# Impact of the Chemical Composition of *Pinus radiata* Wood on its Physical and Mechanical Properties Following Thermo-Hygromechanical Densification

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The thermo-hygromechanical densification process changes the chemical composition and the physical and mechanical properties of wood. The aim of this work was to study the impact of the chemical composition of Pinus radiata wood on its physical and mechanical properties following the thermo-hygromechanical densification process. The samples were initially segregated by lignin content. Density, hardness, modulus of elasticity (MOE), and modulus of rupture (MOR), in addition to lignin, a-cellulose, hemicellulose, and extractive contents, were determined before and after the densification process. The results indicated that densified wood with high initial lignin content had greater rate of increases in density and MOE than wood with lower initial lignin content. Additionally, densified wood with lower initial lignin content had greater rate of increases in hardness. The rate of increase of MOR did not show significant differences within both groups. Carbohydrates present in the control and the densified wood played an important role in the mechanical strength of the final product.

Keywords: Pinus radiata; Thermo-hygromechanical process; Wood densification; Chemical components

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# INTRODUCTION

Densification is a modification method in which the wood cell structure is compressed in a hot press to obtain a higher-density material (Laine *et al.* 2014). The natural elastic properties of the wood, as well as its density, moisture content, orientation of the sample, and compression ratio play important roles in the densification process (Kutnar and Šernek 2007; Pelit *et al.* 2014). This technique yields a reduction in the void volume of the wood, which increases its density and enhances its mechanical properties (Navi and Heger 2004; Fang *et al.* 2012a; Chávez 2015).

The thermo-hygromechanical (THM) densification process can be performed in an open system by compression combined with steam injection (Navi and Sandberg 2012). THM densification reduces wood hygroscopicity, improves dimensional stability, enhances resistance to microorganisms, and releases internal stresses (Fang *et al.* 2011; Diouf *et al.* 2011; Navi and Sandberg 2012; Rautkari *et al.* 2013; Chávez 2015). Some wood densification studies have shown increases in density and Brinell hardness of 100% or more (Kamke 2006; Fang *et al.* 2011; Bustos *et al.* 2012). The modulus of elasticity (MOE) and modulus of rupture (MOR) in static bending of THM densified wood increase by 50% and 100%, respectively (Mariotti 2010; Fang *et al.* 2011; Chávez 2015).

The chemical composition of wood changes when it is subjected to modification processes involving steam, heat, and mechanical compression (Navi 2011; Kariz *et al.* 2017). The THM densification process in softwood increases the Klason lignin content, and extractive substances are evaporated or decomposed (Boonstra *et al.* 2007; Rousset *et al.* 2009; Liu *et al.* 2014). Fourier-transform infrared spectroscopy (FTIR) analyses in densified softwoods show a reduction in the degree of polymerization of hemicelluloses and lignin condensation reactions. This results in an increase of lignin-carbohydrate complexes, increased crystalline cellulose content, glucomannan decomposition, and loss of C=O groups bound to the lignin backbone (Yin *et al.* 2011; Guo *et al.* 2015).

Although there are studies that report the effects of the densification process on the physical and mechanical properties of wood and its chemical composition (Diouf *et al.* 2011; Sandberg *et al.* 2013), there is little information on how the chemical components of wood are related to its physical and mechanical properties, especially those involved in the THM process. Therefore, the objective of this work was to study the impact of the chemical composition of wood on the physical and mechanical properties of *Pinus radiata* after THM densification.

### **EXPERIMENTAL**

#### Materials

For this study, 28 commercial planed sawn boards of *Pinus radiata* provided by CMPC Maderas sawmill (Los Ángeles, Chile) were used. Their dimensions were 7 mm  $\times$  80 mm  $\times$  1000 mm. Their average moisture content (dry basis) and density (at 9% moisture content) were 9% and 500 kg/m<sup>3</sup>, respectively. Each board was graded visually to obtain pieces free of visible defects such as knots, cracks, and bark pockets. Additionally, only sapwood was considered within the boards. A ferric chloride stain was used to discard the heartwood. The boards were cut into two parts: a control sample and a sample to be used for densification. The 28 control samples and 28 densified samples were characterized in terms of chemical composition, physical properties, and mechanical properties as depicted in Fig. 1.



**Fig. 1.** Schematic representation of the distribution of test samples for measurement of density, color, bending properties, hardness, and chemical composition of control and densified wood

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### **Determination of Chemical Composition**

The chemical composition was determined in the control and densified wood. Both control and densified wood were milled in a knife mill (FRITSCH, Germany) and sieved to 45 to 60 mesh. To determine the amount of extractives, the milled wood was extracted in a Soxhlet apparatus with acetone for 16 h according to TAPPI T280 pm-99 (2015). Extractive-free milled wood was used in the chemical characterization assays.

The holocellulose and  $\alpha$ -cellulose were measured according to the TAPPI T 9 m-54 (2015). Holocellulose was prepared with 250 mg of extractive free milled wood and then adding 5 mL of deionised water, 2 mL CH<sub>3</sub>COOH, and 5 mL of 80% NaClO<sub>2</sub>. The samples were immersed in a water bath at 90 °C for 1 h. After this period, an additional 4 mL CH<sub>3</sub>COOH and 10 mL of 80% NaClO<sub>2</sub> were added to the flask, and the reaction was carried out for another 1 h at 90 °C. The reaction was stopped by immersing the flask in a water bath at 10 °C. Solids were filtered and washed with deionised water, and dried at 105 °C to constant weight, with the remaining weight quantified as holocellulose. Later, 100 mg of holocellulose was treated with 8 mL of 17.5% (w/v) NaOH for 30 min at room temperature with stirring every 10 min. Next, 8 mL of distilled water was added to the solution, and the reaction was carried out for an additional 30 min. Solids were filtered, washed with of distilled water, and impregnated with 20 mL of 1.0 M CH<sub>3</sub>COOH for 5 min. The residue was washed with excess water, dried at 105 °C to constant weight, and quantified as  $\alpha$ -cellulose. All analyses, holocellulose and  $\alpha$ -cellulose, were performed in triplicate.

The lignin content was determined as described by Aguayo *et al.* (2010). Samples of 300 mg were weighed in a test tube, and 3 mL of 72% (w/w) H<sub>2</sub>SO<sub>4</sub> was added. Hydrolysis was performed in a water bath at 30 °C for 1 h with stirring applied every 10 min. Subsequently, the acid was diluted to 4% (w/w) and transferred to a 250 mL Erlenmeyer flask and autoclaved for 1 h at 121 °C. The residual material was cooled and filtered. Solids were dried to constant weight at 105 °C and classified as insoluble lignin. Soluble lignin was determined by measuring the solution absorbance at 205 nm (Dence 1992). Total lignin was calculated as the sum of insoluble and soluble lignin. Analyses were performed in triplicate for each sample.

## Segregation of Samples

Lignin is a native plasticizer embedded in the cell walls. If all the lignin in the cell walls could be softened, then the wood would exhibit plasticizing during its modification (Wang *et al.* 2011). To analyze the behavior and effects of the chemical composition in *Pinus radiata*, the samples were segregated by lignin content in control wood (C). Two groups were identified: group A, with low lignin content, and group B, with high lignin content. After undergoing the THM densification process, both groups were identified with the letter D.

## **Densification Process**

Planed sawn boards of 7 mm  $\times$  80 mm  $\times$  500 mm were densified using a thermohygromechanical (THM) process. The densification process was carried out at the Renewable Materials Research Center (*Centre de recherche sur les matériaux renouvelables*, CRMR), Université Laval, Quebec City, Quebec, Canada. A steam injection press (Dieffenbacher, Alpharetta, GA, USA) with dimensions of 862 mm  $\times$  862 mm was used for the densification treatment (Fang *et al.* 2012b). Steam injection holes with a diameter of 1.5 mm were distributed uniformly at 32 mm intervals on both the upper and lower platens of the press. The two platens were preheated to the target temperature before treatment. Steam was continuously injected throughout the densification process at a maximum pressure of 550 kPa. The *Pinus radiata* boards were densified at 180 °C and 9000 kPa of pressure with 550 kPa of steam pressure for 7 min according to Chávez (2015), providing a densification ratio of 50%. The press was kept closed for 5 min to prevent an increase in thickness of the samples due to the springback effect. After the THM process, the boards were conditioned at 20 °C and 65% relative humidity until constant weight.

#### **Determination of Physical and Mechanical Properties**

#### Density

The samples were placed in a conditioning room at 20 °C and 65% relative humidity to reach an equilibrium moisture content of 12%. The dimensions of the control samples were 7 mm  $\times$  50 mm  $\times$  50 mm and the dimensions of the densified samples were 3.5 mm  $\times$  50 mm. Following the conditioning stage, the samples were measured and weighed for apparent density determination (kg/m<sup>3</sup>) according to ASTM D1037 (2012).

#### Static bending

Three-point static bending tests were performed according to ASTM D1037-12 (2012) on densified and control samples with a Zwick Roell Z020 Universal Testing Machine, with a capacity of 20 kN. The span was 24 times the nominal thickness of the samples. The load was applied continuously throughout the test at a uniform rate. The modulus of rupture (MOR) and the modulus of elasticity (MOE) were determined with Eqs. 1 and 2, respectively,

$$MOR = \frac{3PL}{2bd^2} \tag{1}$$

$$MOE = \frac{\Delta PL^3}{4\Delta \delta b d^3} \tag{2}$$

where *b* is the width of the sample (mm), *d* is the thickness of the sample (mm), *L* is the span (mm), *P* is the maximum load (N),  $\Delta P$  is the loading increment in the proportional section of the load-deflection diagram (elastic zone) (N), and  $\Delta \delta$  is the deflection measured at mid-span (mm).

#### Brinell hardness

Brinell hardness tests were conducted using a universal testing machine according to the European standard EN 1534 (2000). The testing machine was equipped with a hardened steel ball indenter with a diameter of 10 mm. A maximum load of 1000 N was reached in 15 s and maintained for 25 s. The load was then released. The measurement of the diameters of the indentations were made with a digital caliper with  $\pm$  0.01 mm sensitivity and a magnifier. The Brinell hardness HB (N/mm<sup>2</sup>) was calculated using Eq. 3,

(3)

$$HB = \frac{P}{\frac{\pi D}{2}(D - \sqrt{D^2 - d^2})}$$

where P is the maximum load (N), D is the diameter of the steel ball indenter, and d is the average diameter of the indentation (mm).

#### Color analyses

In order to evaluate color differences of densified wooden surfaces, color measurements on the control and densified samples were carried out. Color measurements were conducted by a portable color spectrometer (spectro-guide sphere gloss meter, model CD-6834, BYK-Gardner GmbH, Geretsried, Germany). The colorimeter was calibrated at D65 lighting and observing angle of 10°. The CIE  $L^*a^*b^*$  chromaticity system was used for color measurements. The color is described by 3 coordinates:  $L^*$  represents the lightness,  $a^*$  represents the content from red to green, and  $b^*$  represents the content from yellow to blue. According the CIE  $L^*a^*b^*$  color system, the total color difference was determined using Eq. 4 (Mitani and Barboutis 2014) from two measurements taken for each piece:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{4}$$

where  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  represent the differences between the tested sample and the standard piece. These quantities can be calculated by the difference between the coordinate value of the sample and the coordinate value of the control. The total color change  $\Delta E^*$  represents the color difference.

#### FTIR spectroscopy

The control and densified wood samples were analyzed by FTIR spectroscopy. The spectra were acquired in transmittance mode using the KBr technique for sample preparation. The spectra range was between 4000 and 400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and 32 scans, using a Spectrum BX FTIR spectrometer (PerkinElmer Inc., Waltham, MA, USA). A spectrum was obtained for each control and densified sample. The spectra were normalized in the 1030 cm<sup>-1</sup> band and averaged by groups for analysis.

#### **Statistical Analysis**

The normality (Shapiro-Wilk) of the physical and mechanical properties and chemical composition data distribution, ANOVA, Tukey test (Tables 1 and 2) and a t-test (Table 3) were performed using the software Statgraphics Centurion XVII (Statpoint Technologies, Inc., The Plains, VA, USA). The principal component analysis (PCA) was performed using all the physical and mechanical properties. The chemical composition data were obtained in order to evaluate the spontaneous separation of samples, using the software Pirouette 4.5 (Infometrix, Inc., Bothell, WA, USA) after a scaling of the data. Correlations between chemical composition and physical and mechanical properties were determined using Pearson's coefficient.

# **RESULTS AND DISCUSSION**

## **Chemical Composition of Control and Densified Wood**

Table 1 shows the chemical composition of the *P. radiata* samples analyzed, from the two groups of segregated control wood (C) and densified wood (D).

Group AC (14 pieces) presented low lignin content values (from 25.2% to 27.3%). In contrast, group BC (14 pieces) contained samples with higher lignin content (from 27.6% to 32.7%). These control groups presented significant differences at p < p0.05 (Tukey test). After the densification process, group AD (14 pieces) presented lignin content values from 31.6% to 36.8%, and group BD (14 pieces) presented lignin content values from 32.1% to 47.6%. It is known that, after densification, the wood presents changes in its chemical composition (Kutnar and Šernek 2007; Diouf *et al.* 2011; Neyses et al. 2016; Yin et al. 2017). In this study, it was observed that lignin content increased for both groups (low lignin content and high lignin content). This may be due to a partial depolymerization of lignin and a rearrangement of the hemicelluloses (Navi and Pizzi 2015), as the hemicelluloses easily degrade due to their amorphous structure and low molecular weight (González-Peña et al. 2009). Degradation of hemicelluloses in the densification process has been reported in previous works (Tjeerdsma and Militz 2005; Boonstra 2008). Similar results were obtained in this study, where average hemicellulose contents were 28.9% and 29.5% (groups AC and BC, respectively). These numbers decreased drastically following the densification process (5.5% and 7.6% for groups AD and BD, respectively).

The average  $\alpha$ -cellulose content in control groups AC and BC was 41.7% and 38.4%, respectively. After densification, the  $\alpha$ -cellulose increased to 53.4% and 50.7% for groups AD and BD, respectively. There was a significant difference in mean extractive content between groups AC and BD, as can be seen in Table 1. The extractive content may increase due to the degradation of hemicelluloses and lignin, which may generate new extractives (Liu *et al.* 2014; Li *et al.* 2016).

Component		AC	BC	AD	BD	<i>p</i> -value	
Lignin (%)	Range	25.2-27.3	27.6-32.7	31.6-36.8	32.1-47.6	. 0.0001	
	Ā	26.5 <sup>d</sup>	29.3 °	34.2 <sup>b</sup>	37.7 ª	< 0.0001	
Holocellulose (%)	Range	66.8-73.6	62.5-72.1	55.8-63.8	52.7-65.3	. 0.0001	
	x	70.6 <sup>a</sup>	67.9 <sup>b</sup>	58.9 °	58.3 °	< 0.0001	
α-Cellulose (%)	Range	38.6-45.0	34.6-42.4	46.3-62.9	40.9-70.0	< 0.0001	
	x	41.7 °	38.4 <sup>d</sup>	53.4 ª	50.7 <sup>b</sup>	< 0.0001	
Hemicelluloses * (%)	Range	26.2-31.8	26.4-32.0	0-16.0	4.7-14.7	10.0001	
	x	28.9 <sup>a</sup>	29.5 ª	5.5 °	7.6 <sup>b</sup>	< 0.0001	
Extractives (%)	Range	0.56-3.11	0.26-4.29	1.56-3.53	0.40-4.27	0.0407	
	x	1.84 <sup>b</sup>	2.11 <sup>ab</sup>	2.20 <sup>ab</sup>	2.34 ª	0.0107	

Table 1. Chemical Composition of Densified and Control Samples of P. radiata

\* Hemicellulose content was calculated as holocellulose content –  $\alpha$ -cellulose content (Li *et al.* 2016). Values within a row with different letters present a significant difference at p < 0.05 (Tukey test). AC: control samples with low lignin content; BC: control samples with high lignin content; AD: densified samples with low lignin content; BD: densified samples with high lignin content

## **Physical and Mechanical Characterization**

Table 2 shows the results obtained for the physical and mechanical properties of the samples from the groups low in lignin content and high in lignin content. Following densification, the samples' density increased from 546 kg/m<sup>3</sup> to 1163 kg/m<sup>3</sup> for group A and from 506 kg/m<sup>3</sup> to 1101 kg/m<sup>3</sup> for group B. This can be explained by the decrease in the volume of cavities and the increase in the amount of cell wall per unit volume according to the compression ratio of 50% (Navi and Sanberg 2012; Pelit *et al.* 2015). The Brinell hardness also showed a considerable increase, from 16 to 97 MPa for group A and 17 to 96 MPa for group B. In the case of bending, the MOE values of densified wood were 18100 MPa and 17300 MPa for groups A and B, respectively, while the MOR presented values of 216 and 192 MPa for groups A and B, respectively. Similar results were found by Kutnar *et al.* (2009), Fang *et al.* (2012a), and Chávez (2015).

The total color change was observed by a decrease in  $L^*$ , indicating a loss of lightness (reflectance, evaluated in the green wavelengths), possibly due to a degradation of the hemicelluloses in thermally treated wood and therefore an increase in lignin content (Huang *et al.* 2012; Bekhta *et al.* 2014). For the value of  $a^*$ , the samples had a more reddish color in group B. This color can be associated with the extractive content of the wood (Gierlinger *et al.* 2004). The values of  $b^*$  increased, with the wood becoming more yellow. This color results from the photochemistry of the basic components of wood, particularly lignin (Pelit 2016). The color change ( $\Delta E$ ) showed no significant difference between the two groups of densified wood.

Property		AC	BC	AD	BD	<i>p</i> -value	
Density (kg/m <sup>3</sup> )	Range	473-624	394-574	1066-1308	919-1334	- 0.0001	
	x	546 <sup>c</sup>	506 °	1163 ª	1101 <sup>b</sup>	< 0.0001	
Hardness (MPa)	Range	13-19	10-25	76-132	60-136	< 0.0001	
	x	16 <sup>b</sup>	17 <sup>b</sup>	97 <sup>a</sup>	96 <sup>a</sup>		
MOE (MPa)	Range	10100-17600	5710-15800	16000-20500	6700-25800	< 0.0001	
	x	14010 <sup>b</sup>	12131 <sup>b</sup>	18091 <sup>a</sup>	17335 <sup>a</sup>		
MOR (MPa)	Range	92-136	62-109	190 -243	97- 270	< 0.0001	
	x	108 <sup>c</sup>	89 <sup>c</sup>	216 ª	192 <sup>b</sup>		
L*	Range	70-82	74-82	67-78	69-78	- 0.0001	
	x	76 <sup>a</sup>	<b>78</b> ª	73 <sup>b</sup>	74 <sup>b</sup>	< 0.0001	
a*	Range	4-9	4-8	9- 10	6-8	0.0000	
	x	6.5 <sup>b</sup>	6 <sup>b</sup>	<b>7</b> a	7 <sup>ab</sup>	0.0002	
b*	Range	23-30	22-29	24-31	24-31	. 0.0001	
	x	25 <sup>b</sup>	24 <sup>b</sup>	28 <sup>a</sup>	27 <sup>a</sup>	< 0.0001	
ΔE	Range	-	-	1-8.6	2-10	0.4000	
	x	-	-	4.8 <sup>a</sup>	5.5 <sup>a</sup>	0.4608	

**Table 2.** Physical and Mechanical Properties of Control and Densified Wood

Values within a row with different letters present a significant difference at p < 0.05 (Tukey test). AC: control samples with low lignin content; BC: control samples with high lignin content; AD: densified samples with low lignin content; BD: densified samples with high lignin content

# **FTIR Analysis**

FTIR spectra of control and densified wood were analyzed (Fig. 2). Band assignments were made according to Pandey (1999) and Faix (1992). Figure 2 shows the spectra of groups A and B for control and densified wood. Small differences were found among the spectra, which is most likely a consequence of the short processing time (Kutnar *et al.* 2008).

The analysis was focused on characteristic bands of the infrared spectra of the control and densified wood in groups A and B: 1740 cm<sup>-1</sup> (C=O stretch in unconjugated ketones), hemicellulose characteristic band; 1640 cm<sup>-1</sup> (water associated with lignin or cellulose); 1510 cm<sup>-1</sup> (C=C stretching of the aromatic ring (with G unit of lignin)); 1458 cm<sup>-1</sup> (C–H deformation in –OCH<sub>3</sub> in lignin and CH<sub>2</sub> symmetric scissoring in pyran ring), and 1269 cm<sup>-1</sup> (C–H of guaiacyl ring in lignin), characteristics of lignin. The bands 1374 cm<sup>-1</sup> and 1169 cm<sup>-1</sup> (CH bending in cellulose I and cellulose II and hemicellulose and C–O–C asymmetric stretching in cellulose I and cellulose II), which characterize the carbohydrates, were also considered.



**Fig. 2.** FTIR spectra of control and densified wood. AC: control samples with low lignin content; BC: control samples with high lignin content; AD: densified samples with low lignin content; BD: densified samples with high lignin content

## Effect of Chemical and Physical-Mechanical Features in THM Process

In the THM densification of wood, factors such as temperature and pressure affect the wood's chemical components (individually and their interactions) and therefore its mechanical properties (Boonstra *et al.* 2007). All the results obtained (chemical composition and physical and mechanical properties) were also analyzed by PCA, which is a multivariate data analysis method suitable for describing major trends in a data set and the relationships among samples and among variables (Aguayo *et al.* 2010).

Figure 3A shows the PCA results of control and densified samples. The PCA identified patterns to highlight their similarities and differences. The results show that the

first component accounted for 73.8% of the variance of the data. The main separation of the groups was defined by PC1 and PC2, obtained following the process of densification. The more relevant components for this separation were lignin, hemicellulose,  $\alpha$ -cellulose, density, and MOE (Fig. 3B). Hardness and MOR mainly characterized the densified samples, while the control was characterized by MOE and chemical composition (lignin, α-cellulose, hemicellulose, and holocellulose). Figure 3C shows the PCA of the control and densified samples of group A, in which the first main component explained 84.8% of the variance of the data. The main separation of the data was defined by PC1 and PC2, and the components that most influenced this separation were lignin,  $\alpha$ -cellulose, hemicellulose, MOE, color, and density (Fig. 3D). Density mainly characterized group AD, while group AC was characterized by lignin,  $\alpha$ -cellulose, hemicellulose, MOE, and color. Figure 3E shows the PCA of the control and densified samples of group B, in which the first main component explained 73.7% of the variance of the data. The main separation of the data was defined by PC1 and PC2, and the components that most influenced this separation were lignin,  $\alpha$ -cellulose, hemicellulose, density, MOE, extractives, and color (Fig. 3F). Holocellulose, hemicellulose, and  $L^*$  characterized group BC, while group BD was characterized by hardness, MOR, extractives, and  $a^*$ .

This information was in agreement with the data for the control samples (Tables 1 and 2), where there were significant differences between groups A and B in chemical composition but not in physical and mechanical properties. In contrast, the densified wood showed differences in chemical composition and also in some physical and mechanical properties.

The main chemical components of the cell wall contribute to different degrees to the mechanical properties of wood (Winandy and Rowell 2005). With the segregation of the samples by lignin content, it was possible to establish groups that could provide information about the behavior of the wood's chemical components during THM densification and to analyze whether segregation affected the various properties of the final product. Table 3 shows the increases in density, hardness, and MOE in densified wood by group, with significant differences in the properties studied. Density increased by 118% in group B but by 109% in group A.

When grouping all the data of density and lignin content, a correlation coefficient of r = 0.9 was observed for group A and r = 0.7 for group B, with a greater dispersion of data for group B (Fig. 4A). Hardness increased by 512% for group A and 415% for group B, compared to the control samples. High correlation coefficients between hardness and lignin content were seen in both groups, with r = 0.8 for group A and r = 0.7 for group B (Fig. 4B).

This strong relationship may occur because the hardness of the cell wall is dominated by the matrix composition (Gindl *et al.* 2004). In the densification process, a reduction in hemicellulose content has been reported (Li *et al.* 2016). This chemical component of the wood is relevant because the main role of the hemicelluloses is to act as a bonding material between the microfibrils, allowing their mobility in the deformation process (Keckes *et al.* 2003). This information may explain this study's results for MOE, where the higher increase, 57%, was obtained for group B. This can be related to the residual hemicellulose content in the densified wood of group B (7.6%), while group A had a lower MOE increase, 28%, and a lower hemicellulose content in its densified wood (5.5%) (Tables 1 and 3).

MOE and hemicellulose showed high correlation in both groups (Fig. 4C). MOR increased by 104% for group A and 106% for group B: a statistically insignificant

difference between the groups. Figure 4D shows a high negative correlation between MOR and hemicellulose content in both groups (r = -0.935 and r = -0.840, for groups A and B respectively).



**Fig. 3.** Principal component analysis of chemical composition and physical and mechanical properties. A: scores of control and densified wood; B: loadings of control and densified wood; C: scores of control wood; D: loadings of control wood; E: scores of densified wood; F: loadings of densified wood. AC: control samples with low lignin content; BC: control samples with high lignin content; AD: densified samples with low lignin content; BD: densified samples with high lignin content

**Table 3.** Rate of Increase in Physical and Mechanical Properties of Groups A

 and B

Property	Increase in Densifie	n voluo	
	A	В	<i>p</i> -value
Density	109 <sup>b</sup>	118 ª	0.0041
Hardness	512 ª	415 <sup>b</sup>	0.0473
MOE	28 <sup>b</sup>	57 <sup>a</sup>	0.0018
MOR	104 <sup>a</sup>	106 ª	0.9001

Values within a row with different letters differ significantly at p < 0.05 (t-test).



**Fig. 4.** Relationships between chemical composition and physical and mechanical properties of control and densified woods. A: density *vs.* lignin content; B: hardness *vs.* lignin content; C: MOE *vs.* hemicellulose content; D: MOR *vs.* hemicellulose content. AC: control samples with low lignin content; BC: control samples with high lignin content; AD: densified samples with low lignin content; BD: densified samples with high lignin content

# CONCLUSIONS

- 1. The wood samples of high initial lignin content increased more in density and MOE after the densification process than did the samples of low initial lignin content. However, the rate increase of hardness after THM densification was greater for wood of low initial lignin content than for wood of high initial lignin content.
- 2. The carbohydrates ( $\alpha$ -cellulose and hemicelluloses) present in the control and densified samples play a major role in determining the mechanical strengths of the final products, contributing significantly in MOE and density.

3. The principal component analysis indicated that lignin content is not the only important factor in the separation of the groups; hemicellulose and  $\alpha$ -cellulose contents are important, too. In contrast, the physical and mechanical properties that contribute to the separation of groups were density and MOE.

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