

Composition and structure of organosolv lignins from four eucalypt species

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Abstract Lignins were extracted from different species using organosolv process (ethanol/water). Obtained organosolv lignins were characterised by various methods to determine their composition, structure and functional groups with the purpose of evaluating their potential use for obtaining value-added compounds. The purity of organosolv lignins was determined. The total phenols content and the antioxidant power were analysed in order to know the reactivity of lignins. The ratio S/G was determined by nitrobenzene oxidation. In addition, molecular weight distribution, infrared spectroscopy and thermo gravimetric analysis were carried out in order to determine the physical and chemical properties of organosolv lignins. Obtained organosolv lignins have very high purity and low sugar and inorganic contamination. All organosolv lignins samples have high polydispersity, and lignin from grey ironbark wood had the highest molecular weight average. Among the organosolv lignins, lemon-scented gum showed the highest average value of S/G ratio and the lowest average value of total phenols.

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Introduction

Wood is a lignocellulosic material with many applications due to its characteristics and availability (Abdul Khalil et al. 2011). Wood from eucalypt species is one of the mostly used raw materials in the industry due to the high productive capacity and adaptability to distinct sites. According to Brazilian Association of Forest Plantation Producers (ABRAF 2012), Brazilian eucalypt plantations in 2011 represent approximately 4,873,952 ha, of which most of the production is destined for pulp and paper industry.

One of the main wood components is lignin, which is defined as an amorphous polyphenolic material created through enzymatic polymerisation of the three monomers, coniferyl, sinapyl and p-coumaryl alcohols (Stephen and Carlton 1992; Pelaez-Samaniego et al. 2013). The separation of wood components is related to chemical pulping, which is performed through a delignification process. Lignin is considered as a side product in the process of pulp and paper production and is used for generating energy required by the process. The extracted lignin in the pulping process is estimated at over 70 million tons per year, and <2 % is used as chemical product (Lora 2008).

However, the use of lignin for the synthesis of new polymeric materials is a great alternative to its revalorisation. Several works reported on the use of lignin in phenolic resin (Jin et al. 1990; Sarkar and Adhikari 2000; Tejado et al. 2007; Cavdar et al. 2008), in polyethylene oxide/organosolv blends (Kubo and Kadla 2004), as emulsifier (Boeriu et al. 2004) and in rigid polyurethane foam (Li and Ragauskas 2012). Lignin could be also used as a promising precursor for the production of chemicals (Toledano et al. 2010).

Currently, organosolv pulping processes are the most eco-friendly method for the fractionation of lignocellulosic materials and obtaining of value-added products (lignin and hemicelluloses) besides high quality cellulose pulp. According to a study on the production of fermentable sugars from lignocellulosic materials by Hidenó et al. (2013), organosolv treatment with alcohol reduced the treatment time while increasing the final sugar yield from enzymatic hydrolysis. According to Araque et al. (2008), by using an organosolv process a considerable part of the lignin was separated from the pulp, mainly cellulose. Li and Ragauskas (2012) affirmed that the lignin from organosolv process is industrially interesting due to its lower molecular weight, and it is a sulphur-free product. The conversion of biorefinery lignin into value-added co-products could help to reduce the costs of production of biofuels, but this application of lignin is still a challenge (Araque et al. 2008).

The new classification of eucalyptus proposed by Brooker (2000) based on comparative morphology has incited the discussion about the inclusion or not of lemon-scented gum in the *Corymbia* genus. In the present work, wood chemistry and lignin from different eucalypt species and *Corymbia* species were analysed in order to identify possible differences in these properties, which could significantly affect final uses of these products. In this context, this study aimed to characterise the composition and structure of organosolv lignins from three different eucalypt species and compare with lemon-scented gum lignin obtained through organosolv process. The raw material, black liquor and obtained organosolv lignins were

characterised using several analytical techniques such as ATR-IR, GPC described by Glasser et al. (1993) as an excellent method for acetylated lignin, TGA, antioxidant power and phenolic composition for alkaline nitrobenzene oxidation.

Materials and methods

Raw material

Sixteen trees—four trees for each species of bangalay (*Eucalyptus botryoides* Sm), grey ironbark (*Eucalyptus paniculata* Sm), forest red gum (*Eucalyptus tereticornis* Smith) and lemon-scented gum (*Corymbia citriodora* Hook) were harvested from a homogeneous population located in Southern Brazil (29°57'17"S 51°37'31"W). Disks were cut at DBD height (1.30 m) from four trees of each species and were then placed in a climatic chamber at 20 °C and 65 % of relative humidity in order to obtain equilibrium moisture content (~12 %). Then, all the disks were milled in a knife mill (40 mesh) to prepare the samples for the experiments.

Raw material characterisation

Milled raw material from each of the four species were chemically characterised according to established standard methods TAPPI (2007): moisture content (TAPPI 412 om-94), ash content (TAPPI 211 om-93), ethanol-toluene extractives (TAPPI 204 cm-97), solubility in 1 % sodium hydroxide (TAPPI 212 om-98), solubility in hot water (TAPPI 207 om-93), Klason lignin (TAPPI 222 om-98), holocellulose (Wise et al. 1946) and α -cellulose (TAPPI 203 om-93).

Organosolv delignification

Delignification reaction was performed using the organosolv process described by García et al. (2010). Each experiment was carried out with ethanol/water (60/40 % volume) and a 1:10 solid/liquid ratio in a stirred reactor at 180 °C for 90 min. The solid fraction was separated from the liquid fraction by filtration and then cellulose pulp was washed with ethanol/water solution (60/40 % volume) and then with water. Finally, cellulose pulp was dried in an oven at 100 ± 3 °C for 24 h in order to prepare the material for its characterisation. The cellulose pulp was characterised using the methods mentioned above for raw material characterisation.

Composition of black liquor

The physical and chemical properties of obtained black liquor were determined. Inorganic matter was determined after combustion of the sample at 525 °C using a method based on TAPPI T211 om-93 to determine the ash content. Organic matter was determined by the difference between total dissolved solids and inorganic matter. Dry matter was determined using a method based on TAPPI T264 cm-97 to determine the moisture content in the raw material. PH was determined with a

digital SELECTA pH-meter “pH-2005”. Density in (g/mL) was determined by measuring the weight of the black liquor in a known volume previously weighed. Lignin content was determined by a gravimetric method after that lignin has been isolated from the black liquor by precipitation with an aqueous solution of sulphuric acid (72 % w/w).

Composition and characterisation of lignin

In the precipitation process of organosolv lignins, the black liquor was diluted in 1.5 volumes of water acidified to pH 2 with the sulphuric acid (72 % w/w) method described by Alriols et al. (2010). Moisture content, ash content and acid insoluble lignin, the latter using a method described by Toledano et al. (2013), were determined for the organosolv lignin samples obtained.

Acid-soluble lignin was determined using a Jasco V-630 spectrophotometer UV–VIS. The filtrated material was diluted in an aqueous solution containing H₂SO₄ 1 M until the absorption of the samples was between 0.1 and 0.8 nm. The solution absorbance was measured at 205 nm.

The content of main sugars (glucose, xylose and arabinose) was determined by HPLC technique. To achieve this, filtrated liquid from Klason lignin tests was analysed.

The infrared spectroscopy was done through attenuated total reflectance (ATR-IR) by direct transmittance in a single-reflection ATR System (ATR top plate fixed to an optical beam condensing unit with Zn Se lens) with an MKII Golden Gate SPECAC instrument. Spectrum data were 30 scans in a range of 4,000–600 cm⁻¹ and resolution of 4 cm⁻¹.

The thermo gravimetric analysis was performed in order to obtain the organosolv lignin degradation profile with temperature. To achieve this, Mettler Toledo equipment was configured to measurements between 25 and 800 °C at a constant heating rate of 10 °C min⁻¹ under a constant inert atmosphere of nitrogen (N₂). Organosolv lignins were subjected to high performance size exclusion chromatography (HPSEC) to evaluate lignin molecular weight (MW) and MW distribution (MWD) using a JASCO instrument equipped with an interface (LC-NetII/ADC) and a reflex index detector (RI-2031Plus). Two Polar Gel-M columns (300 × 7.5 mm) and Polar Gel-M guard (50 × 7.5 mm) were employed. Dimethylformamide +0.1 % lithium bromide was the eluent. The flow rate was 0.7 mL/min, and the analyses were carried out at 40 °C. Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 70,000 to 266 g/mol.

The total phenols content in organosolv lignins samples were determined using a method described by García et al. (2010) and Amendola et al. (2010). To achieve this, a volume of 2.5 mL Folin–Ciocalteu reactive and 5 mL of 20 % Na₂CO₃ solution was mixed with 0.5 mL of lignin solution (20 mg in 10 mL of DMSO). The mixture was kept for 30 min at 40 °C before measuring the absorbance at 750 nm. The intensity of blue colour was measured at 750 nm in a UV–VIS spectrophotometer, and the total phenols content was determined using a standard curve with gallic acid solutions.

The antioxidant power of organosolv lignin samples as the lignin capacity to reduce ABTS radical was measured through a spectrophotometric method described by Amendola et al. (2010) and García et al. (2012) using a UV–VIS spectrophotometer. The chemical composition of the phenolic and carboxyl groups was determined as described by Toledano et al. (2013).

Phenolic composition was determined by alkaline nitrobenzene oxidation according to the method described by Nadji et al. (2009). The oxidation products were analysed by JASCO HPLC instrument equipped with an interface (LC-Net II/ADC) and a photodiode array detector (MD-2018). Teknokroma Mediterranean sea 18 column (25 × 0.46 cm) was used for the experiments and a mixture of acetonitrile and water (1:8, m/m) with 1 % acetic acid mobile phase was used. The flow rate was 0.5 ml/min, and the analyses were conducted at 40 °C. Calibration was performed using pure compounds patterns (Sigma-Aldrich) vanillic acid, syringic acid, p-hydroxybenzoic acid, p-hydroxybenzaldehyde, vanillin, syringaldehyde, acetovanillone and ferulic acid.

Data analysis

The collected data were assessed using descriptive statistics and analysis of variance ($p < 0.05$). When the null hypothesis was rejected, the average values were compared with Tukey test at the level of significance of 5 %.

Results and discussion

Raw material characterisation

Table 1 describes the chemical characterisation of the raw material and cellulose pulp from each species studied.

Grey ironbark showed highest mean value of Klason lignin both in the raw material and the cellulose pulp, which was higher than the results found by Rencoret et al. (2007). Moreover, Klason lignin in cellulose pulp was lower than in the raw material for all species, which confirmed the significant elimination of lignin during the organosolv delignification process (Alriols et al. 2009).

Composition of the black liquors

As observed in Table 2, all properties of the black liquor from organosolv delignification showed a significant difference, except inorganic matter and density. The lignin content varied between 17.25 and 30 %, where bangalay showed the highest value, approximately 42 % higher than the value found for black liquor from lemon-scented gum.

Table 1 Chemical composition of raw material

Parameter (%)	Bangalay		Forest red gum		Grey ironbark		Lemon-scented gum	
	R.M.	Cellulose pulp	R.M.	Cellulose pulp	R.M.	Cellulose pulp	R.M.	Cellulose pulp
Ash	0.15 ± 0.02a	0.24 ± 0.04a	0.23 ± 0.04a	0.32 ± 0.01a	0.23 ± 0.1a	0.27 ± 0.02a	0.64 ± 0.1b	0.82 ± 0.09b
Extractives	2.2 ± 0.4ab	3 ± 1a	1.1 ± 0.3a	5.7 ± 0.7b	2.9 ± 0.6b	3.9 ± 0.4ab	4.4 ± 0.4c	5.8 ± 0.3b
Water solubility	5.6 ± 0.8a	6.2 ± 0.8a	5.4 ± 0.6a	6.0 ± 0.5a	6.5 ± 0.6a	7.0 ± 0.2a	5.6 ± 0.3a	5.7 ± 0.5a
NaOH solubility	17.2 ± 0.9c	10.9 ± 0.4b	18.22 ± 0.06c	11.1 ± 0.1b	15.0 ± 0.5b	8.4 ± 1a	12.9 ± 0.6a	8.1 ± 0.3a
Klason lignin	28 ± 1ab	17.9 ± 0.5ab	32.4 ± 2.9bc	17.9 ± 0.9a	36.7 ± 0.9c	21.2 ± 2.2b	25.3 ± 0.7a	18.1 ± 0.8ab
Holocellulose	59.6 ± 0.6c	74.3 ± 0.9a	55.4 ± 1.6b	74.8 ± 0.8b	52 ± 1a	74.6 ± 0.9b	55.9 ± 0.5b	76.4 ± 0.3b
Cellulose	42 ± 2ab	58 ± 6a	40.1 ± 0.3a	63.5 ± 0.5a	43.3 ± 1.2b	63.02 ± 0.06a	41.2 ± 0.6ab	61.2 ± 0.9a
Hemicelluloses	16.7 ± 1.9b	16.2 ± 6.3a	15.4 ± 1.3b	11.3 ± 0.5a	8.9 ± 0.2a	11.5 ± 0.06a	14.7 ± 0.7b	15.1 ± 0.7a
Pulp yields*	–	58.7	–	58.3	–	60.5	–	60.8

Mean values in the same line for the same material (raw material or cellulose pulp) followed by the same letter are not statistically different at level of 5 % by the Tukey test

* Referred to the content of dry raw material (w/w)

Table 2 Characterisation of black liquor

Parameter	Bangalay	Forest red gum	Grey ironbark	Lemon-scented gum
Inorganic matter (%)*	0.03 ± 0.01a	0.016 ± 0.003a	0.4 ± 0.6a	0.0083 ± 0.0004a
Organic matter (%)*	2.87 ± 0.03a	3.5 ± 0.3ab	5 ± 1b	3.4 ± 0.2ab
Dry matter (%)	2.91 ± 0.02a	3.54 ± 0.28a	5.21 ± 0.56b	3.4 ± 0.2a
pH	4.08 ± 0.02b	3.99 ± 0.02c	3.90 ± 0.029a	4.24 ± 0.04d
Lignin (%)*	30.1 ± 0.7b	25 ± 2ab	19.62 ± 0.92a	17.2 ± 0.8a
Density (g mL ⁻¹)	0.9100 ± 0.0007a	0.900 ± 0.001a	0.9000 ± 0.0001a	0.910 ± 0.002a
Total solids (g/L)	13.30	11.33	18.22	13.32

* % in dry matter (p/p); mean values in the same line followed by the same letter are not statistically different at level of 5 % by the Tukey test

Composition and structure of lignin

Table 3 shows the mean values of the parameters analysed in order to characterise lignin composition.

Among the sugars, only glucose and xylose were detected; both sugars were statistically different between species. The highest content of glucose and xylose was found in lignin from lemon-scented gum. Grey ironbark was the most impure lignin when compared to lignin from other species because it showed the lowest total lignin content.

In general, all the spectra from 4,000 to 600 cm⁻¹ (Fig. 1) showed the same typical peaks of the organosolv lignins. However, some differences in relative intensity of the peaks were observed.

The peak at 1,712 cm⁻¹ is referred to conjugated carbonyl vibration. Many peaks related to functional groups present in lignin were found, such as 1,592 cm⁻¹ which is related to aromatic skeletal vibrations and (C=O)stretching. The peak at 1,510 cm⁻¹ is related to aromatic skeletal vibration and 1,456 cm⁻¹ to methyl and methylene groups. The peaks found at 1,328 and 1,271 cm⁻¹ correspond to the syringyl and guaiacyl condensed vibration. Peaks common in both lignin and cellulose were found at 1,420, 1,111 and 1,030 cm⁻¹. Moreover, a peak at 830 cm⁻¹ and a shoulder at 1,159 cm⁻¹ representing G and S units (Kline et al. 2010) were observed.

Table 4 shows the thermal properties of different organosolv lignins. The process of lignin degradation is characterised by three regions. The first region is between 80–100 °C and corresponds to the loss of moisture content. The second region at 150–280 °C is related to the degradation of hemicelluloses. The third region was found between 280–400 °C and corresponds to the lignin degradation.

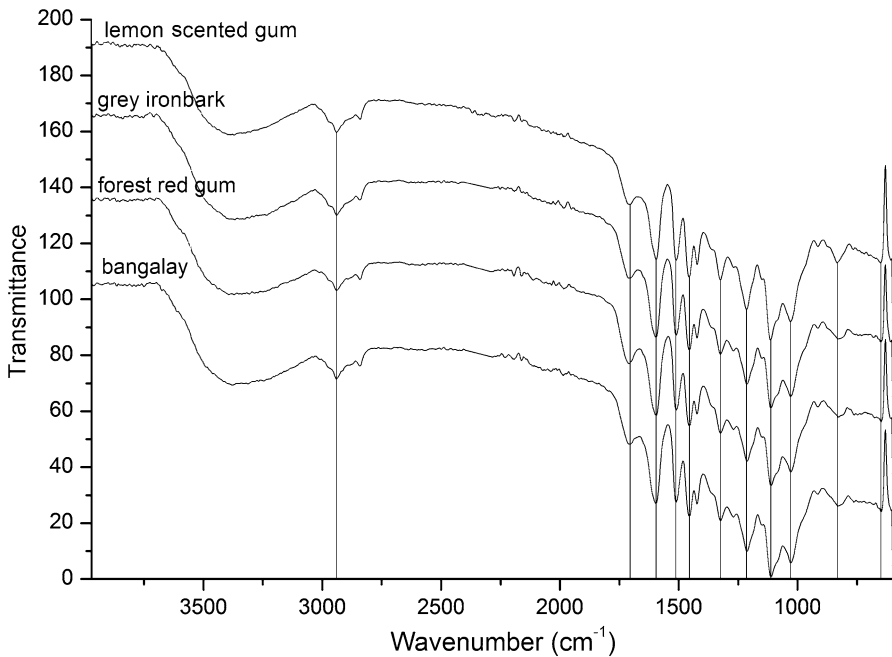
The lignin from lemon-scented gum showed narrowest peak at 350 °C when compared to other samples.

Moreover, a high residual mass (37–43.5 %) was observed for all organosolv lignins from three *Eucalyptus* species and *Corymbia* species. According to García et al. (2011), a high percentage of residual mass is related to a high thermal stability,

Table 3 Characterisation of lignins from four eucalypt species

Parameter	Bangalay	Forest red gum	Grey ironbark	Lemon-scented gum
Ash content (525 °C)	0.6 ± 0.2ab	0.150 ± 0.009a	1.1 ± 0.5b	0.4 ± 0.1ab
Ash content (800 °C)	0.41 ± 0.07ab	0.120 ± 0.001a	1.0 ± 0.5b	0.2 ± 0.1a
Glucose	0.21 ± 0.01b	0.10 ± 0.01a	0.090 ± 0.002a	0.62 ± 0.01c
Xylose	0.89 ± 0.02a	0.87 ± 0.03a	1.09 ± 0.06b	1.69 ± 0.02c
Arabinose	ND	ND	ND	ND
Insoluble lignin	82.5 ± 0.9b	89.20 ± 0.60b	73 ± 2a	87.1 ± 0.2b
Soluble lignin	0.9 ± 0.1a	0.90 ± 0.04a	1.6 ± 0.2b	1.2 ± 0.3ab
Total lignin	83 ± 1b	90.1 ± 0.5b	75 ± 2a	88.3 ± 0.1b

ND not detectable; mean values in the same line followed by the same letter are not statistically different at level of 5 % by the Tukey test

**Fig. 1** ATR-IR spectra of lignin from four eucalypt species

i.e. a more complex three-dimensional structure. Decrease in residual mass with increasing xylose content (see Table 3) was observed. Higher xylose content means lower residual mass (see Tables 3, 4), which is related to the linear structure of xylose and its thermal instability. According to Xu et al. (2007), degradation of hemicelluloses occurs at low temperatures (220–315 °C) because they are amorphous and have random structure. Thus, lignin with a low percentage of

Table 4 Thermal properties of different lignins

	DTmax (°C)	Peak temperature (°C)	Weight loss (%)	Residue (%)	Mass loss rate at DTmax (%/°C)
Bangalay	355.43	71.5	3.0	43.5	0.00243
		189.5	3.1		
		350.6	50.4		
Forest red gum	354.05	80.6	2.7	43.4	0.00250
		174.5	3.6		
		357.8	50.3		
Grey ironbark	358.18	71.7	3.6	42.6	0.00232
		175.0	3.9		
		217.6	2.6		
		358.0	23.6		
		481.4	23.7		
Lemon-scented gum	351.19	69.1	3.0	37.93	0.00371
		167.9	5.5		
		350.9	53.6		

Table 5 Weight average (M_w), number average (M_n) and polydispersity (M_w/M_n) of lignins from four eucalypt species

	M_w	M_n	M_w/M_n
Bangalay	8,848	2,052	4.31
Forest red gum	8,444	1,745	4.84
Grey ironbark	10,193	1,916	5.32
Lemon-scented gum	8,604	1,534	5.61

xylose could be considered purer and, consequently, presents more difficulty to be thermally degraded, which means a great residual mass.

Table 5 shows the molecular weight average (M_w), number average (M_n) and polydispersity (M_w/M_n) of different organosolv lignins.

M_w , M_n and M_w/M_n of organosolv lignins from all the species were significantly different. The highest M_w (10,193) was found for lignin from grey ironbark, while the lowest average value was 8,444 for lignin from forest red gum. M_w of lignin from forest red gum was similar to that found by Guerra et al. (2008) for lignin from *Eucalyptus globulus* (8100). According to Lora (2008), organosolv treatments produce low molecular weight lignin.

Table 6 shows the total phenols content as a percentage of gallic acid equivalents of different organosolv lignin. According to Barclay et al. (1997), damages in free radical peroxidation in lignin-containing pulps and paper could be avoided by the presence of phenolic groups.

In this study, the results found for lignin from lemon-scented gum presented the lowest value of total phenols content, while the highest value was found for forest

Table 6 Total phenols content in the lignins from four species

	EAG/100 g Lig. (%) [*]
Bangalay	48.4
Forest red gum	50.2
Grey ironbark	46.7
Lemon-scented gum	34.4

^{*} Total phenols content in the lignin expressed as % gallic acid equivalents

Table 7 Antioxidant power of lignins from four species

	Inhibition ABTS (%) [*]
Grey ironbark	94.8
Bangalay	94.6
Forest red gum	94.6
Lemon-scented gum	94.9

^{*} Antioxidant power expressed as a percentage of decrease of ABTS radical

red gum. Decrease in sugars content with increasing total phenols content (see Table 3) was observed, which was expected. Vázquez et al. (2012) have extracted a total phenols content of 21.9 g GAE/100 g from eucalyptus bark using slightly alkaline aqueous solutions, the value being much lower than found in this study.

The increase in the content of the residue TGA was proportional to the increased content of phenolic. This effect can be explained by the difference in structure, because the presence of a phenolic structure associated with the high number of conjugated double bonds lead to formation of self-condensed aromatic structures, which have a lower amount of H and O in the sample and hence suffer less weight loss. For TGA, analysis was carried out under N₂ (inert atmosphere). Thus, only O and H are lost during mass degradation. The inorganic residues of lignins remained between 37 and 44 %. According to Tejado et al. (2007), in the TGA analysis after heating to 800 °C, 40–50 % by weight of lignin are not volatilised due to the formation of condensed aromatic structures.

Antioxidant properties based on antioxidant power of lignins from different species are shown in Table 7.

The results obtained in this study are similar to those reported by García et al. (2010). All the lignins presented the antioxidant power between 94 and 95 %.

According to Ugartondo et al. (2008), free phenolic hydroxyl groups are essential for the antioxidant activity and aliphatic hydroxyl groups have a negative relationship with the antioxidant power of lignin. High molecular weight could be one of the main factors that influence the activity of caption of free radical. Moreover, heterogeneity of lignins varies with the isolation method used. Pan et al. (2006) affirmed that high molecular weight, heterogeneity and polydispersity (M_w/M_n) reduce the activity of free radical catching. The authors also reported that low molecular weight causes an extensive lignin depolymerisation, which results from the formation of new aromatic hydroxyl groups, the centre to trap radicals.

Table 8 Yields (% wt/wt) of the detected phenolic acids and aldehydes compounds released from the lignins alkaline nitrobenzene oxidation

	Bangalay	Forest red gum	Grey ironbark	Lemon-scented gum
Vanillic acid	0.47	0.29	0.14	1.36
Syringic acid	0.85	0.35	0.15	0.03
4-Hydroxybenzaldehyde	ND	ND	ND	ND
Vanillin	20.48	15.52	28.78	4.61
Syringaldehyde	37.00	36.12	58.94	25.43
4-Hydroxybenzoic acid	ND	ND	ND	ND
Acetovanillone	0.55	0.43	0.81	0.25
Ferulic acid	ND	ND	ND	ND
Total	59.35	52.72	88.82	31.68
S/G ratio	1.76	2.24	1.99	4.09

S corresponds to the sum of syringic acid and syringaldehyde yields; G to the sum of vanillic acid, vanillin, and acetovanillone yields; *ND* not detected

The analytical techniques for quantification of the lignin are very complex due to bonds heterogeneity. As observed in Table 8, the results of nitrobenzene oxidation were similar for the organosolv lignins from bangalay and forest red gum, which was observed in the aforementioned analyses.

Nitrobenzene oxidation analysis of all lignins produced the highest quantities of vanillin, syringaldehyde and showed the absence of 4-hydroxybenzaldehyde and 4-hydroxybenzoic acid, indicating that the studied lignins belong to the GS type (typical of hardwood). The highest S/G ratio (4.09) was found in the lignin from lemon-scented gum, which was 45–57 % higher than values of other organosolv lignins. These values were similar to those reported by Lima et al. (2008), who found S/G ratio between 2.0 and 3.2 for lignins from five eucalypt species.

Conclusion

The organosolv delignification did not influence the antioxidant power of the lignins studied. All the organosolv lignins showed signals of contamination, whereby lignin from grey ironbark wood presented the highest level of contamination, mainly due to its high molecular weight and low total lignin content. All the organosolv lignins were characterised as GS type. The lowest total phenols content was found in the lignin from lemon-scented gum, which showed the highest content of contaminant sugars. Nevertheless, composition of lemon-scented gum wood was similar to that found for the other eucalypt species analysed in this study, which does not justify the modification of the genus as a function of chemical composition.

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