Effect of Partial Pre-Extraction of Hemicelluloses on the Properties of *Pinus radiata* Chemimechanical Pulps

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Extraction of hemicelluloses prior to pulping and conversion of the extracted hemicelluloses to other bioproducts could provide additional revenue to traditional pulp and paper industries. The effect of hemicelluloses pre-extraction with a hydrothermal (HT) process on *Pinus radiata* chemimechanical pulp (CMP) properties was investigated in this study. The HT extraction resulted in a release of 7% to 58% of the initial amount of hemicelluloses from the wood. The extraction yield increased with temperature and extraction time. This hemicellulosic fraction was in the form of low molar mass oligomers with molecular weights varying from 1.5 to 100 kDa. Compared with the control (unextracted) CMP pulp, the HT pre-extraction significantly reduced the refining energy to obtain a given fibrillation degree (freeness). The pulp yield with the HT/CMP process was in the range of 56% to 75%. Fiber properties of the pulps from pre-extracted wood, such as fiber length, were reduced, while increases in fiber width, fines content, fiber coarseness, and kink index were observed in comparison with the control pulps. The strength properties of CMP pulps decreased with increasing amounts of hemicellulose removal during the stage prior to pulping.

Keywords: Chemical pulping; Hemicelluloses extraction; Fiber biometry; Pulp strength properties

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INTRODUCTION

The forest-based industry has played an undeniable and pivotal role for ensuring sustainable development as well as being one of the major economic contributors for many countries, especially for the production of cellulosic pulp. Pulp varieties can be produced from wood by mechanical, semi-chemical, or chemical pulping processes (Gellerstedt 2009; Höglund 2009). Chemimechanical pulping (CMP) is based on the pre-impregnation of wood chips with chemicals, such as NaOH and/or Na_2SO_3 solution, before a mild cooking followed by atmospheric pressure disc refining. The combined processes cause the fibers to swell, which increases the water retention and partial solubilization of hemicellulose, lignin, and extractives (Biermann 1996; Konn *et al*. 2006). The chemical pretreatment reduces the energy required for wood defibration and refining, resulting in pulp yields in the range of 75% to 95% and pulps with good strength properties for newspaper, cardboards, and tissue paper (Smook 1992; Banavath *et al*. 2011). During pulping, part of the carbohydrate component (mostly hemicelluloses) is released from the raw material into the process liquor, causing an increase in the biological oxygen demand of the effluent. Boluk *et al*. (2008) indicated that approximately 2% to 5% of hemicelluloses are dissolved and dispersed into the process

liquor in a mechanical pulping process. The recovery of hemicelluloses at an early stage before the CMP process can be an alternative for the production of new value-added products and improved economics of pulp mills under the concept of "Value Prior to Pulping" (VPP), thus improving the utilization of woody biomass (Thorp and Raymond 2004; van Heiningen 2006). The VPP concept proposes that the hemicelluloses are either partially or completely extracted for production of biofuels and biomaterials.

Several researchers have studied hemicellulose extraction using hot water and alkaline or acidic liquors, particularly before kraft pulping (Yoon and van Heiningen 2008; Liu *et al.* 2012; Jun *et al*. 2012; Reyes *et al.* 2015). The hydrothermal (HT) extraction of hemicelluloses from wood chips can be considered feasible and well-integrated with the existing infrastructure of a pulp mill as an environmentally friendly process (Ormsby *et al.* 2012; Chen *et al.* 2015). In HT extraction, temperatures vary between 120 and 240 °C, with an extraction time from minutes to hours. The dissolution of acidic components in water causes the liquor pH to decrease and effectively generates protons to catalyze polysaccharide hydrolysis. As a result, most of the amorphous hemicelluloses and part of the lignin can be dissolved in water, while cellulose crystallinity may decrease and wood porosity may increase due to breakdown of the lignocellulosic complex (Mosier *et al.* 2005; Hou *et al.* 2014).

Most of the VPP studies have focused on the kraft pulping process (Yoon and van Heiningen 2008; Helmerius *et al.* 2010; Duarte *et al.* 2011; Vila *et al.* 2011; Chirat *et al.* 2012), and there have been only a few studies applied to semi-chemical or mechanical pulping (Liu *et al.* 2012; Hou *et al.* 2014), with most of them highlighting an important reduction in refining energy and an excellent opportunity to increase additional revenue by producing high-value bio-based chemicals and materials. A key consideration for extracting hemicelluloses prior to chemimechanical pulping is maintaining the yield and quality of the pulp obtained. The aim of this study was to determine the effects of HT extraction of hemicelluloses prior to chemimechanical pulping of *Pinus radiata* wood chips relative to yield, fiber biometry, and pulp strength properties.

EXPERIMENTAL

Raw Material

Pinus radiata wood chips were provided by a pulp mill located in the Biobío Province of Southern Chile. The wood chips, of approximately 2.0 × 2.5 × 0.5 cm, were air-dried to a moisture level of 10% (w/w) and stored in plastic bags until use. The average composition is given in Table 1 (Reyes *et al.* 2013). The chemical composition showed that hemicelluloses represented 26% of wood dry weight; of this, hexoses (glucose, mannose, and galactose) are responsible for 64% of this composition. The cellulose and lignin contents were 41.2% and 27.8%, respectively.

Hydrothermal Extraction of Hemicelluloses

The HT extraction was based on a study by Reyes *et al.* (2013). Wood chips (100 g) and 500 mL of deionized water were placed in a rotary digester equipped with four independent 1.5 L vessels model AU/E-27 (Regmed, Brazil). The extraction experiments were performed according to Table 2. A prehydrolysis factor (P-factor) based on the Arrhenius equation combining the effect of time and temperature, similar to the H-factor in kraft pulping, was used as a measure of hydrothermal extraction intensity (Sixta 2006).

Table 1. Chemical Composition of *Pinus radiata* Wood Chips

Component		g/100 g wood
Cellulose		41.2
Hemicelluloses [a]		26.0
	Arabinose	1.3
	Galactose	3.1
	Glucose	3.9
	Mannose	9.7
	Rhamnose	0.7
	Xylose	5.0
	Uronic acids	2.3
Lignin		27.8
Extractives		1.9

Reyes *et al.* 2013; [a] Determined by acid methanolysis.

After each reaction, the residual material was cooled to room temperature, filtered, and washed with 100 mL of water. The solids were air-dried, the exact moisture content was determined, and the residual wood chips were weighed. The liquid fractions were concentrated in a vacuum to approximately 100 mL. The concentrates were mixed with 400 mL of 95% ethanol to precipitate the oligosaccharides. The precipitated material was retained in a 0.45 µm membrane filter, washed with ethanol, and dried in a vacuum oven at 40 °C. The solids were weighed to determine the crude hemicellulose recovery yield and stored for further chemical analysis.

Chemimechanical Pulping (CMP)

The CMP process with unextracted (control) and extracted wood chips was performed in an 800 mL stainless-steel reactor under the following conditions. Wood chips (100 g) were placed in the reactor and mixed with 600 mL of cooking liquor composed of 7.5% NaOH, 17.5% Na_2SO_3, and 0.1% anthraquinone. The mixture was heated to 170 °C at a rate of 4.5 °C min^{-1} and kept at maximum temperature (T_{max}) for 45 min. After each reaction, the liquor was drained and the biomass was washed with tap water and disintegrated in a 10 L laboratory blender (Metvisa, Brazil) equipped with dull blades for 1 h with 8.0 L of water (to simulate the 1st refining step in the CMP process). The material was washed inside a 1.0 m x 150 mm diameter PVC column with a 200 mesh screen at the bottom to avoid losses of fines (particles smaller than 0.2 mm). Fines initially passing through the screen were pumped back to the column top. Filtrate recirculation enabled the formation of a fiber mat at the column base that retained the fines. Water recirculation was stopped when the wash water was free of turbidity and reached a neutral pH. The washed material was centrifuged to a consistency of approximately 30%. Six parallel reactions were performed to provide enough solids for the refining step. The defibrated material was suspended in water to a final volume of 25 L (approximately 2.0% consistency), and was refined in a Bauer MD-3000 disk refiner (Regmed, Brazil) with a disc clearance of 0.1 mm (2nd refining step). Refining was performed with 300 to 1200 Wh of energy consumption in the disk refiner. The refined pulps were assayed for the fibrillation degree using Canadian Standard Freeness (TAPPI

T227 om-04, 2004) and centrifuged to 35% consistency.

Wood and Hemicelluloses Characterization

Approximately 50 g of wood chips were milled in a knife mill and sieved with a 40/60 mesh screen. Three grams of milled wood was extracted with a 90% acetone solution for 16 h in a Soxhlet apparatus. The amount of acetone-soluble extractives was determined on the basis of the dry weight of extracted and unextracted wood samples. Extractive-free wood (300 mg) was hydrolyzed with 72% sulfuric acid. The acid-insoluble and soluble lignins were determined by gravimetry and UV-Vis spectrophotometry (model UV-1650PC, Shimadzu, Japan), respectively. Glucose was determined using a high-performance liquid chromatography (HPLC) system (Merck-Hitachi LaChrom, Merck Hitachi, Germany) and further converted to glucans using a 0.9 hydrolysis factor (Ferraz *et al.* 2000). The monomeric composition of the hemicelluloses in the wood and the ethanol precipitates was determined using acid methanolysis followed by a gas chromatography system (Clarus 600, Perkin Elmer, USA), according to the methodology described by Sundberg *et al.* (1996). All experiments were performed in triplicate.

The weight-average molecular weight (M_w) of the hemicelluloses obtained from the different extraction conditions was determined by size-exclusion chromatography (SEC). Measurements were performed using a JASCO SEC system (degasser DG980-50, pump PU-980, refractive index detector RI-930, Suprema precolumn, columns Suprema 1000 and Suprema 30, from Kromatek, Essex, UK), in an aqueous 0.1 M $NaNO_3$ solution containing 0.05% NaN_3 as the eluent (1.0 mL/min). Pullulans were used as the standard to determine the M_w of hemicelluloses.

Strength Properties and Fiber Properties

Handsheets of pulps from the CMP processes were prepared according to the TAPPI standard T205 sp-02 (2002). Tensile strength and breaking length (TAPPI T494 om-01, 2001), tear index (TAPPI T414 om-04, 2004), and burst strength (TAPPI T403 om-02, 2002) were determined. Mean fiber length, fiber width, kink index, coarseness, and fines were determined using Fiber Tester equipment model 912 1.1e (Lorentzen & Wettre, Sweden), where 100 mg of sample was previously disintegrated in 100 mL of distilled water for 10 min. During the analysis of this suspension, the equipment measured approximately 35,000 fibers per sample.

Scanning Electron Microscopy (SEM)

Images of fibers were obtained using a Jeol JSM-6380LV microscope (Jeol, USA) operating in secondary electron mode at a bean current of 100 mA and an accelerating voltage between 15 and 20 kV. Image magnification was performed at 100X/ and 50X.

RESULTS AND DISCUSSION

Hemicelluloses Extraction and Characterization

The P-factor was used for comparison of different hemicellulose extraction conditions. The amount of precipitated hemicelluloses recovered from the HT treatment is shown in Table 2. The hemicelluloses recovered from water-soluble fractions were increased with an increase of the P-factor from 2.2 to 15.2 g/100 g of wood, performed at

P-factors of 6 and 1200, respectively (or from 7% to 58% of the initial amount of hemicelluloses in the wood). The average M_w of the hemicellulosic fraction ranged from 1.5 to 100 kDa. The increase in the severity increased the hydrolysis of the hemicelluloses during the extraction process, resulting in fast depolymerization of hemicelluloses and forming low M_w oligomers that were soluble in the aqueous media. Oligomers product are partial depolymerized in the aqueous phase to render monomeric sugars. During the HT extraction, the pH gradually decreased from 5.4 to approximately 3.6 (Table 2). The pH decrease was attributed to the release of acidity from the acetyl groups and carbohydrate degradation to formic acid (Lehto and Alén 2012).

Table 2. Amount and Molecular Weight of Ethanol-Precipitated Hemicelluloses from the Hydrothermal Treatment

Experiment	Time (min)	Temperature (°C)	P-factor	Final pH	Hemicelluloses recovered (g/100g wood)	Hemicelluloses removal (%)	Molecular weight (kDa)
P-6	30	120	6	5.4	2.2	8.4	14
P-20	120	120	20	5.1	6.4	24.6	4
P-110	75	145	110	4.9	5.8	22.3	6.6
P-410	30	170	410	4.1	10.8	41.5	100
P-1200	120	170	1200	3.6	15.2	58.5	1.5

The chemical composition of ethanol-precipitated hemicelluloses showed that mannose, glucose, and galactose from galactoglucomannans (GGMs) were the major components in all conditions, as shown in Fig. 1. The hexose concentration present in the extracts exhibited values from 47.6 to 91.6 mg hexoses/g of hemicelluloses, indicating an efficiently extraction of GGMs

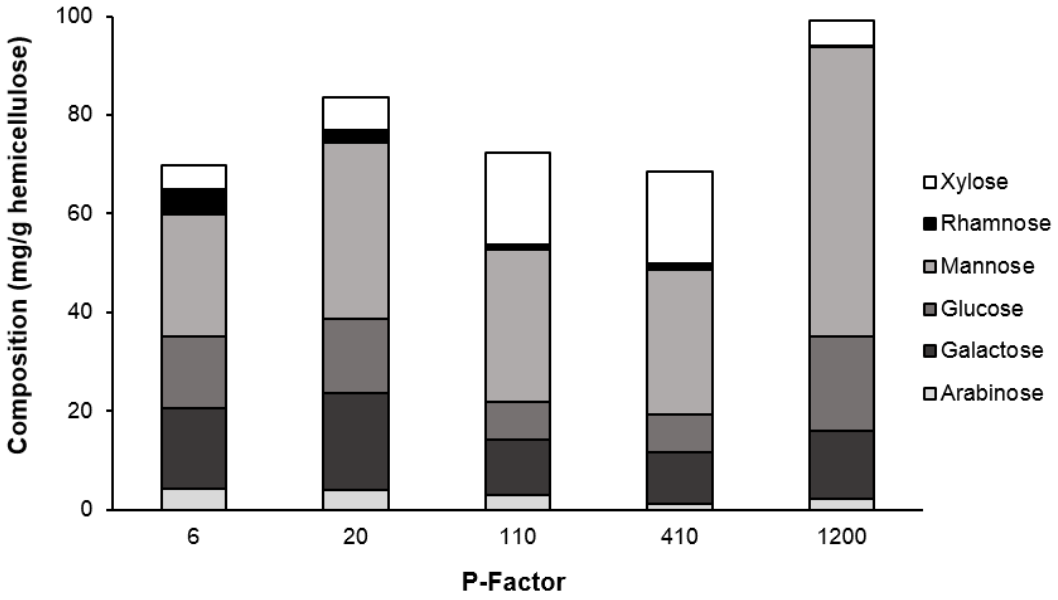

Fig. 1. Sugar composition of ethanol-precipitated hemicelluloses from the HT extractions

In *P. radiata* wood, the GGMs accounted for 64% of the non-cellulosic carbohydrates. Arabinose and xylose were preferentially hydrolyzed from xylans and arabinogalactans, and the concentrations of arabinose and xylose decreased with increased severity. This was probably caused by their acidic degradation to furfural (Lai 2001), especially when working at high temperature and pressure.

Chemimechanical Pulping (CMP)

Two conditions were selected to evaluate how the pre-extracted wood performed under CMP. In the present work, hydrothermal treatment P-20 was performed at 120 °C/120 min (mild treatment with a P-factor of 20) and P-1200 was performed at 170 °C/120 min (severe treatment with a P-factor of 1200), providing hemicelluloses extracts with the characteristics shown in Fig. 2. These HT extractions removed 25% and 58% of the hemicelluloses present in the wood, respectively. This amount is representative and aimed to demonstrate the effect of extraction of hemicelluloses from wood prior CMP pulping. The CMP pulps prepared from the control (untreated) and hemicellulose-extracted wood chips presented pulp yield between 56.5% and 74.6%, depending on the severity of the extraction process (Fig. 2).

The decrease in yield could have been attributed to the formation of oligomers that became hydrolyzed and solubilized in the subsequent alkaline treatment of the CMP process. The mass balance indicated that the cellulose was retained in the pulps, with percentages of retention over 99% for P-20 and 95.6% for P-1200. Regarding the hemicelluloses, the retention was 73% for P-20 and 44% for P-1200. The delignification degree presented values of 32.3% and 37.4% for P-20 and P-1200, respectively. Lignin removal was increased in the HT wood chips and contributed to the pulp yield decrease. The amount of lignin removed from the fiber surface can improve significantly the fiber inter-fiber bonding.

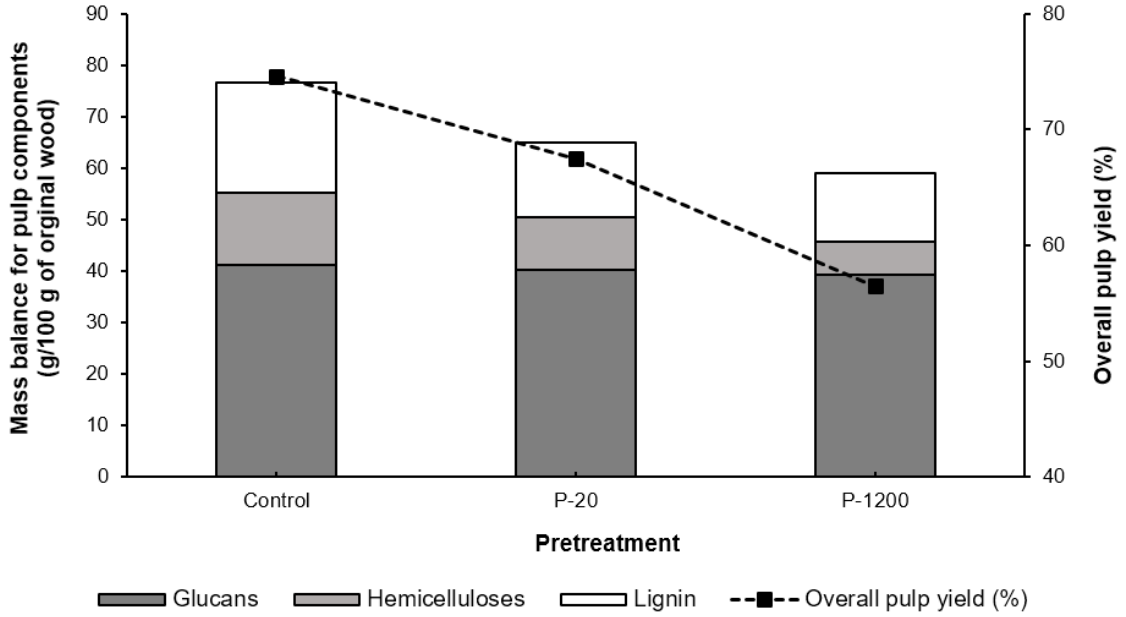

Fig. 2. Pulp yield and chemical composition of *P. radiata* CMP pulps from control and extracted wood at P-factors 20 (P-20) and 1200 (P-1200)

CMP Fibers Characteristics

The combined effect of HT pre-extraction and CMP on fiber properties of the obtained pulps are shown in Table 3. A difference in the average fiber length of pulps from the control and HT-extracted wood was observed. In control pulp, fiber length was 1.4 mm, while in P-20 and P-1200 the values were 1.2 mm and 1.0 mm, respectively. The amount of fines (fragments of less than 0.3 mm long) for the control pulp samples was 4.6%, while in P-20 and P-1200, the values were increased to 7.0% and 8.0%, respectively. The increase in fines content in HT pulps seemed to be related to a decrease in fiber length because of the hemicelluloses extraction that caused the release of the fines during the mechanical refining. High fibrillar content fines have been reported to influence positively sheet tensile index and negatively on the sheet light-scattering coefficient (Retulainen 1997). Average fiber width slightly increased in pulps from the HT wood chips from 42.5 µm in the control pulp to 43.5 µm and 44.1 µm for P-20 and P-1200, respectively.

Fiber coarseness (defined as the weight per unit fiber length) in the control, P-20, and P-1200 pulps were similar values in the range of 2.5 to 2.6 mg/100 m. The kink index (a deformation on the fiber that can be a weak or breaking point) was higher in pulps from the HT extractions, with values of 0.58 and 0.60 in P-20 and P-1200, respectively, when compared with the 0.42 value of the control pulp. Fibers were more likely to bend and break because of their low hemicelluloses content.

Table 3. Characteristics of CMP Fibers from Control and HT-Extracted Wood Chips (Values at 200 mL of Freeness)

Characteristics	Control	P-20	P-1200
Average fiber length (mm)	1.4	1.2	1.0
Average fiber width (µm)	42.5	43.5	44.1
Coarseness (mg/100 m)	2.52	2.53	2.60
Kink index	0.42	0.58	0.60
Fines content (%)	4.6	7.0	8.0

The SEM images of the fibers obtained in the different conditions are presented in Fig. 3. The surface structure of CMP fibers are important in the interfiber bonding in the final product. A higher fibrillation was observed in pulps from the HT-extracted wood (Fig. 3c to 3f) than in pulps from the unextracted control (Fig. 3a and 3b) obtained at different refining energy consumption. During refining, the fiber shape was changed from tubular to flat, which also can be associated with a higher fiber width, as shown in Table 3.

The refining process initially caused a shearing in the fiber wall, followed by an increase in the surface roughness and release of superficial layers (Mou *et al.* 2013). In fibers of the HT samples, P-20 and P-1200, exhibited this effect which was observed as compression and wrinkles in the structure of the fibers produced by mechanical actions of the disk refining. Page (1989) indicated that the hemicelluloses content influences the deformation tendency of fibers; this can affect the flexibility of the pulps.

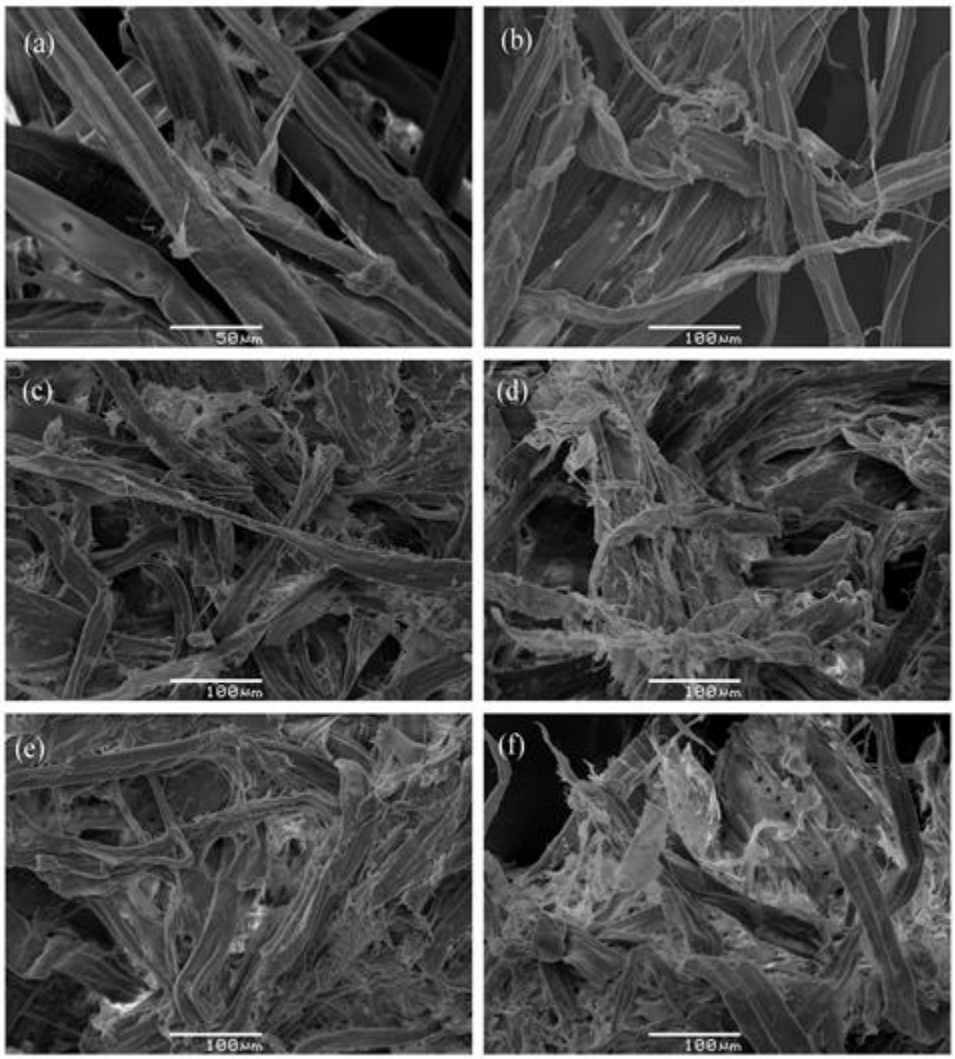

Fig 3. SEM micrographs showing the fiber morphology of *P. radiata* CMP pulps: (a-b) control pulps at 600 and 1200 Wh of refining energy, (c-d) P-20 pulps at 500 and 1100 Wh refining energy, and (e-f) P-1200 pulps obtained at 300 and 900 Wh

Strength Properties

Figure 4a shows that the HT extraction significantly reduced the refining energy to obtain a given freeness. Pulps from which hemicelluloses had been partially extracted were more rapidly refined, providing higher water retention with less energy consumption. Pulps with 200 mL of CSF were obtained at 1200, 790, and 500 Wh for the control and treated wood samples P-20 and P-1200, respectively. The specific refining energy was reduced by 34% and 58%, respectively, in comparison with the control; this may have been a result of the loss of lignin and hemicelluloses during the extraction and pulping process. This would have produced more loose, collapsible, and easily separable fibers. In addition, this indicated that the extraction of hemicelluloses could save energy in the refining, which is a significant portion of the total production cost (Kenealy *et al*. 2007; Liu *et al*. 2012).

The pulp strength, when in a handsheet, is a very complex function of several physical characteristics of the fibers. These characteristics include dimension (length, wall thickness, and diameter or coarseness), potential of bonding (bonding strength and

bonding area), and fiber strength (tensile and stiffness). The pulp properties were compared at similar freenesses (CSF) (Fig. 4b) and the results showed that the tensile index did not differ appreciably between the control pulp and P-20; however a decrease was observed for P-1200 pulp. The negative effect of extraction of hemicelluloses in the tensile strength is likely caused by the low inter-fiber bonding ability of the pulps from hemicelluloses-extracted wood compared at the same CSF. The inter-fiber bonding strength increased when hemicelluloses were present, which may be related to the increase in the amount of bonds per unit of contact area. This effect probably occurs because of the mobility in the hemicellulose chains, which increases the probability of hydrogen bonding with the cellulosic fibers (Hartler and Mohlin 1975; Hardacker 1984). The tensile strength is an important propertiy of papers with low basis weight used as wrapping papers. Nevertheless, it can be expected that chemi-mechanical pulps are not a material suitable for this purpose. The burst index of CMP versus its freeness are shown in Fig. 4c. By increasing the removal of hemicelluloses in wood, the burst index decreased in the pulps produced. The tear strength measures the ability of the sheet to resist the propagation of a tear. The tear strength is truly a measure of the amount of energy required to fracture a sample. A rule of thumb is that as tear strength decreases as the tensile strength increases. The tear index was slightly higher in pulps from extracted wood. According to Spiegelberg (1966), the removal of hemicelluloses decreased the strength properties of the fibers product to replacing the flexible hemicellulose-cellulose bond by a more rigid cellulose-cellulose bond.

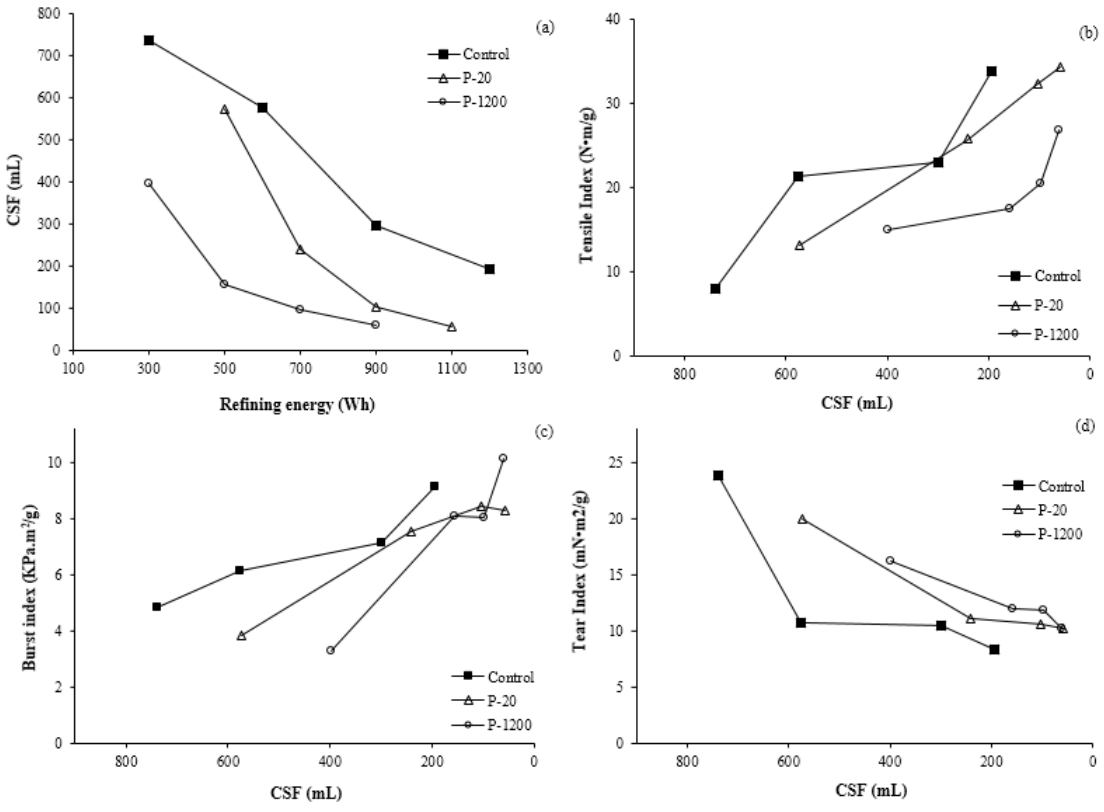

Fig. 4. Freeness and strength properties of handsheets prepared from *P. radiata* CMP pulps obtained at various energy inputs during disc refining

Many studies have investigated the effects of hemicelluloses on pulp and fiber properties over the years. The addition of a small amount of hemicellulose to pulp can produce remarkable improvements in the tensile strength properties of the subsequent handsheets. It has been generally accepted that GGMs in softwood pulp are more effective in fiber bonding than xylans in hardwood pulps because of their primary hydroxyl groups (Spiegelberg 1966). The bursting strength is the maximum pressure that can be exerted perpendicularly to the surface of a paper, before rupture occurs; this relationship can be observed in Fig. 4c. The CMP pulps from HT extraction had less resistance than that of the control pulps, which exhibited more bonding between the fibers. The tearing index increased in pulps P-20 and P-1200 in comparison with the control pulp.

CONCLUSIONS

1. The labile hemicelluloses fraction from *P. radiata* wood was partially extracted using a hydrothermal (HT) pretreatment.
2. Mannose, galactose, and xylose are the main sugars present in the extracts, and their relative amount varied according to the extraction conditions.
3. Low-molecular weight molecules were found in most of the recovered hemicelluloses.
4. The yield of chemimechanical pulp (CMP) prepared from HT chips was lower than in unextracted wood because of the higher solubilization of lignin and hemicelluloses.
5. In the CMP process, less energy input is necessary in the refining step; however, fiber length was decreased, which affected the strength properties of the pulps from HT wood chips. These were similar or lower in pulps from unextracted control wood. Depending on the use of the CMP, the pulping and refining conditions should be adjusted for the pre-extraction process and for the use of hemicelluloses obtained in a biorefinery, producing animal feed additive or as a feedstock for producing biofuels (ethanol, butanol), chemical intermediates (furfural), or pure sugars and substitutes (xylose, xylitol).

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