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Performance of Side-Streams from Eucalyptus Processing as Sources of Polysaccharides and Lignins by Kraft Delignification

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Supporting Information

ABSTRACT: The performance of bark, branches, sawdust, forest biomass, and short-rotation eucalyptus in kraft delignification to produce polysaccharides and lignin is reported and discussed. A positive correlation was found between pulping severity required for delignification and lignin reactivity. Among all, branches feedstock is the best source of polysaccharides due to the high pulp yield (48−54%) with a satisfactory delignification degree. Branches lignin was characterized for the first time, evaluating syringyl/guaiacyl/*p*-hydoxyphenyl (65:22:13), β-O-4 units (71/100C$_6$) and condensed structures (12%). Kraft lignins (KL) were isolated from black liquors, including industrial one, and analyzed by NMR demonstrating remarkable differences. Among all, bark KL reveals the highest depolymerization (lowest β-*O*-4 content, 18/100 C$_6$) and condensation (50%) as a consequence of higher active alkali required for pulping. Sawdust and branches KLs have similar degree of condensation, but the former revealed slightly less β-*O*-4 (25/100 C$_6$) and more hydroxyl phenolic groups (6.6 mmol/g) than branches KL (28/100C$_6$, 5.9 mmol/g).

1. INTRODUCTION

Eucalyptus globulus is the dominant hardwood species in Southern Europe and South America for pulp production, mainly by kraft pulping. Pulp mills are well established as multiproduct platforms producing pulp for materials (paper, viscose, cellulose acetate), steam, power, and recovering inorganic chemicals. Depending on the wood species and process, other low/medium volume products with commercial importance have been also generated, such as tall-oil, turpentine, ethanol, specialty lignins, and vanillin, among others.[1,2] These already established valorization paths and also the current research and demonstration plants on other bioproducts and bioenergy have made the pulp and paper industry a privileged platform to set up the biorefinery concept.[1−7]

The harvesting of *Eucalyptus globulus* generates several lignocellulosic residues in the plantation, such as foliage, tree tops, branches, stumps, roots, and even some bark released during logging processing. In Portugal, the logistic chain of pulp and paper companies assures the transport of these forest residues to the mill site for power generation in their own biomass boiler. For a company producing 500 000 tons of pulp per year, about 220 000 tons of branches and 135 000 tons of forest biomass (foliage, small branches and tree tops, stumps, roots, some bark) are produced. Boles are usually debarked at the mill site before wood chip production, generating an additional power source based on the 120 000 tons of bark produced. Furthermore, the sawdust resulting from the woodchip production (15 000 tons, < 1 mm particle size) is also exploited for the same purpose. This weight distribution demonstrates that about 1/3 of the *E. globulus* plantation biomass (Figure S1 (Supporting Information)), representing 500 000 tons of lignocellulosic material per year, are currently available at the mill site to be integrated in a valorization chain, as an alternative to burning.

Considering an average composition of 50% of cellulose and 25% of lignin, about 250 tons of cellulose and 125 000 tons of lignin could be produced from these side streams. Miranda and co-workers[8] have studied the incorporation of bark and tree tops in *E. globulus* wood kraft pulping, concluding that it is possible to use them at levels below or similar to the whole-stem without compromising conventional pulp properties. Other studies concerning chemical composition[9] and detailed structural analysis of wood components, such as lignin[10] have pointed out the main differences between the commercial bole wood and some peripheral parts of the tree, such as bark. However, neither of these *E. globulus* morphological parts have been exploited or even studied as a source, *per se*, of polysaccharides (pulp) and lignin on a biorefining perspective. Therefore, the current effort is to evaluate the performance of these materials in the conventional kraft pulping aiming to generate a source of sugars and lignin. This is one of the objectives of this work.

The current concept of biorefineries is still based on feedstock logistic, pretreatment, or delignification processes, and hydrolysis of polysaccharides followed (or integrated) by sugar fermentation. Most of lignin produced is burned due to its high calorific value, supporting the energetic integration of some processes. However, it is widely recognized that lignin could be turned into products of high value and, as such, to be a competitive advantage for the biorefineries economic and environmental sustainability.[11−13] Because of its aromatic

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structure and functional groups,[14,15] lignin is a renewable source of several commodities such as adhesives, dispersants, emulsifiers, concrete additives, foams, resins, and thermoplastics, and also low molecular weight phenolic compounds.[1,11,12,15,16] However, this is still restricted to a low fraction of the lignin produced around the world, being a challenging task for the next years due to the lignin availability increase as a consequence of lignocellulosic biorefineries activity. The main constraints and challenges have been quite well highlighted in the literature.[11] In accordance, the first step for lignin upgrading is acquiring the knowledge about the characteristics of lignin generated in the biorefining processes. In a last instance, its characteristics could be tailored by raw-material, processing technologies, or conditions for delignification,[11,17] as had been done for the polysaccharide fraction for many years. In this work, besides the evaluation of pulping performance of bark, branches, forest biomass (material collected in the plantation, composed by foliage, small branches and tree tops, stumps, roots, some bark), sawdust (generated during woodchip production), and eucalyptus energetic crops, the aim is to assess the main characteristics of the generated kraft lignins for their evaluation as a side stream from kraft pulping of *Eucalyptus* biomass. Therefore, this paper has two main parts: one for the evaluation of pulping performance of the *eucalyptus* biomass components and it includes the results of kraft pulping and the characterization of the native lignins; the second part is devoted to the evaluation of black liquor and kraft lignins presenting the composition of the generated black liquors and respective isolated kraft lignins, as well as characterization by ^{13}C and ^{31}P NMR.

2. MATERIALS AND METHODS

2.1. *Eucalyptus globulus* Components. Bark, forest biomass, branches, and sawdust are coproducts of *E. globulus* that are generated in wood preparation for pulp production. Branches and forest biomass were collected directly at *E. globulus* short-rotation plantations (10−12 years long) in Portugal. Bark and sawdust were collected at the mill site in the wood debarking and wood chipping section, respectively. *E. globulus* wood from an energetic plantation (shorter rotations cycles, 4 to 6 years, than in plantations for pulp and paper industry) in the North of Portugal was considered for comparison purposes. The average productivity of eucalyptus energetic crops is in the range 5−15 ton/ha/year, depending of the edaphoclimatic conditions.

All the eucalyptus-derived materials were air-dried until constant moisture content and milled for characterization. For pulping experiments, branches and eucalyptus energetic crops (hereby referred as energetic eucalyptus) were processed to obtain laboratorial woodchips, while bark and forest biomass were roughly cut for loading the laboratory pulping reactors. Extractives, 1% sodium hydroxide (NaOH) solubility, ashes and lignin content were quantified according to TAPPI Standards: TAPPI T 204, 413, 222, 212, respectively. Carbohydrates were quantified after acid hydrolysis by anion-exchange chromatography using a Dionex DX 500 series chromatograph equipped with pulse amperometric detector (Dionex ED 50) and a CarboPac PA-1 column (guard column 4 mm × 50 mm and analytical column 4 mm × 250 mm). The eluent was 2 mM NaOH solution at a flow rate of 1 mL/min and room temperature. The composition is summarized in Table S1 (Supporting Information).

2.2. Kraft Pulping. Kraft pulping comprises delignification of the material at high temperature (160−180 °C) by pulping (white) liquor containing sodium sulfide (Na_2S) and NaOH. Depending on pulping conditions and lignocellulosic material, about 90−95% of the initial lignin is removed. Residual lignin and other chromophore/oxidizable compounds in the final pulp are usually measured by Kappa number (KN), which is correlated with lignin content as follows: lignin (%) = KN× 0.13.

Kraft pulping experiments were performed in MK System reactors (model 409 MII), with liquid recirculation and temperature control with a capacity for 1 kg of dried material and 4 L of pulping liquor, using the conditions depicted in Table 1, reporting active alkali (AA) and *H* factor. *H* factor, hereby referred as *H*, is the combination of temperature and time in the same variable.[19] The ratio of white liquor/wood chips (hydromodule, HM) is usually 4; however, for some materials, because of their lower density, a higher HM is required to ensure the liquid recirculation. This was the case of bark (HM 8), sawdust, and forest biomass (HM 6). Industrial pulping conditions for *Eucalyptus globulus* wood chips are *H* factor of 478 (160 °C, 180 min), HM of 3−4, and 20% AA. The lignin isolated from industrial black liquor was used as reference in this work.

Table 1. Conditions of Kraft Pulping Experiments for Each Material

raw material	HM	pulping time, min	max temp, °C	*H*	AA, % (as Na_2O)
bark	8	180	160	478	16, 18, 21, 24
			170	1101	20, 22, 24, 26, 27, 28
		210	170	1568	16, 18, 21, 24
extracted bark	8	180	170	1101	24, 26
forest biomass	6	180	160	478	16, 18, 20, 22
			170	1101	
		210	160	680	
branches	4	180	160	478	16, 18, 20, 22
			170	1101	
		210	160	680	
sawdust	6	180	160	478	16, 18, 20, 22
			170	1101	
		210	160	680	
			170	1568	
energetic eucalyptus	4	180	160	478	16, 18, 20, 22
			170	1101	
		210	160	680	

The bark of *E. globulus* was extracted in the same MK system reactors as described for pulping using ethanol/water (HM 8) according to the selected conditions to maximize the extraction of phenolic compounds (52/48% v/v ethanol/water, 264 min, 82.5 °C[20]). The material was then cooked in the same conditions as the untreated bark (intermediate conditions were chosen—Table 1) aiming to test the effect of the partial removal of these extractives on the pulping performance of the material.

Resulting pulps were washed and the uncooked material was removed before pulp weighing. All pulps produced were defiberized in a disc refiner, thoroughly washed with distilled water, centrifuged, and weighed. The partially delignified material was separated in the disc refiner step and quantified separately as rejects. After moisture quantification, resulting

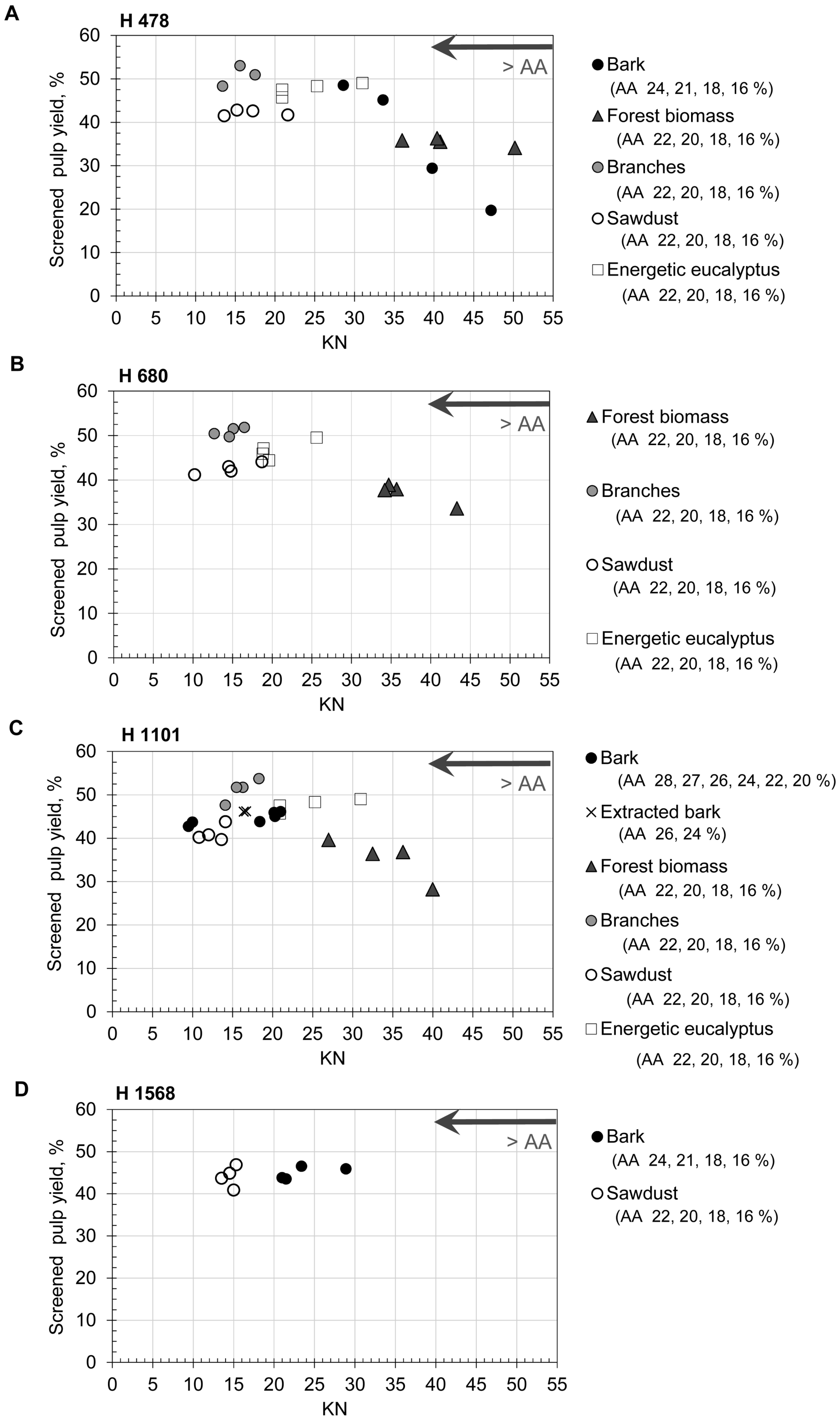

Figure 1. Screened pulp yield and KN of kraft pulps of bark, extracted bark, branches, forest biomass, sawdust and energetic eucalyptus grouped for the same pulping H: (A) *H* = 478 (160 °C, 180 min); (B) 680 (160 °C, 210 min); (C) 1101 (170 °C, 180 min), (D) 1568 (170 °C, 210 min). For each material and each *H*, the decreasing order of KN follows the increasing order of AA % of the pulping.

pulp weight was reported as screened pulp yield (oven-dried, o.d.). KN was determined according to TAPPI Standard T 236. This method measures the $KMnO_4$ (oxidant) demand of the pulp due to residual lignin, and also to other structures, such as hexenuronic acids and extractives.[18] Black liquors (BL) (also designated as kraft liquors, the liquid streams resulting from pulping) were collected directly after each essay with simultaneous cooling down to room temperature. Liquors were then degassed with nitrogen, and stored at 4 °C until the next step to avoid any further modification of the dissolved lignin. BL and respective lignins were analyzed and characterized as described in the next section.

2.3. BL Composition Analysis, Lignins Isolation, and Characterization. BL were analyzed for nonvolatile solids, inorganics, and carbohydrate content using the methods described elsewhere.[18,21] For nonvolatile solids, briefly, 10.0 mL of BL was added to previously dried crucibles containing calcinated sand. The crucibles with BL were dried at 105 °C until constant weight. Then, crucibles were submitted to incineration at 650 °C for 8 h for ash quantification. For carbohydrate content, the freeze-dried black liquors, and isolated lignins were submitted to acid methanolysis,[20] briefly: 10−15 mg of sample was suspended in 2 mL of 2 M HCl methanolic solution, at 100 °C, for 4 h. Then, 100 μL of pyridine and 1.00 mL of sorbitol solution 0.1 mg/mL were added to the mixture. The dried mixture was then dissolved in 150 μL of pyridine, and the partially methylated monosaccharides were converted to trimethylsilylated derivatives. The products were identified by GC−MS and quantified by GC−FID (oven temperature program: 100−175 °C at 4 °C/min and 175−290 °C at 12 °C/min). Quantification was carried out with calibration curves built with standards for each monosaccharide. Lignins from BL (the one corresponding to the selected condition for each lignocellulosic material) were isolated by precipitation with 2 M H_2SO_4:[18] around 350 mL of BL was kept below 10 °C, under continuous stirring. The acid was gradually added to the BL until pH 3. The suspension was centrifuged (15 min, 3000 rpm). The supernatant was rejected, and the solid obtained was washed with distilled water for three times, rejecting the washing solution. The isolated material from each BL, hereinafter designated as kraft lignin (KL), was freeze-dried and stored in sealed containers.

Lignin from *E. globulus* branches was isolated by acidolysis using a solution of dioxane/water (9:1, v/v) containing 2 M HCl under reflux in mild conditions.[10,22] The solution (containing dissolved lignin) was concentrated through reduced pressure and the lignin was recovered by adding the dioxane solution to cold water under vigorous stirring. Lignin was finally separated by centrifugation, washed with water, and freeze-dried.

Native lignins, BLs and KLs were characterized by nitrobenzene oxidation (NO).[18] KL resulting from bark, branches and sawdust pulping and acidolysis lignin from branches were analyzed by ^{13}C NMR and ^{31}P NMR:[10] ^{13}C NMR spectra were recorded in a sample of 170 mg of dried lignin dissolved in 0.5 mL of deuterated dimethyl sulfoxide using a Bruker AVANCE III 400 spectrometer operating at 400 MHz, temperature of 45 °C, acquisition time of 72 h. For ^{31}P NMR spectra, samples were previously phosphitylated: dried lignin (40 mg) was dissolved in 400 μL of pyridine and deuterated chloroform (1.6:1,v/v); then cholesterol (200 μL, 19 mg/mL, internal standard) and chromium(III) acetylacetonate (50 μL, 11.4 mg/mL, relaxation agent) were added. After 2 h, the phosphitylating reagent (100 μL, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) was added and the mixture was then analyzed using the same equipment as described for ^{13}C NMR. ^{31}P NMR spectra were acquired at 25 °C for 30 min with 10 s relaxation time, 45° pulse angle, and 4 s pulse delay. For comparative purposes, lignin isolated from industrial BL of *E. globulus* was also analyzed.

3. RESULTS AND DISCUSSION

3.1. Evaluation of Pulping Performance of the Eucalyptus Biomass Components. KN and screened pulp yield (after removal of uncooked material, referred as rejects) were the two parameters considered for comparison of the response of the materials to the kraft pulping conditions. It is important to note that as rejects increase, screened pulp yield decreases. Figure 1 presents the results for each material indicating the AA applied and grouped by *H*. For each *H* and material, the AA charges applied were 16%, 18%, 20%, and 22%, except for bark and extracted bark. For these materials, the percentage of rejects in the final pulp was very high for this range of AA. Therefore, for bark and for extracted bark, the range of AA was extended to 28% and to 26%, respectively. For each material and each *H*, the decrease of KN follows the increasing order of AA applied as indicated in the legend of Figure 1.

3.1.1. Bark and Forest Biomass. Bark of *E. globulus* used in this study presents a high content in lignin and low content of glucose (Table S1 (Supporting Information), when compared to some reference values from literature.[8,23] However, with reference to the other materials in this work, the total content of lignin is equivalent. Glucose and xylose content of bark and forest biomass are lower than for the other materials, indicating a probably lower pulp yield. These two materials have the higher content of material soluble in NaOH solution. In particular, bark contains nearly twice the solubility found for energetic eucalyptus of this work, and also for *E. globulus* wood.[8] This factor and the remarkable high content of inorganic material could be pointed out as the main drawbacks of bark on the perspective of kraft pulping. Polar extractives are alkali consuming components and, as such, pulping experiments with bark were performed with a wide range of AA for evaluation of the effect of this parameter. Forest biomass composition (high level of extractives in ethanol/toluene and NaOH 1% and low carbohydrate content) also suggest a probable low performance toward kraft pulping.

Figure 1A (results for the lowest *H*) demonstrates that for a similar range of AA, bark and forest biomass pulps present a KN higher than 25 (being near 50 for AA 16%) indicating an incomplete delignification. However, for the same *H*, the increase of AA to 21% and 24% benefices the pulp yield of bark (reaching to 45−50%) due to a better delignification, which is confirmed by the lower rejects percentage (2−5%). In the case of forest biomass, a pronounced improvement of delignification was achieved with the increase of AA, but screened pulp yield was kept at a constant and low level (about 35%) for the lowest *H* (Figure 1A). Probably, this is due to a high rate of material solubilization in pulping liquor. Interesting to note is that KN did not decrease with *H* (Figure 1A to 1C), except for AA 22% at H 1101, noticing a decrease of 7 KN units (relative to H 680 for the same AA). In that most favorable condition for forest biomass pulping, pulp has a KN of 27 and low rejects (1%); nevertheless, pulp yield is still low (40%). These observations led to the conclusion that some fractions of the forest material become overcooked (loosing material by this way) while other fractions keep some resistance to delignification, maintaining a high KN (27). The low homogeneity of the material could be the main reason for this. Low average cellulose content and/or a quite soluble fraction of polysaccharides are probably also contributing to unfavorable performance of forest biomass as source of carbohydrates when compared with the other

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materials. Considering the low yield vs delignification of forest biomass, no further attempts were made to improve delignification.

In the case of bark, the response to kraft pulping was improved with the increase of *H* (compare Figure 1A with 1C for AA 20−24%); for $H = 478$, the screened pulp yield is 46.8 ± 2.4%, while for $H = 1101$ the value is 45.7 ± 0.6%. Figure 1C and 1D demonstrated that yields of about 45% could be achieved with KN 20−24 (AA 18−24%) and negligible rejects percentage. An increase of AA to 27 and 28% at H 1101 (Figure 1C) has led KN to change from 20 to 10 with a low decrease on pulp. Probably, for polysaccharide hydrolysis purposes, it is not necessary to achieve such quite low KN; however, these experiments demonstrate the interesting aptitude of bark for kraft pulping denoting some selectivity demonstrated by the preservation of carbohydrates with the increase of delignification. Therefore, in spite of the higher AA consumption (probably due to the extractives) and the higher HM required for bark (Table 1 for experimental conditions), the results demonstrate that this could be an interesting source of carbohydrates, with yields closer to, for example, sawdust (disclosed in section 3.1.2). The selected conditions were $H = 1101$ and AA = 26% for a pulp yield of 43.9% and KN of 18.4 as indicated in Table 2.

Table 2. Selected Conditions, KN, and Screened Pulp Yield for Eucalyptus-Derived Materials

	pulping conditions			results	
material	HM	*H*	AA, %	KN	pulp yield, %[a]
bark	8	1101	26	18.4	43.9
forest biomass	8	1101	22	27.0	40.0
branches	4	680	22	12.7	50.4
sawdust	6	680	22	12.8	41.8
energetic eucalyptus	4	1101	20	16.8	44.9

[a] Screened, oven-dried yield.

In an attempt to improve the pulping performance of *E. globulus* bark, a previous extraction of bark with ethanol/water was performed in conditions stated in the literature as those promoting the maximum extraction of total phenolic compounds (extraction yield 1.5%).[20] The aim of this stage was also to evaluate a possible sequence of processes for bark valorization, starting with the extraction of polyphenols with antioxidant and biological activity[20] and the subsequent kraft pulping, taking advantage, at the same time, of the lower content of polar extractives in the material before pulping. Comparative pulping essays of extracted bark were performed for $H = 1101$ and AA = 24% and 26% (Figure 1C). The KN decreased from 20/18 (bark) to 16 (extracted bark) with no noteworthy change of pulp yield (44/45 to 46%). These preliminary results give some support to the suggestion that these extractives hinder the delignification by consuming the alkali necessary for lignin reactions. As such, it should stimulate further research on the direction of an integration of an extraction stage (eventually more extensive than the one performed in this work) with kraft pulping for a complete bark valorization.

3.1.2. Branches, Sawdust, and Energetic Eucalyptus.

Kraft pulping results for branches, sawdust, and energetic eucalyptus are mainly located on the upper quartile of the performance graphics presented in Figure 1. Among all, branches showed the highest pulp yield (48−54%) for KN in the range 12−18, whatever the AA and *H*. This advantage and the low HM and AA required for pulping have led to the classification of this material as the one with best pulping performance.

Screened pulp yields of sawdust are in the range 40−44% for KN between 11 and 22 − Figure 1. It is noticeable that the AA effect on KN decreases as the severity of pulping rises (higher H). For H 1568, corresponding to a pulping time of 210 min and 170 °C, the KN (14−15) did not change significantly with AA. Kraft pulping yields of *E. globulus* bole wood is, in general, about 59%[8,24] for KN around 18. Usually, for optimum delignification of bole wood for pulp production a lower AA is required than that applied in this work. This is one of the factors leading to higher yields than for the eucalyptus-derived components studied in this work. Sawdust has a very low particle size compared to standard chips. As a consequence, there is a higher impact of pulping chemicals on the polysaccharide fraction, leading to an additional dissolution/degradation, promoted also by the higher HM (6) required for liquid recirculation. Furthermore, sawdust is generated during woodchips production and, as such, this fraction of fines could be composed by a higher proportion of parenchyma cells, leading to higher polysaccharide dissolution rates. Also noticeable is the high content of glucose in sawdust, similar to branches; however, sawdust contains a higher percentage of alkaline soluble material. These three factors, together, could be the main reasons for low pulp yields of sawdust when compared, for example, with branches wood (both with low rejects percentage). For both branches and sawdust, the pulping conditions selected were $H = 680$ and AA = 22%, as indicated in Table 2. Among all, branches wood is the material with highest pulp yield (48−54%) for KN of 12 to 18.

Pulp yields of energetic eucalyptus were between 42% and 50% (negligible rejects), with KN in the range 18−32 for the conditions tested (Figure 2A−C). Chemical composition of this material is close to branches wood: low lignin content and high glucose percentage, indicating high content of cellulose. However, the xylose content of energetic eucalyptus (Table S1 (Supporting Information)) suggests a higher proportion of hemicelluloses in the polysaccharide fraction which, due to its higher dissolution rate, could be contributing to the lower yields observed for energetic eucalyptus pulp as compared with branches for $H = 1101$ (Figure 1.C) for the same range of KN (10−15). Whatever the *H*, for AA from 16% to 22%, the pulp yield of energetic eucalyptus is always between sawdust and branches. In this work, the selected conditions for this material were H = 1101 and AA = 20% as depicted in Table 2.

Based on the KN and screened pulp yield for each material a selection of essays was made, as depicted in Table 2. The selection was based on the best combination of *H* and AA, favorable to pulp yield with a KN between 13 and 18, in the range of conditions studied. The exception was forest biomass: the resulting pulp KN (27) exceeded the upper limit of the above-mentioned range; however, due to the already low pulp yield (40%), it was decided not to increase the AA (22%) for this biomass. From these essays, the collected BL were considered to further analysis and lignin isolation.

3.1.3. Native Lignins and Correlation with Pulping Conditions.

The native lignin of each material (bark, forest biomass, branches, sawdust, and energetic eucalyptus) was analyzed by NO. This analysis method allows assessing the relative proportion of noncondensed lignin in the biomass by the total yield obtained in phenolic aldehydes and carboxylic

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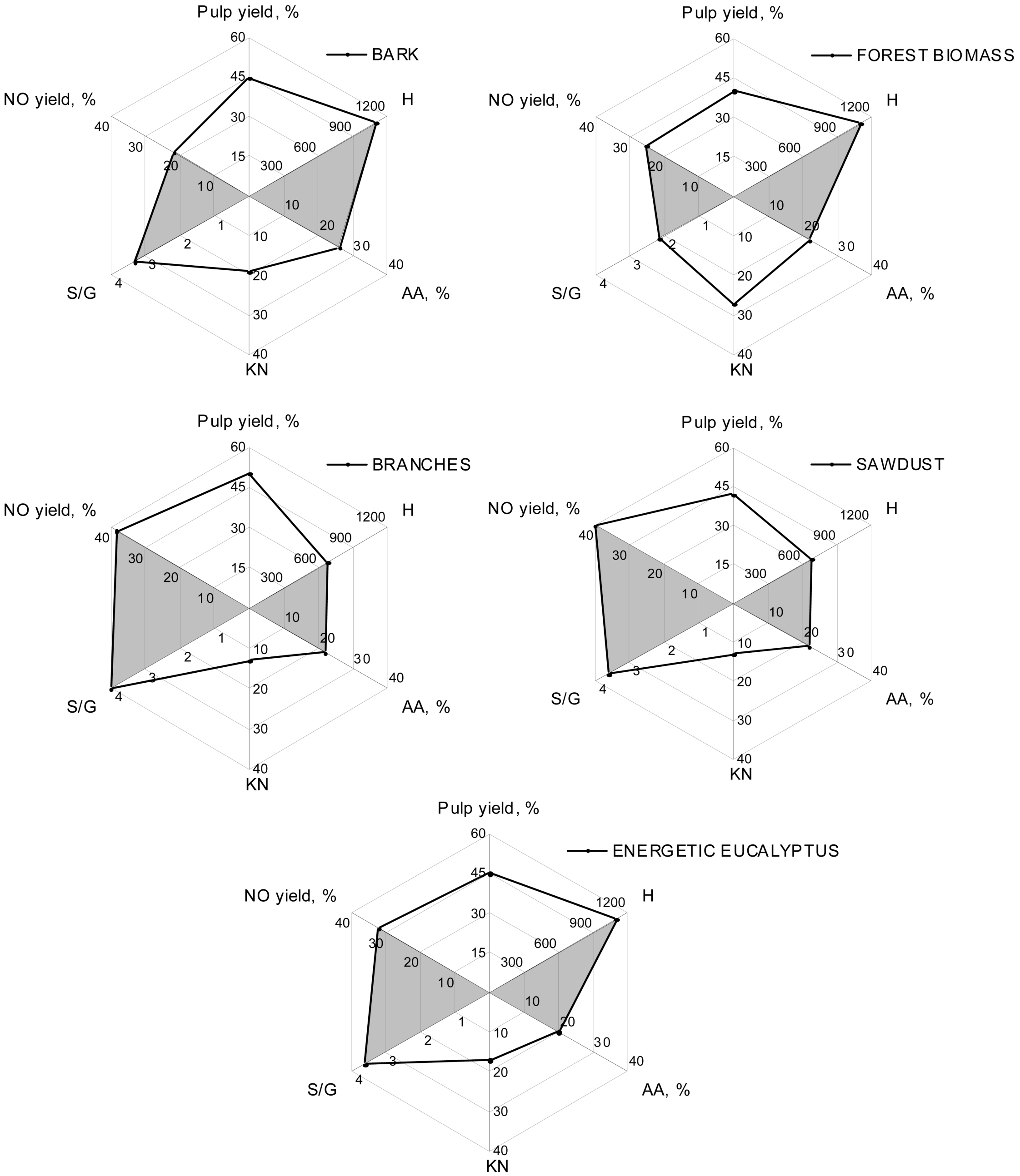

Figure 2. Radar plots showing pulping conditions (*H*, AA), resulting screened pulp yields, and respective KN, and the main lignin characteristics (NO yield on lignin basis, S/G) assessed by analysis of the native lignin of the five materials.

acids. Also, the relative content of NO products provides information about the ratio between syringyl (S) and guaiacyl (G) (S/G) moieties in the noncondensed fraction of lignins. These structural features are important factors contributing to the lignin reactivity during kraft pulping;[24] as such, it is possible to draw a comparison between the reactivity of native lignin of the five materials. NO yield (reported to lignin basis in material) and S/G ratio are plotted in the radar graphics presented in Figure 2 in which the data on *H* and AA applied in each kraft pulping is also shown and highlighted by the filled area. To complete the key data set on each material, radar plots also present the output of each pulping, represented by screened pulp yield and KN in the upper and lower (opposite) positions.

NO yield (% w/w on lignin basis) resulting from analysis of native lignin is remarkably lower for bark (22%) and forest biomass (25%) than for branches (38%), sawdust (40%), and energetic eucalyptus (32%), demonstrating that the first two are the lignins with highest degree of condensation. Also S/G presents some important differences: branches presented the highest ratio (4), followed by sawdust and energetic eucalyptus (3.7), bark (3.4), and finally forest material (2.2). Among all, branches, sawdust, and energetic eucalyptus reveal lower differences concerning these parameters as compared with bark and with forest biomass. Although several factors determine the required pulping conditions for delignification of the lignocellulosic material, the lignin structure is one of them.[24] In an attempt to verify this correlation, the area values of radar plots defined by NO yield and S/G and by *H* and AA were calculated and normalized. The correlation between these two areas is presented in Figure 3.

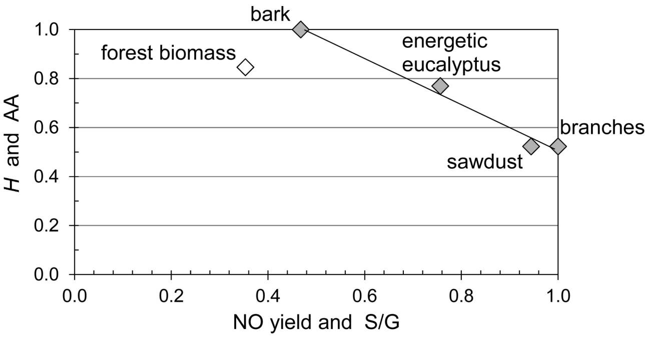

Figure 3. Correlation between the conditions of pulping (normalized area defined by *H* and AA in radar plots Figure 2) and lignin characteristics in the material (normalized area defined by NO yield and S/G in radar plots Figure 2); point corresponding to forest biomass was not included in the correlation; correlation coefficient r = 0.991; confidence interval (with 95% confidence) for the average of normalized area of NO yield and S/G [0.557; 1.027], and for the average of normalized area of *H* and AA [0.479; 0.928].

This plot shows that the lower is the combined NO yield and S/G ratio, the higher must be the *H* and AA to attain a satisfactory degree of delignification, stated in this work as KN in the range 13−18. Forest biomass is out of the trend defined by the other materials because of the higher pulp KN (27). To achieve a KN in the range of the other materials, the combination *H* and AA should be even higher than that applied to bark, with the consequent adverse effect on pulp yield. This is unfavorable for a sustainable polysaccharide production as compared with the others, in particular with branches, which is in the opposite position: best pulp yield and one of the lowest KN, followed by sawdust (Figure 2). Radar plots and the correlation found between the combined parameters provide a useful tool for evaluation of lignocellulosic materials performance, taking into account the contribution of the lignin structure.

3.2. Evaluation of Black Liquors and Kraft Lignins.

3.2.1. Composition. Figure 4 summarizes the main composition of BL and respective KL. The results are reported to kilogram of BL. From the data presented it is possible to figure out the yield of lignin isolation by the comparison of the adjacent column height for each material.

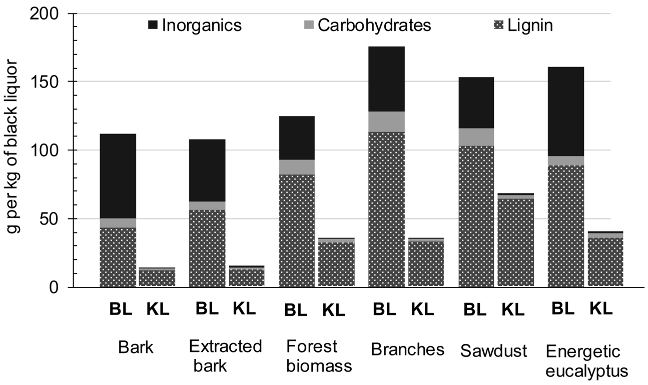

Figure 4. Content of inorganic compounds, carbohydrates, and lignin in BL and in KL, both reported to respective BL weight.

The content of total nonvolatile solids in the BL is in the range 11−18%. The contribution of inorganic content is higher for bark representing 55% of the solids, whereas for the other liquors the contribution is between 40% and 25%. The main reasons pointed out for this are the higher content of inorganics in bark (9%) than in the other materials (Table S1 (Supporting Information)) and the higher AA used in the pulping. The BL resulting from extracted bark shows a lower content of inorganic material (42%, close to that from energetic eucalyptus, 40%) probably due to the leaching effect of the ethanol/water previous extraction. Carbohydrates are a minor fraction accounting for 5% to 9% of the nonvolatile solids of BLs.

The material isolated from BLs was also analyzed to assess the main contaminants contribution. In all cases, the content of inorganics and carbohydrates were drastically reduced when compared with BL solids. The resulting material from the isolation process is almost composed by lignin (83−94%).

The isolation yield reported on the lignin basis is between 22% and 29% for bark and branches and between 38 and 62% for forest biomass, energetic eucalyptus, and sawdust.

The detailed analysis of carbohydrates in both materials, reported as mass fraction, is shown in Figure 4. In BL, xylose (Xyl) is the main component resulting from xylans dissolution/depolymerization during kraft pulping. Galactose (Gal) and arabinose (Ara) were also identified in proportions varying from 2 to 30% of the total of carbohydrates; galactose is particularly important in BL of forest biomass, indicating the presence of material with high content of galactans. After isolation, the proportion of retained Xyl in the KLs increases as a consequence of preferential elimination of the other carbohydrates. The same trend was also observed for BLs and KLs from the hardwoods mimosa and willow.[18]

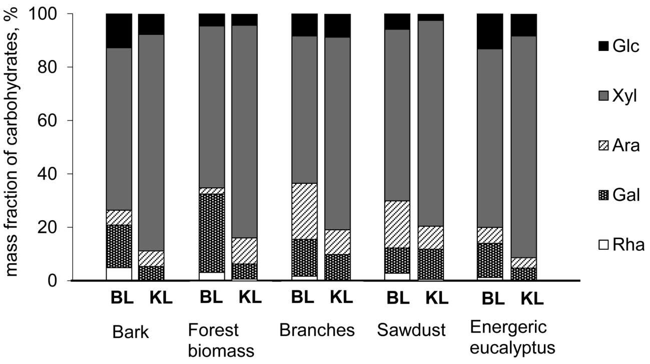

Figure 5. Monosaccharide composition (mass fraction) of the BL and respective KL. Glc, glucose; Xyl, xylose; Ara, arabinose; Gal, galactose; Rha, rhamnose.

3.2.2. Analysis of Kraft Lignins. The materials isolated from BL by acidification, designated as KL, were analyzed by NO. NO products are the phenolic aldehydes syringaldehyde (Sy), vanillin (V), and *p*-hydroxybenzaldehyde (Hy) and the carboxylic acids syringic acid (SA) and vanillic acid (VA).

In addition to the selected pulping essay for bark (conditions: *H* = 1101, AA = 26%) indicated in Figure 6 as "Bark", data on BL and KL resulting from bark pulping with AA = 28% and extracted bark pulping are also reported. Data on industrial BL and respective KL are also depicted in Figure 6.

In the pulping process, lignin is partially depolymerized and it suffers several reactions leading to noteworthy changes on its

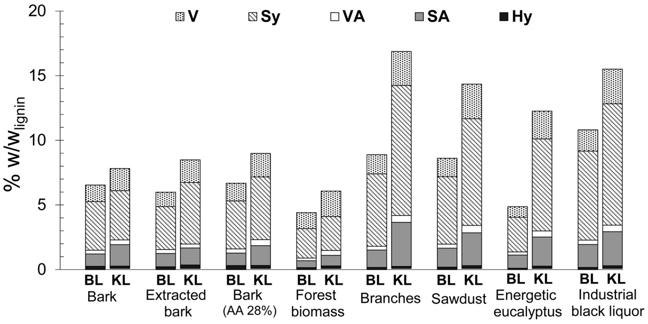

Figure 6. NO products of BL and respective KL, reported to dry lignin basis.

structure. This is particularly evident by comparing NO yields of native lignin (radar plots, Figure 2) and the values of the respective KL in Figure 6. The quite lower NO yields in BL and KL are due to the increase of condensation degree defined as frequency of units linked via one C position of the aromatic ring,[15] as stated before.[10,17]

Total NO yields in BL are in the range 5−9% while for isolated lignins a wider range was obtained: 6−17%. The general observation is that the KL present a lower proportion of condensed structures than the respective BL. This was also reported before for BL and KL from other species.[18]

The lowest NO yields were obtained for forest biomass (for both BL and KL). The low S/G ratio suggests that this material could comprise biomass from other species than *Eucalyptus* (which typically have a high S/G[10,22,24]), as already observed for native lignin.

Forest biomass produces a highly condensed lignin (low NO yield) when submitted to kraft pulping, even at milder conditions than bark (see Table 2 for conditions). Considering pulp yield and lignin characteristics, as compared with the others, this lignocellulosic material is not favorable for a valorization route involving deconstruction by kraft pulping and aiming to produce sugars and reactive lignin for upgrading.

BL and KL resulting from bark pulping show the closest values among all the pairs BL and KL, denoting a lower impact of the lignin isolation on the lignin reactivity assessed by NO. Moreover, no noteworthy differences were found between bark lignins produced by pulping with two different AA and after previous ethanol/water extraction. Energetic eucalyptus lignin in BL is almost as condensed as forest biomass. Sawdust and branches lignin presented the highest NO yields, resemble the industrial KL, as depicted in Figure 6. For sawdust, branches, and also for energetic eucalyptus, there is a noticeable increment of NO yields in KL as compared with BL. This fact could be due to a greater elimination of a nonproductive fraction in the isolation process of these biomass BLs, as compared with bark and with forest material ones. Industrial BL stands out as the one with highest NO yields, while branches KL shows the highest NO yield (Figure 6).

3.2.3. Characterization of Lignins by ^{13}C NMR and ^{31}P NMR.

The material isolated by acidification of BLs produced from sawdust, branches, and bark is mainly composed by lignin (more than 93%) and therefore a further purification process was not considered, being referred to as KL. Branches and sawdust are the materials generating KL with NO yields close to that of industrial KL (Figure 6), and with better performance toward kraft pulping (Table 2 and Figure 2). On the other side, bark KL was produced at higher AA, and it presents a remarkably low NO yield (Figure 6). This prompts a more insightful analysis of these three generated lignins, and comparison with industrial KL, which was performed by ^{13}C NMR and ^{31}P NMR. Additionally, lignin from branches was isolated by mild acidolysis aiming to report for the first time its main structural parameters assessed by ^{13}C NMR.

Figure S2 (Supporting Information) shows the typical ^{13}C NMR and ^{31}P NMR spectra and the main signal assignments for KL resulting from branches pulping.

The main results of quantitative ^{13}C NMR (branches, sawdust, bark and industrial KLs, and mild acidolysis lignin from branches, AcL branches) and ^{31}P NMR (branches and sawdust KLs) are presented in Table 3 and in Table 5, respectively. The assignments and the explanation for calculations based on ^{13}C NMR and ^{31}P NMR spectra of lignins can be found in the literature.[10,17,25−28]

Aromatic OCH_3 (Table 3, entry 2) reflects the proportion between the phenylpropane units (ppu) that compose lignin: syringyl/guaiacyl/*p*-hydroxyphenyl (S:G:H). Branches AcL has lower content of OCH_3 (1.51/C_6) than that reported before for bole wood lignin (1.75/C_6[10]), also isolated from the same

Table 3. Quantification (number/per aromatic ring) of the Main Structures Identified by ^{13}C NMR in KL of Sawdust, Branches, Bark, Industrial KL and Acidolysis Lignin (AcL) of Branches

		amount (number/C_6)				
	assignments	Kraft lignins*				
entry	spectroscopic range	sawdust	branches	bark	industrial	branches AcL
1	Cβ in β-5 and β−β structures (δ 51.0−53.8 ppm)	0.11	0.14	0.14	0.12	0.14
2	Aromatic OCH_3 (δ 54.3−57.3 ppm)	1.26	1.39	1.12	1.50	1.51
3	Cγ in β-*O*-4 structures without Cα=O (δ 59.3−60.8 ppm)	0.11	0.16	0.11	0.18	0.44
4	Cγ in β-5 and β-*O*-4 structures with Cα=O; Cγ in β-1 (δ 62.5−63.8 ppm)	0.16	0.16	0.22	0.14	0.12
5	Cα in β-*O*-4 structures; Cγ in pinoresinol/syringaresinol and β−β structures (δ 70.0−76.0 ppm)	0.68	0.69	0.85	0.69	0.92
6	Cβ in β-*O*-4 structures; Cα in β-5 and β−β structures (δ 80.0−90.0 ppm)	0.36	0.42	0.33	0.43	0.84
7	Aromatic C−H (δ 103.0−123.0 ppm)	1.97	1.91	1.84	1.97	2.10
8	C_4 in H (δ 157.0−162.0 ppm)	0.07	0.10	0.10	0.01	0.13
9	CHO in benzaldehyde structures (δ 191.0−192.0 ppm)	0.05	0.04	0.05	0.03	0.01
10	CHO in cinnamaldehyde structures (δ 193.5−194.5 ppm)	0.06	0.03	0.04	0.02	0.03
11	CO in aldehydes and ketones (δ 195.0−210.0 ppm)	0.81	0.59	0.24	0.37	0.45

*Isolated from respective liquors with no further purification procedure.

Table 4. Summary of the Calculated Parameters Based on Analysis of Lignins by ^{13}C NMR

parameter	KL sawdust	KL branches	KL bark	industrial KL	branches AcL
β-O-4 structures (number/100C_6)	25	28	18	31	71
DC (%)	34	35	50	41	12
S:G:H	62:30:8	64:26:10	55:34:12	75:25	65:22:13

sample by mild acidolysis and analyzed by ^{13}C NMR (in the same conditions). This is certainly due to the presence of H units (which has no methoxyl groups) in branches AcL (Table 3, entry 8). The calculated S:G:H for branches AcL is 65:22:13, whereas for bole lignin the proportion is 80:20:0[10]. Also noticeable is the lower content of OCH_3 in KLs due to the demethylation reactions during pulping.[14] Compared with industrial KL, sawdust and branches KLs are those with lower OCH_3 content. In accordance, the calculated S:G:H proportions are 62:30:8 and 64:26:10 for sawdust and branches KLs, respectively, while for the industrial one, the proportion is 75:25:0. Bark KL has the lowest content of OCH_3 which is in accordance with higher proportion of G and H units (55:34:12) as compared with the other lignins.

Alkyl-aryl ether structures (β-*O*-4) are the main linkage type between ppu of lignin as revealed by entries 3 to 6 in Table 3. However, because of the interference of carbons in other chemical environments, one of the approaches to estimate β-*O*-4 content is to subtract entry 1 from entry 6.[10] Entry 1 refers to Cβ in β-5 and β−β structures, and no major differences were found between lignins (11−14/100 C_6); for bole wood lignin, the reported content of these structures is about one-half (6/100Ar).[10] On the basis of that subtraction, branches AcL contains 71 β-*O*-4 linkages per 100 C_6 or 100 ppu (assuming the lateral chain of ppu was not degraded, aromatic ring C_6 is equivalent to ppu), a lower value than that found for bole wood (76 β-*O*-4/100C_6).[10] For KL the content of this linkage is rather lower; this was expected due to the depolymerization induced by kraft pulping: 25 and 28 β-*O*-4/100C_6 for sawdust and branches, somewhat lower than for industrial KL (31 β-*O*-4/100C_6). These data are gathered in Table 4. The content of β-*O*-4 in processed lignins is related to the content of these linkages in the initial material, albeit kraft conditions could also be a contributing factor. For example, bark acidolysis lignin (isolated from the same sample and characterized in the same conditions) contains 65/100C_6[10] and the respective KL produced in this work (pulping conditions AA 26%, H 1101) contains 18/100C_6. The decrease percentage of β-*O*-4 content is 72% for bark, while for branches and bole is about 60%. The higher depolymerization of bark lignin is certainly related with higher severity applied which promotes alkyl−aryl ether cleavage. Entry 4 (Table 3) indicates that, among all, the KL of bark has the highest content of β-*O*-4 structures with carbonyl at Cα of lateral chain; this feature was not observed in mild acidolysis lignin of bark[10] pointing out, once more, the effect of the higher pulping severity applied to this material.

The interlinkage of the lateral chain of ppu is given by entry 5 (Table 3). While for branches AcL the higher value is related with high β-*O*-4 content (less modified lignin), for bark KL the high value clearly stated a high level of pinoresinol/syringaresinol structures; the estimation indicates that about one-half of lignin units are involved in these structures. No differences were found for sawdust, branches, and industrial KL. Finally, the content of benzaldehydes and cinnamaldehydes (entries 9 and 10, Table 3) is low for all lignins: however, carbonyl groups content is noteworthy, in particular for sawdust KL.

From ^{13}C NMR data it is possible to estimate the degree of condensation (DC) of the lignins.[10,26] Condensation is usually low for native lignins, increasing due to coupling reactions between aromatic rings during the delignification reactions.[15] In accordance with this, DC of branches AcL is quite low (12%) and close to that reported to bole wood lignin (15%).[10] For KL, DC is about 3-fold (34% for sawdust, 35% for branches, and 41% for industrial KL), while for bark KL the DC reaches to 50%. Table 4 summarizes the main results discussed. Once more, this high level of modification is certainly due to the high severity applied in the bark pulping, since the DC of mild acidolysis lignin of bark is low (16%[10]) being similar to bole wood lignin.

The content and distribution of hydroxyl groups in sawdust and branches KL is depicted in Table 5.

Table 5. Quantification (number/ppu) of Hydroxyl Groups (Aliphatic, Phenolic and Carboxylic) by ^{31}P NMR Analysis of Sawdust and Branches KL

group	KL sawdust mmol/g lignin	KL branches mmol/g lignin
aliphatic OH	1.72	2.14
carboxylic acids	0.38	0.39
total phenolic units	6.55	5.92
condensed	1.52	1.38
S	3.64	3.36
G	1.38	1.15
H	0.01	0.03

Compared to branches, sawdust presents a lower content of aliphatic hydroxyl groups, but more phenolic groups (in both condensed and noncondensed units). The distribution of S and G units is similar for both lignins, denoting no differences in the content S and G involved in etherified structures. Interesting to note is the almost inexistent H units with free phenolic group, whereas the total proportion of H units for sawdust and branches KL was 8 and 10, respectively. This observation suggests a high involvement of the phenolic hydroxyl group of H units in ether linkages. Carboxyl group content is similar for both lignins.

4. CONCLUSIONS

Lignocellulosic materials generated in *E. globulus* plantations and at mill sites during wood preparation for pulping were analyzed for chemical composition and then deconstructed by kraft pulping at different process conditions. The chemical composition, the required pulping conditions, and the pulp yields versus the delignification achieved demonstrated a high potential of branches and sawdust as polysaccharides feedstocks. However, sawdust requires a higher liquid/solid ratio than branches which could be a disadvantage considering the dimensioning of the reactors required to process that material. Bark revealed also a good performance with pulp yields close to sawdust but requiring a higher alkaline charge for an effective kraft pulping. The previous extraction of bark with ethanol/water slightly improves the delignification, giving an insight about the presence of alkali-consuming compounds that can be removed before pulping with favorable effects on delignification; according to the previous works of the authors, that extract having high added-value compounds would be interesting to upgrade, supporting a possible sequence of processes for bark valorization. The drawback of the bark as feedstock is also the higher liquid/solid ratio required for kraft pulping, resulting in a similar constraint of that referred to sawdust. Forest material provided the lowest pulp yield in the range of conditions tested. Energetic eucalyptus was also tested for comparison purposes, revealing to be more difficult to delignify, although the pulp yields were satisfactory between sawdust and branches values.

Radar plots for all materials were built based on pulping conditions (AA and *H*), characteristics of biomass lignin (NO yields and S/G), and pulping results (yield and KN). The combination of these three pairs provided a useful tool for evaluation of materials: a positive correlation was found between the pulping severity (temperature, time, and AA required for an effective delignification) and the native lignin reactivity assessed by NO and the ratio S/G.

Lignin was isolated from branches and characterized by ^{13}C NMR. The assignment to H units was found in the spectrum of branches AcL, leading to a calculated S:G:H proportion of 65:22:13 (S/G 3). Although such H unit content in eucalyptus biomass is not expected, this proportion is in accordance with OCH_3 content also assessed by ^{13}C NMR (152/100C_6). Branches AcL was revealed to have a slight lower content of β-*O*-4 (71/100C_6) and condensed (12%) structures than bole eucalyptus lignin.[10] Lignins isolated from BLs have some remarkable differences in their main interunit linkages and functional groups. KL of bark has the lowest β-*O*-4 content (18/100 C_6) revealing a higher depolymerization of native lignin when compared with sawdust (25/100 C_6), branches (28/100 C_6), and industrial (31/100 C_6) KLs; it has also higher DC and pinoresinol/syringoresinol content. KL of the two most promising lignocellulosic materials, sawdust and branches, were similar; the main difference found was the higher content of free phenolic groups in both condensed and noncondensed fractions of sawdust KL.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b03712.

> Distribution of component weight in *Eucalyptus globulus* plantations in Portugal; NMR spectra of kraft lignin resulting from *E. globulus* branches pulping (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AA = active alkali
AcL = acidolysis lignin of branches
Ara = arabinose
BL = black liquor
DC = degree of condensation
G = guaiacyl unit
Gal = galactose
Glc = glucose
H = *H* factor
H = *p*-hydroxyphenyl unit
Hy = *p*-hydroxybenzaldehyde
HM = hydromodule
KL = kraft lignin
KN = kappa number
NMR = nuclear magnetic resonance
NO = nitrobenzene oxidation
ppu = phenylpropane unit
Rha = rhamnose
S = syringyl unit
Sy = syringaldehyde
SA = syringic acid
S:G:H = syringyl:guaiacyl:*p*-hydroxyphenyl
V = vanillin
VA = vanillic acid
Xyl = xylose

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