

## Comparison of Py-GC/FID and Wet Chemistry Analysis for Lignin Determination in Wood and Pulps from *Eucalyptus globulus*

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The kraft pulps produced from heartwood and sapwood of *Eucalyptus globulus* at 130 °C, 150 °C, and 170 °C were characterized by wet chemistry (total lignin as sum of Klason and soluble lignin fractions) and pyrolysis (total lignin denoted as py-lignin). The total lignin content obtained with both methods was similar. In the course of delignification, the py-lignin values were higher (by 2 to 5%) compared to Klason values, which is in line with the importance of soluble lignin for total lignin determination. Pyrolysis analysis presents advantages over wet chemical procedures, and it can be applied to wood and pulps to determine lignin contents at different stages of the delignification process. The py-lignin values were used for kinetic modelling of delignification, with very high predictive value and results similar to those of modelling using wet chemical determinations.

*Keywords:* Klason lignin; Soluble lignin; Wet chemistry; Pyrolysis; *Eucalyptus globulus*

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### INTRODUCTION

Lignin content in wood and other lignocellulosics is a major property that is determinant for the material resistance and reactivity. The methods for lignin determination were therefore developed early, based on the different reactivity of the cell wall components, and gradually developed into standardized procedures. Today, the standards include a lignin determination procedure based on the complete depolymerization of polysaccharides. Lignin is then quantified as the sum of two fractions: the remaining solid, designated as acid-insoluble lignin or Klason lignin; and the acid-soluble lignin fraction that is solubilised in the reaction solution (Sjöström and Wertermark 1998). The sample is treated with 72% sulfuric acid for 1 h at 30 °C, followed by 3% sulfuric acid for 1 h at 120 °C in an autoclave. The lignin is filtered, leaving the Klason lignin as a solid residue. The minor amounts of lignin solubilised in the process, namely the units associated to hemicelluloses, are determined by UV spectroscopy at a wavelength of 205 nm, as acid-soluble lignin (Biermann 1996).

These standard lignin determination procedures are time consuming and labor intensive, and several attempts have been made to develop methods to overcome such shortcomings. For instance, a recent proposal was described by Aldaeus *et al.* (2011) that does not include the primary acid hydrolysis with 72% sulfuric acid and reduces the time in the autoclave.

The lignin content (Klason and soluble lignin) in *Eucalyptus globulus* wood varies from 21.9 % to 25.4 % (Patt *et al.* 2006; Ramírez *et al.* 2009) and in pulps depending on the degree of delignification (Lourenço *et al.* 2010). The method used in the pulp industry for determination of residual lignin in delignified wood is the Kappa number, which is defined as the volume (in mL) of 0.1 N potassium permanganate consumed by lignin oxidation in 1 g of moisture-free pulp (TAPPI T236 cm-85). Klason lignin content is calculated from the Kappa number by multiplication by 0.13. However, in addition to lignin, other components formed during pulping (*e.g.* hexenuronic acids) can be oxidized, inducing misleading results (Pedroso and Carvalho 2003).

Other methods are also used to determine lignin in wood and pulps, in particular from *E. globulus*: by FTIR (Ibarra *et al.* 2005), NIR (Tsuchikawa 2007), and NMR (Rencoret *et al.* 2008). The hyphenated analytical techniques composed by pyrolysis gas chromatography, mass spectrometry, and FID (Py-GC/MS and Py-GC/FID) have been proposed as useful techniques for the chemical characterization of wood (Rodrigues *et al.* 2001; Yokoi *et al.* 1999) and pulps (del Rio *et al.* 2001). The sample is thermally degraded in the absence of oxygen, and its macromolecules break down at specific lower bonding energy points forming volatile fragments that provide useful structural information about the macromolecule as a whole. The pyrolysis of wood produces degradation products from lignin and carbohydrates that can be separated by gas chromatography and identified by mass spectrometry (Meier and Faix 1992). The lignin-derived pyrolysis compounds are of phenolic type, in which the propanoid side chain of the lignin has been completely broken or shortened to one or two carbons. This result in clear recognition of the lignin derivatives during identification by GC-MS, because of the abundance of molecular ions compared to those of carbohydrates (Meier and Faix 1992).

Pyrolysis requires only a small sample (in the µg range (Brunow *et al.* 1998)), is a reproducible method (Rodrigues *et al.* 2001), and does not require previous isolation of the lignin (Meier and Faix 1992; Faix and Meier 1989), although the sample should be free of extractives (Meier and Faix 1992).

The objective of this paper is to compare the standard wet chemical method of lignin determination using Klason and acid-soluble lignin quantification with analytical pyrolysis quantification (Py-GC/FID) of total lignin in the analysis of wood and of pulps obtained at different delignification levels along a pulping process. The results obtained by both methods were used for delignification modeling, and the corresponding kinetic parameters were compared.

## EXPERIMENTAL

### Wood and Delignified Material

This study was performed using a stemwood disc with 10 cm thickness removed at 1.3 m height level of an 18-year-old *Eucalyptus globulus* tree. The disc was separated into sapwood and heartwood, and each part was milled, sieved, and the 20 to 40 mesh fraction used for kraft pulping.

The kraft pulping conditions were: sulfidity 30% (as Na<sub>2</sub>O); active alkali 20% (as Na<sub>2</sub>O); and liquor-to-wood ratio 4:1 (mL/g). The pulping was performed in stainless steel rotating autoclaves in an oil-temperature-controlled bath under isothermal conditions at three cooking temperatures of 130 °C, 150 °C, and 170 °C for several cooking times ranging from 0 min to 180 min. The time zero refers to the point when the pulping

temperature was attained; a 5 min heating period was needed to reach the temperature. After each pulping time, the autoclaves were removed and cooled in ice to stop the reaction. The samples that still presented a wood-like structure were thoroughly washed with deionized hot water, while the delignified samples that were pulps were defibrated in a blender.

All samples were extracted before chemical analysis in a Soxhlet apparatus: the wood samples were extracted with a sequence of dichloromethane (6 h), ethanol (12 h), and water (12 h). The pulps were extracted with ethanol and water (70:30) for 48 h to wash out the extractable residues present after delignification.

### Lignin Determination by Wet Chemistry

The wood and the delignified samples were dried and homogenized before chemical analysis by milling using a 0.12 mm output sieve. The determination of lignin content was made by acid hydrolysis as Klason lignin (adapted from TAPPI T222 standards), soluble lignin (TAPPI UM 250), and total lignin by sum of both.

The wood and delignified material were treated with a solution of H<sub>2</sub>SO<sub>4</sub> (72%, w/w concentration) for 1 h at 30 °C, then further hydrolyzed in dilute 3% H<sub>2</sub>SO<sub>4</sub> for 1 h at 120 °C in an autoclave. The samples were filtered and the solid residue dried and weighed for Klason lignin determination. The soluble lignin was determined in the hydrolysis liquor by spectroscopy at 205 nm wavelength (with an absorptivity coefficient of 110 g.L<sup>-1</sup>cm<sup>-1</sup>). A minimum of two replicates were performed.

### Lignin Determination by Py-GC/FID

Aliquots of the samples of wood and of delignified materials were dried and powdered in a Retsch MM200 mixer ball mill for 60 min (milling time was determined experimentally). These aliquots were characterized by pyrolysis-gas-chromatography associated to mass spectrometry and FID respectively for identification and quantification.

Approximately 100 µg of sample was weighed and pyrolysed in a quartz boat at 650 °C for 10 s with a temperature rise time of *ca.* 20 °C/ms (ramp-off) with the interface kept at 260 °C (CDS platinum coil Pyroprobe 2000 apparatus with a CDS 1500 valved interface). The pyrolysates were purged from the pyrolysis interface into the GC injector with a helium gas flow programmed as follows: 2.0 mL/min (1 min hold), decreased to 1.5 mL/min using a rate of 0.5mL/min<sup>2</sup> and then to 1.0mL/min at 0.2 mL/min<sup>2</sup>, held for the remaining time. The fused-silica capillary column used was an Equity-1701 (60m x 0.25 mm x 0.25 µm) from Supelco. The conditions used were: GC injector 240 °C, FID detector 280 °C and GC-MS interface 280 °C. The GC oven program was: 40 °C, held for 4 min, 10 °C/min to 70 °C, 5 °C/min to 100 °C, 3 °C/min to 265 °C, held for 3 min, 5 °C/min to 270 °C, held for 9 min.

The identification of the pyrolysis products was performed using a Py-GC/MS (Thermo Trace Ultra Polaris Ion Trap) apparatus with the following conditions: electronic ionization at 70 eV and 220 °C for the ion source temperature, using 0.3 mL of damping helium gas. The obtained mass spectra were compared to the mass spectra of NIST and data from Faix *et al.* (1990a,b). The samples used for the compounds identification were the wood samples and the pulps with the longest cooking time at the three temperatures to maximize the number of products identified.

The quantification analysis was performed using Py-GC/FID, and the total area of the pyrogram was obtained by automatic integration (Thermo Excalibur software). A

manual correction of some peaks was performed for all the samples to ensure adequate peak integration since: i) there were differences between samples in the shape and intensity of the peaks; ii) some peaks presented shoulders that were not identified automatically. For quantification, the FID response factors of pyrolysis products were considered to be all equal to 1.0. To our knowledge, Faix and Meier (1989) were the only authors to apply different response factors.

The lignin-derived pyrolysis products were summed up corresponding to total lignin (py-lignin).

### Modeling Kinetics

Kinetic models of delignification were created as described by Labidi and Pla (1992) and Miranda and Pereira (2002a), using the results of Klason lignin (by wet chemistry) and of Py-lignin (by pyrolysis) from the delignified samples. The equation used was,

$$L/L_0 = a_i \exp(-k_i t) + a_b \exp(-k_b t) + a_r \exp(-k_r t) \quad (1)$$

where  $L$  is the lignin present in the sample;  $L_0$  is the lignin in the first point of delignification;  $t$  is the time (min);  $k$  is the rate constant ( $\text{min}^{-1}$ ), and  $a$  is the mass fraction of lignin removed (%) during each of the three phases: initial (i), bulk (b) and residual (r). It was assumed that at  $t = 0$ :  $a_i + a_b + a_r = 100$ , according to Labidi and Pla (1992).

The kinetic parameters were obtained by minimizing the residual sum-of-squares (SQR) of the fitting curve, using single, double or triple first-order reactions, by “solver” add-in from Excel for Windows.

## RESULTS AND DISCUSSION

### Chemical Characterization

Heartwood and sapwood samples were chemically characterized by summative analysis. Heartwood had less ash content than sapwood (0.17% vs. 0.44%) and more extractives (9.8% vs. 3.9%). There were no differences with respect to monosaccharides, as described by Lourenço *et al.* (2010).

### Lignin Determination by Wet Chemistry

The results from wet chemical determination are presented in Table 1. The wood samples presented different values for total lignin, expressed as the sum of Klason lignin and soluble lignin (in % of extracted wood): 25.3% in sapwood (21.4% + 3.9%) and 25.8% in heartwood (21.8% + 4.0%). However, due to the higher extractives content in heartwood, when the total lignin is reported to original wood, the values are slightly different: 24.3% and 23.5%, respectively for sapwood and heartwood (Lourenço *et al.* 2010). These are values in the range of values reported for *E. globulus* wood of 24.2% to 27.9% (Miranda and Pereira 2002b); 24.7% to 31.2% (Poke *et al.* 2006); 25.4% (Ramírez *et al.* 2009); or 24.5% (Rencoret *et al.* 2011), while a somewhat lower value of 21.9% was reported by Patt *et al.* (2006). It is known that such amplitude of values is due to different factors such as wood origin (Miranda and Pereira 2002b; Poke *et al.* 2006) or age of the tree (Miranda and Pereira 2002c).

1 **Table 1.** Values of Lignin Content in Wood and Delignified Samples (% of sample), Obtained by Pyrolysis and Wet Chemistry

Cooking conditions		Sapwood					Heartwood				
		Wet chemistry				Pyrolysis	Wet chemistry				Pyrolysis
Temperature (°C)	Time (min)	Klason-lignin	Soluble-lignin	Total	Klason/sol.	Py-lignin	Klason-lignin	Soluble-lignin	Total	Klason/sol.	Py-lignin
	Wood	21.4	3.9	25.3	5.6	23.0	21.8	4.0	25.8	5.5	23.7
130 °C	0	19.7	3.7	23.4	5.4	25.7	21.3	3.7	25.1	5.7	28.3
	1	19.5	3.5	23.3	5.5	24.2	21.5	3.5	25.0	6.2	24.9
	3	19.7	3.5	23.1	5.6	23.9	21.1	3.5	24.6	6.1	26.5
	5	19.6	3.5	23.1	5.6	24.3	20.8	3.7	24.5	5.7	27.1
	10	18.5	3.6	22.0	5.2	23.3	20.3	3.6	23.9	5.6	24.8
	20	17.4	3.6	21.0	4.9	22.0	19.1	3.6	22.7	5.3	22.9
	65	14.2	3.2	17.4	4.4	19.0	16.2	3.1	19.3	5.2	19.2
	95	12.0	2.8	14.8	4.3	15.2	13.7	2.7	16.5	5.0	14.7
	180	7.6	2.2	9.8	3.4	10.5	10.0	2.4	12.5	4.1	11.6
150 °C	0	19.0	3.9	22.9	4.8	25.0	20.9	3.9	24.7	5.4	26.7
	1	18.6	3.5	22.1	5.3	24.0	20.5	3.6	24.1	5.7	25.7
	3	18.1	3.6	21.6	5.1	22.8	20.2	3.6	23.8	5.6	26.6
	5	16.9	3.3	20.3	5.1	20.9	19.2	3.6	22.8	5.4	25.3
	10	15.4	3.1	18.5	5.0	19.3	17.3	3.2	20.5	5.4	19.8
	20	10.9	2.6	13.5	4.2	15.3	12.2	2.7	14.9	4.5	17.1
	65	3.5	1.0	4.5	3.5	3.9	3.8	1.3	5.1	2.9	5.3
	95	1.0	1.0	2.0	1.1	2.8	2.0	0.9	2.9	2.2	3.1
	180	0.7	1.2	1.9	0.6	2.8	1.5	1.2	2.7	1.3	2.5
170 °C	0	18.3	3.6	21.9	5.1	22.8	19.3	3.8	23.0	5.1	22.8
	1	16.5	3.5	20.0	4.7	17.3	17.7	3.5	21.2	5.0	18.8
	3	14.1	3.2	17.3	4.4	15.9	15.8	3.2	19.0	5.0	18.8
	5	9.8	2.5	12.3	4.0	12.5	11.9	2.6	14.5	4.6	13.2
	10	4.3	1.5	5.8	2.8	6.6	7.2	1.8	9.0	4.0	8.2
	20	0.9	1.1	1.9	0.8	2.9	2.4	1.2	3.6	2.0	3.1
	65	0.4	0.9	1.3	0.4	2.7	1.2	1.0	2.1	1.2	2.3
	95	0.4	0.8	1.2	0.5	2.4	1.1	0.9	2.0	1.2	2.3
	180	0.2	0.9	1.1	0.2	2.2	0.7	1.3	2.0	0.5	2.3

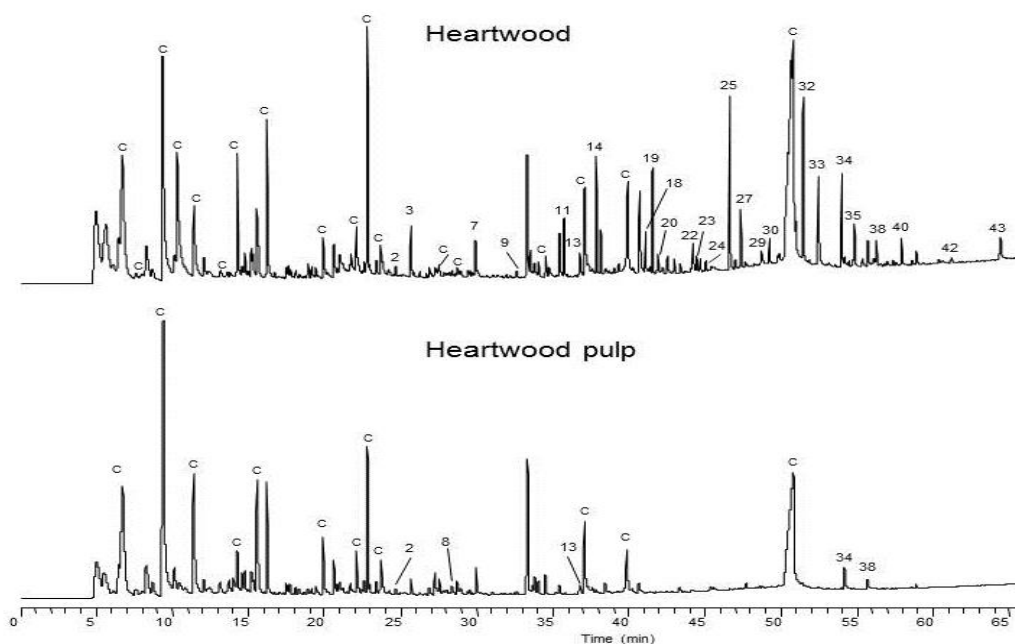
The values of soluble lignin observed for wood material (3.9% and 4.0%, Table 1) are comparable with the reported 3.6% (Pereira 1988) and are in the range of 4.4% to 8.1% (Poke *et al.* 2006). The values of Klason lignin (21.4 % and 21.8 %) were observed to be in the range of 18.9% to 25.5% reported by Poke *et al.* (2006) and near the reported 19.8% (Rencoret *et al.* 2011). This relation between acid-insoluble and soluble lignin is similar for other hardwoods, *i.e.* in beech (Yasuda *et al.* 2001).

The values of total residual, Klason lignin and of soluble lignin in the delignified samples are shown in Table 1. At 130 °C, the first points of delignification presented values of soluble lignin similar to those of wood (3.9 %), in line with the fact that lignin was still barely depolymerized, and the samples maintained a wood structure. However, during the delignification process, the lignin undergoes marked structural changes in both soluble and Klason fractions (Brunow *et al.* 1998), resulting in a change of the ratio of Klason to soluble lignin. The Klason/soluble ratio decreases during delignification, meaning that more soluble lignin is obtained along the reaction compared to Klason lignin. The Klason/soluble lignin ratio was 5.0 (at time 0, at all temperatures), which was similar to the 5.5 of wood lignin (Aldaesus *et al.* 2011), and decreased to nearly 0.5 in the pulps after 180 min at 170 °C. The relative increase of soluble lignin during delignification can be explained by the formation of different types of lignin-carbohydrate complexes (LCC) during pulping (Capanema *et al.* 2004). As mentioned by Lawoko *et al.* (2003), 90% of the residual lignin in softwood kraft pulps is covalently bonded to carbohydrates (of which 92% is bonded to xylan and glucomannan and 8% is bonded to cellulose). Besides the LCC fragments become insoluble in the kraft liquor, which occurs frequently in *E. grandis* kraft pulps (Capanema *et al.* 2004).

The Klason lignin of the pulps produced at 150 °C and 170 °C after 180 min were around 1%, whereas Pinto *et al.* (2005) obtained 1.3% for *E. globulus* pulps. The residual lignin in pulps is usually determined as Kappa number in the industry and research laboratories to evaluate the performance of the kraft cook (Gellerstedt 2009). The results depend upon the conditions used; *i.e.* reported values for *E. globulus* kraft pulps were 14.2 (Ibarra *et al.* 2007), and a range of 18.0 to 16.7 (Miranda and Pereira 2002a) corresponding to 2.5% and 2.7% of residual lignin.

### Lignin Determination by Py-GC/FID

Examples of the pyrograms obtained for wood and pulp (170 °C and 180 min) are presented in Fig. 1, and lignin-derived compounds obtained by pyrolysis are listed in Table 2. The peaks in the pyrograms corresponding to lignin-derived compounds are numbered as in Table 2, while those from carbohydrates are designated by C. The comparison of the wood program and the pulp program shows a notable decrease in the number and area of the lignin-derived peaks in the pulp, as expected since the objective of pulping is to remove the lignin from wood. The lignin quantification using the results of lignin degradation by pyrolysis of the wood and of the delignified samples is presented in Table 1. For wood, a total of 43 lignin-derived compounds were obtained by pyrolysis, mainly of the guaiacyl (21 compounds) and syringyl (17 compounds) type, with only 5 compounds from the hydroxyphenyl type, corresponding to respectively, 5%, 18%, and 1% of total identified compounds. Sapwood and heartwood presented similar values of total lignin, respectively 23.0% and 23.7%. Oudia *et al.* (2009) determined 21.6%, also using pyrolysis, but most of *E. globulus* lignin characterization involving pyrolysis has been focused mainly on the determination of the S/G ratio (Ibarra *et al.* 2005), without mentioning the total lignin present in the samples.



**Fig. 1.** Py-GC/FID chromatograms of heartwood and heartwood pulp produced at 170 °C and 180 min. The peaks of lignin derived compounds are represented by numbers and those from carbohydrates are represented by C.

During kraft pulping, the wood lignin is degraded by alkaline attack in the side-chain, a partial loss of C $\gamma$  atoms, and cleavage of  $\beta$ -O-4 and  $\alpha$ -O-4 bonds (Gierer 1980), inducing lignin solubilisation, thereby decreasing lignin content in the pulps, and allowing fiber separation. The decrease of lignin during pulping was confirmed by  $^{13}\text{C}$ -NMR and Py-GC/MS (del Rio *et al.* 2001) for *E. globulus*, and our results also showed this variation, as can be seen in Table 1.

**Table 2.** Identification of the Lignin-Derived Pyrolysis Products (as % of total identified lignin derivatives) in Sapwood and Heartwood of *E. globulus*

Peak no.	RT	Compound	Origin*	% of Total Lignin	
				Sapwood	Heartwood
1	20.18	benzaldehyde	H	0.77	0.57
2	24.65	phenol	H	0.73	0.62
3	25.65	2,3-Dihydro-5-hydroxy-6-methyl-(4H)-pyran-4-one / guaiacol	cH / G	n.d.	n.d.
4	26.66	o-cresol	H	0.38	0.31
5	28.36	m-/p-cresol	H	0.57	0.42
6	28.61	methylguaiacol	G	0.15	0.18
7	29.91	4-methylguaiacol / anhydrosugar	G / C	n.d.	n.d.
8	30.27	dimethylphenol	H	0.23	0.02
9	32.63	3-ethylguaiacol	G	0.43	0.61

10	33.35	4-ethylguaiacol / 4-hydroxy-3-methyl-(5 <i>H</i> )-furanone	G / C	n.d.	n.d.
11	35.72	4-vinylguaiacol	G	3.54	3.89
12	36.75	eugenol	G	2.49	2.12
13	36.85	4-propylguaiacol	G	0.25	0.28
14	37.84	syringol	S	10.14	7.33
15	38.49/38.65	isoeugenol isomer	G	0.84	0.76
16	39.00	isoeugenol ( <i>cis</i> )	G	0.37	0.36
17	39.32	unknown (M/Z 107,109,138)	G	0.70	1.07
18	41.09	Isoeugenol ( <i>trans</i> )	G	2.45	2.63
19	41.54	4-methylsyringol	S	5.47	6.51
20	41.88	vanillin	G	1.50	1.62
21	42.52/42.96	C <sub>10</sub> H <sub>10</sub> O <sub>2</sub>	G	2.31	2.41
22	44.20	homovanillin	G	2.29	2.47
23	44.43	4-ethylsyringol	S	1.28	1.18
24	45.05	acetoguaiacone	G	0.68	0.70
25	46.63	4-vinylsyringol	S	12.07	11.47
26	46.99	guaiacyl acetone	G	0.69	0.73
27	47.34	4-allylsyringol	S	4.09	3.81
28	48.21	propioguaiacone	G	0.34	0.19
29	48.69	coniferyl alcohol ( <i>cis</i> )	G	1.03	1.13
30	49.23	4-propenylsyringol ( <i>cis</i> )	S	2.16	1.85
31	50.62/50.95	C <sub>11</sub> H <sub>12</sub> O <sub>3</sub>	S	7.04	8.00
32	51.44	4-propenylsyringol ( <i>trans</i> )	S	10.32	10.47
33	52.45	syringaldehyde	S	7.50	7.39
34	53.99	homosyringaldehyde	S	5.47	6.46
35	54.81	acetosyringone	S	3.46	3.58
36	55.44	coniferyl alcohol ( <i>trans</i> )	G	0.14	0.13
37	56.10	coniferaldehyde	G	0.81	0.74
38	56.25	syringyl acetone	S	1.48	1.79
39	57.36	propiosyringone	S	0.28	0.27
40	57.91	sinapyl alcohol isomer	S	1.85	1.84
41	60.38	dihydrosinapyl alcohol	S	0.35	0.34
42	61.17	sinapyl alcohol ( <i>cis</i> )	S	0.55	0.59
43	64.42	sinapinaldehyde	S	2.80	3.15
			<b>Total H</b>	<b>2.7</b>	<b>1.9</b>
			<b>Total G</b>	<b>21.0</b>	<b>22.0</b>
			<b>Total S</b>	<b>76.3</b>	<b>76.0</b>
<b>Total lignin (sum of lignin derivatives, in % of identified area)</b>				<b>23.0</b>	<b>23.7</b>
			<b>S/G ratio</b>	<b>3.63</b>	<b>3.45</b>



## Comparison of Wet Chemistry and Pyrolysis Lignin Determination

Wet-chemical determinations of total lignin and Klason lignin were plotted against total lignin content determined by pyrolysis (py-lignin); these results are presented in Fig. 2. The values of py-lignin were comparable with the wet-chemical total lignin determinations, and the values are aligned along the plot diagonal (Fig. 2a), with a correlation coefficient of 0.990. In relation to Klason lignin, the values of py-lignin were consistently higher by 2% to 5%, and the regression line was consequently below the plot diagonal (Fig. 2b) ( $r = 0.988$ ). This shows the importance of soluble lignin for the accurate determination of the lignin present in the samples.

The results from wet chemistry and pyrolysis analysis were correlated linearly as: Klason-lignin =  $0.86 * \text{Py-lignin} - 1.03$  ( $R^2 = 0.977$ ,  $R^2_{\text{adjust}}=0.976$ ); and Total lignin =  $0.97 * \text{Py-lignin} - 0.16$  ( $R^2$  of 0.980,  $R^2_{\text{adjust}}=0.979$ ). Such high coefficients of determination indicate the strength of the linear relation between the results obtained from both methodologies and with samples that have a wide range of lignin contents (from 26 % to 1.0 %).

Studies that compare lignin determination by pyrolysis and by wet chemistry are scarce for hardwood species and in particular for *Eucalyptus*. For softwood pulps Alves *et al.* (2006) obtained a high coefficient of determination ( $R^2=0.93$ ) when Klason lignin values were plotted against those obtained from pyrolysis. Fahmi *et al.* (2007) obtained also a high coefficient of determination for such lignin determinations in grasses ( $R^2=0.88$ ). These results show that pyrolysis can be used to determine residual lignin in lignocellulosic materials and in pulps with different degrees of delignification and with different lignin monomeric composition.

The two analytical procedures that were used require sample preparation. For lignin determination by wet chemistry: i) the sample has to be extracted first, because otherwise some extractives interfere with the determination of Klason lignin, but a small part of the lignin may be removed during the extraction with ethanol and water (Dence 1992); ii) if the sample has high content of proteins, tannins or silica, then this can artificially increase the results for Klason lignin (Brunow *et al.* 1998; Prozil *et al.* 2012); and iii) the determination of soluble lignin requires an absorptivity value, which is usually taken as  $110 \text{ l.g}^{-1}.\text{cm}^{-1}$  (obtained for milled wood lignin), although ideally it should be determined for each sample (Dence 1992). With regard to pyrolysis, homogeneity of the samples is fundamental, and therefore a preliminary step is sample grinding. If this is not taken in account, the formation of pyrolysis products is affected, and their quantification will not be comparable (Meier and Faix 1992). In fact, small changes in the experimental conditions of pyrolysis can affect the reproducibility of the results (Faix and Meier 1989).

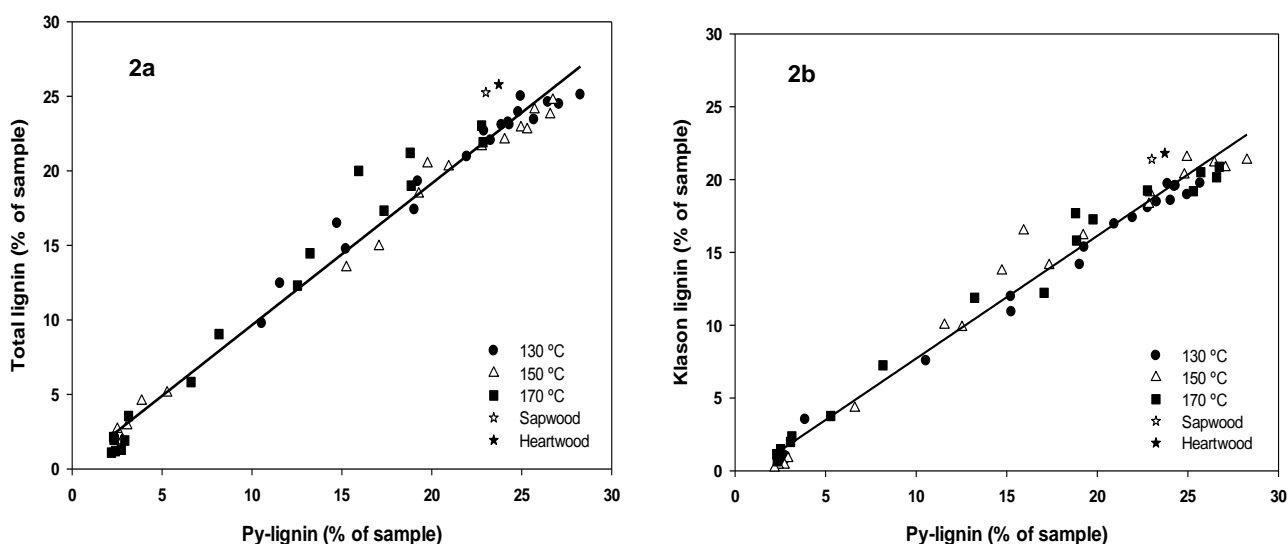
Pyrolysis has two important advantages in relation to wet chemistry: (i) the pyrolytic reactions apply to the lignin and other cell wall components in their *in-situ* context without selective chemical fractionation or modification; and (ii) in addition to lignin quantification, the pyrolysis products allow additional information to be obtained on the type of its monomeric units and of lignin composition (*i.e.* the S/G ratio can be calculated).

## Delignification Kinetics

Studies on delignification kinetics are interesting and important in order to understand the pulping phenomena and also to improve delignification. Most kinetic studies are based on results of lignin obtained from wet chemistry (Miranda and Pereira

2002a; Lourenço *et al.* 2011) and, to our knowledge, only one set of results was obtained using pyrolysis analysis (Lourenço *et al.* 2012).

Modeling the delignification kinetics of sapwood and heartwood by application of Eq. 1 was made using the lignin determination by pyrolysis and wet chemistry (using Klason values). Two delignification stages were identified under the experimental conditions used: at 130 °C, the model presented a lignin removal of 30%, during the initial phase, followed by a bulk phase. At 150 °C and 170 °C the initial phase was not identified, and instead a combined phase designated as initial+bulk, followed by a residual phase was considered. This approach was already described by Lourenço *et al.* (2012) for total lignin values. The kinetic parameters attained are presented at Table 3, for the lignin values determined by both experimental methods (Klason and pyrolysis). The reaction rates and the mass fraction values were very similar in both cases.

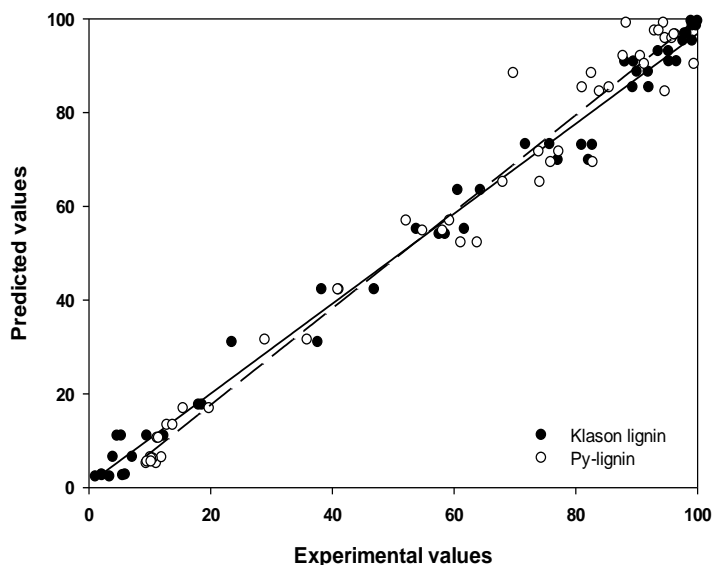


**Fig. 2a.** Correlation between total lignin and py-lignin (both % of sample) using wood (heartwood and sapwood) and all samples obtained by delignification at 130 °C, 150 °C, and 170 °C. The regression line has a  $R^2$  of 0.980; **2b.** Correlation between Klason lignin and py-lignin (both % of sample) using wood (heartwood and sapwood) and all samples obtained by delignification at 130 °C, 150 °C, and 170 °C. The regression line has an  $R^2$  of 0.977

**Table 3.** Models Equations for the Klason-lignin and Py-lignin Obtained from Delignified Samples at 3 Cooking Temperatures (130 °C, 150 °C, and 170 °C)

		$L/L_0 = a_{i+b} \exp(-k_{i+b} t) + a_r \exp(-k_r t)$
130 °C	Klason	$L/L_0 = 30.0 \exp(-0.023 t) + 70.0 \exp(-0.002 t)$
	Pyrolysis	$L/L_0 = 30.0 \exp(-0.022 t) + 70.0 \exp(-0.003 t)$
150 °C	Klason	$L/L_0 = 90.0 \exp(-0.035 t) + 10.0 \exp(-0.003 t)$
	Pyrolysis	$L/L_0 = 85.0 \exp(-0.039 t) + 15.0 \exp(-0.006 t)$
170 °C	Klason	$L/L_0 = 97.0 \exp(-0.124 t) + 3.0 \exp(-0.001 t)$
	Pyrolysis	$L/L_0 = 93.0 \exp(-0.133 t) + 7.0 \exp(-0.001 t)$

The performance of the kinetic delignification models is presented in Fig. 3, where the predicted lignin values during delignification are plotted versus the respective experimental data. There was a good correlation, with the majority of the points near the diagonal and similar trend lines with very high correlation factors (with  $R^2$  values of 0.990 and 0.975, respectively for Klason lignin and py-lignin). The models can predict the experimental results with high precision for the Klason and pyrolysis results, showing that the models can be used for the estimation of lignin content in samples obtained within the range of conditions applied in this study.



**Fig. 3.** Experimental values of delignification plotted against the values predicted by modeling (in % of original wood lignin). Trendline for Klason-lignin (solid line,  $R^2 = 0.990$ ), and trendline for Py-lignin (dashed line,  $R^2 = 0.975$ ), using all points of delignification.

## CONCLUSIONS

The results obtained by wet chemistry and pyrolysis for lignin determinations in wood and delignified wood in the course of a pulping process, showed that:

1. Both methods can be applied to quantify lignocellulosic materials (wood and pulps) with a broad range of lignin contents, although pyrolysis presents advantages over wet chemical procedures.
2. The pyrolysis-determined lignin contents correlated well with the total lignin determined by wet chemistry (Klason lignin and acid soluble lignin). The values for py-lignin were higher by 2% to 5% in relation to Klason-lignin, showing the importance of acid-soluble lignin for an accurate appraisal of the lignin amount, especially in delignified samples, where the relative importance of soluble lignin is higher.
3. Pyrolysis lignin values can be used for kinetic modelling of delignification with very high predictive value, making it possible to obtain results similar to those from modelling when using wet chemical determinations.

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