

## EVALUATION OF CHEMICAL COMPOSITION AND LIGNIN STRUCTURAL FEATURES OF *SIMAROUBA VERSICOLOR* WOOD ON ITS PULPING PERFORMANCE

Teresa Cristina F. Silva,<sup>a,\*</sup> José Lívio Gomide,<sup>a</sup> and Ricardo Balleirini Santos<sup>b</sup>

*Simarouba versicolor* wood was evaluated relative to its kraft pulping ability and compared with *Eucalyptus urograndis* wood. Comprehensive chemical analysis of wood and milled wood lignin (MWL) was performed, aiming to correlate wood and lignin structural features with kraft pulping response. Wood characterization of *S. versicolor* revealed higher lignin content (37.3%) and lower cellulose content (45.1%) than *E. urograndis*. <sup>13</sup>C NMR spectroscopy was performed to characterize MWL, and the results showed a lower syringyl to guaiacyl ratio (S/G), higher degree of condensation, and lower β-O-4 linkages for *S. versicolor*. The gross heating value of *S. versicolor* was slightly higher than that for *E. urograndis*. Significant variations were observed in chemical charge demand and in pulping yield for the two species. This behavior was attributed mainly to the S/G ratio and degree of condensation of the lignin, although total and insoluble lignin, as well as cellulose contents may have affected pulping efficiency too.

**Keywords:** *Simarouba versicolor*; Milled wood lignin; Kraft pulping; <sup>13</sup>C NMR

**Contact information:** Laboratório de Celulose e Papel, Departamento de Engenharia Florestal, Universidade Federal de Viçosa, Viçosa, MG, 36570-000 Brazil; b: Department of Forest Biomaterials, North Carolina State University, Raleigh, NC, 27695-8005 USA;

\* Corresponding author: [teresa.silva@ufv.br](mailto:teresa.silva@ufv.br)

### INTRODUCTION

The *Simarouba* genus grows throughout Brazil, especially in the Northeast region. Species belonging to the *Simaroubaceae* family are commonly used as a source for pharmaceutical and insecticidal applications. Its potential as a renewable resource to generate biomaterials has not yet been exploited. For instance, the abundance and fast growth of the *Simarouba versicolor* species in Brazil may justify its use as a raw material for pulp and paper making. Currently, *Eucalyptus urograndis* wood is probably the most widely planted eucalyptus clone in Brazil for pulp and paper production, and it has been extensively used in forest improvement programs. Therefore, *E. urograndis* was used in this study for comparison purposes.

Many studies have already demonstrated the dependency of wood's chemical composition with pulping performance and yield (Collins *et al.* 1990; Fengel and Wegener 1984; Khiari *et al.* 2010; Lawoko *et al.* 2005; Miranda and Pereira 2002; Pilate *et al.* 2002; Pinto *et al.* 2005; Rydholm 1967), although in some cases, the lack of a complete wood chemical characterization may lead to inconclusive interpretations.

It is well known that wood for pulping must meet certain requirements, such as species suitability for pulping and fiber morphology. Besides, pulping performance is highly dependent on the relative abundance, structure, and reactivity of wood components, mainly cellulose, hemicellulose, and lignin. Lignin reactivity is considered the major obstacle to wood pulping efficiency, and emphasis has been given to determine the ratio of syringyl (S) to guaiacyl (G) structures (Bose *et al.* 2009; Gomide *et al.* 2005; Tsutsumi *et al.* 1995), although some investigations have indicated that besides S/G, other lignin structural features are also important to predict pulping yield (Guerra *et al.* 2008).

Kraft pulping is the most widely employed process for wood chemical pulps production, and it is extensively applied for eucalypts species. Hardwood species that are used industrially for kraft pulping and paper production present considerable variability toward wood properties and industrial processing behavior. *Eucalyptus*, *Acacia*, and *Betula pendula* are among the hardwood species most important in terms of kraft pulping processing worldwide, even though the kraft process can accept a wide variety of wood types.

During pulping, the alkaline media degrades and dissolves lignin extensively (90 to 95%), resulting in separation between individual wood fibers. Thus, lignin chemical structure plays a crucial role in determining pulping ability and efficiency. It has been reported that lignin's chemical features influence the pulping characteristics of different eucalyptus clones (Guerra *et al.* 2008). Because the lignin structure can be built from more than one kind of unit, *i.e.* syringyl, guaiacyl, and H-type phenyl propane, lignin structure exhibits a seemingly random, highly polydispersed, highly cross-linked polymeric network characterized by monomeric phenylpropane units cross-linked through ether linkages and carbon-to-carbon bonds.

In the present study, wood chemical characterization, as well as milled wood lignin (MWL) of *Simarouba versicolor* and *Eucalyptus urograndis* wood species were investigated with respect to their structural features, aiming to find a correlation between chemical structures and pulping performance, considering Brazil's most pulped species, *i.e.* *E. urograndis*, as a reference.

## EXPERIMENTAL

Hardwood species *Simarouba versicolor* and *Eucalyptus urograndis* were chemically characterized and evaluated by means of kraft pulping, gross heat of combustion, and CHNO analysis in order to determine their suitability for pulping and energy combustion. Isolated milled wood lignins (MWL) from both hardwood species were obtained, and their structures were quantitatively characterized by <sup>13</sup>C NMR technique.

### Materials

*E. urograndis* and *S. versicolor* wood samples were obtained from Bahia and Goiás State (Brazil), respectively. MWL was isolated by means of a slightly modified Björkman procedure (Björkman 1956), described as follows: 40- to 60-mesh wood

sawdust fraction from appropriate wood chips was extracted with 0.3% NaOH solution for one hour (liquid:wood ratio = 50:1) under reflux. The extracted wood was thoroughly washed with distilled water until the filtrate reached neutral pH, and then it was dried at 30°C under vacuum. Alkaline extracted wood sawdust was ball milled using a planetary ball mill (Pulverisette 7, Fritsch). After the necessary milling time achieved a 30% yield, the wood sawdust was suspended in 96:4 dioxane:water (v:v) and agitated for 12 hours at 40°C. The mixture was centrifuged and the liquid phase collected. This operation was done in triplicate. The filtrates were combined, rotatory-evaporated to remove the solvents, and finally dried in a vacuum oven. No purification step was necessary because the lignin isolated from the alkaline extracted wood had a low sugar content (<3%).

### Chemical Analyses

Wood chemical analyses were run on sawdust and screened according to TAPPI T257-cm85 standard procedure. Wood basic density, total extractives, acid insoluble lignin, acid soluble lignin, lignin S/V ratio, sugar composition, total uronic acids, and acetyl groups were measured according to SCAN CM-46:92, TAPPI T264 CM-97, TAPPI T222 OM-98, TAPPI UM 250, Chen (1992), Wallis *et al.* (1996), Scott (1979), and Sólár *et al.* (1987).

Carbohydrate composition was determined by high performance liquid chromatography combined with pulse amperometric detection after acid hydrolysis. Wood sawdust and milled wood lignin were first pre-hydrolyzed by 72% (w/v) sulfuric acid at 30°C for 1 hour followed by sulfuric acid (3.5% w/v) catalyzed hydrolysis at 120°C for 1 hour. The resulting solutions were diluted with ultra-pure water to the desired concentration and filtered through a 0.45µm nylon filter (Millipore, Billerica, MA) before chromatography analysis. They were then analyzed by using a Dionex ICS 3000 IC system equipped with a CarboPac PA1 cartridge. The mobile phase was 0.3 M sodium hydroxide, and all analyses were conducted with a column temperature of 27°C.

### Gross Heat of Combustion and CHNO-Elemental Analysis

The higher heating values of extractive-free wood sawdust were determined by weighing approximately 0.5 g of wood sawdust and burning the samples in an automatic adiabatic calorimeter (Parr 6300, Moline Illinois). The samples were oven-dried prior to analysis to avoid moisture content effect.

The CHNO-elemental analyses were carried out on extracted-free wood sawdust. The samples were dried at 103°C, and the elemental analyses were performed with a LecoTruSpec® Micro Series.

### Kraft Pulping

Laboratory-made wood chips were air-dried to 20% moisture content. Kraft pulping of wood chips was carried out in a rotating digester equipped with four cylindrical reactors of 2 liters capacity each (Regmed, Brazil). Before heating, the digester was loaded with 250 g of wood chips (dry weight basis) and cooking liquor at a 1:4 ratio (w/v). The pulping liquor concentration contained sufficient quantities of NaOH and Na<sub>2</sub>S to provide 30% sulfidity, and active alkali concentrations were adjusted to reach kappa numbers ranging from 15 to 20. Heating time required to raise the temperature to

165°C was 60 minutes, and once this temperature was reached it was maintained for an additional 60 minutes. Cooking yields were measured gravimetrically.

### <sup>13</sup>C-NMR of the isolated lignin

<sup>13</sup>C-NMR spectra of the lignin preparations in DMSO-*d*<sub>6</sub> were recorded on a Bruker AVANCE 500 MHz spectrometer at 300 K using a 90° pulse width, a 1.4 s acquisition time, and a 1.7 s relaxation delay. Chromium (III) acetylacetonate (0.01 M) was added to the lignin solution to provide complete relaxation of all nuclei. A total of 20,000 scans were collected. The integral over the spectral 162 to 102 ppm region was set as the reference, assuming that it included six aromatic carbons and 0.12 vinylic carbons. In this way, the integral values divided by 612 would give results equivalent to a hundred aromatic rings (Ar). The integral range related to the signal assignment in the <sup>13</sup>C NMR spectrum of nonacetylated and acetylated MWL were performed according to previous work (Capanema *et al.* 2004; Chen and Robert 1998).

## RESULTS AND DISCUSSION

Chemical compositions of *Simarouba versicolor* and *Eucalyptus urograndis* woods are presented in Table 1.

**Table 1.** Wood Chemical Compositions

	Glc	Xyl	Gal	Man	Ara	Klason Lignin %		Extract.	Uronic Acid %	Acetyl Groups %
	%	%	%	%	%	Soluble	Insoluble			
<i>S. versicolor</i>	45.1	7.6	1.3	1.4	0.7	1.5	35.8	1.22	2.6	2.1
<i>E. urograndis</i>	48.5	10.8	0.9	0.6	0.3	3.5	26.1	0.87	5.6	1.9

*S. versicolor* presented 5% less carbohydrate than *E. urograndis* because of its lower cellulose and xylans content. The lower content of uronic acids in *S. versicolor* presented good agreement with the minor percentage of xylans, indicating that this side chain group was attached to this polysaccharide. Acetyl groups were present in similar quantities for both species, being slightly higher for *S. versicolor*, which may be attributed to a considerable higher degree of acetylation of xylan and/or the presence of this side group in another hemicellulose main chain. Lignin content and its structural features are important parameters to evaluate pulping yield. The *S. versicolor* species showed relevant differences in total lignin content (37.3%) compared to eucalyptus (29.6%). This result revealed over 25% higher total lignin content for *S. versicolor*, which would lead to lower pulping yield. In addition, it is worth mentioning that the soluble lignin content was much higher for eucalyptus than for *S. versicolor* (3.5% and 1.5%, respectively). The poor lignin solubility of the latter species suggests that more severe pulping conditions would be required to achieve the same degree of

delignification. Acetone-extractives content was higher for *S. versicolor* (Table 1), which is probably due to the presence of considerable amounts of quassinoids, conferring to this species' antiviral, anti-inflammatory, and antimalarial properties (Polonski *et al.* 1978).

Basic density determination for both woods demonstrated that *E. urograndis* presented higher density ( $499 \text{ kg m}^{-3}$ ) than *S. versicolor* ( $389 \text{ kg m}^{-3}$ ). As a matter of fact, the woods of *E. urograndis* and *S. versicolor* could be classified as medium density and the latter as a low density wood. It is worth noting that low density of woods is considered to have negative impacts on both industrial production of kraft pulp and on energy production (charcoal).

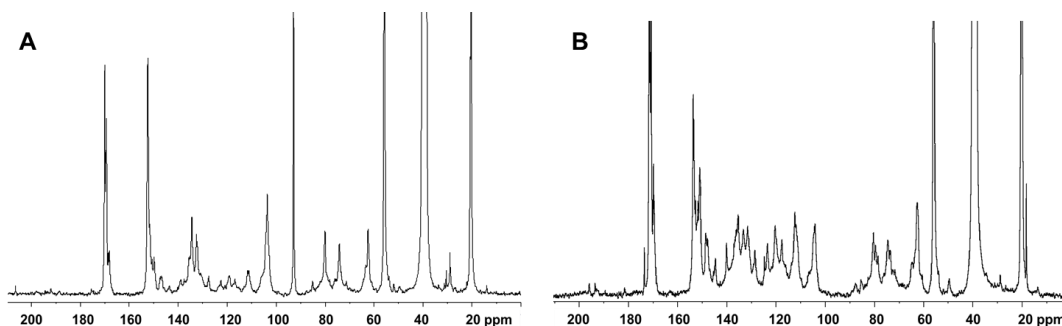
Extractives-free wood sawdust was analyzed for its gross heat of combustion (heating values: HV) and CHNO elemental analysis (Table 2). The heating values were quite similar for *S. versicolor* and *E. urograndis* woods, though *E. urograndis* presented a slightly lower value. The HVs were expected to present greater variation between the two wood species since the heating value of a lignocellulosic material is a function of its lignin content and *S. versicolor* presented much higher lignin content. Previous studies have revealed a highly linear correlation between gross heating value of extractives-free wood and lignin content (Ayhan 2004; Telmo and Lousada 2011; White 1987). Even though the lignin content was different for the two species, the HVs were similar. This can be noted by the similarity in CHNO elemental analysis.

Surprisingly, differences in C, H, N, and O elements between woods were rather low (Table 2), which was not expected due to the great difference between lignin and carbohydrates content in both samples. *S. versicolor* presented higher C content but lower H and O contents. The higher C content of *S. versicolor* may justify its higher HV compared to *E. urograndis*. The greater O content of *E. urograndis* is probably due to the abundance of methoxyl groups present in its syringyl lignin.

**Table 2.** HV and CHNO Elemental Analysis of Wood  
Percentage on dry weight

Wood	C	H	N	O	HV (MJ/kg)
<i>E. urograndis</i>	48.2	6.1	0.0	45.6	19.8
<i>S. versicolor</i>	49.2	5.9	0.2	43.1	20.1

Milled wood lignin (MWL), representing a "true" lignin structure in wood, was isolated from both wood species and analyzed by  $^{13}\text{C}$  NMR (Fig. 1).



**Fig. 1.**  $^{13}\text{C}$  NMR spectra of MWL of *E. urograndis* (A) and *S. versicolor* (B)

Quantification of lignin substructures (syringyl and guaiacyl) along with the wood characterization could probably lead to a better understanding of pulping behavior.  $^{13}\text{C}$ -NMR is a powerful technique that provides valuable lignin structural information, having advantages such as relatively short experimental acquisition time and high accuracy. The substructures determined by  $^{13}\text{C}$ -NMR are shown in Fig. 2.

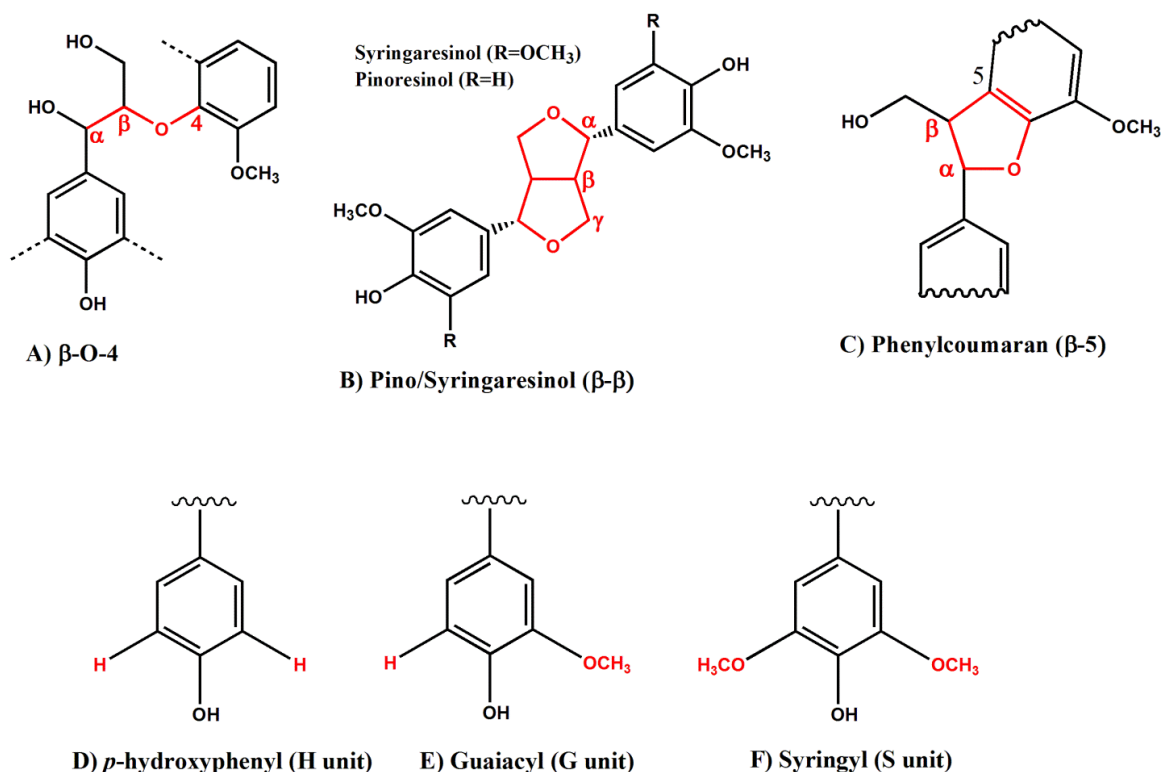


Fig. 2. Lignin substructures determined by  $^{13}\text{C}$  NMR

Table 3. Lignin Chemical Structure based on 100 C9 units

Lignin substructure	<i>S. versicolor</i>	<i>E. urograndis</i>
Primary OH	63	75
Secondary OH	46	53
Aliphatics OH	109	128
Phenolic OH	15	25
Total OH	124	153
Total $\beta$ -O-4	47	58
$\beta$ -5 + $\beta$ - $\beta$	11	11
H units	6	4
S/G	0.40	1.76
S/(S+G+H)	0.27	0.61
Methoxyl	119	168
Degree of condensation,%	32	20

MWL lignins were subjected to analysis of the principal functional groups by  $^{13}\text{C}$  NMR, and their amounts were calculated per phenylpropane unit ( $\text{C}_9$ ). The results are summarized in Table 3.

MWL of *S. versicolor* presented a lower proportion of  $\beta$ -O-4 linkages (Fig. 1A) and a higher proportion of condensed structures (carbon-carbon linkages) than *E. urograndis*.  $\beta$ -O-4 linkages are the dominant linkage pattern in lignin and appear to correlate well with the S/G ratio (Silva *et al.* 2012). Moreover, the additional methoxyl group linked to the C5 in the syringyl structure provides less condensed lignin, therefore facilitating wood delignification. The lignin from eucalypts showed considerably higher content of methoxyl groups (168/100  $\text{C}_9$ ), confirming that lignins from *Eucalyptus* wood have remarkably higher methoxyl groups content than those found for other hardwood lignins (Fengel and Wegener 1984). Small amounts of  $\beta$ -O-4 ether linkages having  $\alpha$ -carbonyl group were also detected (not shown). Those oxidized structures could have been produced from the ball milling process, even though they may be generated during wood lignification.

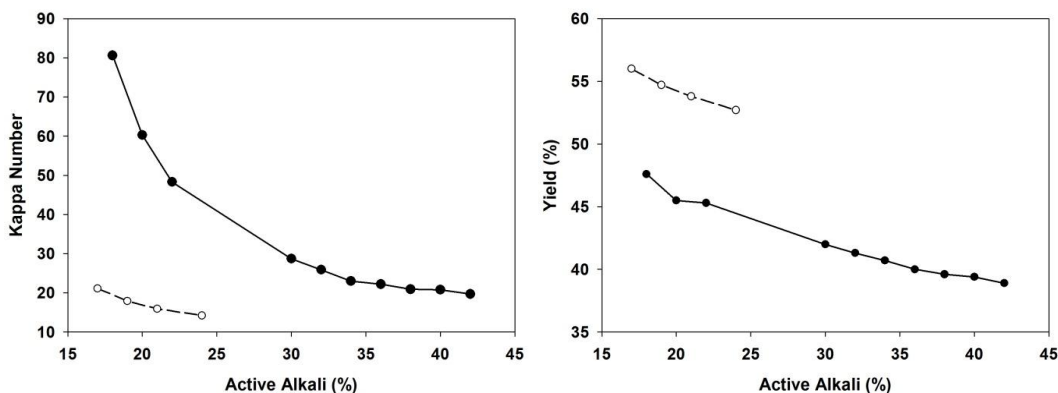
It is worth mentioning that alkaline pulping conditions are rather effective for the cleavage of  $\beta$ -O-4 ether linkages, whereas condensed linkages resist alkaline cooking conditions (Gierer 1980). So, it is not surprising that the better cooking performance for *E. urograndis* species could be expected.

Lignin structures such as  $\beta$ - $\beta$  substructures (pino/syringaresinol – Fig. 2B) and  $\beta$ -5 (phenylcoumaran – Fig. 2C) were identified in MWL for both species. The abundance of phenylcoumaran substructures was rather low and presented no significant difference between the two species. Total OH groups, consisting of aliphatic and phenolic groups, were lower for *S. versicolor* MWL. In Table 3, it can be observed that either aliphatic or phenolic OH groups contributed to minimize the total OH concentration for *S. versicolor*, although phenolic OH affected it most. The effect of syringyl (S) to guaiacyl (G) ratio has been pointed out as being a very important parameter to predict alkali consumption and pulp yield during kraft cooking. Investigation of the S/G effect on kraft pulping of hardwoods has been extensively studied (Bose *et al.* 2009; Pinto *et al.* 2005; Santos *et al.* 2011). The influence of S/G ratio on pulping yield of *E. globulus* wood has led to the use of lignin S/G ratio as a selection parameter in clonal breeding programs for pulpwood production (del Rio *et al.* 2005).

Table 3 shows the S/G and S/S+G+H ratios for both species studied. The data clearly show a minor proportion of p-hydroxyphenyl propane units (H) for both woods. *E. urograndis* presented syringyl content two times higher than guaiacyl. Linkages between carbons (at the free C5 position) are more frequent between guaiacyl units due to the two available pathways for monolignol coupling with a guaiacyl phenolic endgroup (Gomide *et al.* 2005; Guerra *et al.* 2008). On the other hand, higher syringyl lignins have a higher content of  $\beta$ -O-4 coupling, which is of uncondensed nature, indicating a lower degree of condensation, as previously concluded (Evtuguin *et al.* 2001; Rencoret *et al.* 2009; Silva *et al.* 2012). The *S. versicolor* species exhibited the opposite result, showing an S/G ratio of 0.40 and therefore higher degree of condensation, so it would be expected to be more difficult to react in kraft pulping.

The S/G values found for MWL are in agreement with S/V (syringyl/vanillin) values found for these species determined by nitrobenzene oxidation (*S. versicolor*: 0.6 and *E. urograndis*: 2.9) (Chen 1992).

The primary components influencing pulp yield are considered to be lignin and cellulose contents and also wood basic density. Cooking characteristics (kappa number and yield) were plotted against active alkali to characterize the pulping selectivity of both species and are presented in Fig. 3.



**Fig. 3.** Kappa number (A) and yield (B) versus active alkali for kraft cooking of *S. versicolor* (solid line) and *E. urograndis* (dashed line)

The two hardwood species showed quite different selective profile curves. As the active alkali charges were increased, *S. versicolor* wood (Fig. 3A) presented much higher kappa numbers. When using 18% active alkali, *S. versicolor* resulted in very high kappa (80.6) whereas, at the same active alkali, the kappa number of *E. urograndis* was four times lower (23.6), revealing much easier delignification for eucalyptus. To obtain 19.7 kappa for *S. versicolor*, it was necessary to use 42% active alkali, a charge that could be considered industrially unviable, resulting in very low yield (38.9%). Eucalyptus pulping provided a yield of 54.7% and a kappa number of 17.9 when 19% of active alkali was used. Therefore, the relative ease and difficulty of kraft pulping found respectively for *E. urograndis* and *S. versicolor* were in agreement with the  $^{13}\text{C}$  NMR spectra of their MWL. *S. versicolor* presented lower  $\beta$ -O-4 ether linkages and a higher degree of condensation (Table 3), in accordance with its low pulping efficiency. During alkaline pulping, condensed linkages resist degradation, whereas  $\beta$ -O-4 ether linkages are cleaved (Gierer 1980). Cleavage of  $\beta$ -O-4 ether linkages leads to an increased content of phenolic groups and to reactions resulting in elimination of methylol groups ( $-\text{CH}_2\text{OH}$ ).

Another important parameter to be considered is the lignin S/G ratio. Considerable variation in kraft pulping performance for different hardwood species has been reported, and S/G ratio has been pointed out as one of the reasons for this behavior (Bose *et al.* 2009; Pinto *et al.* 2005; Santos *et al.* 2011). A study with model compounds has indicated easier cleavage of  $\beta$ -aryl ethers in syringyl lignins than in guaiacyl lignins (Tsutsumi *et al.* 1995). The unavailability of reactive C5 in the syringyl structure has the advantage of providing less condensed lignin and therefore facilitates wood delignification. Some authors have attributed the relative ease of kraft pulping to the structural



features of lignins, such as the S/G ratio rather than the lignin content in wood (Santos *et al.* 2011). In this study *S. versicolor* presented the highest lignin content (37.3%), very little acid soluble lignin (1.5%), and its S/G ratio was four times lower than *E. urograndis*, indicating a synergy-like behavior with parameters such as degree of condensation and  $\beta$ -O-4 linkages.

## CONCLUSIONS

1. *S. versicolor* wood showed a very low ability for kraft pulping compared to *E. urograndis*.
2. Reasons to account for this behavior of *S. versicolor* wood were supported by its lignin chemical structural features and also lignin content. *S. versicolor* presented higher lignin content, lower S/G, and a high degree of condensation.
3. Total and insoluble lignin content in *S. versicolor* wood showed a rather high level relative to that of *E. urograndis*.
4. The gross heating value of *S. versicolor* wood, as well as the C content of the wood, was slightly higher than of *E. urograndis*.

## ACKNOWLEDGEMENTS

The authors are grateful to FAPEMIG (Fundação de Amparo e Pesquisa do Estado de Minas Gerais) for financial support.

## REFERENCES CITED

- Ayhan, D. (2004). "Combustion characteristics of different biomass fuels," *Prog. Energ. Combust.* 30(2), 219-230.
- Björkman, A. (1956). "Studies on finely divided wood. Part 1. Extraction of lignin with neutral solvents," *Sven. Papperstidn.* 59, 477-485.
- Bose, S. K., Francis, R. C., Govender, M., Bush, T., and Spark, A. (2009). "Lignin content versus syringyl to guaiacyl ratio amongst poplars," *Bioresource Technol.* 100(4), 1628-1633.
- Capanema, E. A., Balakshin, M. Y., and Kadla, J. F. (2004). "A comprehensive approach for quantitative lignin characterization by NMR spectroscopy," *J. Agr. Food Chem.* 52(7), 1850-1860.
- Chen, C.-L. (1992). "Nitrobenzene and cupric oxide oxidations," In: *Methods in Lignin Chemistry*, S. Y. Lin, and C. W. Dence (eds.), Springer-Verlag Berlin Heidelberg, New York.
- Chen, C.-L., and Robert, D. (1988). "Characterization of lignin by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy," In: *Methods in Enzymology*, W. A. Wood and S. T. Kellogg (ed.), Vol. 161, Academic Press, 137-174.

- Collins, D. J., Pilotti, C. A., and Wallis, A. F. A. (1990). "Correlation of chemical composition and kraft pulping properties of some Papua New Guinea reforestation woods," *Appita J.* 43(3), 193-198.
- del Río, J. C., Gutiérrez, A., Hernando, M., Landín, P., Romero, J., and Martínez, Á. T. (2005). "Determining the influence of eucalypt lignin composition in paper pulp yield using Py-GC/MS," *J. Anal. Appl. Pyrol.* 74(1-2), 110-115.
- Evtuguin, D. V., Neto, C. P., Silva, A. M. S., Domingues, P. M., Amado, F. M. L., Robert, D., and Faix, O. (2001). "Comprehensive study on the chemical structure of dioxane lignin from plantation *Eucalyptus globulus* wood," *J. Agr. Food Chem.* 49(9), 4252-4261.
- Fengel, D., and Wegener, G. (1984). *Wood Chemistry, Ultrastructure, Reactions*, Berlin.
- Gierer, J. (1980). "Chemical aspects of kraft pulping," *Wood Sci. Technol.* 14(4), 241-266.
- Gomide, J. L., Colodette, J. L., Oliveira, R. C., and Silva, C. M. (2005). "Caracterização tecnológica, para produção de celulose, da nova geração de clones de *Eucalyptus* do Brasil," *Revista Árvore* 29, 129-137.
- Guerra, A., Elissetche, J. P., Norambuena, M., Freer, J., Valenzuela, S., Rodríguez, J., and Balocchi, C. (2008). "Influence of lignin structural features on *Eucalyptus globulus* kraft pulping," *Ind. Eng. Chem. Res.* 47(22), 8542-8549.
- Khiari, R., Mhenni, M. F., Belgacem, M. N., and Mauret, E. (2010). "Chemical composition and pulping of date palm rachis and *Posidonia oceanica* – A comparison with other wood and non-wood fibre sources," *Bioresource Technol.* 101(2), 775-780.
- Lawoko, M., Henriksson, G., and Gellerstedt, G. (2005). "Structural differences between the lignin-carbohydrate complexes present in wood and in chemical pulps," *Biomacromolecules* 6(6), 3467-3473.
- Miranda, I., and Pereira, H. (2002). "The variation of chemical composition and pulping yield with age and growth factors in young *Eucalyptus globulus*," *Wood Fiber Sci.* 34(1), 140-145.
- Pilate, G., Guiney, E., Holt, K., Petit-Conil, M., Lapierre, C., Leple, J. C., Pollet, B., Mila, I., Webster, E. A., Marstorp, H. G., Hopkins, D. W., Jouanin, L., Boerjan, W., Schuch, W., Cornu, D., and Halpin, C. (2002). "Field and pulping performances of transgenic trees with altered lignification," *Nature Biotechnol.* 20(6), 607-612.
- Pinto, P. C., Evtuguin, D. V., and Neto, C. P. (2005). "Effect of structural features of wood biopolymers on hardwood pulping and bleaching performance," *Ind. Eng. Chem. Res.* 44(26), 9777-9784.
- Polonski, J. E. P., Varon, Z., Jacquemin, H., and Pettit, G. R. (1978). "The isolation and structure of 13,18-dihydroglauucarubinone, a new antineoplastic quassinoid from *Simarouba amara*," *Experimenta* 34, 1122-1123.
- Rencoret, J., Marques, G., Gutiérrez, A., Nieto, L., Jiménez-Barbero, J., Martínez, Á.T., and del Río, J.C. (2009). "Isolation and structural characterization of the milled-wood lignin from *Paulownia fortunei* wood," *Ind. Crop. Prod.* 30(1), 137-143.
- Rydholm, S. A. (1967). *Pulping Processes*, Interscience, New York.
- Santos, R. B., Capanema, E. A., Balakshin, M. Y., Chang, H.-m., and Jameel, H. (2011). "Effect of hardwoods characteristics on kraft pulping process: emphasis on lignin structure," *BioResources* 6, 3623-3637.

- Scott, R. W. (1979). "Colorimetric determination of hexuronic acids in plant materials," *Anal. Chem.* 51(7), 936-941.
- Silva, T. C. F., Santos, R. B., Jameel, H., Colodette, J. L., and Lucia, L. A. (2012). "Quantitative molecular structure–pyrolytic energy correlation for hardwood lignins," *Energ. Fuel.* 26(2), 1315-1322.
- Solar, R., Kacik, F., and Melcer, I. (1987). "Simple method for determination of O-acetyl groups in wood and related materials," *Nord. Pulp Pap. Res. J.* 4, 139-141.
- Telmo, C., and Lousada, J. (2011). "The explained variation by lignin and extractive contents on higher heating value of wood," *Biomass Bioenerg.* 35(5), 1663-1667.
- Tsutsumi, Y., Kondo, R., Sakai, K., and Imamura, H. (1995). "the difference of reactivity between syringyl lignin and guaiacyl lignin in alkaline systems," *Holzforschung* 49(5), 423-428.
- Wallis, A., Wearne, R., and Wright, P. (1996). "Chemical analysis of polysaccharides in plantation eucalyptus wood and pulps," *Appita J.* 49(4), 258-262.
- White, R. (1987). "Effect of lignin content and extractives on the higher heating value of wood," *Wood Fiber Sci.* 19(4), 446-452.

Article submitted: April 10, 2012; Peer review completed: June 24, 2012; Revised version received and accepted: July 3, 2012; Published: July 10, 2012.