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The relationship between *Eucalyptus grandis* lignin structure and kraft pulping parameters

Luis Reina[a,*], Alejandra Galetta[a], Vittorio Vinciguerra[b], Fernando Resquin[c], Pilar Menéndez[a]

[a] *Departamento de Química Orgánica, Facultad de Química, Universidad de la República, Avenida General Flores 2124, Montevideo 11800, Uruguay*
[b] *Dipartimento per la Innovazione nei sistemi Biologici, Agroalimentari e Forestali, Università della Tuscia, l.go dell'Università, 01100 Viterbo, Italy*
[c] *Programa de Producción Forestal, Instituto Nacional de Investigación Agropecuaria Tacuarembó, Ruta 5 km 386, Tacuarembó 45000, Uruguay*

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ABSTRACT

The syringyl/guaiacyl (S/G) ratio of *Eucalyputs grandis* lignin was determined and its relation with kraft pulping parameters was studied. Twenty one wood samples obtained from 10-year-old trees grown in the same place were analyzed using Py-GC–MS to determine the syringyl/guaiacyl (S/G) ratio. The samples were pulped to the same final lignin content (Kappa number 18) obtaining pulp yields between 48.8% and 54.3%. Relationships were observed between pulp yield and S/G ratio ($r = 0.51$) also between alkali charge used in pulping and S/G ratio ($r = -0.60$).

1. Introduction

Pulpwood production involves different mechanical, chemico-physical and chemical steps, which affect the yield and quality of the pulp, such as the final quality of paper. In order to improve the knowledge of the relationship between wood characteristics and kraft pulp production it is necessary to determinate the factors related to wood that affect pulp production. One factor is wood chemical composition [1], that including the quantity of different chemical components (e.g. cellulose, hemicelluloses and lignin) and also the structural features of those components. The lignin, present in wood in the proportion of 15–25%, is a complex polymer, consisting of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) phenylpropanoid units. It is produced from polymerization of three monolignols, *p*-coumaryl alcohol (the less abundant component), coniferyl alcohol and sinapyl alcohol [2]. The structure of the polymer depends on the proportion of those units and the linkages among them [3].

In kraft pulping process wood chips are digested using a solution of sodium hydroxide and sodium sulfide at 130–170 °C. Lignin dissolution is the first objective of the process. When about 90% of lignin is dissolved fibers from wood can be separated [4]. Cellulose and hemicelluloses are also dissolved in the proportions of 7–15% for cellulose and 60–70% for hemicelluloses [5–7].

As the delignification step of the pulpwood production considerably influences the pulpwood yield and paper quality, the knowledge of lignin structure represents an important subject of study to foresee the ability to remove lignin from the pulpwood.

The relation between lignin removal and kraft pulping yield depends on the lignin quantity and its structure. Some authors have found a negative relationship between lignin content in wood and pulping yield [8–10], although other authors have found that pulp yield depends rather on lignin structure [8,11,12]. In these works they analyzed samples from different ages, sites [11] or species [12]. However, to carry out an efficient breeding program the wood samples should be collected from trees grown in the same location so only their genetic potential can be expressed.

In lignin the phenylpropanoid units are linked by ether bonds and carbon–carbon bonds and the latter are more difficult to break, in kraft pulping process, than ether bonds [13,14]. Therefore, when the lignin structure consists in high amounts of C—C linkages a harder pulping process (high alkali requirements) will be required to achieve satisfactory delignification. In these conditions, one consequence is higher dissolution of cellulose and a drop of pulping yield [5].

Of the different analytical techniques to determine lignin structure [15] pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS) is considered a rapid and very sensitive method. It consists of a thermal degradation of lignin, the separation of the

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* Corresponding author. Tel.: +598 29244543.
E-mail address: lmreina@fq.edu.uy (L. Reina).

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degradation compounds in the GC, and their identification using the mass spectrometer. The technique has been used for 50 years to characterize lignin [16]. It has also proven to be able to study the lignin structure of wood [17,18] and pulp [19–21] and to evaluate the behavior of lignin during kraft pulping delignification [22]. Coniferyl alcohol and sinapyl alcohol are the principal units in lignin of hardwoods such as *Eucalyptus* and their pyrolysis produce derivatives of guaiacol (2-methoxyphenol) and syringol (2,6-dimethoxyphenol). These derivatives are grouped as syringyl and guaiacyl units so that syringyl/guaiacyl ratio (S/G) can be calculated and used as indicator of lignin structure. It is known that higher S/G ratio implies more units with two methoxy groups and less free positions available to form carbon–carbon bonds [12]. Thus lignins with high S/G ratio are less cross-linked and easier to degrade in pulping process than lignin with low S/G ratio.

The objective of the present work is to evaluate the relationship among *Eucalyptus grandis* lignin structure and kraft pulping parameters, alkali charge and pulping yield, to establish the ease of delignification. The wood samples selected for analysis were collected from trees with same age and grown in the same site, in order to attribute the changes in S/G variation to natural (tree to tree) variability. These conditions seem reasonably representative of the situation used in a field dedicated to breeding. To characterize lignin structure, S/G ratios have been determined in wood samples by direct introduction in a Py-GC–MS system using a vertical microfurnace pyrolyzer [23].

2. Materials and methods

2.1. Wood samples

E. grandis samples were taken from trees of 10-year-old located in Tres Bocas, Rio Negro department, Uruguay. The trees came from trials in which were used seven different seeds collected in Coff Harbour in New South Wales State, Australia in the range of 30.05–30.14 latitude, 153.01–153.07 longitude and 100–300 altitude.

Three samples were obtained for trees of each seed origin (21 total samples) using the following criteria: 3 trees from low diameter group (F), 5 trees from intermediate diameter group (M), and 3 trees from high diameter group (G). From each Tree 5 trunk sections were obtained at different height, 0%, 25%, 50%, 75% and 100% total length of trunk. The maximum height of the trees was taken at a diameter of the stem (with bark) of 6 cm. Each disk was manually chipped and chips from the same group of trees (F, M and G) were mixed to obtain a representative sample.

2.2. Pulping parameters

A 250 g of each sample were cooked using the following conditions: 170 °C maximum temperature; 25% sulfidity; time to reach maximum temperature: 90 min; time at maximum temperature: 50 min; 3.5 liquor/wood ratio. Alkali charge was the variable condition used to reach a final Kappa number of 18 ± 1. In order to obtain the same kappa different alkali charges were tried in the same cook. For that a laboratory digester were charged with 4 steel sealed vessels. Kappa number was determined according to TAPPI Test Method T 236cm-85.

2.3. Pyrolysis-gas chromatography/mass spectrometry

All samples were analyzed by Py-GC–MS to determine lignin and carbohydrate structures. The chips were milled to 40–60 mesh, pressed into pellets using a special syringe and directly introduced in the pre-heated microfurnace pyrolyzer (Fig. 1) PYROJECTOR II (SGE). It was mounted on a split/splitless injector of a Hewlett-Packard HP 5890 II plus gas chromatograph connected to a 5971 mass selective detector (Hewlett-Packard). Pyrolysis was performed at 450 °C, introducing each sample in the pre-heated and equilibrated microfurnace. The separation of pyrolysis products was performed using a capillary column OPTIMA 1701 (Macherey-Nagel, 30 m × 0.25 mm i.d., 0.25 μm film thickness).

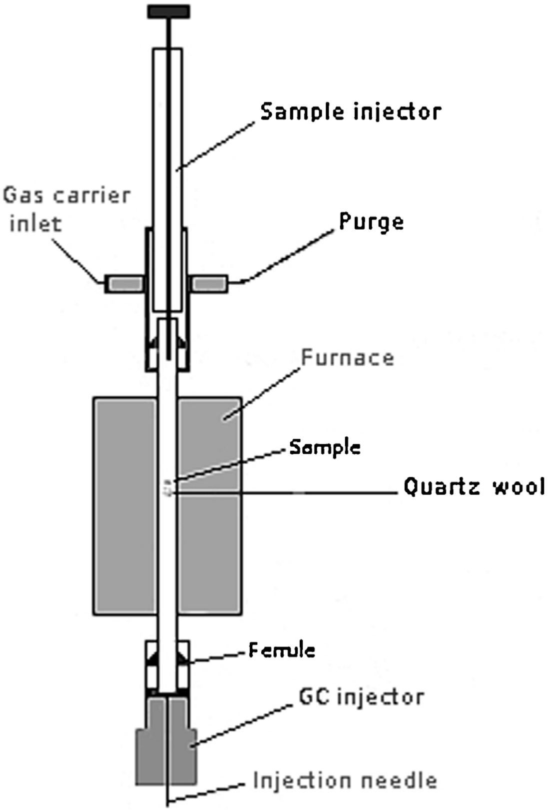

Fig. 1. Scheme of the pyrolyzer.

The carrier gas was He at 170 kPa in the pyrolyzer and 50 kPa (initial, constant flow conditions) in the GC injector that was set at 250 °C in the split mode (1:20 split ratio). The chromatograph oven temperature was programmed from initial temperature 45 °C held for 4 min, to 240 °C at 4 °C min^{-1} and then to 290 °C at 25 °C min^{-1} holding the final temperature for 1 min. The transfer line was set at 300 °C and the mass spectrometer operated in EI mode (70 eV, 180 °C) with a mass in the 40–300 m/z interval.

The pyrolysis products were identified by interpretation of their mass spectra and by comparison with the NIST and Wiley computer libraries and with literature data [24–27].

2.4. S/G calculation.

Quantification of guaiacyl (G) and syringyl-type (S) lignin breakdown products was based on percent peak areas (total integral of pyrolysis products identified equal 100). S/G ratio was determined as the ratio of the sum of the percent peaks areas of S and G-types compounds.

3. Results and discussion

3.1. Pyrolysis-gas chromatography–mass spectrometry

A typical pyrogram obtained from the pyrolysis of one sample of eucalypt wood is shown in Fig. 2. The 21 pyrograms are very similar from the qualitative point of view and show the presence of eighteen lignin derivates as listed in Table 1. Seven of them (peaks