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In situ determination of the syringyl/guaiacyl ratio of residual lignin in pre-bleached eucalypt kraft pulps by analytical pyrolysis

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ABSTRACT

Pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) was used for evaluating the syringyl/guaiacyl (S/G) ratios of residual lignins in oxygen pre-bleached kraft pulps from 24 *Eucalyptus* wood clones. The optimization of the method showed that the best conditions were achieved when pyrolysis is carried out at 550 °C, using a 60 m length SPB-1701 capillary column and the mass spectrometer operating in SIM mode. Pulp pyrograms were analyzed and the compounds produced by pyrolysis of residual lignins identified by mass spectrometry. A total of 18 compounds were identified, being nine derived from guaiacyl units and nine derived from syringyl lignin. The S/G ratios were calculated using the relative area of S-lignin (syringol, 4-methylsyringol, 4-vinylsyringol and *trans*-4-(prop-2-enyl) syringol) and G-lignin (guaiacol, 4-methylguaiacol, 4-vinylguaiacol and *trans*-isoeugenol) as lignin markers. These studies showed that Py-GC/MS-SIM is an efficient tool to characterizing the chemical composition of residual lignin in oxygen pre-bleached *Eucalyptus* pulps.

1. Introduction

Lignin is an amorphous substance, of aromatic and complex nature, present in the cell wall and in the middle lamella of vegetables [1]. It acts as an essential component of wood, strengthening cell walls, facilitating the transport of water and preventing the degradation of wall polysaccharides [2]. It also protects wood from the attack by pathogens, insects and other herbivores.

Lignin is composed of monomeric phenylpropanoid units known as *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S), originated from three primary precursors: *trans*-*p*-coumaryl, *trans*-coniferyl and *trans*-sinapyl alcohols, respectively [3].

However, this natural polymer is an undesirable component in the conversion of wood to pulp, and its content is an important parameter for the industry, since its removal is a major step in the manufacture of pulp and paper [4,5]. Wood formed by lignin with higher proportion of syringyl (S) over guaiacyl units (G) (higher S/G ratio) are more easily delignified and provide higher pulp yield using less chemicals [6–8] This behavior is due to the fact that in the guaiacyl units the C_5 position in the aromatic ring is available for the formation of very strong carbon–carbon bonds, making the resultant lignin more resistant to depolymerization during the pulping process [8]. Furthermore, cleavage of ß-aryl-ether in syringyl lignin takes place more easily than in guaiacyl lignin under alkaline conditions for cooking, contributing to increased delignification rates [9]. Thus, the structural composition of lignin is an important feature in *Eucalyptus* clone selection processes, in order to obtain better quality wood for paper production in terms of delignification rate, pulping yield and chemical consumption in pulping and bleaching [4].

Although several methodologies have been employed to study the structure of lignin in woods [7,10–13], the most common method used by the industries to determine the syringyl/guaiacyl ratios in woods is the oxidation with nitrobenzene in an alkaline medium. This procedure, however, demands prolonged periods of analysis and consumption of large amounts of reagents [14], and therefore, further analytical procedures that are faster, safer and less reagent consuming are required.

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Table 1
Description of the wood clones, and kappa number of the brown and oxygen pre-bleached kraft pulps.

Sample	Wood clone	Plantation site	Brown pulp Kappa number	Oxygen pre-bleached pulpKappa number
1	Natural *Eucalyptus grandis*	Cocais	17.5 a	10.8
2	Hybrid	Guanhães	17.3 a	10.7
3		Rio Doce	16.5 a	10.4
4		Santa Bárbara	17.2 a	10.5
5	Hybrid *Eucalyptus*	Cocais	15.7 b	9.80
6	*grandis* × *Eucalyptus*	Guanhães	15.3 b	9.70
7	*urophylla*	Rio Doce	17.3 a	10.5
8		Santa Bárbara	15.1 b	9.60
9	Hybrid *Eucalyptus*	Cocais	15.2 a	9.70
10	*grandis* × *Eucalyptus*	Guanhães	15.7 a	9.80
11	*urophylla*	Rio Doce	16.1 a	10.2
12		Santa Bárbara	14.6 a	9.50
13	Hybrid *Eucalyptus*	Cocais	15.7 b	9.80
14	*grandis* × *Eucalyptus*	Guanhães	17.0 a	10.4
15	*urophylla*	Rio Doce	17.1 a	10.5
16		Santa Bárbara	16.0 b	9.90
17	Hybrid *Eucalyptus*	Cocais	16.7 b	10.2
18	*grandis* × *Eucalyptus*	Guanhães	17.4 a	10.9
19	*urophylla*	Rio Doce	17.2 a	10.6
20		Santa Bárbara	16.4 b	10.4
21	*Eucalyptus grandis*	Cocais	16.9 a	10.5
22		Guanhães	16.4 b	10.4
23		Rio Doce	15.5 b	9.40
24		Santa Bárbara	16.5 a	10.5

Pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) is an alternative analytical technique widely used in the study of polymer samples, as lignin [15]. The technique consists of the thermal degradation of lignin, producing volatile components that can then be analyzed by gas chromatography/mass spectrometry. This technique is also distinguished by being fast and requires very small amounts of sample (approximately 100 μg), without any previous preparation [15–17].

Considering that the structure of lignin residues present in the oxygen pre-bleached pulp can have significant impact on the bleaching chemical demand in subsequent bleaching process, on brightness reversion and on the demand of optical brightening agents in papermaking, the knowledge of the S/G ratio of the oxygen pre-bleached residual lignin is important. However, and due to the small amounts of lignin present, to the best of our knowledge, there is no routine method efficient to carry out such analyses. Py-GC/MS has been successfully used to measure the S/G ratios in extracted lignins and also in woods [17–23], and therefore, we envisaged that such method could also be extended to analyze the S/G ratios in oxygen pre-bleached kraft pulps. In fact, Py-GC/MS has already been used to analyze residual lignin markers in chemical pulps [24,25]. In this paper we describe a new method based on the use of Py-GC/MS that can be routinely used to analyze *in situ* the S/G ratios of residual lignins in eucalypt brown and oxygen pre-bleached kraft pulps, without the need of their previous isolation.

2. Experimental

2.1. Production of the brown (unbleached) and oxygen pre-bleached pulp samples

The brown (unbleached) and oxygen pre-bleached pulp samples were obtained after kraft pulping and oxygen delignification of various three-year old *Eucalyptus* woods. Table 1 describes the six *Eucalyptus* wood clones from different regions of Brazil, and the kappa numbers of the brown and oxygen pre-bleached pulp samples. The Brazilian regions selected for the study were: Barão de Cocais (latitude 19°24′53″S, longitude 42°55′51″W), Guanhães (latitude 18°41′0″S, longitude 42°l55′37″W), Rio Doce–Ipaba (latitude 19°43′48″S, longitude 42°29′01″W), and Santa Bárbara (latitude 20°7′49″S, longitude 43°l21′01″W). For each clone and location three trees were cut, totaling 72 samples. Five 50 cm long bolts were cut from each tree at different heights (0, 25, 50, 75, 100%) to have a representative sample of the whole tree. All bolts were debarked and chipped in a laboratory chipper (Chogokukikai – Japan). The chips produced were screened (35 × 35 mm and 8 × 8 mm screens) and air dried to uniform moisture content to approximately 20%. After mixture, all samples were homogenized in a rotary 250 liter chips mixer and stored in polyethylene bags to maintain uniform moisture content. The chips derived from the three trees collected for each one of the 24 samples were mixed together. A small fraction of the chips were grinded in a Wiley mill and converted to sawdust used for milled wood lignin preparation. The remaining chip samples were stored in polyethylene bags for further use. Kraft cooking of the chips was carried out at constant conditions for all 24 samples. Cooking processes were carried out in a 7 L M/K digester equipped with a heat exchanger, circulating pump and computer-controlled time and temperature. The cooking parameters used for all batch cooks were as follows: active alkali – 18.4%; sulfidity – 35%; maximum temperature – 170 °C, achieved during 90 min and remained at 170 °C for 90 min; liquor/wood ratio – 4/1; H-factor – 1525. After kraft cooking the pulps were screened and washed thoroughly. The kappa numbers of the brown pulps were in the range of 14.6–17.5. The 24 brown pulp samples were then pre-bleached in an oxygen delignification stage using a high shear mixer/reactor (Quantum Technologies, Springfield, USA). The following fixed conditions were used: consistency – 10%; pressure – 500 kPa; temperature – 100 °C; time – 60 min; oxygen dosage – 20 kg/*t* pulp; NaOH dosage – 18 kg/*t* pulp. After the oxygen delignification the pulps were thoroughly washed with water. The 24 oxygen pre-bleached pulp samples had their kappa number in the range of 9.4–10.8 (Table 1).

2.2. Preparation of milled wood lignin

For the isolation of milled wood lignin, the extractive-free sawdust was initially submitted to sequential extraction with 1% NaOH solution and acetone. This treatment was followed by the procedure described by Björkman [26], which is based on grinding wood dust in a ball mill for three weeks, in the presence of toluene, and subsequently extracting lignin from the macerated material with a mixture of dioxane:water (9:1 v/v).