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Defibration mechanisms of autohydrolyzed *Eucalyptus* wood chips

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Abstract

The objective of this study was to evaluate the influence of autohydrolysis on mechanical defibration of *Eucalyptus* wood chips. The autohydrolysis process changed notably the mechanical properties of *Eucalyptus* chips, which led up to 78% decrease in specific energy consumption. The removal of mainly hemicelluloses undoubtedly decreased the overall pulp yield. Hemicellulose losses cannot be solely accounted for the changes in the wood and pulp properties, because the autohydrolysis also caused changes in the content and structure of lignin. When comparing the

TMP fibers of the original wood chips with the fibers resulting from the autohydrolyzed wood material, it was clear that the rupture point shifted from the secondary wall to the middle lamella, confirmed by X-ray photoelectron spectroscopy measurements. This study revealed the mechanical behavior of autohydrolyzed wood chips and can provide useful information for integration of mechanical pulp mills into the biorefinery concept in the future.

Keywords: Autohydrolysis**;** Defibration; energy consumption; *Eucalyptus*; FTIR; pulp properties; TMP; XPS.

1. Introduction

Eucalyptus wood is currently an established raw material for pulp and paper industries, due to its fast growth in certain regions, low cost and good wood quality {{2 Magaton,Andréia da Silva 2009}}. As the complete utilization of wood has become an important topic with the advent of the so-called biorefineries, *Eucalyptus* wood certainly will also have an important role.

Ethanol production from lignocellulosic biomass comprises the following main steps: hydrolysis of cellulose and hemicellulose, sugar fermentation, separation of lignin residue and, finally, recovery and purifying the ethanol to meet fuel specifications {{124 Alvira,P. 2010}}. Various wood pretreatments for the enhancement of hemicelluloses extraction can be found in literature, such as alkaline treatments (NaOH, alkaline peroxide, ammonia fiber explosion, ammonia recycling percolation), acid hydrolysis (concentrated and diluted) as well as hydrothermal (autohydrolysis and steam explosion)

{{120 Carvalheiro,Florbela 2008}}. Amongst these pretreatments, autohydrolysis is the main technique used for hemicelluloses extraction in the pulping industry, especially in dissolving pulp production. Autohydrolysis studies started back in the 1940's (Overbeck and Muller, 1942) and this technique consists of the treatment of wood with water only at elevated temperatures and pressures {{6 Colodette,Jorge L. 2011}}. Some studies regarding the extraction of hemicelluloses prior to mechanical pulping can be found in literature. {{121 Houtman,Carl 2011}} showed that a combined oxalic acid/bisulfite pretreatment of hardwoods resulted in ca. 20% refining energy savings, as well as 13% gains in brightness. Moreover, {{122 Bilek,E.M. 2011}} confirmed the economic feasibility of such approach. A different approach of hemicelluloses removal from hardwoods has been recently published {{119 Liu,Wei 2012}}, in which wood pretreatment prior to CTMP process is performed with sulfuric acid. Such approach led to refining energy savings and higher pulps' strength properties. However, the defibration mechanisms, which are of high importance for mechanical pulp production and have a great influence in specific energy consumption, have been neglected.

The concept of value prior to pulping (VPP) consist on the utilization of partially or completely extracted hemicelluloses for biofuel production{{123 van Heiningen,A. 2006}}. However, the feasibility of using autohydrolyzed chips for mechanical pulping remains uncertain. Nonetheless, fundamental studies regarding the mechanical properties of autohydrolyzed chips, their behavior during mechanical defibration and the defibration mechanism are worth pursuing. Such study can provide useful information for integration of mechanical pulp mills into the biorefinery business in the future,

especially when considering decreasing the energy for the mechanical size-reduction of wood, as well as the chemical and morphological structure of the resulting fiber material.

The objective of this study was to evaluate the influence of autohydrolysis on the defibration mechanisms of *Eucalyptus* wood chips during thermomechanical pulping. Moreover, the properties of the produced pulps were investigated.

2. Experimental

A novel *Eucalyptus* hybrid (*E. urophylla x E. globulus,* coded as U2xGL1*)*, which is from the Brazilian Network of *Eucalyptus* Genome Research – Genolyptus (a nationwide network of laboratories and forestry companies devoted to an integrated molecular breeding approach {{104 Grattapaglia,Dario 2004}}, was used in this study. The general characteristics of the wood material are presented in Table 1 (shown as REF).

Wood density was evaluated according to TAPPI standard method (T258 om-06). The carbohydrate composition was analyzed by HPAEC-PAD after acid hydrolysis following the procedure described by {{36 Wallis,Adrian F.A. 1996}}. Klason and acid soluble lignins were measured according to {{38 Gomide, J.L. 1986}} and {{39 Goldschimid,O. 1971}}, respectively. Total lignin content was defined as the sum of Klason and acid soluble lignin as described by {{40 Dence,C.W. 1992}}. Lignin syringyl/guaiacyl ratio (S/G) was evaluated according to {{41 Lin,Stephen Y. 1992}}. Total uronic acids and acetyl groups were evaluated according to Scott (1979) and Solar et al. (1987), respectively.

Autohydrolysis was carried out with 500 o.d. grams of chips in a

rotating digester. The reaction temperature was 120ºC, and such a low temperature was chosen in order to minimize changes in lignin structure. Time-to-temperature was 60 minutes and time-at-temperature varied accordingly to the pre-defined P-factors (200, coded as AH-200 and 800 coded as AH-800). P-factor describes the intensity of the autohydrolysis treatment, being analogous to the H-factor concept used for pulping (Sixta et al. 2006). After the autohydrolysis stage, the spent liquor was collected and gravimetric yield was determined for the solid material. Reference chips were pre-impregnated with deionized water in a rotating digester, under 10 bar pressure of pure oxygen, during 5 hours, at 4 L:W (Liquid-to-wood ratio), to ensure complete saturation of the chips, and rested for at least 48 hours under room temperature and atmospheric pressure (Muguet et al. 2013).

The mechanical defibration was carried out on 100 g o.d. chip samples in a wing defibrator, consisting of four static blades; the refining gap between the blades and the inner refiner wall was 1.0 mm. Other parameters: ca. 750 rpm, at ca. 37% consistency, 130°C, and refining times of 5, 10, and 15 min. Prior to the refining experiments, the chips were pre-heated inside the refiner for 5 min, and the condensate was released before the refining process started. Pulps were screened with a slot screener of 0.17 mm and tested for Canadian Standard Freeness (ISO 5267-2:2001).

Handsheets were prepared (ISO 5269:1:2005) and tested for grammage (ISO 536:1995), density (ISO 534:1988), tear strength (ISO 1974:1990, Elmendorf method), tensile index (SCAN-P38) and optical properties (ISO 2470:1999). X-ray photoelectron microscopy (XPS) measurements were performed according to {{125 Johansson,Leena-Sisko

2004}}. Fourier transform infrared spectroscopy with photoacoustic detection (FTIR-PAS) and normalization of the spectra were performed according to {{33 Suchy,Miro 2010}}. Fiber morphological analyses were performed with FiberLab analyzer (Metso Automation, Finland). Scanning electron micrographs were obtained with a Hitachi TM-1000 scanning electron microscopy, after coating the samples with gold.

3. Results and Discussion

3.1 Autohydrolysis

Autohydrolysis is a technique used for the production of high purity cellulose pulps in industrial scale, with the removal of hemicelluloses {{68 Sixta,Herbert 2006}}. It is well known that the higher the P-factor of the treatment, the higher amount of hemicelluloses is removed {{6 Colodette,Jorge L. 2011; 118 Liu,Wei 2011}}. In this study the same trend was seen (Table 1), even though the final yield was substantially lower than in other studies with *Eucalyptus* {{6 Colodette,Jorge L. 2011}}. This can be an indication that the P-factor concept should not be an accurate approach when performing the autohydrolysis at low temperatures.

Table 1: General chemical composition and yield of untreated and autohydrolyzed *Eucalyptus* wood chips expressed in % of wood dry weight.

		REF	AH-200	AH-800
Carbohydrates	**Glucans**	46.8	46.1	37.5
	Xylans	13.7	8.3	3.3
	Others*	2.3	0.7	0.6
Lignin	**Klason**	24.3	21.2	19.7
	Acid Soluble	5.8	2.5	1.2
	Total	30.1	23.7	20.9
Syringyl/Guaiacyl ratio		4.0	4.0	3.6
Acetyl groups		2.7	ND	ND
Uronic Acids		4.1	1.6	0.4
Yield		-	86.3	67.8

* For AH-200 and AH-800 samples, only mannans were found.

Comparing the results presented in Table 1, cellulose was quite stable for AH-200, with only 1.5% of original content in wood lost throughout the treatment. However, with the 800 P-factor, a significant amount of cellulose was dissolved (19.9% of its original content in wood). The possible explanation is that due to the low treatment temperature, the reaction time was extremely long, *ca.* 96 hours for P-factor 800, which caused undesired dissolution of cellulose, reflecting directly on the final yield.

In order to minimize the changes in the lignin structure, which could affect the defibration phenomena, a strategy of using low temperature (120ºC) treatments was adopted. Lignin seems to be dissolved in early stages of the treatment and is more stable at longer treatment times, since *e.g.* with P-factor 200 (*ca.* 23 hours), one fifth of original lignin content in wood was already dissolved, whereas with P-factor 800 (*ca.* 96 hours) about one third was removed. Moreover, the lignin S/G ratio remained constant at P-factor 200, which could indicate that the residual lignin in the chips might still have its original structure. However at P-factor 800 S/G ratio decreased, indicating that syringyl lignin was removed in larger extent (*ca.* one third) than guaiacyl lignin (*ca.* one forth). Changes in lignin structure during autohydrolysis have been

already shown in recent literature ({{16 Leschinsky,Moritz 2008; 15 Leschinsky,Moritz 2008; 116 Rauhala,Tiina 2011}}, such as cleavage of β-O-4 linkages, increase in phenolic groups, decrease of S/G ratio and molar mass, however all studies were performed at high temperature (150 – 170°C), differently from our approach (120 °C).

FTIR spectroscopy was applied to investigate the changes in wood structure and composition in more details. {{115 Pandey,K.K. 2003}}, based on extensive literature review, listed the most important peak assignments for FTIR spectra of wood. In Fig. 1, changes due to the severity of the autohydrolysis process are mainly seen in two different peaks: (1) 1738/1734 cm^{-1} for unconjugated C=O in xylans, which is related to dissolution of acetyl groups during autohydrolysis {{22 Garrote,Gil 2002}}, what could also be detected via other method (Table 1) and; (2) 1244 cm^{-1} for xylan and syringyl ring C-O stretch in lignin, which corroborates the high xylan and syringyl lignin losses with increased severity (Table 1).

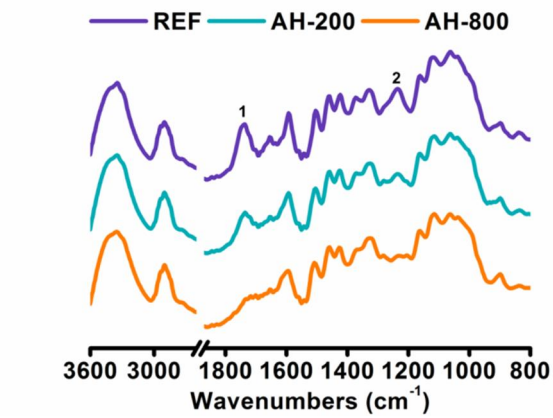

Figure 1: FTIR-PAS spectra of untreated and autohydrolyzed *Eucalyptus* wood chips. (1) 1738/1734 cm^{-1} and; (2) 1244 cm^{-1} peaks.

3.2 TMP refinings

Mechanical pulping requires a great amount of energy, and such demand is a key limiting factor for the process feasibility, especially for hardwoods like *Eucalyptus* {{48 Browne,T.C. 2001}}. The refiner used in this study, based on blades, consumes more energy than pilot scale or industrial disc refiners {{57 Xu,Eric C. 1999}}. It was assumed that, at least as an approximation, the total applied energy with different refining systems will be proportional to the energy that manifests itself as changes to the fibers (Muguet et al. 2012). Table 2 shows the summary of the refining results.

Table 2. Summary of the results of TMP refining experiments of untreated and autohydrolyzed Eucalyptus wood chips.

	Time (min.)	S.E.C. (MWh/odt)	Freeness (ml)	Rejects (%)	Fines (%)
REF*	5	2.59	445	3.4	21.8
	10	4.39	320	2.5	22.2
	15	5.87	200	2.5	22.0
AH-200	5	1.36	625	3.3	16.8
	10	1.60	580	3.8	15.7
	15	1.83	580	4.4	17.6
AH-800	5	0.70	650	4.1	38.8
	10	1.16	590	4.5	36.1
	15	1.28	590	5.0	40.4

*Muguet et al., 2013

The autohydrolyzed wood chips had significantly lower specific energy consumption (S.E.C.), *ca.* 47-78% of energy savings when compared to traditional TMP process, shown as the reference (Fig. 2A), which indicates changes in the mechanical properties of the wood chips after the autohydrolysis. Such improved refinability is usually seen when *Eucalyptus* wood is chemically pre-treated, such as in CTMP or APMP processes or enzymatically pre-treated prior to refining {{57 Xu,Eric C. 1999; 58 Hart,Peter

W. 2009}} . However, the possible roles of xylans and of the partial fiber wall deconstruction are inconclusive at this stage. Even though the energy demand was clearly lower for the autohydrolyzed chips, the development of drainage properties was poor. Fig. 2B shows that on early refining stages, there is a slight decrease in freeness, but it reaches a plateau with longer refining times. Such properties are strongly dependent on the fiber morphology and surface properties, which will be discussed in the next section.

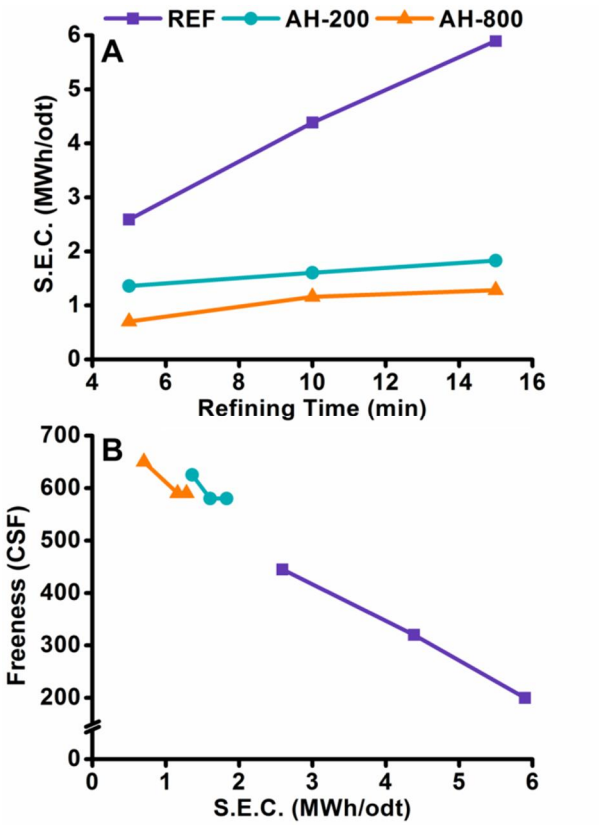

Figure 2: A) Specific energy consumption (S.E.C.) versus refining time and; B) Freeness versus S.E.C. for the untreated and autohydrolyzed *Eucalyptus* wood chips.

3.3 Fiber morphology and surface properties

Fiber morphological characteristics such as coarseness and fiber

length (El-Hosseiny and Anderson 1999) and curl index {{90 Fellers,Christer 2001}}, have been shown to be of extreme importance for pulp and paper properties. Moreover, morphological characteristics may serve as an indicator of changes in the wood structure taking place inside refiners, during the conversion to mechanical pulp. Fig. 3 shows that AH-200 pulps had higher fiber length when compared to the reference pulps. However, AH-800 pulps did not show such behavior; instead they displayed the lowest fiber length values. As a consequence, AH-800 pulps had substantially higher amounts of fines in relation to reference or AH-200 pulps, with the latter showing the lowest amounts of fines.

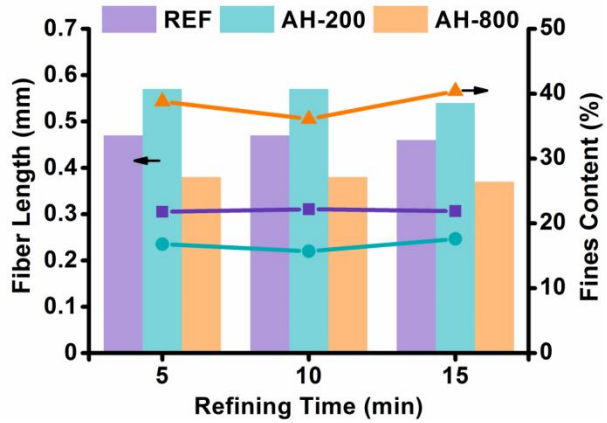

Figure 3: Length (bar graph) and fines content (line graph) of the fiber samples from the untreated and autohydrolyzed *Eucalyptus* wood chips.

Such results indicate that the AH-200 and AH-800 samples behaved in a similar way as the chips in CTMP and APMP processes, where the chips are pretreated with sulfite and alkaline peroxide, respectively{{57 Xu,Eric C. 1999; 58 Hart,Peter W. 2009; 93 Muguet,Marcelo Coelho dos Santos 2012}}. In such treatments, lignin present in the middle lamella is modified, leading to lower glass transition temperature (Tg). At temperatures below the lignin Tg, the cell wall consists of largely tangentially oriented

lamellae of two zones, each of which has both hard and soft components. This is the case in the TMP process, which is the reference of this study (Muguet et al., 2013), where the lignin as the main component of the compound middle lamella, remains hard, whereas the rest of the cell wall is more softened. In this case, the defibration takes place mostly in the segment between the primary wall and the S1 layer of the secondary fiber wall. However, in chemimechanical processes, such as CTMP and APMP processes, where wood is treated with chemicals before defibration, the lignin properties are altered in such a way that the softening temperature is lowered. This leads to improved defibration, which takes place mostly in the middle lamella (Franzén 1986).

The aforementioned results and discussion suggest that the strategy of performing the autohydrolysis at low temperatures to avoid lignin structural changes, and evaluating solely the role of hemicelluloses was not successful. This was confirmed by X-ray photoelectron spectroscopy measurements (Fig. 4), which is a well-known surface characterization technique for wood fiber materials {{125 Johansson,Leena-Sisko 2004}}. Wood surface lignin in Fig. 4 resembles the average amount of lignin present in the middle lamella. The reference pulp showed the lowest surface lignin content among the samples, indicating that the defibration took place inside the fiber wall, more specifically along the S1 layer of the secondary wall, as expected {{81 Franzén,Rune 1986}}. However, the high surface lignin content of both AH-200 and AH-800 pulps at 5 minutes refining indicate that the defibration took place on the middle lamella, resembling chemimechanical processes, due to lignin structure changes during the autohydrolysis treatment.

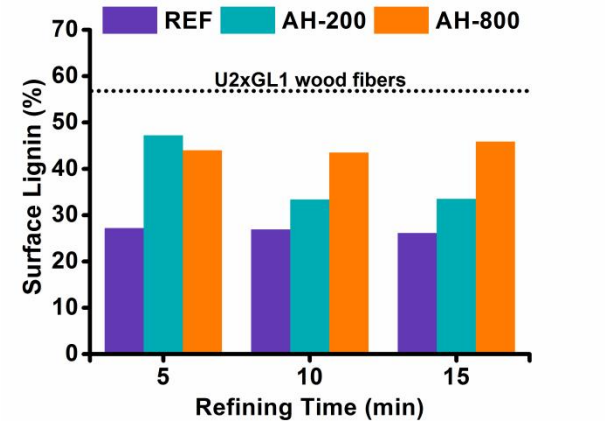

Figure 4: Surface lignin content of untreated wood and pulps from the untreated and autohydrolyzed *Eucalyptus* wood chips.

When comparing AH-200 and AH-800 refinings, different behaviors can be seen. Surface lignin content tended to decrease with increasing refining time for AH-200 pulps, whereas it remained somewhat constant for AH-800 pulps. It seems that the depletion of carbohydrates inside the fiber wall during milder autohydrolysis (P-factor 200) was not enough to decrease the intrinsic wood fiber's strength. In that case, the refining would serve as a surface cleaning stage, alongside with the traditional effects of refining such as delamination and fibrillation {{111 Fernando,Dinesh 2011}}. On the other hand, the harsher autohydrolysis (P-factor 800) decreased the intrinsic wood fiber strength to the point where the fiber would not resist the mechanical forces inside the refiner, which can explain the lowest fiber length and highest amount of fines (Fig. 3). Such theory can be corroborated by SEM micrographs (Fig. 5). The reference and AH-200 pulp fibers show uneven breaking point (white arrows), seeming like fibers resisted to a certain extent the forces inside the refiner, whereas AH-800 fibers show a flat breaking point, indicating that the fibers were weak, not resisting the high forces inside the refiner.

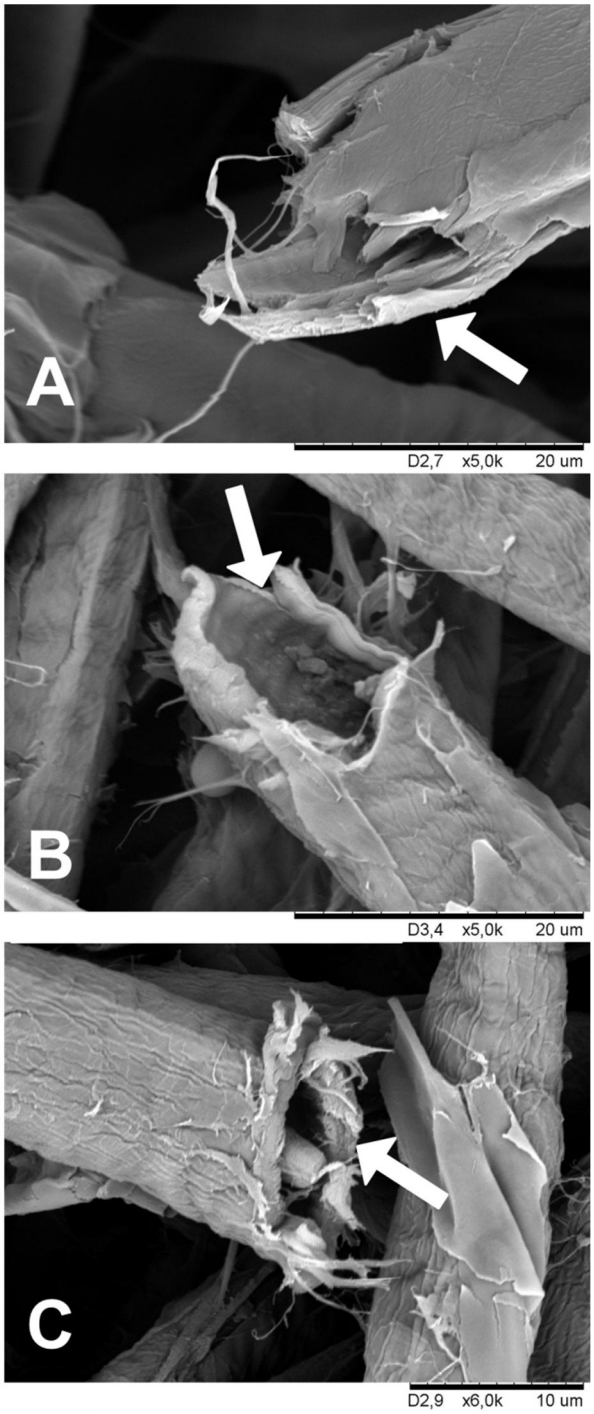

Figure 5: SEM micrographs from the 5 minutes refining samples of; A) Reference; B) AH-200; C) AH-800. The white arrows point out the types of breaking points of the fibers during the TMP process.

3.4 Pulp physical, mechanical and optical properties

The pulps from the autohydrolyzed wood chips show inferior properties when compared to the reference (Table 3). The mechanical properties might be negatively influenced by the high surface lignin content, and especially by the low amount of xylan in the pulps. Our previous studies suggest that xylan is extremely important for fiber bonding and mechanical properties in *Eucalyptus* pulps {{1 Muguet,Marcelo Coelho dos Santos 2011}}.

The main drawback is the optical properties. Even though the opacity is high, which is desirable in mechanical pulps, the brightness is extremely low, due to chomophores formation in the wood during the autohydrolysis, restricting the uses of such pulps. The dark color likely derives from acid induced lignin condensation and cleavage of β-O-4 linkages giving rise to new phenolic hydroxyl groups {{15 Leschinsky,Moritz 2008}}.

Table 3: Summary of physical, mechanical and optical properties of pulps derived from the untreated (REF) and autohydrolyzed *Eucalyptus* wood chips.

		Freeness (ml)	Sheet Density (kg/m^3)	Tear Index ($mN.m^2/g$)	Tensile Index (kN.m/kg)	Opacity (%)	Brightness (% ISO)
REF	5	445	290.0	1.18	7.8	99.0	49.7
	10	320	311.2	1.51	11.7	99.2	49.9
	15	200	335.7	1.75	14.8	99.5	50.0
AH-200	5	625	362.8	0.95	7.9	99.7	17.7
	10	580	371.4	0.97	8.8	99.9	17.8
	15	580	368.0	1.09	9.2	99.9	18.0

AH-800	5	650	372.5	0.91	4.2	99.9	11.3
	10	590	383.1	0.96	5.6	99.9	11.7
	15	590	379.0	0.97	6.2	99.9	11.6

4. Conclusions

This study revealed the mechanical behavior of autohydrolyzed wood chips. The autohydrolysis process changed notably the mechanical properties of *Eucalyptus* chips. However, the role of hemicelluloses during defibration could not be solely assessed due to changes in the lignin structure. With this, the defibration of autohydrolyzed *Eucalyptus* wood chips takes place in the middle lamella, differently from traditional thermomechanical pulping, where the fiber separation takes place along the fibers' secondary wall. This was confirmed by the results of XPS studies. The high surface lignin content of the fibers can be positive if using such fibers as reinforcement for green biocomposites, where the poor optical properties would not be a drawback. Moreover, the low energy consumption during the mechanical defibration can open possibilities for such process as a pretreatment to enhance biomass accessibility in complete hydrolysis and bioethanol production. This study provides useful information for integration of mechanical pulp mills into the biorefinery concept in the future.

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6. References