 48 h prior to filtering and drying at room temperature. Miscanthus fibers, cut at ~2 cm length, were used as received. The soda/anthraquinone pulping process was used to extract lignins from the bagasse and Miscanthus fibers. The pulping reaction was performed on the fibers (100 g) in 1 L of sodium hydroxide (1 M) in the presence of commercial anthraquinone (0.1 g) using a closed stainless reactor placed in an oil bath and
stirred with an electric rotative apparatus. The reactor was progressively heated over 1 h from 25 to 172 °C, where it was maintained for 1.5 h. After cooling, the black liquor was removed, and the pulp (fibrous materials) was washed to neutral pH and dried. The black liquor was precipitated following the conditions described by Mousavioun and Doherty (2010). Sulfuric acid was added to the black liquor to reach a pH of 3. After transferring to a water bath (65 °C), the mixture was centrifuged. The lignin was separated and washed with hot water (50 °C) before drying in a vacuum oven at 35 °C. The purity of the lignins was determined by measuring their Klasson lignin content according to the Tappi-T222 om-88 method. The residual sugars in the sugarcane and Miscanthus lignin samples were analyzed by HPLC after depolymerization into simple sugars by sulfuric acid hydrolysis.

2.3. Depolymerization of lignins

The depolymerization reactions were performed in the presence of one catalyst, namely, a monomeric anthraquinone acid, AQCOOH (Fig. 1).

2.3.1. Catalyst AQCOOH

The anthraquione acid, 3-(9,10-dioxo-9,10-dihydroanthracene-2-yl) propanoic acid (AQCOOH), was prepared by permanganate oxidation of 3-(9,10-dioxo-9,10-dihydroanthracene-2-yl) propanal (AQCHO), which was prepared according to Miguel Del Corral et al. (1998). AQCHO (3 g, 11.36 mmol), Na2CO3 (2.3 g, 14.55 mmol) and water (25 mL) were vigorously stirred at 25 °C for 30 min. The reacting mixture was cooled with an ice-cold water bath, and potassium permanganate (2.3 g, 14.55 mmol), dissolved in 30 mL of water, was added dropwise for 2 h. The mixture was stirred at 25 °C for 6 h, and the manganese dioxide that formed during the reaction was then discarded by filtration. The solution was acidified with HCl (10%) to a pH of 1 to precipitate a solid, which was filtered and washed with water (10 mL). The solid, which was dried under vacuum at 30 °C, corresponded to AQCOOH (1.5 g, yield 50%). It yielded one spot in TLC (Rf 0.4; silica gel plate, eluent was ethyl acetate containing 0.5% acetic acid (v/v)). FTIR (KBr 1%, μ (cm−1)): 3500–2000; 3447; 2907; 2623; 1700; 1673; 1589; 1406; 1384; 1234; 1291; 1176; 972; 930; 858 and 708. 1H NMR (DMSO d6, δ (ppm)): 8.21–7.72 (m, 7H, ArH); 3.05 (t, 2H, H2); 2.45 (t, 2H, H3); 13C NMR (DMSO d6, δ (ppm)): 182.0; 182.0 (C=O, C9 and C10); 173.4 (COOH); 148.3 (quaternary, C1); 134.5; 134.4; 134.3 (CH, C1, C6, C7); 132.86; 132.83; 132.80; 131.1 (quaternary, C11, C12, C13, C14); 126.9; 126.6; 126.5; 126.2 (CH, C1, C4, C5, C9); 34.2 (CH2, H16) and 30.2 (CH2, H15). The assignments were based on COSY, DEPT135 and HMBC experiments. Compound AQCOOH was previously prepared as an intermediate in the synthesis of antisense oligonucleotides by De Mesmaeker et al. (1997), but no characterization of the compound was provided.

2.3.2. Attempt to depolymerize lignins

The lignin depolymerization reactions were performed under nitrogen and magnetic stirring on lignin fraction (1 g), anthraquinone acid AQCOOH (30 mg), glucose (100 mg), sodium hydroxide (400 mg) in water (20 mL). The reacting mixture was refluxed for 4 h, and the solvent was then evaporated to dryness. The residual solid was washed with water to remove as much of the inorganic salts and sugars as possible. The solid was dried under vacuum over phosphorous pentoxide. Similar experiments were conducted without the anthraquinone derivative to assess
the catalytic effect. A fraction of the depolymerized lignin was acetylated for SEC analyses (see Section 2.1).

2.4. Syntheses of phenolic-type resins

Lignophenolic resins were prepared by reacting the lignins [2 g (Bg, Mc, Og)], potassium hydroxide (0.6 g, 10.5 mmol), glutaraldehyde (2 g, 19.6 mmol) and water (5 mL). The solutions were stirred for 4 h at 80 °C, and the mixtures were acidified to pH 6 with HCl (10%). Toluene was added to the mixtures, which were stirred for 2 h to allow the resins to precipitate. The solids were filtered, and residual water was eliminated by co-distillation with toluene (5 mL) under vacuum at 40 °C. The resins were characterized by $^{31}$P NMR spectrometry (see Section 2.1).

Og-glutaraldehyde resin was used to prepare composites (next item), and for comparison purposes, Og-formaldehyde and phenol–formaldehyde resins were also prepared.

2.5. Composites

2.5.1. Composites preparation

Resorcinol (a cure accelerator) was added (1:10, w/w,) to the resin (Og-glutaraldehyde, Og-formaldehyde or phenol–formaldehyde), and the mixture was stirred (25 min, 50 °C). The resin–resorcinol mixture was added through a metallic duct (50 °C), drop by drop, to the sugarcane bagasse fibers (30 wt%, average length: 15 mm) prior being placed into a rotating drum (JV mixer, Pardinho, SP, Brazil). The fibers impregnated with the resin/resorcinol mixture were placed in a metallic mold (300 mm × 140 mm × 5 mm), and the composites (randomly distributed fibers) were prepared using following the cure cycles: (a) 50 °C/100 min; (b) 38.1 kgf cm$^{-2}$, 65 °C/60 min, 80 °C/60 min, 95 °C/30 min, 105 °C/30 min, 115 °C/60 min, 125 °C/120 min, 150 °C/60 min.

2.5.2. Composite characterization

The Izod impact test (unnotched samples) was performed following ASTM D256 using a CEAST Resil 25 system (Brazil). Twenty test-pieces (63.5 mm × 12.7 mm × 4.0 mm) were cut and shaped from each plate of thermoset and composite. Scanning electron microscopy (SEM) analysis of the post-impact fractured surfaces was performed using a Zeiss–Leica apparatus model 440 (Brazil) using the same conditions described by Silva et al. (2011). Flexural tests were conducted according to ASTM-D790 using a INSTRON machine (model 5569) (Brazil).

3. Results and discussion

3.1. Isolation and characterization of the lignin fractions

The isolation of lignin from sugarcane bagasse (Bg) and Miscanthus (Mc) fibers was accomplished using the soda/anthraquinone pulping reaction, which is very well suited for non-woody plants (Labidi et al., 2008). The Klasson lignin content of sugarcane bagasse and Miscanthus fibers were 25.3% and 27.7%, respectively. From 100 g of the bagasse and Miscanthus fibers, 11 g and 14 g of lignin fractions were isolated, respectively. These fractions were not pure (Table 1); they contained both lignin (approximately 70%) and carbohydrates (approximately 30%). The carbohydrates were analyzed after acid hydrolysis (H$_2$SO$_4$, 72%), indicating the presence of xylose (Bg: 23%; Mc: 17%, based on mass of lignin fractions) and glucose (Bg: 5.5%; Mc: 13.5%) (Fengel and Wegener, 1989). From the Klasson lignin amounts that were measured for the sugarcane bagasse and Miscanthus fibers, the lignin isolation yields corresponded to 31% and 34%, respectively. In Table 1, we report the lignin contents, extinction coefficients, SEC molecular weights and SEC polydispersities of the isolated lignin fractions from Bg, Mc and Og (an industrial acid organosolv lignin from sugarcane bagasse).

The alkaline lignins Bg and Mc exhibited very similar UV–vis absorption spectra, whereas the organosolv lignin displayed a significant absorption at 300 nm, which is very characteristic of carbonyl structures that are formed in acidic conditions (Fengel and Wegener, 1989). The molar extinction coefficients of the pure lignins at 280 nm (corrected for their Klasos contents) reported in Table 1 provided an easy way to estimate the lignin contents of the fractions.

The FTIR spectra (not shown) of the acetylated lignins showed weak bands at 3400 cm$^{-1}$, which might be partially assigned to non-acetylated hydroxyl groups on the C6 carbons of lignin units, which are the hydroxyl groups the most resistant to esterification (Paulsson et al., 1996). Bands between 2840 and 3100 cm$^{-1}$ were assigned to aliphatic and aromatic C–H stretching, and absorption corresponding to aromatic groups appeared at 1600, 1515 and 1470 cm$^{-1}$. Bands of condensed syringyl and guaiacyl units were found at 1330 cm$^{-1}$. The band at 825 cm$^{-1}$ corresponded to p-hydroxyphenyl units. Moreover, the bands at 1272 and 910 cm$^{-1}$ were typical of HGS lignin types (Fengel and Wegener, 1989).

The lignin fractions Og, Bg and Mc were analyzed by $^{1}H$ NMR (spectra not shown) after acetylation. The results were similar for all of the lignins, and the observed signals were assigned as follows: 3.7 ppm, methoxy group; 6.2–7.6 ppm, aromatic protons; 2.1–2.5 ppm, aromatic acetates; 1.7–2.1 ppm, aliphatic acetates.

The $^{31}$P NMR spectra of lignins Og, Bg and Mc (Fig. 2) obtained after their derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Argyropoulos, 1995) allowed an estimation of the different hydroxyl groups found in the lignin samples (Fig. 3).

Previous results on the organosolv lignin (Og) indicated similar values: OH aliphatic: 0.75 mmol g$^{-1}$; 5–OH: 0.58; G–OH: 0.47; H–OH: 0.53; condensed phenol OH: 0.27 and carboxylic acids: 0.17 (Ramires et al., 2010). The differences were likely due to the natural variations encountered in different samples of this industrial lignin. The total phenolic contents, equal to 1.8, 6.6, and 7.1 mmol g$^{-1}$ of lignin for Og, Bg, and Mc, respectively, indicated a more significant phenolic content in the alkaline lignins than in the acidic Og. Nevertheless all lignin fractions were very suitable for phenolic substitutions in applications such as phenolic resins.

SEC analyses of the lignin fractions indicated that the alkaline lignins Bg and Mc had lower $M_w$ values (1220 and 1210 g mol$^{-1}$, respectively) than the acidic organosolv lignin Og (4020 g mol$^{-1}$). Thus, the alkaline process resulted in fractions containing lower molecular weights than the acidic process (Table 1).

3.2. Attempt to depolymerize the lignin fractions in alkaline medium in the presence of AOOCOH

Anthraquinone derivatives are known to be efficient catalysts of delignification. Their mechanism of action involves the single electron transfer between anthrahydroquinone (a reduced form of anthraquinone) and quinone methide, which is formed from phenolic β-O-4 lignin units (Fig. 4) (Dimmel et al., 1987). The β-O-4 bond cleavage by anthraquinone derivatives in alkaline aqueous

| Table 1 Lignin contents, extinction coefficients ($\varepsilon$, L g$^{-1}$ cm$^{-1}$) at 280 nm for lignin, molecular weights and polydispersities of lignin fractions Og, Bg and Mc. |
|-----------------|-----------------|-----------------|-----------------|
| Lignin fractions | Lignin content (%) | $\varepsilon$ (L g$^{-1}$ cm$^{-1}$) | $M_w$ | $M_n$/$M_w$ |
| Bg               | 70.3             | 33.9            | 1220           | 9.1            |
| Mc               | 69.9             | 28.5            | 1210           | 6.5            |
| Og               | 95.0             | 30.6            | 4020           | 12.4           |
solution was applied to depolymerize the lignin fractions Og, Bg, and Mc. The catalyst AQCOOH was chosen for its higher solubility in aqueous solutions compared to anthraquinone. Although some carbohydrates were present in the lignin fractions, glucose was added to the reaction mixture to increase reduction efficiency of the anthraquinone derivatives (Dimmel et al., 1987).

Fig. 5 shows the $M_w$ values given by SEC analysis of the lignins before and after depolymerization in the presence and absence of AQCOOH.

For Og and Bg, the depolymerization reaction occurred even without catalyst, but the presence of the catalyst increased the rate of the depolymerization process. In the absence of catalyst, the $M_w$ values changed from 4020 to 3050 g mol$^{-1}$ and from 1220 to 1000 g mol$^{-1}$ for Og and Bg, respectively. In the presence of AQCOOH, an additional depolymerization was obtained with $M_w$ values equal to 2860 and 900 g mol$^{-1}$ for Og and Bg, respectively. The depolymerization of lignosulfonates in alkaline medium has already been observed by El Mansouri et al. (2006). In contrast, for the lignin fraction Mc, the reaction without a catalyst led to an increase in the $M_w$ from 1210 to 1500 g mol$^{-1}$, whereas slight depolymerization was observed ($M_w$ = 1090 g mol$^{-1}$) with the AQCOOH catalyst. This peculiar behavior is likely due to different phenolic structural units that are able to partially condense via methylene quinone intermediates. These intermediates are reduced in presence of the anthrahydroquinone catalyst, leading to the depolymerization of the radical anion intermediate (Fig. 4).

Analysis of the lignin fractions by $^{31}$P NMR following the reactions in the presence of the catalyst AQCOOH indicated a significant increase in carboxylic acid functional groups, from 0.15 to 1.10 mmol g$^{-1}$, 0.75 to 1.30 and 0.08 to 0.32 mmol g$^{-1}$ for Og, Bg and Mc, respectively. Moreover, a decrease in the total phenolic content was observed, resulting in phenolic contents of 35%, 41% and 73% for Og, Bg and Mc, respectively. These observations were likely due to the oxidation of the phenols by the unreacted anthraquinone catalyst because it was also observed in a lignin polymer model (Megiatto et al., 2009). The behavior of the carbohydrate part of the lignin fractions was not studied because its evolution is masked by the addition of the glucose used to reduce AQCOOH to anthrahydroquinone COOH; nevertheless, it is likely that the carbohydrate and the added glucose are oxidized and contribute to the increase in the carboxylic acid content. Based on the low aliphatic content determined by $^{31}$P NMR, it is likely that a major portion of the polysaccharides was degraded during the depolymerization and was eliminated with the final wash.

3.3. Resins and composites

The resins were prepared according to a classical procedure for lignophenolic resins (Hoareau et al., 2006) using the lignin materials (Og, Bg and Mc), potassium hydroxide and glutaraldehyde, which was used as a model of dialdehydes that can be obtained by the oxidation of compounds from biomass.

The quantification of the hydroxyl groups in the resins made from Og, Bg and Mc lignins by $^{31}$P NMR of resins is shown in Fig. 6.

The spectra of the resins (not shown), when compared to those of the starting lignin materials, displayed new peaks in the aliphatic hydroxyls area in accordance with the mechanism of aldehyde reactions with phenols in alkaline media. For all resins, a sharp decrease in the phenol content was observed (Figs. 3 and 6), which might be due to the existence of the equilibrium between phenolic groups and ketones (i.e. keto–enol equilibrium) after the reaction, thereby limiting the quantification of the total true phenolic content.

Og is currently available in greater quantities than Mc and Bg; hence, it was selected to prepare the composites. The preparation and characterization of the composites aimed to assess the suitability of the use of glutaraldehyde, which can be obtained from natural resources, instead of formaldehyde in the preparation of phenolic-type matrices. Sugarcane bagasse was chosen as the reinforcement, which led to a composite with a high content of raw material...
**Fig. 4.** Mechanism of anthraquinone action on phenolic β-O-4 guaiacyl lignin units (Dimmel et al., 1987).

**Fig. 5.** Average molecular masses ($M_w$) given by SEC analysis of lignin fraction Og, Bg and Mc before and after the depolymerization reaction in the presence or absence of the AQCOOH catalyst (solution: water, NaOH and glucose).

**Fig. 6.** Quantification of hydroxyl groups by $^{31}$P NMR (mmol g$^{-1}$) in the resins from Og, Bg and Mc that were prepared with glutaraldehyde.
coming from this source because the Og, used as the phenolic-type reagent in the preparation of the matrix, was also obtained from the sugarcane bagasse. To assess the effects of substituting formaldehyde with glutaraldehyde and the effect of substituting phenol with Og, composites based on Og-formaldehyde and phenol-formaldehyde resins were prepared. Fig. 7 shows the results of the impact and flexural tests.

With respect to the impact strength, the substitution of phenol with Og in the preparation of phenolic-type resins was advantageous because the composite prepared from the Og-formaldehyde resin (COgLigF) exhibited a higher impact strength than the composite prepared from the phenol-formaldehyde resin (CPhF) (Fig. 7a). When in addition to replacing phenol with Og, formaldehyde was replaced with glutaraldehyde, the resulting resin
(Og–glutaraldehyde) generated a composite (CoGligG) with an impact strength that was even higher (Fig. 7a).

Fig. 8 shows that all of the composites exhibited good adhesion at the fiber–matrix interface. The presence of aromatic rings and polar hydroxyl groups in both the fiber and the matrix favors intermolecular interactions at the interface, leading to good adhesion. However, when the Og–formaldehyde resin was used to impregnate the fibers, the fibers appeared to be better covered by the matrix in the composite (Fig. 8b), and when the fibers were impregnated with the Og–glutaraldehyde resin (Fig. 8c), the inner ducts of the fibers were also filled with the matrix. Thus, the load was better transferred from the matrix to the fiber through the interfaces of CoGligF and CoGligG than through those of CPHF. The fibers filled with the matrix formed composites with higher impact strength (CoGligG, Fig. 7a).

The composites exhibited approximately the same flexural strength at the break point, with a trend toward higher resistance for CoGligF (Fig. 7b). However, the composites prepared from resins obtained from Og exhibited higher resistance to deformation, as indicated by the flexural moduli of CoGligF and CoGligG relative to that of CPHF (Fig. 7c).

4. Conclusions

Attempt to depolymerize an industrial organosolv lignin (Og) (from sugarcane bagasse) and two lignins materials extracted from sugarcane bagasse (Bg) and Miscanthus (Mc) fibers (isolated by a soda/anthraquione process) in presence of an anthraquinone acid catalyst (AQCOOH) was described. The reactions were predominantly analyzed by SEC and 31P NMR spectrometry. The anthraquinone acid catalyst slightly improved the fragmentation of the lignin polymers, likely due to the single electron transfer mechanism. With the aim to substitute formaldehyde by glutaraldehyde, a dialdehyde that can be obtained from natural sources, lignin Og, Bg and Mc were reacted with glutaraldehyde and studied as phenolic-type resins for thermosets. More specifically, Og was used in the preparation of resins (Og–formaldehyde and Og–glutaraldehyde), which, in turn, were used as matrices in composites reinforced with sugarcane bagasse fibers. The results of the impact and flexural strength tests showed that for the production of composites reinforced with sugarcane bagasse fibers, as investigated in the present study, it is advantageous to substitute phenol and formaldehyde with organosolv lignin Og and glutaraldehyde, respectively, in the formulation of the resins, given that the properties of the Og–glutaraldehyde composites were superior or similar to those of the composite based on phenol–formaldehyde resin.

The use of phenolic materials originating from renewable resource for various industrial applications, such as the preparation of phenolic-type resins, could contribute to an increase in the profitability of biorefineries where lignins are generated as byproducts.

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