ALKALINE PEROXIDE MECHANICAL PULPING OF NOVEL BRAZILIAN *EUCALYPTUS* HYBRIDS

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Eucalyptus wood is among the most important biomass resource in the world. Wood mechanical defibration and fibrillation are energy-intensive processes utilized not only to produce pulp for papermaking, but also to produce reinforcement fibers for biocomposites, nanocellulose, or pretreat lignocellulosic material for biofuels production. The structural features of different *Eucalyptus* hybrids affecting the refining energy consumption and produced fiber furnish properties were evaluated. The defibration and fiber development were performed using an alkaline peroxide mechanical pulping (APMP) process, which included chelation followed by an alkaline peroxide treatment prior to wood chip defibration. Despite the similar wood densities and chemical compositions of different *Eucalyptus* hybrids, there was a clear difference in the extent of defibration and fibrillation among the hybrids. The high energy consumption was related to a high amount of guaiacyl lignin. This observation is of major importance when considering the optimal wood hybrids for mechanical wood defibration and for understanding the fundamental phenomena taking place in chemi-mechanical defibration of wood.

Keywords: Alkaline peroxide mechanical pulping; APMP; Defibration; Energy consumption; Eucalyptus; Hybrids; Lignin structure; Pulp properties

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INTRODUCTION

Eucalyptus sp. is one of the most important lignocellulosic fiber sources worldwide and its role is increasing steadily, while the need for biomass as a renewable raw material also is expanding. The major interest in *Eucalyptus* wood originates from its low production cost in certain regions, mainly because of high forest productivity. The increasing understanding of its application in various paper grades makes *Eucalyptus* one of the preferred fiber raw material worldwide (Magaton *et al.* 2009). Part of the success of the Brazilian forest industry relates to its intensive breeding program, focusing on *Eucalyptus* hybrids. Brazilian breeders are investing heavily in the potential of *Eucalyptus globulus*, due to its adequate wood density, fiber length, chemical composition, and lignin structure in relation to other commercial *Eucalyptus* species (Rencoret *et al.* 2008).

Some other generations of Brazilian-grown *Eucalyptus* hybrids have already been evaluated for kraft pulping and papermaking (Gomide *et al.* 2005), but research on the mechanical defibration of *Eucalyptus* wood species is still lacking. *Eucalyptus* woods have already been used in mechanical pulping, but in terms of process design and post-pulping bleachability, only two processes are suitable for high brightness paper grades and packaging: alkaline peroxide mechanical pulping (APMP) and alkaline sulfite mechanical pulping (CTMP) (Xu and Sabourin 1999). The APMP process is an interesting pulping method for *Eucalyptus* woods; especially when producing suitable high-brightness papers, since the wood chips can be fully bleached prior to refining (Cort and Bohn 1991). The APMP process has several pre-treatment stages prior to the actual defibration. In the first one, chelants are used to remove metals (Area and Kruzolek 2000). The metals removal is necessary, since hydrogen peroxide (used on the further pre-treatment stages) is decomposed by their presence, especially manganese (Qiu *et al.* 2003). The process presents high flexibility in processing wood of variable qualities and it delivers fibers of higher density, tear and tensile strength when compared to CTMP fibers (Xu and Sabourin 1999).

Mechanical pulping is an energy-intensive process, and methods for reducing energy demand during refining have been largely investigated. For example, the application of enzymatic treatments (Hart *et al.* 2009), the reduction of raw materials variability (Dundar *et al.* 2009), and the use of chemical treatments (*e.g.* alkaline hydrogen peroxide) are among the many attempts to decrease refining energy demand. However, it is obvious that wood composition and ultrastructure have a distinct impact on the energy consumption. Therefore, understanding the fundamental phenomena of the defibration process and determining the variables affecting the energy consumption are crucial to establishing the possibilities to reduce the energy consumption.

The objective of this study was to evaluate the feasibility of a new generation of top-level *Eucalyptus* hybrids for APMP production. The focus was to investigate the effect of structural components of wood on energy consumption, fiber, and pulp properties.

EXPERIMENTAL

Four different hybrids of Brazilian-grown *Eucalyptus* trees derived from the Genolyptus genetic breeding program were used in this study. The wood samples were coded based on the following crossings: *E. grandis* x [*E. urophylla* x *E. globulus*] (**G1xUGL**), *E. urophylla* x *E. urophylla* (**U1xU2**), [*E. dunnii* x *E. grandis*] x *E. urophylla* (**DGxU2**) and *E. grandis* x *E. urophylla* (**REF**) (Table 1). The hybrid REF was chosen to be the reference since it was already planted and used as an industrial fiber source. The others are being evaluated for their potential as a wood source for the pulp and paper industries.

Table 1. Wood Chemical and Physical Characterization

	Carbs. (%)			Lignin (%)			S/G	Acetyl (%)	UA (%)	Dens. (kg/m^3)
	Gluc.	Xyl.	Oth.	Klas.	ASL	Tot.				
G1xUGL	46.2	13.6	2.1	25.4	5.0	30.4	3.1	2.9	4.0	500
U1xU2	48.0	12.4	1.7	26.8	4.5	31.3	3.0	2.1	3.8	504
DGxU2	46.6	12.9	2.2	26.2	4.5	30.7	2.7	2.6	4.1	496
REF	50.7	12.3	2.5	23.6	4.3	27.9	2.8	2	4.1	480

* Gluc= Glucans, Xyl= Xylans (as backbone), Oth= Other hemicelluloses, Klas= Klason, ASL= Acid Soluble Lignin, Tot= Total Lignin, S/G= Syringyl-to-Guaiacyl Ratio, UA= Uronic Acids, Dens= Density

The carbohydrate composition was analyzed by HPAEC-PAD after acid hydrolysis, following the procedure described by Wallis *et al.* (1996). Total uronic acids were evaluated according to Scott (1979). Klason and acid soluble lignins were measured according to Gomide and Demuner (1986) and Goldschimid (1971), respectively. Lignin content was defined as the sum of Klason and acid soluble lignin as described by Dence (1992). Syringyl/Guaiacyl ratio (S/G) was evaluated according to Lin and Dence (1992). Acetyl groups were evaluated according to Solar *et al.* (1987). Wood density was evaluated according to TAPPI standard T258 om-06.

The APMP process was carried out with a pre-vaporization stage of 20 minutes and double-stage chemical impregnation (Table 2). The first impregnation stage consisted of the application of NaOH and DTPA. It was carried out in a press apparatus that works with compression forces of *ca*. 14 MPa. After the chips were squeezed, the chemicals were added, and after that, the pressure was released so that the chemicals penetrated the chips. The chelation stage was run at 25^{o}C, for 20 minutes, with a liquor-to-wood ratio (L/W) of 4:1. The liquor was then pressed out of the chips and collected for further analyses. The second impregnation stage consisted of the application of alkaline hydrogen peroxide and stabilizers. It was carried out following the same pressing procedure of the first stage, but then transferred in a plastic bag and placed in a warm bath under 60 °C, for 60 minutes, and a L/W ratio of 4:1. The liquor was then pressed out of the chips and collected for further analyses. After pressing, the chips were ca. 43% consistency.

Mechanical pulping was carried out in a wing defibrator, consisting of four static blades, refining gap between blades, and inner refiner wall of 2.5 mm, *ca.* 750 rpm, 100 o.d. grams per run per sample, at *ca.* 43% consistency, temperature of 130 °C, and refining times of 4, 7, 10, and 13 minutes. The liquors obtained after each impregnation stage were subjected to pH and hydrogen peroxide concentration (iodometric titration) measurements. 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 and ISO 9416:1998). X-ray photoelectron spectroscopy (XPS) measurements were done according to Johansson and Campbell (2004), and surface lignin concentration was calculated according to Laine *et al.* (1994). Fiber morphological analyses were done with a FiberLab analyzer (Metso Automation, Finland).

Table 2. Chemical Charges (kg/odt) Applied During Double-Stage Impregnation

Chemicals	1st Impregnation	2nd Impregnation	Total
H_2O_2	-	40	40
DTPA	3	1	4
NaOH	35	25	60
Na_2SiO_3	-	25	25
$MgSO_4$	-	0.6	0.6

RESULTS AND DISCUSSION

APMP Experiments

Double-stage impregnation

In the APMP process, the wood chips were impregnated in two stages: first using chelating agents to remove metals, followed by a second impregnation with alkaline hydrogen peroxide to bleach the wood chips and reduce refining energy consumption. No significant differences were seen among the various wood samples regarding either the end pH of the first and second impregnations or hydrogen peroxide consumption in the second impregnation (Table 3). This was an indication that the pre-treatments behave similarly for all wood samples.

Table 3. Characterization of Liquors from Both Pre-Impregnation Stages

Sample	pH 1st Impreg.	pH 2nd Impreg.	H_2O_2 consumption (% of applied)
G1xUGL	13.75	11.06	45.4
U1xU2	13.73	10.79	45.9
DGxU2	13.74	10.91	45.7
REF	13.74	10.94	45.8

Refinings

High refining energy consumption is a key factor limiting the utilization of mechanical wood defibration (Francis *et al.* 2002). In addition, high energy demand is also problematic in other types of defibration processes, such as microfibrillated cellulose (MFC) production. For example, Spence *et al.* (2011) showed that energy consumption during the production of MFC can be decreased by choosing an appropriate method. In addition, mechanical pulps can be used as raw material for MFC production, and MFC-containing aromatic lignin may reduce production costs and result in new uses and products (Spence 2011). Therefore there is a need to determine the fundamental phenomena affecting the required defibration energy and to find novel methods for its reduction. The use of chemicals has been said to reduce energy consumption (Xu and Sabourin 1999), as well as choosing a suitable wood for such processes. Although the wood characterization, the pre-refining chemical treatments, and progress in the specific energy consumption did not show large differences among the wood hybrids, the development of drainage properties among the samples varied significantly (Fig. 1). It is worth pointing out that the refiner used in this study consumes higher amounts of energy when compared to disc or pilot scale refiners (Jones and Richardson 2000, 2001; Xu and Sabourin 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. Nevertheless, the hybrid G1xUGL shows the best refinability among all hybrids, since it reached lower freeness levels than all the other hybrids at similar energy levels. This refinability could not be explained by the morphological properties, since Prinsen *et al.* (2012) showed that there are no relevant differences on fiber width among the same hybrids studied in this work. Moreover, recent studies (Rusu *et al.* 2011) show that thicker cell walls need less energy to reach a given freeness, however such differences are not enough to explain different behavior between the evaluated species (pine and spruce).

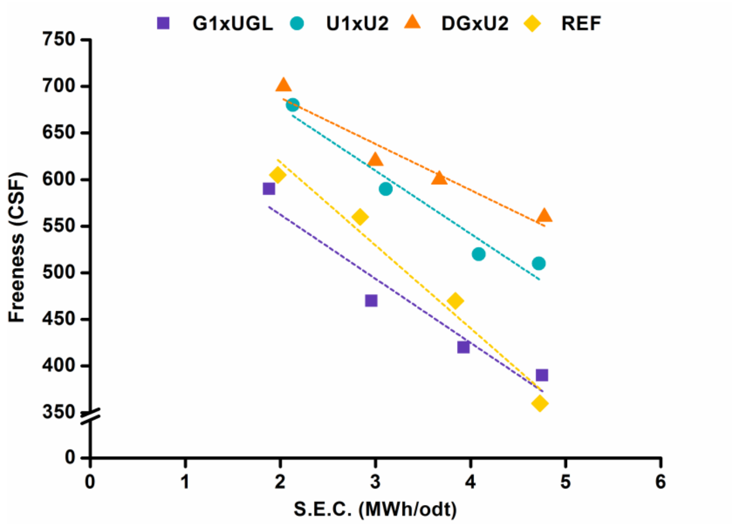

Fig. 1. Specific energy consumption (S.E.C.) vs. freeness for all four *Eucalyptus* hybrids pulp samples

Pulp Physical and Mechanical Properties

If the mechanical fiber furnish is used for paper applications, an ideal mechanical pulp produces paper sheets with high opacity, brightness, bulk, and smoothness, as well as a suitable pore structure at low grammage without excessive use of reinforcement pulp (Lönnberg 2009). On the other hand, if short-fiber pulp is used for composite reinforcement, properties such as aspect ratio and number of fibers per gram are of major importance. Using short fibers and consequently a high number of fibers per gram, the fiber-free areas in the composite is decreased, as well as the aspect ratio, which enhances the fiber dispersion (Chung 2005). Tonoli *et al.* (2010) studied the potential of *Eucalyptus* fibers as cement reinforcement. They observed that such fibers were suitable as reinforcement due to low-energy refining and a higher number of reinforcing elements, providing effective crack bridging and contributing to the maintenance of the mechanical performance of the composite after accelerated ageing cycles.

As illustrated in Fig. 1, relevant differences in refinability were noted among the four *Eucalyptus* hybrids and such differences can play an important role regarding paper properties. Table 4 shows that the density of paper sheets increases with longer refining. The main reasons are that fibers tend to be more flexible, increasing the relative bonding area. In addition, external fibrillation tends to increase the interfiber bonding formation, leading to a more closed and dense fiber network.

Table 4. Summary of Physical, Mechanical, and Optical Properties of Pulp Samples Derived From all Four *Eucalyptus* Hybrids

	Refining Time (minutes)	S.E.C. (MWh/odt)	Sheet Density (kg/m³)	Tear Index (mN.m²/g)	Tensile Index (kN.m/kg)	Brightness (% ISO)	Opacity (%)
G1xUGL	4	1.88	259.09	1.45	6.64	58.7	91.9
	7	2.96	282.99	1.46	9.59	59.8	94.1
	10	3.93	286.79	1.61	11.59	59.1	94.3
	13	4.75	299.38	1.72	12.80	60.0	95.0
U1xU2	4	2.13	242.14	1.07	5.45	55.6	93.5
	7	3.11	248.50	1.26	6.45	54.9	93.9
	10	4.09	260.22	1.35	8.30	56.3	94.0
	13	4.72	265.76	1.41	8.38	56.7	95.1
DGxU2	4	2.03	216.95	0.78	2.49	55.2	92.3
	7	3.00	216.00	0.80	3.66	54.6	93.2
	10	3.67	215.25	0.86	3.83	55.1	94.2
	13	4.78	240.92	1.07	5.98	55.4	94.6
REF	4	1.97	257.41	0.88	4.03	57.7	93.6
	7	2.84	270.71	1.05	6.03	58.8	93.7
	10	3.84	278.61	1.27	8.46	57.4	94.8
	13	4.73	293.31	1.63	10.92	58.0	95.1

Tensile index can indicate how the paper will behave during its manufacturing process, and it can be highly affected by bonding strength between fibers, fiber length, and stiffness. It is shown in Table 4 that in general, all four hybrids produced weaker sheets when compared to *Eucalyptus* chemical fibers at the same freeness levels (Muguet *et al.* 2011). Mechanical pulps can have a higher tensile index than chemical pulps at the same sheet density (Xu and Zhou 2007), but in this study the sheet densities were quite low because of the relatively low refining levels (Fig. 1). However, the results are comparable with the observations of Xu and Sabourin (1999).

Increased fiber strength obviously increases the tear strength. Table 4 shows that fibers from G1xUGL are much stronger than DGxU2 at same refining energy level. In addition, fiber length also influences *e.g.* tear index (Kärenlampi, 1996). Such influence can be seen when comparing Table 4 and Table 6. G1xUGL shows relatively higher fiber length than DGxU2, which might have positively affected the tear index values.

Tear index is better interpreted when correlated to tensile index (Fig. 2). A great correlation index was found among all samples, indicating that if some of the hybrids were refined to lower freeness levels (Fig. 1), they could have reached similar values, showing distinctions in refinability.

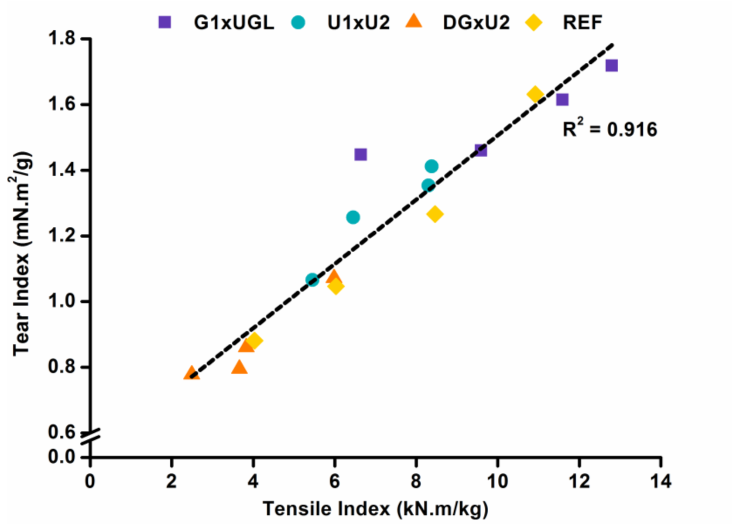

Fig. 2. Tensile index vs. tear index for all four *Eucalyptus* hybrids pulp samples

To illustrate the differences in refinability, the results from all hybrids were plotted together in Fig. 3, revealing high correlation indexes for sheet density, tensile index, and tear index with freeness. This indicated that with more intensive refining, poorly refinable hybrids could achieve similar properties to their refinable counterparts. However, this would require more energy for the refining process. Some studies have confirmed the fact that differences in wood quality can impact the refining process and pulp quality (Dundar *et al.* 2009; Jones *et al.* 2005), but as the hybrids do not show eminent differences among themselves regarding absolute chemical composition, such differences might be related to the wood ultrastructure and/or the fiber wall polymer structure.

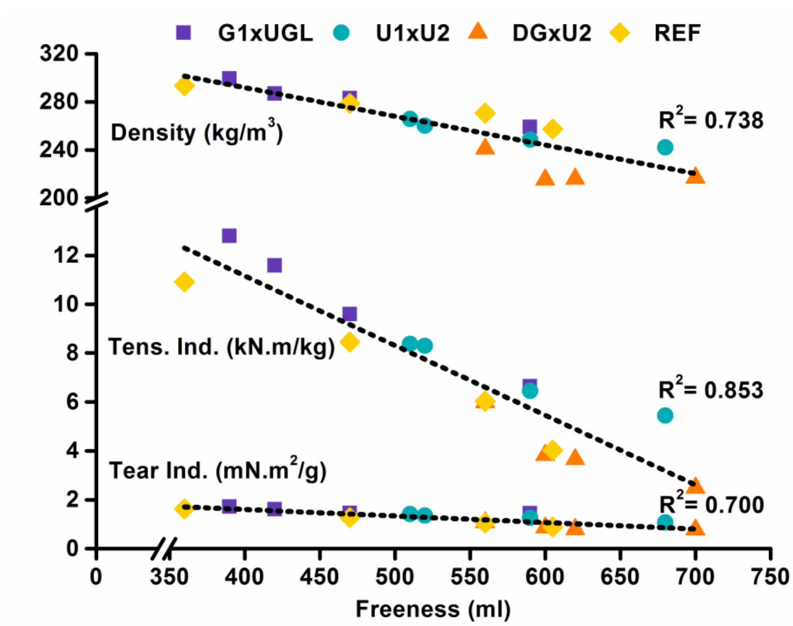

Fig. 3. Sheet density, tensile, and tear index vs. freeness for all four *Eucalyptus* hybrids pulp samples

Surface Properties and Fiber Morphology

The surface composition of fibers defines the fiber bonding properties in papermaking and the compatibility with the matrix in composite production. Therefore, the surface lignin content was evaluated with X-ray photoelectron spectroscopy, which is a well-known surface analytical tool for wood fibers (Johansson and Campbell 2004; Laine *et al.* 1994). The surface lignin content was not significantly affected by the refining time for any of the hybrids. However, the differences among the hybrids were evident (Table 5). The most important aspect is that even though no clear trend was seen among refinings, all values of surface lignin content are substantially higher than the original lignin content of the woods (Table 1 and Table 5). This result agreed with the findings for spruce chemi-mechanical pulps by Koljonen *et al.* (2003) and indicated that the defibration took place on the middle lamella region, which is expected for chemi-mechanical processes (Fig. 4, adapted from Franzén 1986).

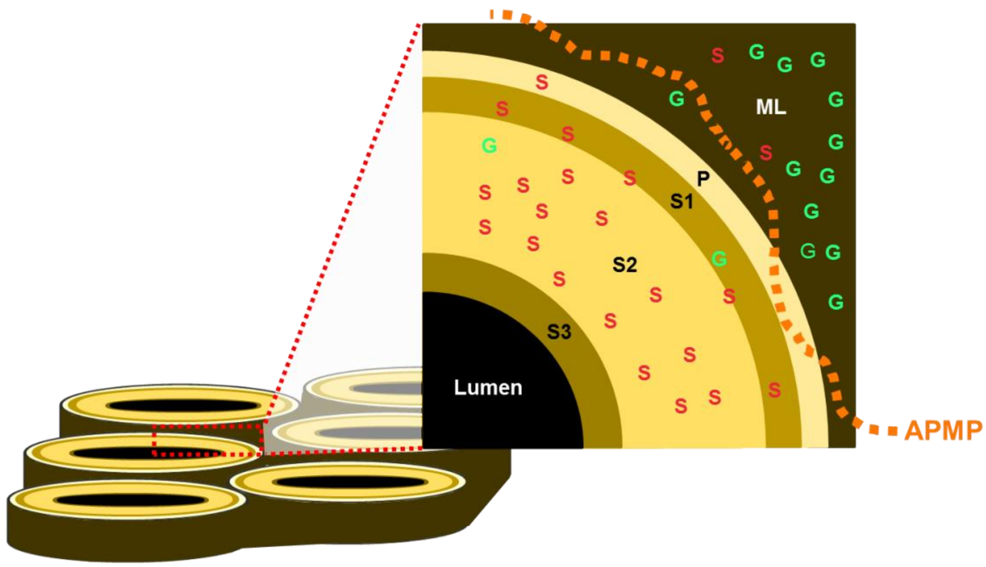

Fig. 4. Defibration mechanism of typical APMP process and illustration of lignin units localization on *Eucalyptus* wood (adapted from Franzén 1986, Watanabe *et al.* 2004). ML = Middle Lamella; P = Primary wall; S1, S2, S3 = Secondary wall layers; G = Guaiacyl lignin units; S = Syringyl lignin units.

Table 5. Surface Lignin Content of Fibers as Analyzed by XPS

Refining Time (minutes)	Surface Lignin (%)			
	G1xUGL	U1xU2	DGxU2	IP-REF
4	30.9	35.8	34.8	34.4
7	28.4	33.5	33.2	32.7
10	29.4	34.4	36.4	33.4
13	30.4	35.4	34.5	30.8

As the defibration process took place mostly at the middle lamella, where the lignin concentration is higher, it was expected that the lignin structure played an important role. The content of guaiacyl lignin in the wood samples varied notably among the samples (Table 1), whereas the lignin content was almost constant. It was noted that guaiacyl units content had a negative effect on the energy consumption in order to reach a certain freeness (Fig. 5). In *Eucalyptus globulus*, for example, Watanabe *et al.* (2004) showed that guaiacyl units are mainly located in the middle lamella and vessels walls (as illustrated in Fig. 4). This concept for hardwoods was also shown in other studies (Musha and Goring 1975). Due to the fact that there is an absence of methoxyl groups, the amount of cross-linking increases. In addition, these lignin units are known to increase the softening temperature of wood lignin (Olsson and Salmén 1997). A low S/G ratio has also been shown to impair chemical pulping processes (González-Vila *et al.* 1999; del Río *et al.* 2005; Pinto *et al.* 2005; Stewart *et al.* 2006; Gomes *et al.* 2008; Santos *et al.* 2011). In this study, the guaiacyl content likely affected the softening temperature of the different hybrids, as well as decreased the reactivity of lignin with the alkaline peroxide treatment, requiring more energy to defibrate the chips, and reaching a certain freeness level (450 CSF). Prinsen *et al.* (2012) revealed that the highest amount of β-O-4 linkages exist between lignin units for the G1xUGL hybrid, whereas DGxU2 had the lowest amount. This corroborates the increased reactivity of the G1xUGL hybrid.

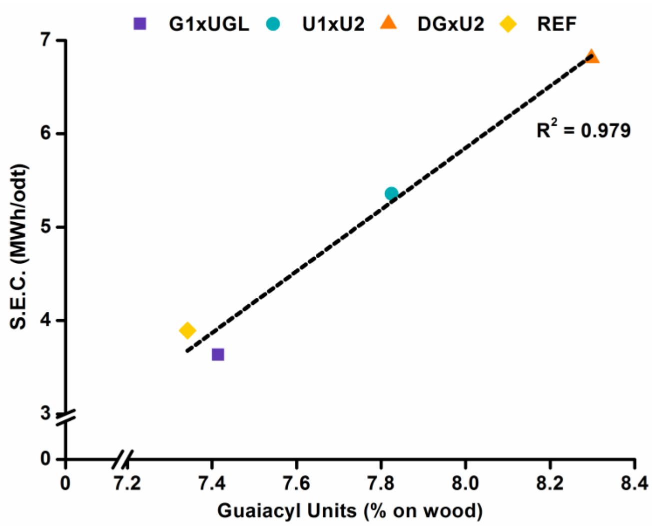

Fig. 5. Influence of guaiacyl units content on the refining energy demand to reach a given freeness of 450 CSF for all four *Eucalyptus* hybrids woods

When plotting the physical and mechanical properties as one set, it was observed that the correlation between surface lignin content and paper properties was weak (Fig. 6). The low correlation indices can be attributed to the fact that besides the number and strength of formed interfiber hydrogen bonds, the structure and intrinsic strength of the fibers are also important to the properties of the finished paper. Thielemans and Wool (2005) studied the deposition of kraft lignin onto natural fiber surfaces. Such lignin samples contain a large amount of hydroxyl groups not found in native lignin, such that these polar ends would interact favorably with the cellulosic fiber. The effect of lignin deposition was positive when producing resin composites due to a better incorporation of lignin to the hydrophobic matrix. Thus, chemi-mechanical pulp fibers with high surface lignin, which was somehow modified by a previous alkaline treatment, could possess potential as the reinforcement phase of composites. The surface extractives content of the fibers were very low (2.5 to 4%) when compared with other mechanical and chemi-mechanical pulps (Koljonen *et al.* 2003; Johansson *et al.* 2004; Zhou *et al.* 2006) and no correlation between the fiber properties and surface extractives content were observed.

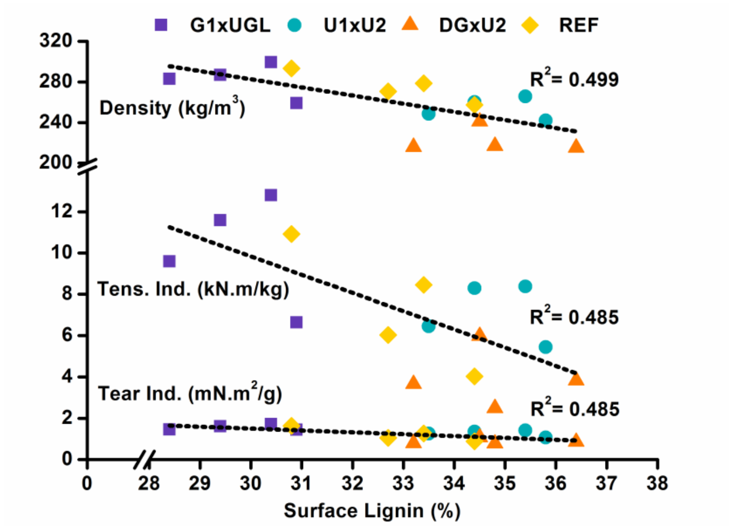

Fig. 6. Sheet density, tensile, and tear index vs. surface lignin content for all four *Eucalyptus* hybrids pulp samples

The morphological properties of single fibers did not show large differences in the fiber length among all pulp samples (Table 6). However, tear strength depends on fiber length, besides fiber strength (Kärenlampi 1996), as discussed in the previous section. Nevertheless, such values are in line with fiber length distribution of the same *Eucalyptus* hybrids' wood fibers (Prinsen *et al.* 2012).

Table 6. Fiber Length Measurements of Pulp Fibers

Refining Time (minutes)	Fiber Length (mm)			
	G1xUGL	U1xU2	DGxU2	IP-REF
4	0.620	0.610	0.560	0.590
7	0.600	0.605	0.565	0.585
10	0.595	0.605	0.560	0.590
13	0.600	0.600	0.570	0.585

Other important fiber properties for bonding strength, such as curl and fibrillation index, were impacted by the amount of lignin on the fiber surface. Figure 7 shows that at a tensile index of 6 kN•m/kg, the fibrillation and curl index decrease with increasing surface lignin content.

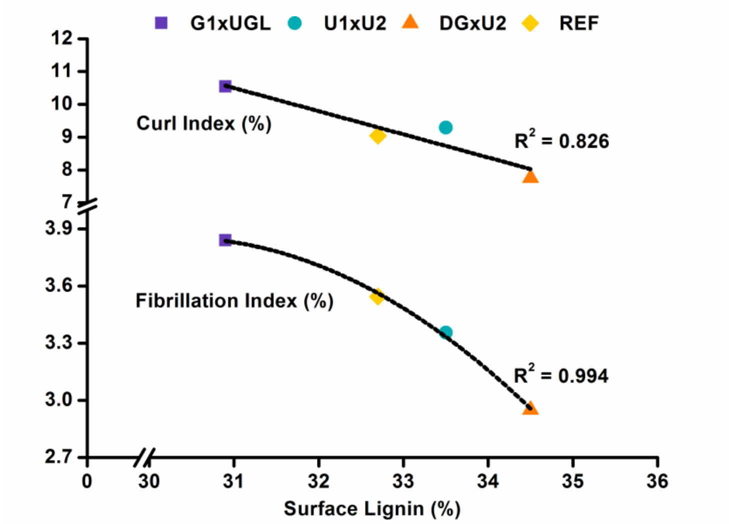

Fig. 7. Surface lignin content vs. curl index and fibrillation index for sample with a tensile index of 6 kN•m/kg for each *Eucalyptus* hybrids pulp samples

The surface lignin decreased the area of carbohydrates that would then fibrillate, and stiffened the fibers at the same time, leaving them more aligned (low curl index). The fact that the fibers were more aligned tended to compensate the lower fibrillation indices, which could explain the similarities in tensile index values.

CONCLUSIONS

1. The chemi-mechanical wood defibration process is a suitable method for the novel Brazilian *Eucalyptus* hybrids.
2. The hybrid with *E. globulus* genome (G1xUGL) showed better performance in all technical properties evaluated than the other *Eucalyptus* hybrids.
3. The major differences observed for the four hybrids were in the amounts of refining energy needed to reach a certain fiber development level.
4. There were indications that the lignin structure, especially the guaiacyl units content, has a definite role in increasing the energy consumption of the defibration process.

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