KRAFT PULPING AND BLEACHING OF PAULOWNIA SUN TZU 104® WOOD

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A trihybrid clone of Paulownia from the varieties *fortunei x tormentosa x elongate* was used for obtaining cellulosic pulp and paper by a kraft process and bleaching. Both bleached and unbleached pulps were subjected to a refining study between 0 and 3000 revolutions in a PFI mill. A fiber length (0.97 mm) similar to that of Eucalyptus, a high holocellulose content (71.4%), a low ash content (0.9%), a lignin content comparable to that of other varieties of Paulownia and an α-cellulose content slightly lower than that of Eucalyptus, but greater than that of other varieties of Paulownia were observed. Also, paper sheets showed good strength properties, comparable to or even greater than those obtained with Eucalyptus or other varieties of Paulownia at comparable refining degrees, between 30 and 40 ºSR. The pulp was successfully bleached in all cases with a value of brightness >90%.

Keywords: Kraft pulp, Paulownia, paper, pulp, bleaching

INTRODUCTION

Pulp and paper industry is facing an ever-increasing demand of quality paper and paperboard, which triggers the search for new and unexploited sources of cellulosic fibers. However, out of nearly 600 known species, less than a dozen are in commercial use for pulp production.[1]

Paulownia crops present very high productions of biomass and resprouting capacity, which are among the highest growing levels.[2, 3] Paulownia is species used for reforestation in China, where it is well-known for more than 2600 years, but has naturalized since its introduction in United States and other parts of the world.[4-6] Most species of Paulownia are extremely fast growing.[7] It could be considered a low-demand water plant, despite not growing in barren zones.[8, 9]

Suggested uses for Paulownia include veneer or plywood, furniture, handicrafts, tools, musical instruments, particleboard, charcoal, and also there have been numerous attempts to generate energy from Paulownia chips,[7, 10-12] one of them is its use as source for pulp.

Kraft is the dominant chemical pulping process used for the production of pulp fibers from various lignocellulosic materials. The reasons for its wide acceptability are (i) superior pulp quality; (ii) an efficient chemical recovery system and (iii) suitability for almost all biomass. During kraft pulping, a significant amount of carbohydrates are removed along with lignin, thus decreasing pulp yield. Normal kraft pulp yield lies between 45% and 50% for hardwoods. Yield improvement is constantly being sought due to the anticipated decline in wood resources in many regions of the world.[13] Thus, the objective of this work is to study kraft pulping, refining and bleaching of Paulownia trihybrid pulp.

EXPERIMENTAL

Raw material. Origin and characterization

A trihybrid variety of Paulownia (*fortunei x tormentosa x elongate* – registered trade name: SUN TZU 104®) clone obtained by *in vitro* replication was used for field experiments. The material was harvested after 3 years of growth in plantations used to exploit biomass crops in southwestern Spain.

For characterization of the raw material, standard analytical procedures were used to determine hot water soluble (TAPPI T 207 cm-08, "Water Solubility of Wood and Pulp"), acetone extractives (TAPPI T 280 wd-06, "Acetone Extractives of Wood and Pulp"), holocellulose contents (Wise method)[14] and ashes (TAPPI T 244 cm-99, "Ash in Wood, Pulp, Paper, and Paperboard: Combustion at 525 °C"). Also, fiber length was determined according TAPPI T 271 om-07 (Fiber length of pulp and paper by automated optical analyzer using polarized light), and % fines was determined with Morphological Fiber Analyzer MORFI LB-1.

The gross calorific values (constant volume) were determined according to "CEN/TS 14918:2005 (E) Solid biofuels – Method for the determination of calorific value" and UNE 164001 EX standards by using a Parr 6300 Automatic Isoperibol Calorimeter.

Aliquots from the homogenized wood (after eliminating compound extractives with ethanol) were subjected to moisture determination (drying at 105 ºC to constant weight), quantitative acid hydrolysis with 5 mL of 72% sulphuric acid for an hour and 20 minutes at 121 ºC in an autoclave. [15] Before HPLC analysis, the solid residue from hydrolysis was recovered by filtration and considered as Klason lignin. Monosaccharides and acetic acid contained in hydrolysates were determined by HPLC in order to estimate the contents of cellulose (as glucan), hemicelluloses (xylan + araban) and acetyl groups. Chromatographic determination was performed using an Agilent 1100 HPLC, equipped with an ion-exchange resin BioRad Aminex HPX-87H column.[16]

Kraft pulp production and characterization pulp

Conventional Kraft cooking was carried out in a rotary digester with electrical heating with four individual 2 L vessels. Pulping yield was determined in weight, also Kappa number (TAPPI T 236 om-06 "Kappa number of pulp") and viscosity (TAPPI T 230 om-04 "Viscosity of pulp [capillary viscometer method]") were determined. The residual alkali was titrated according to TAPPI 625 wd-99b ("Analysis of soda and sulfate black liquor"). All cookings were performed aiming to produce pulp with a kappa number in the range 17-18, which was achieved by keeping all parameters constant (sulfidity: 20%; relation liquor/wood: 5/1; maximum temperature: 165 ºC; time to maximum temperature: 70 min; time at maximum temperature: 60 min). Only active alkali was varied in the cooking process (between 18 and 30% on dry matter).

Bleaching, beating and paper sheet characteristics

Bleaching of pulp was carried out to 90% ISO brightness with the $OD_1(EP)D_2P$ sequences, whereby: O refers to a oxygen delignification; D_1 refers to a time of 60 min and 80 ºC chlorine dioxide stage; (EP) refers to a hydrogen peroxide stage with a time of 90 min and a temperature of 80 ºC; D_2 refers to conventional chlorine dioxide stage with a long time (120 min) and a temperature of 80 ºC, which was carried out with three different concentrations of chemicals (ClO_2 expressed as Cl_2, kg/t, 0.3, 0.6 and 0.9%); P refers to atmospheric peroxide stage for 120 min and a temperature of 80 ºC in the three samples of the previous step. General oxygen delignification and bleaching conditions are listed in Table 1.

Table 1
Bleaching conditions for Paulownia trihibrid pulp

Stage	O	D1	EP	D2			P		
				a	b	c	a	b	c
Consistency, %	10	10	10		10			10	
Temperature, ºC	100	80	80		80			80	
Time, min.	60	60	90		120			120	
Kappa factor (KF)	-	0.24	-	-	-	-	-	-	-
NaOH, % o.d.p	2	-	0.5	-	-	-		0.2	
H_2SO_4, % o.d.p	-	1.4	-	0.15	0.075	-	-	-	-
$MgSO_4$, % o.d.p	0.15	-	0.15	-	-	-	-	-	-
O_2, % o.d.p.	2	-	-	-	-	-	-	-	-
ClO_2 expressed as Cl_2, %o.d.p.	-	2.41	-	0.3	0.6	0.9	-	-	-
H_2O_2, % o.d.p.	-	-	0.5	-	-	-		0.2	
Final pH	11.5	2.4	11.0	4.9	4.7	4.6	10.1	9.6	9.73

o.d.p.: oven dry pulp; O – oxygen; D – chlorine dioxide; EP – hydrogen peroxide; P – peroxide

For characterization of the bleached pulp, in addition to the above, the following standard analytical procedures were used: forming handsheets for testing reflectance (TAPPI T 272 sp-08; "Forming Handsheets for Reflectance Testing of Pulp [Sheet Machine Procedure]"), diffuse brightness of pulp (TAPPI T 525 om-06; "Diffuse Brightness of Paper, Paperboard and Pulp (*d*/0)"), brightness stability (TAPPI T 260 wd-98; "Test to Evaluate the Aging Properties of Bleached Chemical Pulps") and hexenuronic acid (HexA) content (TAPPI T282 pm-07; "Hexeneuronic Acid Content of Chemical Pulp"). The indirect analysis of TOC allowed the evaluation of the total yield of the bleached pulp, as described by Longue *et al.*[17]

Bleached and unbleached pulp samples were refined in a PFI mill between 0-3000 revolutions. ("Forming handsheets for physical tests of pulp"). The laboratory handsheets were conditioned at a temperature of 23±1 ºC and relative humidity of 50 ± 1% and tested for grammage (TAPPI T 220 sp-01 "Physical testing of pulp handsheets"), burst index (TAPPI T 403 om-02 "Bursting strength of paper"), tear index (TAPPI T 414 om-04 "Internal tearing resistance of paper [Elmendorf-type method]"), tensile index (TAPPI T 494 om-01 "Tensile breaking properties of paper and paperboard [using a constant rate of the elongation apparatus]"), Schopper-Riegler degree (ISO 5267/1 "Pulps – Determination of drainability – Part 1: Schopper-Riegler method"), and ISO brightness (TAPPI T 525 om-06 "Diffuse brightness of paper, paperboard and pulp [d/0 degree]")[19].

RESULTS AND DISCUSSION

Raw material characteristics

The mean fiber length of the trihybrid of Paulownia, used in this work, is 0.97 mm weighted average, and 0.52 mm arithmetic Paper sheets were prepared with an ENJO-F-39.71 sheet machine according to the TAPPI T 205 sp-02 average, with a minimum of 0.5 mm and a maximum of 2.9 mm. The wood density is 213 kg·m^{-3}. This is a fiber length similar to hardwoods, like *Eucalyptus globulus*.

The soluble content is lower than that of other raw materials (hot water soluble: 13.3%) and similar to wood species. Specifically, the content of extractives in Paulownia trihybrid is 3.64%, higher than those found for eucalyptus wood (extractives: 2.09%), but lower that for other Paulownia (5.46%)[20]. These compounds could cause problems related to pitch deposits in the manufacturing of pulp, by adhering to machinery and reducing the quality of pulp.[21]

Previous results reported by other authors [2, 7-9, 16, 20, 22-26] about chemical characterization of different varieties of Paulownia are shown in Table 2. *Eucalyptus globulus* is also included as a reference species.

Table 2
Chemical composition of paulownia trihybrid and other pulp raw materials (Percentages on dry basis)

	Paulownia fortunei			*Paulownia tormentosa*		*Paulownia elongata*	*Eucalyptus globulus*	*Paulownia Sun Tzu 104®*
	Ref. 16	Ref. 9	Ref. 22	Ref. 7	Ref. 8	Ref. 23	Ref. 20	This work and Ref. 24
Holocellulose, %	56.9	70.9	69.6	78.8	-	75.7	66.9	65.2
Klasson lignin, %	27.2	22.4	28.0	22.1	20.9	20.5	22.9	27.8
Glucan, %	34.2	37.4	n.d.	48.3	40.7	43.6 (α-cellulose)	46.8-53.4	44.0
Xylan, %	18.3	-	-	-	-	-	14.2-16.6	15.7
Araban, %	1.1	-	-	-	-	-	0.4-0.54	1.1
Acetyl groups, %	3.3	-	-	-	-	-	3.56	4.4
Acetone extractives, %	5.5	-	-	-	-	-	2.09	3.6
Ash, %	1.6[25] - 2.1[26]			2.0[26]		1.9[26]	0.4[25]	0.9[2]
Gross heating value, J/g, o.d.b.	17648[26] - 19843[25]			18339[26]		17690[26]	19324[25]	20335.4

o.d.b. – % on dry basis

Table 3
Characterization of kraft pulp from Paulownia trihybrid

Active alkali, % NaOH	Kappa number	Yield		Residual liquor (NaOH)	
		Total, %	Screened, %	pH	AEr, g/L
18	32.0	53.9	49	11.8	0.01
22	24.2	49.9	48.7	12.7	4.2
24	20.3	49.4	47.8	12.9	6.9
26	17.1	48.1	47.6	13	9.2
28	15.3	47.2	46.9	13.0	11.6
30	14.5	46.4	46.1	13.1	14.2

AEr: residual effective alkali

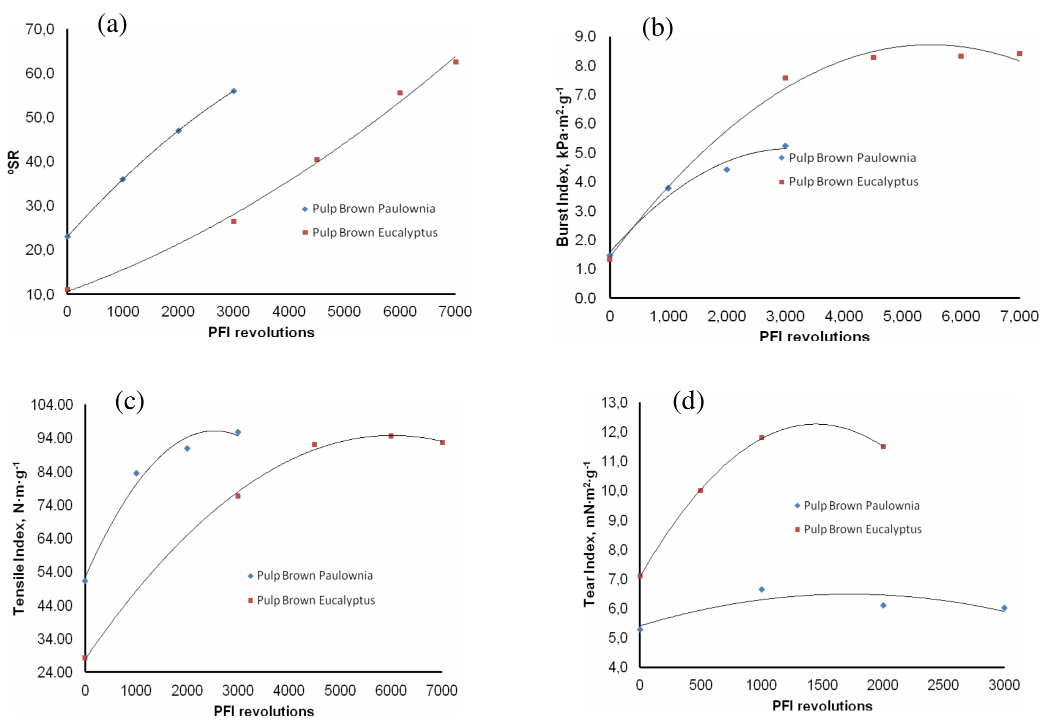

Figure 1: Physical properties of Paulownia trihybrid unbleached kraft pulp versus Eucalyptus kraft pulp[31,34] as a function of milling (ºSR – Schopper Riegler degree; PFI – PFI refining)

The holocellulose content in the Paulownia trihybrid clone (71.4%) was determined with the method of Wise.[14] This value is higher than the results reported by García[26] (as a combination of monomers and oligomers), 6.7% higher than the value for *Eucalyptus globules,*[20] between 25.5% and 0.7% higher than that for *Paulownia fortunei*,[9,16,22] but lower than the results for *Paulownia tormentosa*[7,8] (10.4% lower) and *Paulownia elongata*[23] (6.0% lower). The cellulose content in Paulownia trihybrid, is between 6.0% and 17.6% (expressed as glucan) lower than those found for *Eucalyptus globules*,[20] but higher (22.2%-14.9%) than those found for *Paulownia fortunei*.[9,16,22] Lignin values are slightly higher and xylan, araban and acetyl groups values are similar to those found for other materials, such as *Eucalyptus globules.* [20] The ash content is lower than those found for other species of Paulownia[25-26] (between 52.6% and 57.4% lower). A low ash and silicon content is preferable because silicon entering alkaline pulping processes will cause problems in the chemical recovery line at the pulp mill. The gross heating value for the trihybrid clone of Paulownia was higher than those for other Paulownia varieties[25-26] (between 2.4% and 13%), *Eucalyptus globulus* and other solid biofuels, such as willow and one-year-old poplar (never above 20 MJ kg^{-1}).[27-28] Overall, the lower heating value (between 15.9 MJ kg^{-1} and 16.7 MJ kg^{-1} for Paulownia trihybrid, *P. tormentosa* and *P. elongata* with a 30% humidity) for Paulownia genus is higher than those for other species, such as *Pinus pinaster*, *Pinus radiata* or *Eucalyptus globulus* (between 13.0 MJ kg^{-1} and 15.5 MJ kg^{-1}).[25]

Cooking and beating of kraft pulps

Reaching a fixed Kappa number (Kappa 17) and the efficiency in the cooking process were the two objectives of the experimental designs, besides preserving yield and a moderate consumption of reagents. Table 3 shows the results for Kappa number, total pulp yield, screened yield, final pH and residual alkali for the experiments with different active alkali concentrations. All other variables of cooking were constant.

An increase in active alkali concentration is always accompanied by a decrease in Kappa number and process yield, and an increase in the pH and residual active alkali of the black liquor from the pulping process, indicating an excess of unreacted reagent and overcooked pulp, as happens to the raw material with a concentration above 26%. These data show that the process could be improved, with lower reagent consumption at greater operating temperatures or times.

The active alkali levels used and the results of the screened yield and residual alkali were represented and set by second degree polynomial equations (not shown). So according to the results, Paulownia Kraft pulp achieved a Kappa number of 17-18, at an active alkali concentration of 24.9%. Respecting the conditions of the process, a pulp reaching the maximum area of screened yield (47.9%), and with residual alkali values among the lowest within the rank of results (7.9 g L^{-1}) may be obtained. The pulp obtained using 24.9% active alkali showed 30.6 cP viscosity, 39% ISO brightness and a hexenuronic acid concentration of 43.3 mmol kg^{-1}.

In order to evaluate the potential of the cellulosic pulp from the trihybrid clone of Paulownia, it was subjected to a refining study. Beating and physical properties of paper are correlated not only with the morphological properties of fibers, but also with their chemical composition and structure. [29, 30] Figure 1 shows the evolution of Schopper Riegler degree (ºSR), tensile index, burst index and tear index of the paper sheets versus PFI revolutions.

The increase in Schopper Riegler degree is more pronounced at the beginning – 13 ºSR between 0 and 1000 revolutions versus increments of 11 ºSR between 1000 and 2000 revolutions and 9 ºSR between 2000 and 3000 revolutions. The pulp obtained from the trihybrid clone of Paulownia shows better suitability for refining (lower energy consumption) than the kraft pulps of eucalyptus studied by Mutje.[31] It is observed that, in order to obtain a 36 ºSR, the refining should be performed at 4000 rev. of the PFI mill, decreasing the percentage of beaten pulp (69.5% versus 42.0% in eucalyptus between 0 and 3000 revolutions). The differences from eucalyptus are even more pronounced when compared to studies by Area,[32] where the Schopper Riegler degree varies between 18 ºSR (for unbeaten) and 23.5 ºSR (for 2000 PFI revolutions). It should be noted the low presence of fines (7.8%) in Paulownia, which is logical, because the fines were lost in the formation of the sheets.

Regarding the strength rates, the kraft pulp from the trihybrid clone of Paulownia developed very favorably. Great increments were achieved in the rates studied at 1000 revolutions in the PFI mill: the tensile index increased by 62.8% up to values above 80 Nm/g, the burst index increased by 156.1%, and the tear index increased by 25.5%. As shown in Figure 1, the tensile index and burst index keep increasing along with the refining degree, although less obviously, until they achieve values above 95 Nm/g and 5 $kPam^2g^{-1}$, respectively. However, the tear index shows maximum values in the region between 1000 and 1500 PFI revolutions, which suggests that these pulps should not be refined beyond this point.

These results are very interesting when compared to those obtained for a reference material like eucalyptus. In the study performed by Khristova,[4] where alkaline cellulosic pulps of 4 varieties from Sudan (*Eucalyptus camaldulensis*, *E. citriodora*, *E. microtheca* and *E. tereticornis*) are analysed, the following results are obtained: at 30 ºSR, between 61.7 Nmg^{-1} and 85 Nmg^{-1} for tensile index, between 3.1 $kPam^2g^{-1}$ and 5.6 $kPam^2g^{-1}$ for burst index, and between 6.9 mNm^2g^{-1} and 10.4 mNm^2g^{-1} for tear index. The results reported for the physical properties of *Eucalyptus grandis*[33] kraft pulps are as follows: at 30º SR approximately, between 85.2-103 Nmg^{-1} for tensile index, 5.3-7.1 $kPam^2g^{-1}$ for burst index, and 7.8-9.9 mNm^2g^{-1} for tear index. In another work[34] on the kraft pulp of *Eucalyptus grandis*, (with beating at 40 Wh – 3000 PFI approximately – and Kappa number of 16-17, using residual alkali between 3-18 gL^{-1} and temperatures between 160-170 ºC), values between 95.6-112.1 Nm/g for tensile index, between 6.1-7.9 $kPam^2g^{-1}$ for burst index, and between 9.2-11.2 mNm^2g^{-1} for tear index were achieved. In the work of Mutje[31] on refining of comercial eucalyptus kraft pulp, values of 76.7 Nmg^{-1} for tensile index and of 7.8 kPa m^2g^{-1} for burst index at 26.5 ºSR, 3000 revolutions, have been achieved. Finally, in another article,[35] values between 91.0-66.2 Nmg^{-1} for tensile index for hornbeam, birch, poplar, beech, oak and black locust kraft pulp (30 ºSR) have been reported.

The characteristics of the paper sheets obtained from kraft pulps from the Paulownia trihybrid clone were also better than those obtained by Rai[21] for kraft pulps from *Paulownia fortunei* beaten in a Lampen mill under standard conditions with 45 ºSR, the characteristics were similar in tensile index (between 99.8 Nmg^{-1} and 106.1 Nmg^{-1}) and burst index (between 5.5-6.5

$kPam^2g^{-1}$) and much lower in tear index (between 2.5-2.7 mNm^2g^{-1}).

Pulp bleaching

The previously indicated kraft pulp with a Kappa number of 18 and an active alkali concentration of 24.9% was selected for bleaching. The sequence utilized (Table 1) was selected from a wider experimental design with the objective of obtaining cellulosic pulp with the same brightness degree (90-91% ISO). Variations in the process conditions from the different steps shown in Table 1 have been adopted to achieve this target. Three different concentrations of chemicals (ClO_2 expressed as Cl_2, kg/t, 0.3, 0.6 and 0.9%) were used in D_2 step. The pulp was sucessfully bleached in all cases with a Kappa number lower than 1.5 after the stage (EP) and a value of brightness >90% ISO (90.4%, 90.9% and 91.5%, respectively). Brightness reversion decreased as the amount of chlorine dioxide increased in stage D_2. However, in all cases brightness reversion was below 2%, indicating good brightness of the pulps.

The sequence OD_1EPD_2P with a 0.3% ClO_2 as Cl_2 in step D_2 (final brightness of 90.4% ISO), was selected for full characterization, and beaten pulp and paper sheets were prepared. The yield of bleaching process was 96.0% with Kappa number <1, viscosity of 15.04 cP, brightness reversion of 1.90% and hexeuronic acid content of 5.9 mmol kg^{-1}.

In part, brightness reversion of the bleached pulps is due to the presence of hexenuronic acid (in our case, the hexenuronic acid content was decreased by 86.4% with respect to unbleached pulp). The elimination of the acid increases the stability of pulp brightness, as reported by Buchert and Vuorinen. [36,37]

The consumption of chemical reagents was practically 100% in stages O, D_1, (EP) and D_2. However, the consumption in the final stage with hydrogen peroxide was about 50%, which indicates that the load of this reagent could be reduced in the final stage of bleaching.

Viscosity values decreased in the successive stages, between 30.6 cP in brown pulp and 15.04 cP in bleached pulp, which is explained by cellulose degradation during the bleaching sequence. In this case, the results of TOC yield (9.84 kg ton^{-1}) indicate that cellulose degradation is relatively low, below 1% cellulose, although, on the other hand, significant decreases were observed in tensile index (24.6 to 53.9 Nmg^{-1} for 0-3000 PFI revolutions) and burst index (1.21 to 3.24 $kPam^2g^{-1}$ for 0-3000 PFI revolutions). However, the results of tear index were similar to those for unbleached pulp (3.75 to 6.88 mNm^2g^{-1} for 0-3000 PFI revolutions).

These results are appropriate for pulp and paper making, although they are somewhat lower than those obtained by other authors for a raw material like eucalyptus. Santiago[38] achieved values of tensile index between 80-85 Nmg^{-1}, burst index between 4-6 $kPam^2g^{-1}$ and tear index between 8-10 mNm^2g^{-1} for eucalyptus pulps obtained through modified kraft processes (30 ºSR).

The brightness value obtained in this study was lower than 90-91% ISO, between 84.7% and 87.6% after the reversion test. For bleached kraft and ASAM pulps of *Eucalyptus citriodora* (30 ºSR), Khristova[4] reported values of tensile, burst and tear indexes ranging bewteen 70.2 and 78.3 Nmg^{-1}, 4.4 and 4.8 $kPam^2g^{-1}$, 8.1 and 7.9 mNm^2g^{-1}, respectively. However, García[39] reported more similar values of resistence for kraft pulp from *Eucaliptus grandis* (30 ºSR) bleached with 6 different sequences (brightness of 90.0% ISO approximately): tensile index between 51.9-66.5 Nmg^{-1}, burst index between 2.1-2.6 $kPam^2g^{-1}$ and tear index between 8.9-10.2 mNm^2g^{-1}.

CONCLUSION

This variety of Paulownia has appropriate characteristics for pulp and paper making, presenting a fiber length similar to that of Eucalyptus, a high holocellulose content, a low ash content, a lignin content comparable to that of other varieties of Paulownia and an α-cellulose content slightly lower than that of Eucalyptus, but greater than that of other varieties of Paulownia.

Paper sheets showed good strength properties, comparable to or even greater than those obtained for Eucalyptus or other varieties of Paulownia at a comparable Schopper Riegler degree, between 30-40 ºSR. The pulp was sucessfully bleached in all cases with a Kappa number below 1.5 in EP stage and a value of brightness >90%.

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