STRUCTURAL FEATURES OF DIOXANE LIGNIN FROM *Eucalyptus globulus* AND THEIR RELATIONSHIP WITH THE PULP YIELD OF CONTRASTING GENOTYPES

María Graciela Aguayo [1,2], José Ruiz [2], Marcela Norambuena [3], Regis Teixeira Mendonça [1,2,♠]

ABSTRACT

The chemical structure of dioxane lignins isolated from two groups of *Eucalyptus globulus* genotypes with contrasting pulpwood characteristics were evaluated. Six genotypes were selected and separated in two groups (G1 and G2) based on differences in wood density, pulp yield and chemical characteristics. Lignin was isolated from both milled wood and kraft pulps produced at kappa number 16, and were characterized by different techniques such as FTIR, elemental analysis, molar mass distribution and ^{31}P NMR spectroscopy. From the different characteristics evaluated, some were determined as more relevant, such as syringyl (S) and guaiacyl (G) amounts, S/G ratio and condensed biphenyl units, were correlated with the pulp yield. High correlations were found between pulp yield and syringyl units ($R^2 = 0,69$), and pulp yield and syringyl/guaicyl ratio ($R^2 = 0,88$). The condensed 5-5 biphenyl units presented a negative correlation with pulp yield ($R^2 = 0,76$). The information obtained explained part of the difference in pulpability of the contrasting genotypes and can be used for the selection and improvement of the species for the pulp and paper industry.

Keywords: Dioxane lignin, kraft pulping, *Eucalyptus globulus*, FTIR, ^{31}P NMR spectroscopy.

INTRODUCTION

The study of the characteristics of wood components and their effect during pulping processes is subject of several works (Pinto *et al.* 2002, 2005, Guerra *et al.* 2006, Ramirez *et al.* 2009, Aguayo *et al.* 2013). The characteristics of lignin are among the most important features for understanding the mechanisms of its removal from cell wall during chemical pulping processes. This information is useful not only for the wood of different species, but also for different genotypes of a single species, as found in commercial plantations for the pulp and paper industry. The present work will be focused on *Eucalyptus* wood that is an important raw material for the production of writing and printing paper and, specifically, *Eucalyptus* globulus that represents the main source of short fiber for countries like Chile, Spain, Portugal and Australia.

Structural characteristics of *Eucalyptus* lignin explained some advantages of this species when compared with other hardwoods during pulping and bleaching processes. For instance, Pinto *et al.* (2005), characterized by ^{13}C NMR spectroscopy lignins from different hardwood species. In *Eucalyptus globulus*, more than 80% of lignin units are syringyl-type, higher than the average found in other species as *Eucalyptus grandis*, *Eucalyptus urograndis* and *Betula pendula*, which showed S-type amounts between 65% and 70%. After pulping, the relative content of S-units decreased, however, it still higher in *Eucalyptus*, while in the other wood species, the º-type units become predominant in the residual lignin, affecting bleaching performance. It was also showed that lignin in *Eucalyptus globulus* kraft pulps had lower condensation degree and high frequency of β-O-4 linkages than other species.

[1] Facultad de Ciencias Forestales, Universidad de Concepción, Casilla 160-C, Concepción, Chile.
[2] Centro de Biotecnología, Universidad de Concepción, Casilla 160-C, Concepción, Chile.
[3] BioEnercel S.A., Edificio IdeaIncuba, Universidad de Concepción, Concepción, Chile.
♠Corresponding author: rteixeira@udec.cl

However, there is less information if genotypes from a single species could also present significant differences in structural characteristics of lignin that can be relevant during pulping process. Guerra *et al.* (2008), showed that for different clones of *Eucalyptus globulus*, the lignin content did not correlated with the pulp yield, but significant correlations were found between pulp yield and the content of S-β-O-4 type structures. In a previous work, Aguayo *et al.* (2013), evaluated different *Eucalyptus globulus* genotypes that showed a significant variation in wood density and kraft pulp yield. Wood and pulp samples were analyzed by UV microspectrophotometric (UMSP) and thioacidolysis. Results showed that samples with the lowest lignin levels had also the lowest UV absorption at 278 nm in the secondary wall (0,22 A-units) and low levels of S-type β -O-4 linkages in the lignin structure. In samples obtained during kraft pulping, UV absorbance decreased reaching values as low as 0,08 A-units. Samples with high levels of initial lignin, have significantly higher UV absorbance (A_{278nm} 0,15) and lignin enriched in G-β-O-4 structures. These analyses performed *in situ* revealed that distribution of lignin in the cell wall and, at least one structural characteristic (abundance of S or G units), had important effect in kraft delignification and pulp yield.

To complement the previous study, the present work focused on the chemical and structural characterization of lignin extracted from wood and kraft pulps of selected genotypes of *Eucalyptus globulus* with the aim to determine the existence of other features that could also be associated with the pulping performance in this species.

EXPERIMENTAL

Wood and pulp samples

Eucalyptus globulus trees (15 years old) were sampled from a commercial plantation provided by a Chilean forest company located in the Biobío Province. Six genotypes were selected and separated in two groups (G1 and G2) based on a previous study that showed significant variations in wood density, pulp yield and chemical characteristics (Table 1) according to Aguayo *et al.* (2013). Logs of 35-40 cm were cut along the trunk from each tree. All the logs were visually examined to discard the presence of tension wood determined by pith asymmetry in the longitudinal axis of the log. Selected logs °were chipped and wood chips from each of the samples were submitted to kraft pulping in a rotary digester equipped with 4 independent 1,5-L vessels (Regmed Ltda., Brazil). Each vessel was loaded with 50 g of wood chips (dry basis) and 200 mL of cooking liquor with active alkali (AA) varying from 18,5% to 19,5% and 30% sulfidity (both calculated on dry wood basis and expressed as NaOH equivalents). Reactor heating rate was 2,1oC/min, cooking temperature was 165oC and the H-factor used was 800. Produced pulps were screened through a 0,2 mm slot screen and the screened pulp yield was determined. Kappa number was measured according to TAPPI Standard T236 om-99.

Table 1. Wood and kraft pulps characteristics of *Eucalyptus globulus* genotypes.

	Group 1			Group 2		
	1	2	3	4	5	6
Density (kg/m^3)	563	573	547	485	485	484
Glucose (%)	53,8±0,5	53,3±0,5	52,1±0,5	50,3±0,9	49,2±0,7	48,7±0,8
Xylans (%)	11,6±0,3	11,6±0,7	11,2±0,4	13,1±0,6	12,6±0,6	14,3±0,7
Lignin (%)	23,8±0,5	24,1±0,2	24,9±0,1	28±0,3	27±0,5	25,8±0,8
β-O-4 linkages (%)	60,2±0,4	56,8±0,7	58,4±0,9	56,5±1,3	51,3±1,1	51,5±0,9
Active alkali (%)	19	18,5	19	19,5	19,5	19
Pulp yield (%)	58,4±0,6	58,5±0,7	58±0,6	54,6±0,6	56,4±1,6	54,2±0,2
Kappa number	15,7±0,2	16,7±0,2	15,6±0,6	15,3±0,4	15,6±0,2	16,7±0,2

Isolation of lignin from wood and pulps

The isolation of the lignin from wood and pulps was based on the methodology described by Evtuguin *et al.* (2001), using mild acidolysis and dioxane as solvent. First, milled wood (40/60 mesh) was subjected to extractives removal with acetone (90%) for 16 h in a Soxhlet apparatus. Further, extractive-free milled wood was extracted with NaOH solution at 0,3% (0,075 mol/L) for 1 h (liquid:wood ratio 50:1) under nitrogen atmosphere for removal of tannins. Ten g of extracted wood (dry basis) were placed in a 1-L three-necked flask fitted with a reflux condenser, nitrogen bubbler, and a dropping funnel. The solvent, 100 mL of dioxane/water (9:1, v/v) containing 1,82 g HCl (equivalent to 0,2 M), was added slowly from the funnel. The mixture under nitrogen atmosphere was heated with a heating mantle and refluxed at 90-95°C for 40 min. Then, the mixture was allowed to cool in nitrogen atmosphere until 50°C. The liquid phase was decanted and the solid residue was extracted with 100 mL of acidic dioxane/water solution for 30 min, as described above.

The procedure was repeated more two times. A fourth extraction was performed without addition of hydrochloric acid in the dioxane/water mixture. Each portion of extract was concentrated separately (from 200 mL to 40 mL), the concentrates were combined and lignin was precipitated by addition of cold water in the dioxane solution. Filtered isolated lignin was extracted with diethyl ether (100 mL), then washed with water, and freeze-dried. Purity of lignin was determined using the methodology described by Dence (1992), where 2 mg of lignin were introduced into tubes containing 5 mL of acetyl bromide, acetic acid 25% v/v and 0,2 mL of 70% perchloric acid. The samples were introduced in a water bath at 70°C for 30 min with occasional stirring. Subsequently, the digested sample was transferred to a 100 mL flask with 10 mL 2 M NaOH and 25 mL of glacial acetic acid. The solution was made to a final volume of 100 mL with glacial acetic acid. Purity of lignin was determined by measuring the absorbance at 280 nm, using 20,09 L/g cm as the absorptivity coefficient. Carbohydrates content of the lignins were determined by acid methanolysis according to Sundberg *et al.* (1996).

Elemental and methoxyl analysis

The amount of C, H and O in the lignin samples was determined in an Elemental Analyser EA 1108 (FISONS Instrument). The methoxyl content in dioxane lignin was determined in accordance with methodology described by Li *et al.* (2012). Half milliliter hydroiodic acid (57%) was mixed with 10 mg of sample in headspace test vial, and then sealed with a septum. The vials were placed in an oil bath and heated for 30 min at 130°C. The vials were cooled to room temperature, and 0,5 mL NaOH (6 mol/L) was injected with a syringe into the sealed vial to neutralize the excess hydroiodic acid. The vial was immediately put into the headspace autosampler. All measurements were carried out using a TurboMatrix 40 Trap (Perkin Elmer) automatic headspace sampler and GC-MS 7890A-5975C (Agilent Technologies) with DB-5 capillary column (30 m x 0,25 mm x 0.25 µm) at 40°C, high-purity nitrogen carrier gas 1,0 mL/min flow rate. Detector temperature was 280°C and headspace operating conditions were sample at 50°C; 0,2 min vial pressurization time and 0,3 min injection time. Standard deviation from a triplicate analysis was lower than 1%.

Fourier-Transformed Infrared Spectroscopy (FTIR)

FTIR spectra were recorded using a Perkin Elmer spectrometer model System 2000. The dried lignin samples from wood and pulp were embedded in KBr pellets in the concentration of 1 mg/100 mg KBr. The spectra were recorded in transmittance mode in the range 4000 - 400 cm^{-1}. The bands of each spectrum were assigned according to Pandey (1999), and lignin was classified according to Faix (1991).

^{31}P NMR spectroscopy

The content of phenolic and aliphatic hydroxyl groups in the lignin structure was determined by phosphitylation of lignin samples according to Granata and Argyropoulos (1995). About 40 mg of lignin was weighted and dissolved in 400 µL of a solvent mixture of pyridine and deuterated chloroform (1,6:1). The samples were maintained at room temperature under constant stirring. Subsequently, it was added 100 µL cholesterol as internal standard and 50 µL chromium (III) acetylacetonate as relaxation reagent. Finally, 100 µL of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (phophitylating reagent II). The ^{31}P NMR spectra were acquired using a BRUKER 400 MHz spectrometer. The maximum standard error of the data was 1×10^{-2} mmol/g lignin.

Molar mass distribution

Molar mass distribution of dioxane lignin was performed using the protocol described by Guerra *et al.* (2006). Lignin was acetylated with acetyl bromide before analysis. In a 15-mL round bottom flask it was added 10 mg of lignin and 2,5 mL of a mixture consisting of acetyl bromide and glacial acetic acid (8/92, v/v). The flask was sealed and placed in a water bath at 50°C for 2 h with continuous stirring. The solvent was evaporated in a rotary evaporator. The sample was immediately dissolved in THF and used for the size exclusion analysis. A size exclusion chromatography system (Waters) with UV detection was used. Analyses were performed at 40°C, using tetrahydrofuran (THF) as eluent at 0,44 mL/min and three Styragel columns mounted in series, HR1, HR3 and HR5 (Waters) with a mass range between (100 and 4 x10^{-6} g/mol). The GPC system was calibrated with polystyrene standards. Standard deviation for this analysis is lower than 5%.

RESULTS AND DISCUSSION

Chemical composition of the six genotypes (Table 1) showed that G1 (samples 1, 2 and 3) contained the highest amount of glucans (52,1%-53,8%) and the lowest amount of lignin (23,8%-24,9%), whereas G2 (samples 4, 5 and 6) had lower glucans levels (48,7%-50,3%) and higher lignin contents (25,8%-28,0%). Kraft pulping of these genotypes was performed at H-factor 800 and varied active alkali (AA) from 18,5% to 19,5% with the aim to prepare pulps with similar kappa number (16 ± 1). G1 samples presented higher pulp yields than samples from G2, which were related with their lower original lignin contents, higher proportion of S-type units and β-O-4 linkages, as previously reported by Aguayo *et al.* (2013). With the wood and pulp samples, dioxane lignin was prepared and used for a more detailed analysis of the lignin structure and to determine other possible features affecting pulp yield.

Dioxane lignin is frequently used for structural studies since its preparation allows good extraction yields with minimal structural changes during the procedure (Pascoal Neto *et al.* 1997, Evtuguin et al. 2001, Argyropoulos *et al.* 2002, Jahan and Mun 2007). The yield of dioxane lignin extracted from *Eucalyptus globulus* genotypes was calculated on the basis of the Klason lignin content and were in the range of 60%-71% for G1 and 47%-56% for G2. Residual lignins present in kraft pulps were also extracted, yielding around 44% for G1 and 28%-36% for G2 pulps. The purity of the dioxane lignins extracted from wood and pulps varied between 88% and 99%. Under the conditions used for lignin extraction, small amounts of carbohydrates from the lignin-carbohydrate complex (LCC) can also be extracted (Gellerstedt *et al.* 1994). The carbohydrates contents were quantified by acid methanolysis and revealed values up to 8% that were used to correct the results from the elemental analysis of the lignins (Jahan and Mun 2007).

Elemental analysis

The empirical formula of the dioxane lignins from wood and pulps are shown in Table 2. The number of methoxyl groups per C_9 unit in dioxane lignins from wood did not presented significant difference for G1 and G2 samples and was in the range of 1,3-1,5 methoxyl groups/C_9 units, as expected for *Eucalyptus* species (Pinto *et al.* 2002, Evtuguin and Pascoal Neto 2007). In pulps, the dioxane lignins from G1 samples presented 0,88-0,93 methoxyl groups/C_9 and 0,72-0,76 methoxyl groups/C_9 for G2. The demethoxylation degree in dioxane lignins from G2 was between 46%-51%, higher than in G1, where demethoxylation was 30%-44%. One on the reactions that occurs during kraft pulping is the cleavage of the methyl-aryl ether linkages in lignin. The primary reaction involves an attack of a hydrosulphide ion to the aromatic methyl ether group and formation of methylmercaptan together with a phenolic hydroxyl group (Gellerstedt 2009). A higher demethoxylation of lignin could increase the occurrence of condensation reactions decreasing the efficiency of lignin removal during kraft pulping.

Table 2. Empirical formula* of dioxane lignins isolated from wood and pulp of *Eucalyptus globulus* genotypes.

Samples		Wood lignin	Pulp lignin
G1	1	$C_9H_{8,79}O_{3,98}(OCH_3)_{1,32}$	$C_9H_{6,40}O_{4,26}(OCH_3)_{0,93}$
	2	$C_9H_{8,30}O_{4,07}(OCH_3)_{1,55}$	$C_9H_{7,71}O_{4,04}(OCH_3)_{0,88}$
	3	$C_9H7_{8,62}O_{3,99}(OCH_3)_{1,45}$	$C_9H_{7,53}O_{3,91}(OCH_3)_{0,91}$
G2	4	$C_9H_{7,80}O_{4,88}(OCH_3)_{1,56}$	$C_9H_{8,66}O_{3,48}(OCH_3)_{0,76}$
	5	$C_9H_{8,16}O_{4,23}(OCH_3)_{1,34}$	$C_9H_{8,89}O_{3,31}(OCH_3)_{0,72}$
	6	$C_9H_{8,02}O_{4,02}(OCH_3)_{1,50}$	$C_9H_{8,89}O_{3,55}(OCH_3)_{0,75}$

* Empirical formula $C_xH_yO_z(OCH_3)n$ was calculated as: $n=(\%OCH3)/31,04$; $x=(\%C)/12-n$; $y=(\%H)-3n$; $z=(\%O)/16-n$ (Jahan and Mun 2007).

Molar mass distribution

The weight-average (Mw), number-average (Mn) molecular weight and polydispersity of dioxane lignins were obtained from GPC analysis (Figure 1). The data (Table 3) shows that the lignins isolated from wood samples had values of Mw between 9585-10802 g/mol for G1 and between 11176-11527 g/mol of G2. For Mn the values were between 2439-3052 g/mol for G1 and between 2971-3928 g/mol for G2. Evtuguin *et al.* (2001), reported Mn value of 2180 for dioxane lignin extracted from *Eucalyptus globulus.* Nagy 2009, reported Mw 2400 g/mol and Mn 2150 g/mol for dioxane lignins of *Eucalyptus spp.* Dioxane lignins obtained from pulps had Mw values between 2508-2910 g/mol for G1 and between 2196-2858 g/mol for G2. For Mn the values for G1 were from 854 to 1122 g/mol and from 671 to 717 g/mol for G2. Similar values were reported for dioxane lignins extracted from Eucalyptus globulus kraft pulps (Pinto *et al.* 2002).
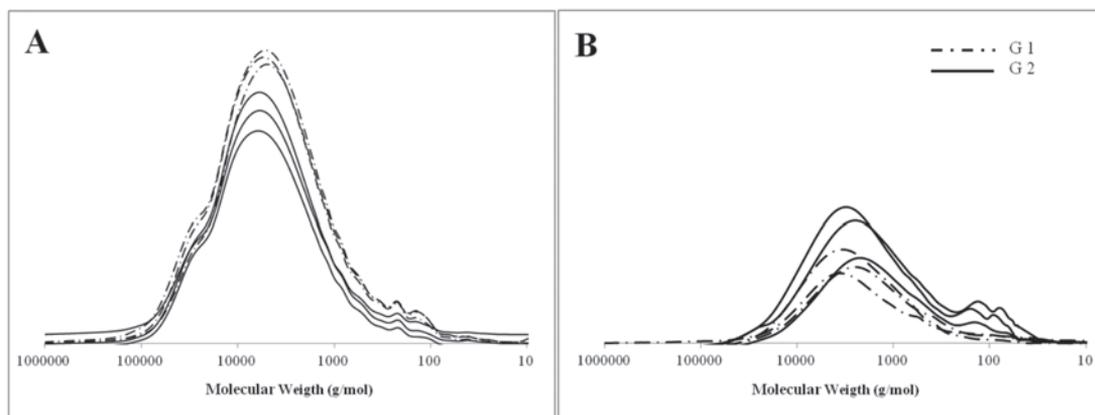
Figure 1. GPC chromatogram of dioxane lignins isolated from
(A) wood and (B) pulp of *Eucalyptus globulus* genotypes.

Table 3. Average molar masses of dioxane lignins extracted from wood
and kraft pulps of *Eucalyptus globulus* genotypes.

Samples		Mw (g/mol)		Mn (g/mol)		D	
		wood	pulp	wood	pulp	wood	pulp
G1	1	10485	2907	3052	1122	3,4	2,6
	2	10802	2910	2647	1084	4,1	2,7
	3	9685	2508	2439	854	4	2,9
G2	4	11315	2196	2980	680	3,8	3,2
	5	11527	2858	3928	717	2,9	3,9
	6	11176	2493	2971	671	3,8	3,7

Standard deviation for Mw and Mn is lower than 5%.

FTIR

FTIR spectra of dioxane lignins were shown in Figure 2 (Fig. 2A, wood lignin and Fig. 2B, pulp lignin). Band assignments were done according to Pandey (1999) and Faix (1991). All spectra showed absorbance bands at 1328 cm^{-1} (syringyl units) and a small shoulder at 1268 cm^{-1} (guaiacyl units), which is typical for hardwood lignins. Another characteristic of the lignins spectra is the band at 1462 cm^{-1} (C-H deformation, methyl and methylene) that was more intense than the band at 1505 cm^{-1} (aromatic skeletal vibration). The band at 1460 cm^{-1} indicates the C-H vibration and deformation in the aromatic ring. The strong band intensity at 1124 cm^{-1} is associated with the structure of the syringyl lignin molecule. The FTIR analysis corroborated that the lignins isolated from wood and kraft pulps are GS4-type, according to the classification of Faix (1991). The presence of the band at 1720 cm^{-1} in dioxane lignins isolated from kraft pulps indicated an increase in the content of carbonyl groups from esters, aldehydes, or carbonyl groups non-conjugated with the aromatic ring (Faix 1992, Lin and Dence 1992). This is an indication that the increase in the content of carbonyl groups in the residual lignin is due to oxidation reactions that occurred during alkaline pulping (Rutkowska *et al.* 2009).
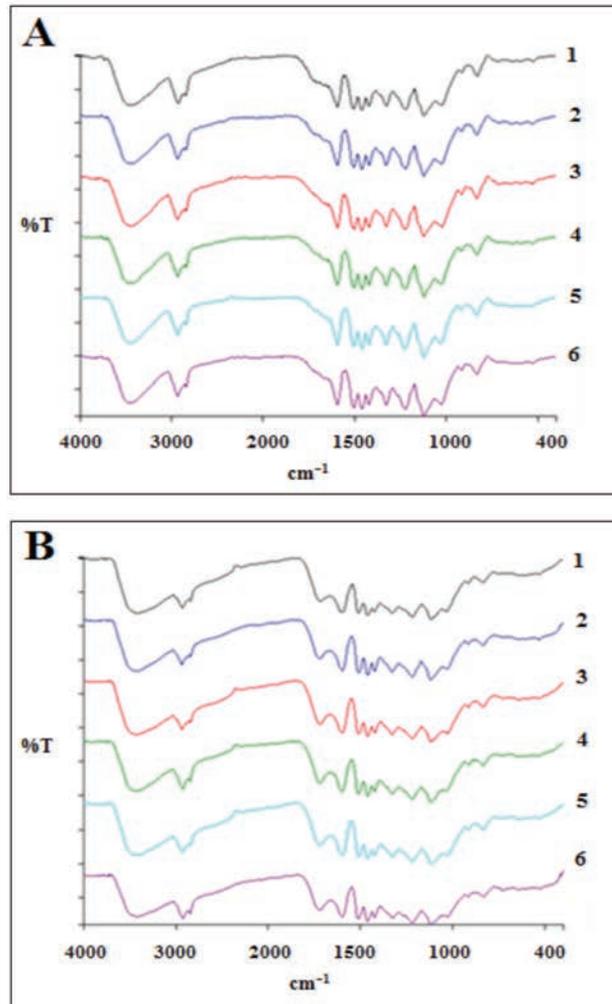
Figure 2. FTIR spectra of dioxane lignins isolated from (A) wood and (B) pulp. Samples 1, 2 and 3 corresponded to G1 and samples 4, 5 and 6 corresponded to G2.

^{31}P NMR

The lignins isolated from wood and pulps were subjected to ^{31}P NMR spectroscopy to determine the contents of phenolic and aliphatic hydroxyl groups associated with the lignin structure. A representative sample of the ^{31}P NMR is shown in figure 3. The integration zones for each structure were determined according to Wu and Argyropoulos (2003). The main structures with hydroxyl groups of the dioxane lignins determined by ^{31}P NMR were: OH-aliphatic, OH-syringyl (S-OH), OH-guaiacyl (G-OH), 5-5 biphenyl, OH-p-hydroxyl, OH-carboxyl and total phenolic hydroxyl (Ph-OH) groups. With S-OH and G-OH data, the syringyl/guaiacyl ratio was calculated (Table 4). The pulp yield was used as a ranking parameter and correlated with the lignin structural traits (Figure 4).
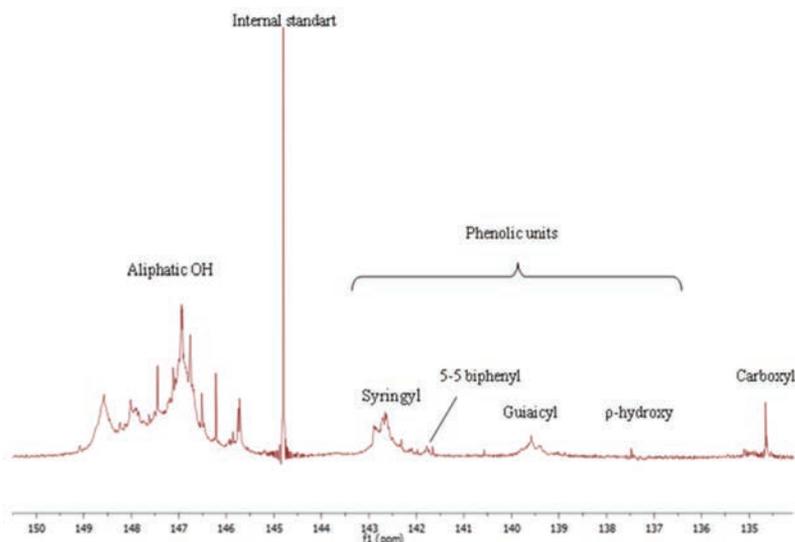
Figure 3. ^{31}P NMR spectrum representative for *Eucalyptus globulus* dioxane lignin (genotype 1).

Table 4. Hydroxyl groups (determined by ^{31}P NMR) and S/G ratio in dioxane lignins isolated from wood and pulps of *Eucalyptus globulus* genotypes.*

		OH aliphatic	OH syringyl	5-5 biphenyl	OH guaiacyl	OH ρ-hydroxyl	OH carboxyl	Total phenolic OH	S/G ratio
		Structures (mmol/g of lignin)							
Integration limits (ppm)		146,6-150	143,4-142,4	141,7-142,3	139,2-140,2	137-138	134,7-135		
Wood lignin	1	4,48	0,73	0,10	0,22	0,02	0,08	1,07	3,4
	2	3,91	0,72	0,11	0,22	0,03	0,03	1,08	3,3
	3	4,48	0,64	0,09	0,19	0,05	0,01	0,97	3,3
	4	3,81	0,58	0,14	0,25	0,02	0,01	1	2,3
	5	4,05	0,58	0,13	0,25	0,01	0,01	0,98	2,3
	6	4,11	0,59	0,14	0,29	0,01	0,01	1,03	2
Pulp lignin	1	2,77	0,68	0,31	0,26	0,06	0,22	1,31	2,6
	2	2,05	0,62	0,30	0,25	0,04	0,20	1,21	2,5
	3	2,47	0,70	0,30	0,26	0,05	0,13	1,31	2,7
	4	1,89	0,50	0,36	0,25	0,05	0,14	1,16	2
	5	2,25	0,49	0,33	0,24	0,05	0,15	1,11	2
	6	1,95	0,47	0,38	0,21	0,04	0,19	1,10	2,2

* The maximum standard error of the data was 1×10^{-2} mmol/g lignin.

High correlations were found for pulp yield *vs.* S-OH, (Fig. 4A), pulp yield *vs.* S-OH/G-OH ratio, (Fig. 4B) and pulp yield *vs.* 5-5 biphenyl, (Fig. 4D). Low correlation was found for pulp yield *vs.* G-OH units (Fig. 4C). High syringyl contents, as well as, high S/G ratio favored the lignin removal during kraft pulping promoting a faster delignification and less recondensation at the ending of the pulping (Sjöström 1993, Gellerstedt 2009). Regarding the condensed structures, the 5-5 biphenyl units are presented in smaller amounts in wood, however, have a negative correlation with the pulp yield (Fig. 4D) since decreased the delignification rate hindering lignin fragmentation (Sjöström 1993, Gellerstedt 2009). The total phenolic hydroxyl groups of dioxane lignins presented a poor correlation with pulp yield (data not showed), same behavior was reported by Guerra *et al.* (2008).

Kraft delignification occurs by modifying the structure of lignin mainly in two ways, the first mechanism is the degradation of lignin by cleaving interunits linkages by means of hydroxy and hydrosulfite anions, while the second is the introduction of hydrophilic groups making the degradation products more soluble in the cooking liquor (Sjöström 1993). These phenomena generated new free phenolic hydroxyl groups, as observed in the isolated lignin from pulp, when compared with lignins from wood (Table 4). Prinsen *et al.* (2013), indicated that a high content of phenolic hydroxyl groups in dioxane lignin in pulps is the result of high levels of β-O-4 bonds in wood lignin. This tendency is also observed in the Eucalyptus globulus genotypes of the present study as shown in figure 5 (r=0,92; p=0,008).

In lignins extracted from pulps it was observed an increase in the content of 5-5 biphenyl units that could be the responsible for the low yields of extraction with dioxane. Furthermore, the content of 5-5 biphenyl structures in residual lignin could also be associated with the content of G-units in lignin from wood, generating more condensed units during pulping. These results were also in agreement with the previously obtained (Aguayo *et al.* 2013), where samples from G2 showed an increase in the UV absorbance during the topochemical study of delignification. Furthermore, the increase of condensed structures in the residual lignin could also have an effect on the subsequent bleaching process, as observed by Pinto *et al.* (2005).
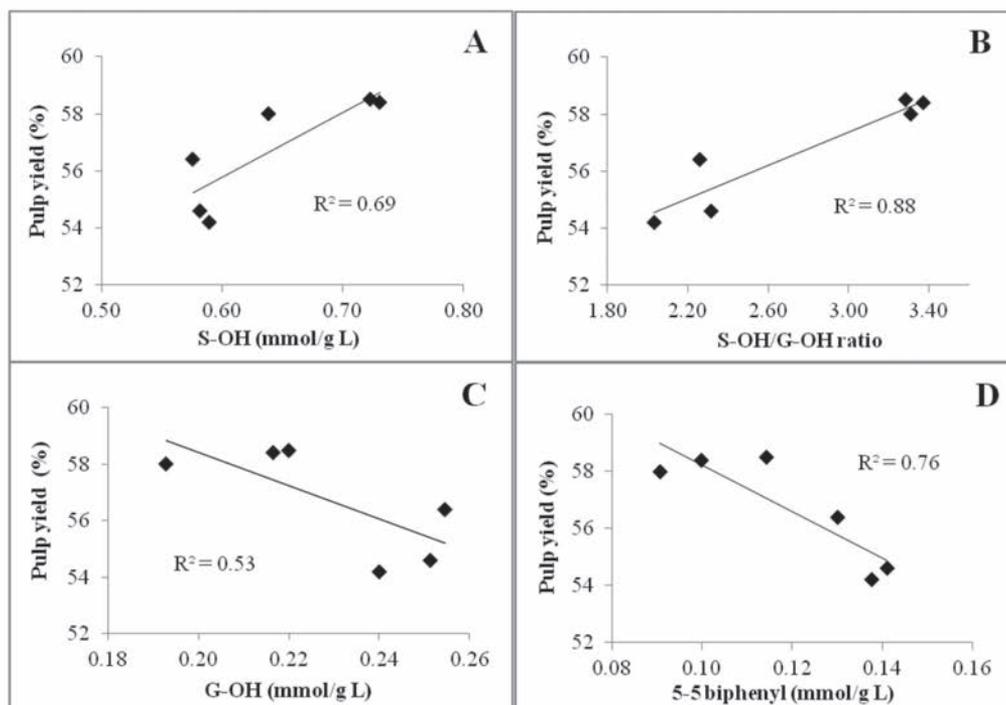

Figure 4. Relationship between pulp yield and (A) S-OH, (B) S/G ratio, (C) G-OH and (D) 5-5 biphenyl units of dioxane lignins isolated from *Eucalyptus globulus* wood. The maximum standard error for pulp yield is 0,5% and for lignin features is lower than 1×10^{-2} mmol/g lignin.
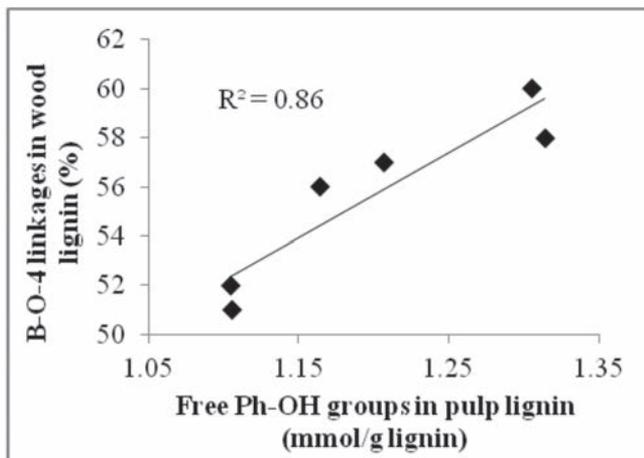
Figure 5. Relationship between β-O-4 linkages in lignin from wood and free phenolic hydroxyl groups in lignin from kraft pulps of *Eucalyptus globulus* genotypes. The maximum standard error for B-O-4 linkages is 3% and for free OH groups is lower than 1×10^{-2} mmol/g lignin.

CONCLUSIONS

The analysis of dioxane lignins isolated from wood and kraft pulps of *Eucalyptus globulus* genotypes revealed structural features of the macromolecule that contributed to explain the contrasting pulpwood characteristics. The main structures that differentiated the two groups and with high correlation with the pulp yield were the content of S-units and S/G ratio. More condensed units (5-5 biphenyl) had a negative impact on pulp yield. These results showed that the structure of lignin in genotypes of a single species also plays a key role in pulp yield and should be considered as a parameter for the selection and improvement of the species in commercial plantations for pulp production.

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