

..... Crespo Gutiérrez, Torres Uribe, Poblete Wilson: Hygrothermal Treatment of Tepa...

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Hygrothermal Treatment of Tepa (*Laureliopsis philippiana* Looser) Fibers: Effects on Chemical and Physical Properties

Hidrotermička obrada iverja drva tepe (*Laureliopsis philippiana* Looser): utjecaj na kemijska i fizička svojstva

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ABSTRACT • The present study consisted in determining the effects of a hygrothermal treatment on wood fibers from the *Laureliopsis philippiana* Looser species. The fibers were treated in autoclave at 150 °C for 90 minutes at a pressure of 430 kPa, which was generated during the evaporation process of the water in autoclave. Physical properties, color, and water retention capacity of hygrothermally treated and untreated fibers were analyzed. The chemical properties determined were the extractable amount in sodium hydroxide, toluene ethanol, hot and cold water, the cellulose, holocellulose and lignin contents, the pH value, the percentage of volatile and washable acids, and the buffer capacity. In hygrothermally treated fibers, a change of color was detected as well as a reduction in the water retention capacity and an increase in the percentage of extractable, cellulose, lignin and a decrease of holocellulose. Also an increase in acidity, amount of volatile and washable acids and buffer capacity were determined. Due to the chemical changes observed in the treated fibers, these would present advantages in the manufacture of fiberboards, facilitating the setting of the amino resins.

Key words: hygrothermal treatment; *Laureliopsis philippiana*; fibers; physical and chemical properties; acidity; fiberboards

SAŽETAK • Cilj rada bio je utvrditi učinke hidrotermičke obrade na vlakna drva *Laureliopsis philippiana* Looser. Vlakna su tretirana u autoklavu, na temperaturi 150 °C tijekom 90 minuta, i pri tlaku 430 kPa, koji je nastao tijekom procesa isparavanja vode u autoklavu. Analizirana su fizička svojstva, boja i kapacitet zadržavanja vode u hidrotermički obrađenim i neobrađenim vlaknima. Od kemijskih svojstava određena je ekstrahirana količina u natrijevu hidroksidu, toluen-etanolu te u toploj i hladnoj vodi, zatim sadržaj celuloze, holoceluloze i lignina, pH vrijednost, postotak hlapljivih kiselina i kiselina koje se mogu isprati te kapacitet pufera. U hidrotermički tretiranim vlaknima zabilježena je promjena boje i smanjenje kapaciteta zadržavanja vode te povećanje postot-

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ka ekstrakta, sadržaja celuloze i lignina, kao i smanjenje sadržaja holoceluloze. Također je utvrđeno povećanje kiselosti, količine hlapljivih kiselina i kiselina koje se mogu isprati te određen kapacitet pufera. Zbog kemijskih promjena uočenih na obrađenim vlaknima takva bi vlakna mogla imati prednost u proizvodnji ploča vlaknatica jer olakšavaju pozicioniranje amino smola.

Ključne riječi: hidrotermička obrada, *Laureliopsis philippiana*, vlakna, fizička i kemijska svojstva, kiselost, ploče vlaknaticе

1 INTRODUCTION

1. UVOD

Heat treatment darkens the color of the wood (Akgül and Korkut, 2012; Karlsson *et al.*, 2012a; Crespo *et al.*, 2013), reducing the clarity and increasing the chromaticity (Karlsson *et al.*, 2012a.). Darkening is proportional to the temperature and time of treatment, being uniform through the width and depth of the wood (Brauner and Conway, 1964), resulting in a greater darkening of hardwoods than of conifers (Schneider, 1973; Sandoval-Torres *et al.*, 2010).

The wettability of heat treated wood particles decreases in treated fibers (Poblete, 1983; Crespo *et al.*, 2013) as well as water retention capacity (Roffael and Kraft, 2012; Weigl *et al.*, 2013). The higher the temperature and the exposure time of heat treatment, the lower the amount of water absorbed by the wood (Poblete, 1983; Kartal *et al.*, 2007.).

Thermal decomposition of the constituent molecules of the wood begins at temperatures below 160 °C (Yamauchi *et al.*, 2005; Esteves and Pereira, 2009). Constitution water loss begins at this temperature, leading to a decrease in the content of OH groups (Hill, 2006). The degradation of the chemical components causes the formation of acetic acid, formic acid and phenolic compounds, as well as the formation of other aromatic and extractable compounds (Jämsä and Viitanie-mi, 2001; Hill, 2006; Awoyemi and Jones, 2011). The formation of organic acids catalyze the hydrolysis of pectins, hemicelluloses and to a lesser extent, the amorphous cellulose. Simultaneously, the lignin is softened and is partially depolymerized (Mitchell, 1988; Garcia-Jaldon *et al.*, 1998). Furthermore, some components of the cell walls are reorganized, and the number of OH-H bonds decreases (Homan *et al.*, 2000). Using an autoclave generates pressure, which has effects that can be important in regards to the composition, structure and properties of wood (Giebel, 1983; Ding *et al.*, 2011.). However, these treatments cause an improvement in certain physical properties (Burmester, 1973).

The production of acetic and formic acid at temperatures below 200 °C (Fengel and Wegener, 1989; Alén *et al.*, 2002) decreases the pH value of the wood (Kollmann and Fengel, 1965; Weiland and Guyonnet, 2003; Wikberg and Maunu, 2004), increasing the amount of volatile and washable acids as well as the acidic buffer capacity (Poblete, 1983; Roffael, 1987a, b; Crespo *et al.*, 2013.).

Acidity is an important factor to consider in the manufacture of wood panels, since the chemical reactions that occur during the setting of the adhesive follow an optimal course with a specific pH range for each

type of adhesive. The variation in pH values affects the properties of fiber bonding, so knowing the acidity of the wood and its changes due to the form of processing are important in predicting the behavior of the wood and adhesive (Crespo *et al.*, 2013).

Considering the changes in the physical and chemical properties of wood due to heat treatments, and its potential impact on production of boards, the aim of this study was to determine the effects of a hygrothermal treatment on fibers from *L. philippiana*, a species with unfavorable chemical characteristics for the production of boards with ureaformaldehyde (Pinto and Poblete, 1992; Poblete and Pinto, 1993). The effects on the physical and chemical properties that affect the production of boards made with *L. philippiana* fibers and amino resins were reported, considering the changes in color, in water retention capacity, in the main cell wall compounds, in the percentage of extractables, in varied pH values, in washable and volatile acids, and in buffer capacity.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

2.1 Materials

2.1. Materijali

L. philippiana wood harvested in the region XIV of Los Rios Pre-Andean mountain range (Chile) was used. The wood was chipped and shredded through a mechanical process, using water to prevent temperature increase during the extraction of fibers. After obtaining the fibers, these were conditioned to room temperature and humidity.

2.2 Methods

2.2. Metode

The fibers were placed into a steel basket in an autoclave at 150 °C for 90 minutes. The autoclave contained water to a height leaving a space of 2 cm between the fibers and water. Due to the steam generated in the autoclave, there was an increase in pressure during the process, which was controlled and reached 430 kPa. After the treatment was finalized, the fibers were conditioned to room temperature and humidity. After being conditioned, the fibers with and without hygrothermal treatment were dried at 70 °C to 4 % moisture content.

The evaluation of color of the fibers before and after the hygrothermal treatment was performed using color tables for soils (Munsell, 1994) and an X-Rite spectrophotometer, with which the measurements were made using built in computer software with the D65/10 brightness option.

The water retention capacity was measured according to the methods employed by Poblete (1983). Therefore, a certain amount of fibers were left in the distilled water for 18 hours. Then, a sample was poured into a pulp testing apparatus and centrifuged at a speed of 2850 rpm for 5, 10, 15 and 20 seconds, to extract the water. After completing each centrifuging process, the fibers were taken to a pre-weighed beaker, then weighed again, and dried in an oven at 103 °C to constant weight. Finally, the beaker was cooled with the fibers in a desiccator and weighed. Water retention capacity (WRC-value) was calculated by the following equation:

$$WRC-Value = \frac{Weight\ of\ wet\ fibres - Weight\ of\ dry\ fibres}{Weight\ of\ dry\ fibres} \times 100$$

The chemical components were determined according to the standards and methods described below:

- Preparation of wood for chemical analysis (TAPPI 264 cm-97).
- Water solubility of wood and pulp (TAPPI 207 cm-99).
- Solubility in 1% of sodium hydroxide (0.25 N) of wood and pulp (TAPPI 212 om-98).
- Extractables in toluene ethanol (TAPPI 204 cm-97).
- Hoffer Kurschner cellulose method according to Hessler and Merola (1949).
- Poljak holocellulose method according to Haas *et al.* (1955).
- Insoluble lignin in acid (Klason lignin) (TAPPI 222 om-98).
- PH value of a filtered sawdust solution with water according to Roffael *et al.* (2000).
- Volatile and washable acids according to Poblete (1983).
- Buffering capacity, according to Roffael *et al.* (2000).

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

3.1 Color

3.1. Boja

According to the comparison made using the Munsell color tables for soils, a change in the color of the yellow fibers (2.5 Y 4/8) to a reddish yellow (10 YR 5/6) was detected. Measurements taken with the spectrophotometer confirm a darkening of the hygrothermally treated fibers, making them less clear (lower L^*

value), redder (higher value of a^*), more blue (lower value of b^*), with a lower color saturation (C^*) and a lower hue angle (h°). The reduction in the hue angle indicates a change of color of the fibers from a greenish yellow to a reddish blue (Table 1).

Sullivan (1967a, b) states that the color variations in the wood will focus on the clarity and saturation, which coincides with the difference in lightness (L^*) and hue angle (h°) between the hygrothermally treated and untreated fibers.

The color changes observed in this experiment are consistent with those detected by different authors who found color changes from light to dark after solid wood vaporization at high temperatures (Brauner and Conway, 1964) and in solid wood subjected to a hygrothermal treatment (Momohara *et al.*, 2003; Oelhafen *et al.*, 2006a, b; Todorovic *et al.*, 2012). Darkening was also determined in *L. philippiana* particles subjected to a hygrothermal treatment (Crespo *et al.*, 2013). In a study with fibers, Widsten *et al.* (2001) stated that by increasing the temperature of defibration from 171-202 °C the fibers become darker, which indicates an increased frequency of chromophore groups, free radicals and quinonic structures on the surfaces of the fibers.

The color change in the heat treated *L. philippiana* fibers is related to the increased amount of extractables (Table 2), since according to Sundqvist and Morén (2002) the extractables participate in the color formation of the heat-treated wood. Karlsson *et al.* (2012a) claim that the degradation of the monosaccharides is an important factor in the formation of the color of the wood during heat treatment. Similarly, Dubey (2010) ensures that compounds degraded by heat, along with the extractables and other compounds such as sugars with low molecular weights and amino acids, tend to migrate to the surface of the wood during the heat treatment process, which results in a darkening.

Thermal oxidation of cellulose (Matsuo *et al.*, 2012), the formation of colored degradation products of hemicelluloses (Sehlstedt-Persson, 2003; Sundqvist, 2004; Dubey, 2010), and the generation of chromophoric groups by oxidation, primarily the increase of lignin carbonyl groups, in particular the appearance of quinones (González-Peña and Hale, 2009; Dubey, 2010), also may have influenced the color change recorded in hygrothermally treated fibers to a lesser extent.

Considering that the market for furniture and construction prefer boards with light surfaces, the darkening recorded in the present study may result in a

Table 1 Color comparison of *L. philippiana* hygrothermally treated and untreated fibers

Tablica 1. Usporedba boje hidrotermički obrađenih i neobrađenih vlakana drva *L. philippiana*

Parameter / Svojstvo	Untreated fibers <i>Neobrađena vlakna</i>	Treated fibers <i>Obrađena vlakna</i>
L^* (lightness 100 "white" 0 "black") / L^* (svjetlina 100 "bijelo" 0 "crno")	60.56	48.36
a^* (chromaticity + a^* "red" - a^* "green") a^* (kromatičnost + a^* "crveno" - a^* "zeleno")	3.13	4.66
b^* (chromaticity + b^* "yellow" - b^* "blue") b^* (kromatičnost + b^* "žuto" - b^* "plavo")	13.11	9.00
C^* (color saturation) / C^* (zasićenost boje)	13.48	10.13
h° (hue angle) / h° (kut boje)	76.59	62.61

disadvantage for marketing boards made with these fibers.

3.2 Water retention capacity

3.2. Kapacitet zadržavanja vode

The variation of the water retention capacity of the fibers with and without hygrothermal treatment, after centrifugation at different times, is presented in Figure 1.

In Figure 1, it can be observed that the water retention capacity in hygrothermally treated fibers permanently decreases with the centrifugation time, which implies that less water is absorbed and retained. The water retention capacity of treated fibers was always less than that of untreated fibers, with an average difference of approximately 15.9 %.

The decrease in water retention capacity coincides with the reduction of wettability with ureaformaldehyde in hygrothermally treated *L. philippiana* particles, reported by Crespo *et al.* (2013). Similarly, in particles thermally modified at 180 °C for 1.5 hours, Weigl *et al.* (2013) reported a decrease of 28.0 % and 46.0 % of the water retention capacity, which is related to the reduction of polarity. Coincidentally, Roffael and Kraft (2012) indicate that the thermal modification of the wood leads to a marked decrease of the water retention capacity. After subjecting particles to heat treatment, these authors reported a decrease in water retention values (after 72 hours in water) of 27.0 % for *Fagus sylvatica*, 19.4 % for *Fraxinus excelsior* and 30.0 % for *Picea abies*.

Jayme and Fengel (1963) claim that excessive drying of wet pulp at 105 °C for 24 hours results in a substantial reduction in the water retention value, even though the fibers still presented expanded cellular walls showing an irregular lamellate structure, which suggests that the OH groups in the fibrils were partially

inactivated. In this way, the resistance of the inner wall is adversely affected and the water retention capacity of the fiber walls is extremely reduced.

The wettability of the thermally modified wood decreases with treatment between 130 and 210 °C with a maximum of approximately 190 °C (Esteves and Pereira, 2009). Hakkou *et al.* (2005) affirm that the change in the wettability may be due to the conformational arrangement of the wood biopolymers resulting in the loss of residual water or, more likely, due to the plasticization of lignin. Meanwhile Chen *et al.* (2012) ensure that the formation of acetic acid, in addition to hydrolyzing the hemicelluloses, also leads to a loss of hydroxyl groups in the form of water, which is why heat treated wood becomes more hydrophobic.

From a practical point of view, the decrease in fiber wettability caused by heat treatment may affect the distribution of the adhesive in the production of boards, and may also have a negative effect on their painting.

3.3 Chemical components

3.3. Kemijski sastav

The average values of different chemical determinations of *L. philippiana* fibers with and without hygrothermal treatment are shown in Table 2.

Extractables in cold and hot water

In Table 2, the average values of extractables in different solvents are expressed as a percentage based on dry wood. An increase was found in hygrothermally treated fibers, from 0.4 % to 8.5 % in the percentage of extractables in cold water and from 0.9 % to 10.3 % in the percentage of extractables in hot water. Crespo *et al.* (2013) found similar variations in a previous study of hygrothermally treated *L. philippiana* particles. Coinciding with the trend found in the pre-

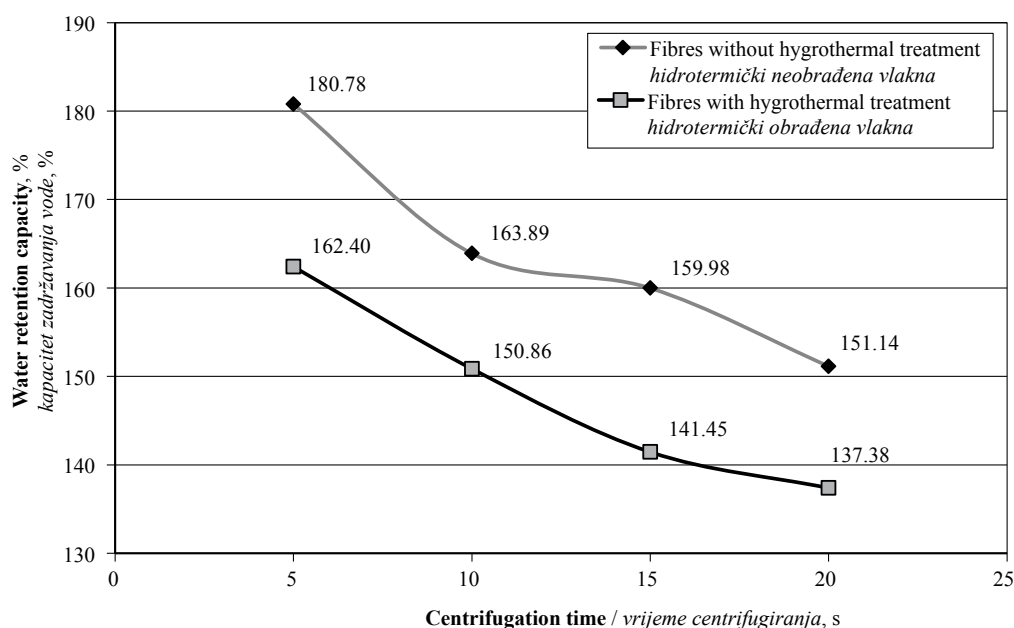


Figure 1 Values of water retention capacity of *L. philippiana* fibers hygrothermally treated and untreated after centrifugation at different times

Slika 1. Vrijednosti kapaciteta zadržavanja vode hidrotermički obrađenih i neobrađenih vlakana drva *L. philippiana* nakon različitog vremena centrifugiranja

Table 2 Chemical components of *L. philippiana* fibers with and without hygrothermal treatment

Tablica 2. Kemijski sastav hidrotermički obrađenih i neobrađenih vlakana drva *L. philippiana*

Property / Svojstvo		Untreated fibers <i>Neobrađena vlakna</i>	Treated fibers <i>Obrađena vlakna</i>
Extractables / Ekstrakti (% DWB)	Cold water / hladna voda	0.35	8.45
	Hot water / topla voda	0.90	10.29
	1% of sodium hydroxide (0.25 N) <i>1 %-tni natrijev hidroksid (0,25 N)</i>	13.32	33.06
	Toluene ethanol / <i>toluen-etanol</i>	0.79	8.40
Wood polymers / Drvni polimeri (% DWBFE)	Cellulose / <i>celuloza</i>	57.39	64.11
	Holocellulose / <i>holoceluloza</i>	62.68	60.20
	Lignin / <i>lignin</i>	24.41	29.63
pH Value / <i>pH vrijednost</i>	Filtered sawdust solution with water after stirring for 4 h / <i>filtrirana otopina piljevine s vodom nakon 4-satnog miješanja</i>	5.65	3.52
Volatile acids, % <i>Hlapljive kiseline, %</i>	Acid as acetic acid <i>kisela kao octena kiselina</i>	0.026	0.071
Washable acids, % <i>Kiseline koje se ispiru, %</i>		0.018	0.207
Buffer capacity NaOH 0.01 mol/l (mmol / 100 g wood) <i>Kapacitet pufera NaOH 0,01 mol/l (mmol / 100 g drva)</i>	NaOH solution consumed <i>potrošena otopina NaOH</i>	0.75	11.91

DWB – Dry Wood Basis / *na bazi suhog drva*; DWBFE – Dry Wood Basis Free of Extractables / *na bazi suhog drva bez ekstrahiranog dijela*

sent investigation, other researchers found an increase in the number of extractables in hot water when treating solid *Cryptomeria japonica* wood (Yilgör and Kartal, 2010) as well as the extractables in water, in *Picea abies* and *Pinus sylvestris* fibers after a defibration process (Widsten *et al.*, 2001). Karlsson *et al.* (2012b) state that the heat treatment of *Picea abies*, *Pinus sylvestris* and *Betula pendula* wood, in saturated steam at 160 and 170 °C, produced higher contents of water soluble carbohydrates, which correspond to the monosaccharides.

Extractables in 1 % of sodium hydroxide

The percentage of extractables in 1 % sodium hydroxide (0.25 N) increased from 13.3 % in untreated fibers to 33.1 % in thermally treated fibers. Crespo *et al.* (2013) also reported an important increase in the amount of these extractables in hygrothermally modified *L. philippiana* particles. Similarly, Yilgör and Kartal (2010), soon after heat treating *Cryptomeria japonica* wood, reported an increase of extractables in 1 % sodium hydroxide. The increase of extractables in 1% sodium hydroxide in the treated fibers is due to the degradation of the hemicellulose and cellulose that were subjected to high temperature. According to TAPPI 222 (om-98), hot alkali solution extracts low-molecular-weight carbohydrates consisting mainly of hemicellulose and degraded cellulose in wood. The solubility of wood could indicate the degree of fungus decay or of degradation by heat, light, oxidation, etc. As the wood decays or degrades, the percentage of the alkali-soluble material increases (Morgan, 1931; Procter and Chow, 1973 cited by TAPPI 222 om-98).

Extractables in toluene ethanol

An increase from 0.8 to 8.4 % in the amount of extractables in the toluene ethanol of hygrothermally

treated *L. philippiana* fibers was detected, which is consistent with what Crespo *et al.* (2013) reported for *L. philippiana* particles. Other researchers also found increases in the amount of extractables in toluene ethanol following heat treatment, in *Pinus patula* wood in a nitrogen atmosphere (Mohareb *et al.*, 2012), in *Pinus sylvestris* wood heat treated with steam and pressure (Ding *et al.*, 2011) and in *Cryptomeria japonica* wood heat treated in an oven (Yilgör and Kartal, 2010).

Changes in extractable content reflect a change of the main chemical components of wood. The increase of extractables in the heat treated fibers is due to the temperature degradation of hemicelluloses; the molecular chains are then broken and extracted by the solvents used.

The increase in the percentage of extractables could affect the strength of the boards made from treated fibers, because during the hygrothermal treatment, the amount of hydrophobic extractables increases, which could prevent a good bond between the wood and adhesive.

Cellulose

In hygrothermally treated *L. philippiana* fibers, the percentage of cellulose increased from 57.4 % to 64.1 %. Crespo *et al.* (2013) also reported an increase in the percentage of cellulose in hygrothermally treated *L. philippiana* particles. Coincidentally, Yildiz *et al.* (2006) stated that heat treatment of *Picea orientalis* wood, in an oven at 150 °C for 2 hours in the presence of air, produced an increase in the cellulose content. According to Tjeerdsma and Militz (2005), the cellulose from *Fagus sylvatica* and *Pinus sylvestris* wood undergoes few changes at temperatures of 165 and 185 °C in wet and dry conditions with nitrogen gas. Fengel and Kollmann (1965) claim that cellulose undergoes significant changes starting from 180 °C

treatments, with small changes at lower temperatures. The increase in percentage of the cellulose presented in Table 2 is not due to an increase of the cellulose content, but rather to the relatively high degradation of the hemicelluloses, which changes the percentage share of the compounds (Esteves *et al.*, 2011).

Holocellulose

The percentage of holocellulose in hygrothermally treated fibers decreased from 62.7 % to 60.2 % in respect to the untreated fibers. In a previous study of hygrothermally treated *L. philippiana* particles, Crespo *et al.* (2013) reported a decrease in the percentage of holocellulose. Coinciding with the results obtained, Akgül and Korkut (2012), following a heat treatment at 150 °C, reported a decrease in holocellulose content, which they attributed to the degradation of hemicelluloses. With the increase of temperature and pressure, holocellulose content decreases (Mohareb *et al.*, 2012; Ding *et al.*, 2011).

The increased cellulose content and the general increase of the extractable compounds identified in this study should be produced by the depolymerization of hemicellulose, which is detected by the decrease in holocellulose.

Lignin

According to Table 2, the percentage of lignin determined in hygrothermally treated *L. philippiana* fibers increased from 24.4 % to 29.6 %. According to Windeisen *et al.* (2007), the lignin starts to degrade in the beginning of treatment but at a lower rate than the polysaccharides. Wienhaus (2005) stated that lignin softens and melts between 120 and 130 °C, and at higher temperatures, the softening is associated with reactions to condensation. Nuopponen *et al.* (2004) and Yilgör and Kartal (2010) state that the percentage share of lignin increases with temperatures above 140 °C, which is probably due to the degradation of hemicelluloses.

The increase in lignin content in hygrothermally treated *L. philippiana* fibers coincides with the increase registered in particles of this species reported by Crespo *et al.* (2013). Widsten *et al.* (2001) also recorded an increase in the amount of lignin, after thermomechanical defibration at 188 °C. However, at 202 °C, their share decreased.

Alén *et al.* (2002) and Nuopponen *et al.* (2004) reported increases in lignin content with increasing treatment temperature. With *Pinus sylvestris* wood, heat treated at 205 °C for 1.5 hours, Ding *et al.* (2011) also determined an increase in the lignin content of 6.6 %, when treated with steam without pressure, and 15.8 % when treated with steam at a pressure of 350 kPa, attributing this increase to the decreased holocellulose content.

The increase in the amount of lignin in hygrothermally treated fibers indicates the formation of polymerized products (Gosselink *et al.*, 2004). In pressurized hygrothermal treatments, there is a correlation between the changes in the ultrastructure and the extractability of lignin. A low extractability of lignin is produced due to

the formation of high molecular weight fractions (Košíková *et al.*, 1990). The heat treated lignin determined in wood is probably not pure, since the reactions of polycondensation with other components of the cell wall result in reticulations, contributing to an increase in the apparent lignin content (Tjeerdsma and Militz, 2005; Boonstra and Tjeerdsma, 2006).

pH value

Table 2 shows that the pH value of the hygrothermally treated fibers is considerably more acidic than that of the untreated fibers. The reduction of pH value in hygrothermally treated *L. philippiana* fibers coincides with the decrease in the pH value of the same hygrothermally treated particle species (Crespo *et al.*, 2013). Yilgör and Kartal (2010) also reported a decrease in the pH value after 2 hours of heat treating *Cryptomeria japonica* wood. Coincidentally, other researchers determined a decrease of the pH in particles coming from logs vaporized at 60 °C, for 16 hours (Çolak *et al.*, 2007) and in fibers obtained through thermomechanical refinement with steam and pressure for 3 minutes (Xing *et al.*, 2006).

The acidification of wood occurs because deacetylation of hemicelluloses and acetylated oligosaccharides is produced at temperatures of 145-190 °C, (Garrote *et al.*, 2001), increasing the emission of formic and acetic acid from the wood (Roffael and Uhde, 2012), the acetic acid being the catalyst of depolymerization and condensation reactions of polysaccharides (Nuopponen *et al.*, 2004).

The decrease in pH of hygrothermally treated *L. philippiana* fibers permits the prediction of better setting of amino resins, which may solve the problems reported by Poblete and Peredo (1990) and Pinto and Poblete (1992) when manufacturing boards with particles of this species.

Volatile and washable acids

The percentage of volatile and washable acids, determined as acetic acid, in hygrothermally treated *L. philippiana* fibers registered strong increases when hygrothermally treated (Table 2). The change in these compounds is an indicator of acidification caused by the treatment. In a previous study, hygrothermally treated *L. philippiana* particles in the same conditions as used in this study, registered an increase in the percentage of volatile and washable acids (Crespo *et al.*, 2013). Poblete (1983) obtained similar results after drying *Fagus sylvatica* and *Picea abies* wood chips at 100 °C for 16 hours.

The percentage increase of volatile and washable acids is beneficial for the manufacture of boards made with *L. philippiana* and amino resins, since it provides the optimal pH environment for the setting of such resins.

Buffer capacity

While the pH of wood measures the specific level of acid activity under given conditions, the buffer capacity measures the resistance of wood to changes in

the pH levels. Wood with a high buffering capacity requires the addition of a larger amount of acid catalyst to reduce the pH until the required level for optimal setting of the resin (Maloney, 1977). Determining the amount of sodium hydroxide consumed is an indirect way of determining the buffer capacity of the wood. The amount of NaOH (0.01 mol/l), in mmol/100g of wood, added to reach a pH value of 7, represents the buffer capacity of the fibers whose values are shown in Table 2.

According to Table 2, in hygrothermally treated *L. philippiana* fibers, the buffer capacity increased drastically; these results being consistent with the registered increment of a previous investigation (Crespo *et al.*, 2013). Xing *et al.* (2006) also showed an increase in the buffer capacity of fibers obtained through a thermomechanical refinement using steam and pressure for 3 minutes.

The decrease of the alkalinity of the fibers when subjected to hygrothermal treatment results in a significant increase in the consumption of NaOH, with a much greater equilibrium capacity of ionization (buffering capacity). This effect is determined by wood extractables. In addition to the decrease of the pH value and the increase of the volatile and washable acids, the decrease in alkalinity is an important parameter to optimally induce polymerization of the amino resins. These changes allow for better adhesion between the fibers and may positively influence the mechanical properties of the boards made with treated fibers. According to Çolak *et al.* (2007), wood acidity plays a very important role in generating the optimal pH environment for setting the ureaformaldehyde resins.

4 CONCLUSIONS

4. ZAKLJUČAK

Hygrothermally treated *L. philippiana* fibers at 150 °C for 90 minutes and 430 kPa of pressure, presented significant changes in their physical and chemical properties. There was a color change from greenish yellow to reddish blue, as well as a lowered water retention capacity. The percentages of extractables in cold and hot water suffered increases that far exceed the original value. The same trend was observed for the amount of extractables in sodium hydroxide and in toluene ethanol. The percentage of cellulose increased from 57.4 % to 64.1 % and lignin percentage increased from 24.4 % to 29.6 %, while the holocellulose percentage decreased from 62.7 % to 60.2 %. A significant decrease in pH value from 5.6 to 3.5 was determined, as well as a sharp increase in the percentage of volatile and washable acids, while the buffering capacity increased about 16 times.

The color change and the reduced water retention capacity of hygrothermally treated *L. philippiana* fibers reported in this study may present a disadvantage for the marketing of MDF as well as for the bonding process in manufacturing. However, the slight degradation of the cell wall components and the increased acidity of the treated fibers may be an advantage for

producing MDF, as it would facilitate the setting of amino resins as adhesive and its reaction with wood. In general, the hygrothermal treatment of this species is presented as a viable alternative for the production of MDF and favors production with resin containing ureaformaldehyde.

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