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Hydrothermal treatment of Eucalyptus wood: Effects on Ion permeability and material removing

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ABSTRACT

Hemicelluloses, the second most abundant polysaccharides in nature after cellulose, can be used for hydrogels, in packaging-films, or biomedical materials, among other purposes. In the case of eucalyptus wood, glucuronoxylans are the main constituents of hemicellulose. Hot water extraction can be used as a pretreatment for purposes of hydrolysis of the biomass followed by fermentation and also as a previous stage in pulping processes. The influence of auto hydrolysis/extraction has been widely studied for different lignocellulosic materials, but the characteristics of the hydrolyzate and aspects like change in wood permeability have not been analyzed in detail. This paper analyzes the hydrothermal treatment of *Eucalyptus grandis* chips and slices under mild conditions, considering temperature and time range corresponding to a P_{factor} of up to 350. The ion permeability of the treated wood slices and its profile in wood chip, as well as the amount of hemicellulose and lignin dissolved from chips are evaluated. The amount of the hemicelluloses and lignin extracted was increased as treatment was intensified. For a P_{factor} higher than 180, the increment in the extracted xylan is clear but the colloidal electric charge in the liquor is reduced due to xylan degradation. Total extracted lignin can be up to 3.0 g/100 g of original wood and the hemicelluloses 6.5 g xylose/100 g of original wood, respectively. The permeability of wood slices is clearly increased by water treatment. In the chip, the diffusion restriction leads to a permeability profile, and the increase at the proximity of the outer faces can be higher compared to that in the chip core.

1. Introduction

Hemicellulose removal by the acid hydrolysis of wood chips prior to the alkaline pulping is usually applied in special pulping processes in order to obtain dissolving low-hemicellulose pulps. The partial removal of hemicelluloses prior to kraft pulping has been proposed by several authors for different reasons. One is that the heat capacity of hemicelluloses is only half that of lignin, which makes it more advantageous to extract them prior to cooking and use them for other purposes instead of burning in the recovery boiler (Yonn et al., 2008, Mendes et al., 2009).

The consumption of alkali in the Kraft process implies fuel consumption and gas emission not only in the boiler but also in the lime kiln. Alkali saving in the process leads to a reduction of the organic load that is sent to the recovery boiler. Several authors have demonstrated that hemicelullose pre-extraction offers advantages: it reduces the demand of chemicals of pulping and/or bleaching and total bleaching time of a kraft pulping (Mendes et al., 2009; Francis et al., 2008; Mao et al., 2008; Al-Dajani and Tschirner 2008); increases bleachability (Francis et al., 2008); leads to pulps of higher brightness (Al-Dajani and Tschirner 2008; Testova 2006) and reduces the whiteness reversal (Mendes et al., 2009). Yoon and van Heiningen (2008) observed an increase in the delignification rate (kinetic constants increased from 10% to 60% depending on conditions) which may be due to increased accessibility of the fiber wall and the cleavage of lignin-carbohydrate bonds during pre-treatment.

The depolymerization of lignin, which can be produced by the hydrothermal treatment, facilitates subsequent delignification stages. Unfortunately, lignin condensation also takes place as was discussed by Li and Gellerstedt (2008). Nevertheless, it has been shown that the modification of the autohydrolisis treatment by addition of NaOH and 2-naphtol clearly enhances delignification and upgrades lignin for potential applications (Li and Gellerstedt 2008).

The ideal situation is to use the hydrothermal treatment to promote alkaline pulping or enzymatic hydrolysis of biomass and, at the same time, separate a useful extract rich in hemicellulose (Ribas Batalha et al., 2015). For the latter point, conditions must be moderate in order to minimize hemicellulose degradation.

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The diffusion rate of ions within the wood is enhanced by the hydrothermal treatment (Inalbon et al., 2014). As the diffusion rate is critical at the beginning of the pulping process, different techniques have been proposed to study diffusion under these conditions (Inalbon et al., 2009, 2013; Montagna et al., 2013). The analysis of the relative ion transport capacity of wood, which is related to the effective capillary cross-sectional area (ECCSA) was proposed by Stone and Green (1958). The determination of ECCSA is based on the analogy of diffusion and conductivity, considering the relation between the electrical conductivities of the wood and the liquid medium. The concept has also been applied to other materials different from wood (Synder 2001; Synder and Marchand 2001).

Local ECCSA allows determining the local effective diffusion coefficient, in wood for any ion, from the corresponding diffusion coefficient in the liquid medium (Inalbon et al., 2009).

$D_{i(effective)} = D_{i(i\ n_{solution})}$. ECCSA.

This work analyzes the hydrothermal treatment of eucalyptus wood under mild conditions. The lignin and hemicellulose dissolution, the polyelectrolytic anionic charge of the hydrolizate as well as changes in the effective capillarity of wood are determined as a function of the treatment severity.

2. Materials and methods

2.1. Materials

Fresh stems of 6-year-old *Eucalyptus grandis* (never dried) provided by UPM (Fray Bentos- Uruguay) were used.

2.1.1. Wood preparation

Wood was considered under three different forms:

- Industrial chips.
- Wood blocks of (3.5 × 3.5 × 1) cm^3 were prepared slicing by microtome to make faces flat and parallel (for ECCSA profiles determination).
- Slices of 300 μm thickness: logs were cut into 3.5 cm high disks using a carpentry saw, and then cubes of 3.5 cm of side length were obtained from disks. Slices of 300 μm thickness were obtained from the radial or tangential face of the cubes using a microtome (for ECCSA determination).

2.2. Hydrothermal treatment

Treatments were performed following the 3^2 experimental design that is shown in Table 1. Wood (200 g chips, 6 blocks, 6 slices) and water, in a liquor to wood ratio of 6:1 $dm^3\ kg^{-1}$, were added into rotating reactor with steam jacket. Temperature was raised to 110 °C in 10 min, the air was purged off after 10 min, and the temperature was raised and kept according to design. The reactor was then cooled to 90 °C and most of the hydrolyzate was collected (1.2 l) at this temperature. Treated wood was washed with distilled water at room temperature and stored at −15 °C. The washing liquid was discarded.

The hydrothermal treatment intensity was determined by the P_{factor} as proposed by Sixta (2006).

$$P_{factor} = \int_0^t \exp\left(40.48 - \frac{15106}{T}\right) dt \quad (1)$$

Table 1
Hydrothermal treatment conditions.

	Temperature (°C)	Time (min)
Water	140–150–160	20–40–80

Where: T is temperature in K, and t is time in hours.

2.3. Liquor analysis

The hydrolysis liquor was filtrated (200 mesh) and quantitatively neutralized with 5.10^{-2}N NaOH. After that, it was centrifuged during 30 min. The supernatant was filtered (fiber glass filter of 1.5 μm) and the precipitate was reserved.

2.3.1. Lignin and hemicellulose content determination

The amount of lignin precipitated during neutralization was determined as the dry weight of the material retained by filter. According to Leschinsky et al. (2009), this solid fraction in the hydrothermal treatment of eucalyptus is mainly lignin.

Concentration of soluble lignin in the supernatant was spectrophotometrically determined based on TAPPI UM 205. The filtered supernatant was diluted and sulfuric acid was added to obtain 4% acid concentration. The absorbance at 205 nm was measured and absorptivity of 110 l $(g\ cm)^{-1}$ was considered.

The hemicellulose concentration in supernatant was evaluated by a rapid and also by chromatographic methods. The first one was the phenol/sulfuric acid method proposed by Hodge and Hofreiter (1962). It was used here to determine xylose concentration. A sample of 1 ml of the supernatant solution, 1 ml of phenol at 5% (m v^{-1}) and 5 ml of concentrated sulfuric acid (95.5–96.5%) were added and shaken in a glass tube. After 10 min, the tube was shaken again and placed in a water bath at 25–30 °C during 20 min. Absorbance was spectrophotometric measured at 480 nm. The xylose content was determined by a calibration curve using xylose provided by Sigma Aldrich.

The concentration of carbohydrates was also determined by a modification of the technique proposed by Sluiter et al. (2011). A sample of 20 ml of the extracted liquor with 0.72 ml of sulfuric acid (72%) was treated in an autoclave for one hour at 121 °C. The sample was filtered and two aliquots of the supernatant were separated. One fraction was neutralized with $Ba(OH)_2$ and diluted for HPLC carbohydrates determination. The other fraction was used for soluble lignin determination. HPAEC-PAD (high performance anion-exchange chromatography with pulse amperometric detector) system (Water Co) and column and guard column CarboPac PA1 (Dionex Co) were used. A 3 mM NaOH solution as an eluent, a flow rate of 0.5 ml min^{-1}, and 30 °C of column temperature were considered. Standards of xylose, glucose, galactose and arabinose were hydrolyzed to estimate the losses of these materials during acid hydrolysis.

The xylose contents obtained by both methods are compared in this work.

2.3.2. Polyelectrolytic charge

Charge of the hydrolizate was determined by polyelectrolyte titration using streaming current equipment (Chemtrac ECA 2100) at ionic strength corresponding to 110 μS cm^{-1}, and pH 7.0. The titrant used was pDADMAC solution (2.5 mN). The zero value in streaming current signal was considered as an indicator of charge neutralization.

2.3.3. Contents of uronic acid group

Uronic acid content was determined using the Scott method (Scott, 1979), which consists in the acid hydrolysis of xylan followed by a colorimetric determination of the chromophore formed with the 3–5-dimethyphenol. A sample of 0.25 ml was mixed with 2% NaCl solution (0.25 ml) in a reaction tube. Concentrated sulfuric acid (4 ml) was later added and the solution was immediately mixed. The tube was placed in a bath at 70 °C for 10 min, and then was cooled to room temperature. Then, 0.2 ml of 3,5-dimethylphenol solution was added to the mixture. Between 10 and 15 min after the addition of the colorimetric reagent, absorbance was read at 450 nm and 400 nm against a water reference having 100% transmission at 450 nm. Calculation of the uronic anhydride concentration was based upon the 450–400 nm absorbance

difference. An average reagent blank for this difference was predetermined. D-Galacturonic acid monohydrate was used as standard, since 4-0- methylglucuronic acid and this compound have the same molar absorptivity in this method. However, it was necessary to multiply the uronic anhydride absorptivity of this standard by the correction factor of 1.12 when they were constituents of polymers.

2.3.4. Molecular mass

Amicon Ultra-15 Centrifugal Filter Devices were used to determine the mass fraction with molecular mass lower than 3000 Da and greater than 10,000 Da. For this purpose, two different molecular mass cutoff membranes were used. The determinations were made for three different liquors corresponding to P_{factor} 148, 162 and 335.

For each molecular mass cutoff membrane, 15 ml of the original diluted solution were spun during 40 min and two fractions were obtained. The filtered fraction was reserved for concentration determination, and the retained fraction was diluted up to 15 ml with NaCl 10^{-3} N and spun again during 30 min. This latter operation was repeated once.

The concentration of hemicelluloses in each fraction was determined using the phenol/sulfuric method explained before in section 2.3.1.

2.4. Wood analysis

Lignin and carbohydrates content was also determined on the extracted wood. About 10 g of wood chip was milled in a Wiley mill and was Soxhlet extracted by ethanol in 24 cycles.

Acid-insoluble and soluble lignin were determined as Sluiter et al. (2011). A sample of 300 mg of extractive-free wood was treated at 30 °C with 72% sulfuric acid for 60 min, and then at 121 °C with 4% sulfuric acid for 60 min. The sample was filtered and washed with water. The filtrated supernatant was used to determine soluble lignin and carbohydrates content, and the solids were dried and weighted to determine insoluble residue. Soluble lignin was spectrophotometrically determined. The absorbance of 240 nm was measured, and an absorptivity of 25 l $(g\ cm)^{-1}$ was considered.

The filtrated supernatant was neutralized with $Ba(OH)_2$ and diluted for HPLC carbohydrates determination.

2.4.1. Acetyl group

The acetyl content of wood was determined by gas chromatography (GC) according to Solár et al. (1987). Butyric acid instead of propionic acid was used as the internal standard. Samples (80–100 mg) were treated at 150 °C for 50 min in closed glass ampoules with 0.9 ml of a liquor containing oxalic acid (63 g l^{-1}), and butyric acid (1.8 ml l^{-1}). Acetyl content was determined by GC and reported as g based on 100 g oven-dry (o.d.) wood. The GC conditions were: Column: DB-5MS– 50 m x 0.25 mm x 0.25 μm; Carrier: N_2 (2 ml min^{-1}); $T_{inyector}$: 260 °C, $T_{detector}$: 300 °C, (air 450 ml min^{-1}, hydrogen 45 ml min^{-1}).

2.4.2. Effective capillary cross-sectional area (ECCSA)

ECCSA was determined by the method proposed by Inalbon and Zanuttini (2008) based on the analogy with the relative electrical conductivities of the wood at 10^{-1} M NaCl solution. A four-electrode-laboratory conductivity cell (WTW-TetraCon 325) was used. An especially designed PTFE frame allowed the use of micrometric slices for the determination, keeping the slice flat and equidistant from the electrodes. The device was introduced in the thermostatic solution for the conductivity determination. The specific conductivity of the wood was calculated considering slice thickness and electrical resistance in a series circuit with the electrical resistance of the free solution that exists between electrodes. The wood slices that were cut in radial direction permitted the determination of the specific conductivity in tangential direction and vice versa. ECCSA was determined at 20 °C using 10^{-1} M NaCl solution. Since no reaction took place during the determination, ECCSA was stable over time.

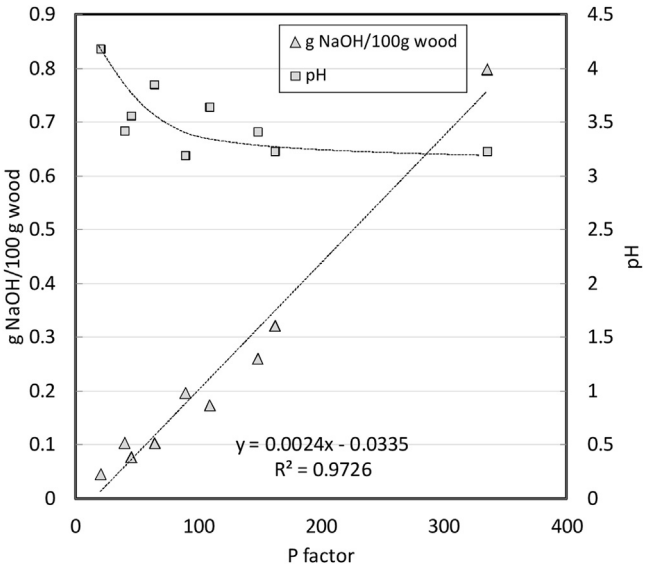

Fig. 1. Acid charge in the extracted liquors as a function P_{factor} reported as pH and NaOH consumed in the neutralization.

ECCSA was determined on the treated slices (6 slices for each conditions) in order to know the effect of the treatment assuming no diffusion restriction. On the other hand, for the determination of the ECCSA profiles of the hydrothermal treated blocks, ECCSA was determined on slices obtained by successively slicing the treated blocks from their external surface. The procedure allowed ECCSA profile determination in radial and tangential wood directions. At least two profiles for each direction and condition were determined.

3. Results and discussion

3.1. Acidic charge of the liquor

Fig. 1 shows pH and the amount of alkali needed to neutralize the hydrolyzate. The intensities of treatments are expressed by P_{factor} which is calculated by Eq. (1) as a function of temperature and time. The pH the hydrolyzate varied between 4.2 and 3.2. Nevertheless, the amount of NaOH consumed in the neutralization linearly depends on the P_{factor}. The higher amount of NaOH consumed is 0.8% on wood, which is relatively low.

3.2. Extracted lignin

Fig. 2 shows extracted lignin. For extracted lignin the amount that can be precipitated after neutralization is indicated as insoluble lignin of the liquor. The amount of extracted lignin is linearly increased reaching the value of 3 g/100 g of original wood. The proportion of insoluble lignin that can be separated by centrifugation after neutralization is between 10–35% of the total extracted lignin.

3.3. Extracted hemicellulose

Fig. 3a shows the xylose concentration determined by phenol/sulfuric against the value obtained by HPLC method expressed as g xylose l^{-1}. A correlation between both methods is obtained. The slight difference between both methods might be due to the presence of others 5-carbon-sugars that are quantified by the phenol/sulfuric method. Nevertheless, it seems that phenol/sulfuric is a simpler method that can be useful to estimate xylose in a liquor of hydrothermal treatment.

Fig. 3b shows the amount of xylose extracted during hydrolysis determined by HPLC as a function of P_{factor}. As expected, the amount of

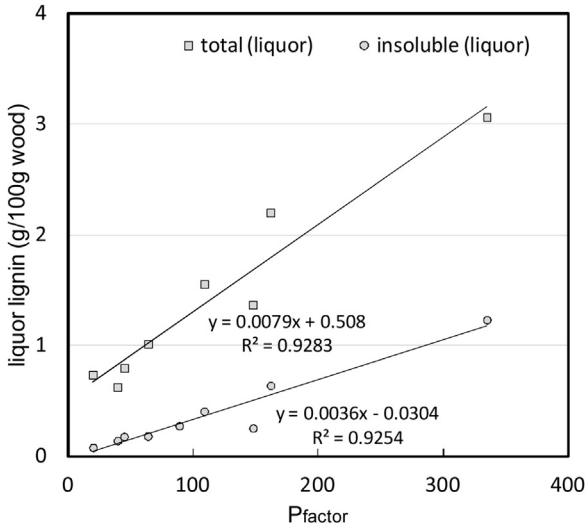

Fig. 2. Extracted lignin as a function of P_{factor}. ■ Total extracted lignin, ● lignin precipitated by neutralization of the hydrolyzate.

extracted xylose increases with the intensity of the treatment. It reaches the level of 6.5% xylose on the original wood. A second order polynomial relation can be established between the xylose extracted and the intensity of the treatment measured by P_{factor}.

3.4. Uronic acid and colloidal content charge of the liquor

Fig. 4 shows the Glucuronic acid content and the charge of the extracted liquor obtained as a function of the P_{factor}. The amounts of glucuronic acid and ion charge are increased when the thermal treatment is intensified up to P_{factor} 160. Nevertheless the treatment at the most drastic condition leads to a reduction in the amount of glucuronic acid and the charge content.

For moderate conditions (up P_{factor} 70), the content of glucuronic or galacturonic acid groups can be explained by the existence of other components like pectins because the xylan content, according to Fig. 3b, is very low. There is a noticeable increase of glucuronic or galacturonic acid groups for P_{factor} between 70 and 180. Those higher values, in relation to the charge of glucuronic or galacturonic acid, indicate that the acids are separated from the polymer structure or that unstable structures are present under these conditions, as can be pectins. Between P_{factor} 100 and 350 there is a drop in the charge content despite that the amount of xylose extracted increases from 0.5% to 6% in wood. This indicates that a notable degradation of xylan, i.e. loss of metilglucuronic, or hydrolysis of xylan chains takes place.

3.5. Molecular mass of xylans

Table 2 shows the fraction of molecular mass lower than 3000 Da and greater than 10,000 Da for liquor of treatment at three different $P_{factors}$. It can be observed that, the proportion of high molecular mass is affected by the intensity of the treatment. For similar P_{factor} (148 and 162) the proportion of high molecular mass is analogous. Nevertheless, the lower molecular mass fraction is increased with temperature (for similar P_{factor}). At the most severe condition (P_{factor} 335) the higher molecular mass fraction is notably reduced to 17%.

3.6. Effect of the hydrothermal treatment on wood

Fig. 5 shows remaining values of lignin, xylose and glucose contents in wood.

For a P_{factor} higher than 160 there is a notable xylan loss since the xylose content is reduced from 14 to 4 g/100 g wood.

The lignin in wood, total and acid insoluble content, is slightly

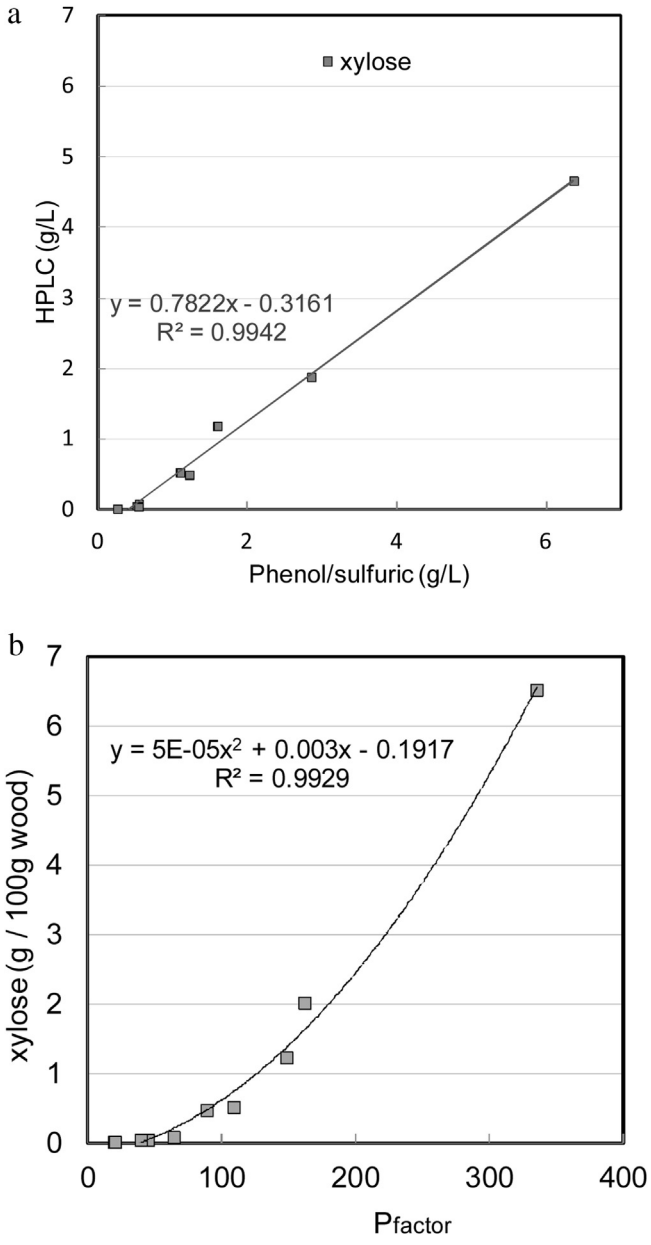

Fig. 3. (a) Relation between xylose concentration ($g\,l^{-1}$) determined by phenol/sulfuric method and by HPLC. (b) Xylose extracted during hydrothermal treatment as a function of P_{factor} (determined by HPLC).

increased by hydrothermal treatment because more polysaccharide materials than lignin are removed. The values showed are absolute. In the hydrothermal treatment hemicellulose is the main extracted component, followed by lignin. As a consequence, the absolute value of glucose content in the extracted wood is increased as well as lignin content, in lower proportion.

3.7. Effective capillary cross section area (ECCSA)

Fig. 6 shows capillarity in both wood directions as a function of the intensity of the hydrothermal treatment. Effects, for radial and tangential direction, are notable different. Tangential capillarity was gradually increased as P_{factor} was increased. A treatment at P_{factor} 109 and 335 duplicated and triplicated tangential ECCSA values of the original wood, respectively. Nevertheless a low value is reached (0.08). Differently, radial ECCSA shows a drastic increase (from 0.06 to 0.14) irrespectively to treatment condition.

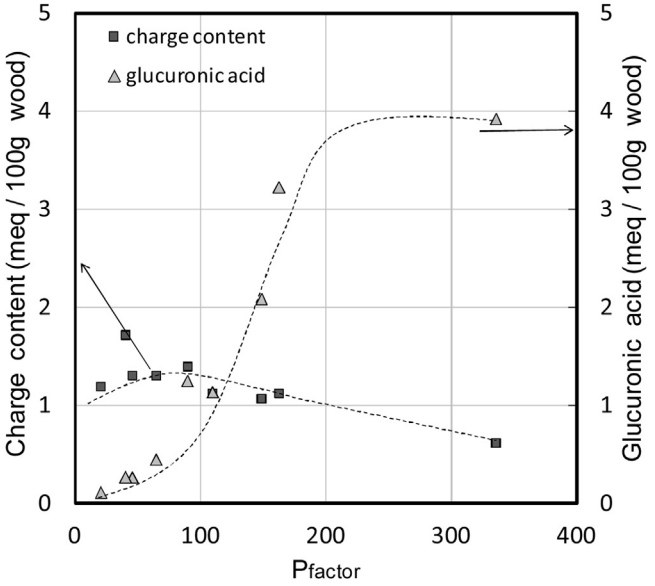

Fig. 4. Glucuronic acid and charge content of the extract as a function of the P_{factor}.

Table 2
Percentage of different molecular mass of tree liquors.

P_{factor}	Time (min)	Temperature (°C)	Greater than 10,000 Da	lower than 3000 Da
148	80	150	39%	39%
162	40	160	39%	47%
335	80	160	17%	54%

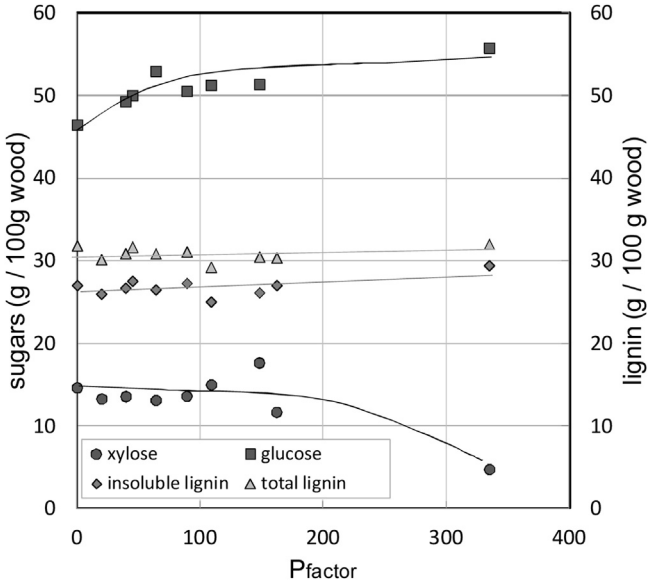

Fig. 5. Values of lignin, glucose and xylose remaining content in the treated wood as a function of the treatment intensity (P_{factor}).

Fig. 7 shows the ECCSA profiles on wood blocks determined as a function of P_{factor}. Only 3 treatments are shown to make the figure clearer. Values of ECCSA of untreated wood for both directions, i.e. radial and tangential are indicated. The ECCSA increase is higher in the proximity of the outer faces of the wood block in comparison the interior of the blocks. This indicates that the dissolution of material is highly restricted by the diffusion of the hemicellulose and lignin toward external liquor.

Figs. 6 and 7 show that ECCSA in radial direction, for which

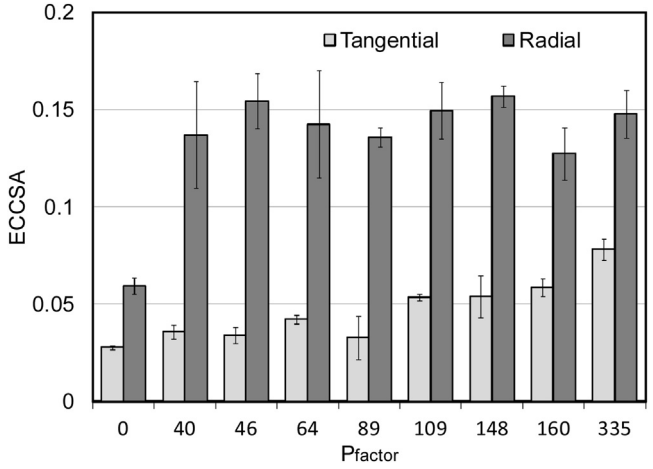

Fig. 6. Capillarity of wood as a function of P_{factor}, determined in radial and in tangential wood direction.

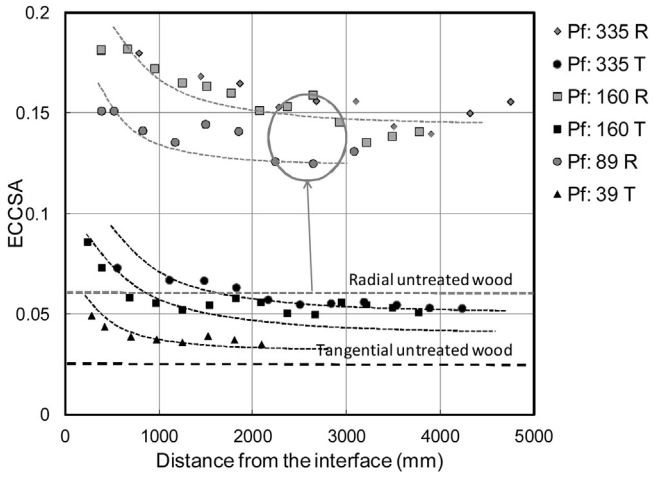

Fig. 7. ECCSA (tangential and radial) of treated and untreated blocks as a function of the distance from the liquor-wood interface.

morphological conduction elements (ray cells) are present, is easily increased, reaching a high value for all cases. This may be due to the opening of the ray cells produced by the hydrothermal treatment. It is clear that the major diffusion limitation exists in the tangential direction of wood for which diffusion in fiber walls is the limiting process.

Fig. 8 shows acetyl group content as a function of radial and tangential ECCSA. Slices individually treated and slices obtained from the core of treated wood under selected conditions (P_{factor}: 64, 160, 335) are considered for this plot.

Deacetylation in the wood has a certain relationship with the increase in tangential ECCSA.

The hydrothermal treatment produces a reduction in acetyl content that is higher than the reduction in xylan content. The reasons of the reduction in acetyl content are the removal of xylan and the partial deacetylation of the remaining one.

4. Conclusion

Under mild conditions, the hemicelluloses and lignin extracted from eucalyptus wood by hydrothermal treatment gradually was increased as the intensity, characterized by P_{factor}, was increased. Hemicellulose and lignin in the liquor reached a value of 6.5 g of xylose and 3 g of lignin/100 g of original wood. An exponential relation between xylose extracted and P_{factor} was found. The extracted lignin can be linearly related with P_{factor}.

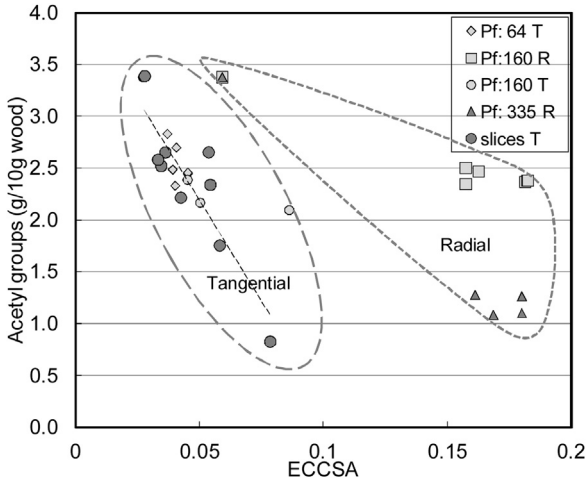

Fig. 8. Acetyl content as a function capillarity (ECCSA) of wood for different hydrothermal intensity (P_{factor}). Values corresponding to slices individually treated and those of solid wood treated under some conditions (P_{factor}: 64, 160, 335) are included.

The acidity of the liquor was also gradually increased but differently, the content of uronic acid and colloidal charge of the liquor was leveled off or reduced as treatment was intensified. The liquor acidity increases due to the acetyl groups removal and the carboxylic acid generation by carbohydrates degradation. They pass into solution during extraction.

A relation between xylose content determined by HPLC and that determined by phenol/sulfuric method shows that this can be useful as a rapid and ease method for this liquor.

Approximately one third of the lignin that was extracted during the hydrothermal treatment can be precipitated by centrifugation after neutralization of the hydrolyzate.

Capillarity in radial direction was easily raised by the hydrothermal treatment. The maximum value is achieved even for the mildest condition. On the contrary, capillarity in tangential direction, which is more dependent on the specific capillarity of the fiber wall, was gradually increased and showed a linear relationship with acetyl content.

The difference between radial and tangential capillarity, existing in the original wood, was even higher after the hydrothermal treatment.

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