

BLEACHED KRAFT PULP PRODUCTION FROM *Pinus tecunumanii* (Eguiluz e Perry)¹

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ABSTRACT – The use of 12-year-old *Pinus tecunumanii* (Eguiluz e Perry) grown in Colombia was evaluated for bleached kraft pulp production. Kraft pulps of kappa number 30 ± 1 were produced, and oxygen delignified and bleached to 90% ISO with ECF processes. The bleached pulps produced under optimum conditions were evaluated with regard to their strength properties. *Pinus tecunumanii* wood required low effective alkali charge to reach the desired kappa number and the unbleached pulp showed high oxygen delignification efficiency and bleachability when a OD(EO)DED sequence was used. The bleached pulps presented good physical-mechanical properties, which are comparable to those obtained with more traditional pines such as *Pinus taeda* and *Pinus radiata*. The results demonstrate that this tropical pine species is a suitable raw material for bleached kraft pulp production.

Key words: *Pinus tecunumanii*, kraft pulp, ECF bleaching, strength properties.

PRODUÇÃO DE POLPA KRAFT BRANQUEADA DE *Pinus tecunumanii* (Eguiluz e Perry)

RESUMO – Foram avaliadas amostras de *Pinus tecunumanii* de (Eguiluz e Perry) com 12 anos de idade procedente da Colômbia, para produção de polpa de kraft branqueada. Produziram-se polpas kraft com número kappa 30 ± 1 , deslignificada com oxigênio e branqueada a 90% ISO por processo ECF. As polpas branqueadas foram produzidas em condições ótimas e avaliadas com relação às suas propriedades de resistência. A madeira de *Pinus tecunumanii* exigiu baixa carga de álcali efetivo para alcançar o número kappa desejado, e a polpa marrom mostrou eficiência na deslignificação com oxigênio e alta branqueabilidade quando submetida à seqüência OD(EO)DED. As polpas branqueadas apresentaram boas propriedades físico-mecânicas, em comparação com aquelas obtidas das espécies tradicionais de *Pinus*, como o *Pinus taeda* e o *Pinus radiata*. Os resultados indicaram que essa espécie de pinus tropical é uma matéria-prima satisfatória para produção de polpa de kraft branqueada.

Palavras-chave: *Pinus tecunumanii*, polpa de kraft, ECF branqueado e propriedades de força.

INTRODUCTION

The Colombian pulp and paper industry is faced with a chronic shortage of wood despite the high growth rate of wood species in this tropical country. Only 45,000 hectares of a total of 2.7 million hectares of potentially reforestable land in Colombia are used for planted forests. Other Latin American countries have much larger areas

covered by forest plantations. For example, Brazil has 5 million hectares of planted forests, Chile, 2 million hectares, Argentina, 770,000 hectares and Venezuela, approximately 530,000 hectares (RESTREPO, 2003).

The planted forest wood supply shortage in Colombia has led to a shortage of pulp production and a permanent dependence on pulp imports, with 96,600 tons imported

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in 1999 and 105,300 tons in 2000. Additionally, all newsprint consumed in Colombia is imported and half the pulp used by the Colombian paper industry comes from recycled fibers (RESTREPO, 2003). The industry depends on two wood species for virgin fiber supply: *Pinus patula* and *Eucalyptus globulus*, as well as sugar cane bagasse. Sustained growth of the Colombian pulp and paper industry depends on development of new raw materials for kraft pulp production. *Pinus tecunumanii* (Eguiluz e Perry), identified officially by Eguiluz-Piedra and Perry in the early 1980's, is a potential new wood raw material for pulping (DVORAK et al., 2000). Preliminary evaluation suggested this species could be used to produce kraft pulp under conditions normally used for softwood kraft pulp production (WRIGHT et al., 1995; WRIGHT et al., 1996). However the detailed characterization of this pine species necessary to guide further tree-improvement programs is still lacking. The objective of this study was therefore to determine the fiber characteristics and the true potential of this species for producing high quality bleached kraft pulp.

EXPERIMENTAL

Twelve-year-old *Pinus tecunumanii* trees planted at a density of 1060 trees per hectare were used in this study. The plantation is located in Yolombó County, northeastern Antioquia, Colombia (altitude 1440 m; average annual temperature 21°C; average annual precipitation 2200 mm). Sample trees came from a 25-meter-diameter circular plot. Average diameter at breast height (DBH) of the trees in the plot was 21.24 cm and average height was 21.44 m. Three logs (1 m long) were cut at base height, half the commercial height and top of the commercial height (10 cm diameter) from each of five trees within the parcel that were of average DBH. The logs were chipped, classified and dried to approximately 80% dryness. Chip density was determined using the TAPPI method 258 om-94. Fiber length, fiber diameter, cell-wall, thickness and lumen diameter were measured using an optical microscope.

Chips were pulped in a 4.7 L capacity M/K laboratory digester. The pulping conditions used were: 30% sulfidity, a 4:1 liquor to wood ratio, time of 90 minutes and maximum temperature of 170°C. The effective alkali charge varied from 13% to 18% Na₂O and time to maximum temperature varied from 40 to 70 min, to obtain pulp of kappa number

30 ± 1. The cooked chips were disintegrated by vigorous agitation and the resulting pulp screened in a Valley flat screen. Pulp kappa number was determined according to TAPPI method T 236 om-85. Pulp metal contents were measured by atomic absorption spectroscopy after wet ashing the pulp according to TAPPI standards. Hexenuronic acids (HexAs) content was measured by high-pressure liquid chromatography using an ultraviolet (254 nm) detector, after complete acid hydrolysis of the pulp.

Table 1 presents the general oxygen delignification conditions used. Single (O) and double (OO) stage oxygen delignification were carried out with 300 g oven-dry (o.d.) samples in a Quantum Mark V mixer/reactor (Twinsburg, USA) with five repetitions. ECF bleaching by the sequences DEoDED and DEopDED was carried out using the conditions listed in Table 2. The bleaching sequences were compared based on total chemical consumption, total yield and pulp quality. The first chlorine dioxide stage (D₀) was carried out with 300 g o.d. samples in polyethylene bags and the alkaline/peroxide extractions (Eo / Eop) with 250 g o.d. pulp samples in the Quantum Reactor equipped with Teflon-lined mixing vessel. The final D stages (D₁ and D₂) were also conducted in polyethylene bags with 150 g o.d. pulp samples. All bleaching stages were run in duplicate and the samples were washed with excess distilled water after each stage. Brightness reversion was measured on hand sheets heated for four hours at 105±3 °C and 0% relative humidity.

Pulp optical and physical-mechanical properties were analyzed according to TAPPI standard procedures. Strength properties were determined on samples refined in a PFI mill (0, 4000, 6000 and 8000 revolutions).

Table 1 – Single (O) and double (OO) stage oxygen delignification conditions

Quadro 1 – Condições para estágio simples (O) e duplo estágio (OO) de deslignificação com oxigênio

Conditions	O	(OO)
Consistency, %	10	10
Time, min	35	15+45
Temperature, ° C	90	90+95
Pressure, kPa	600	600
NaOH, kg/o.d. metric ton	34.8	34.8+19.5
MgSO ₄ .7H ₂ O, kg/o.d. metric ton	1	5

Table 2 – General bleaching conditions
Quadro 2 – Condições gerais de branqueamento

Conditions	Bleaching Stage					
	D ₀	E ₀	E _{0p}	D ₁	E	D ₂
Consistency, %	11	11	11	11	11	11
Time, min	45	20+45	20+45	150	15	180
Temperature, °C	65	85	85	70	70	70
Kappa Factor	0.24	-	-	-	-	-
NaOH, kg/o.d. metric ton	1	11.5	11.5	-	2	-
O ₂ , kg/o.d. metric ton	-	3	3	-	-	-
H ₂ O ₂ , kg/o.d. metric ton	-	-	2	-	-	-
Pressure, kPa	-	200	200	-	-	-

RESULTS AND DISCUSSION

Fiber characteristics

The 12 year-old *Pinus tecunumanii* wood had a relatively high density (466 kg/m³) compared to the values cited in previous studies of the same species and to densities of other *Pinus* species used for pulp production (Table 3). A Brazilian study reported a density of 445kg/m³ for 12-year-old *Pinus tecunumanii* (SILVA et al., 1994) while the density of 8 year-old *Pinus tecunumanii* was found to be 361 kg/m³ in a Colombian study (GOMES et al., 1992). Table 3 presents the results of *Pinus tecunumanii* fiber analysis. This species' fibers are longer (3.96 mm) than those of other pine species used to produce kraft pulp. For example, fibers of 12-year-old *Pinus taeda* from a commercial plantation in southern Brazil are 3.53 mm long (GOMES et al., 1992). Cell-wall thickness and lumen diameter are directly correlated to high density. These properties translate into fibers with elevated resistance against collapse since the more rigid fibers maintain their original form (tubular). The result is a reduction in interfiber bonding and hence lowers tensile and burst strengths and increases tear strength.

Table 3 – Wood density and fibre morphology 12-year-old *Pinus tecunumanii*

Quadro 3 – Densidade da madeira e morfologia das fibras de *Pinus tecunumanii* aos 12 anos de idade

Parameters	Values
Wood density, kg/m ³	466
Fibre length, mm	3.96
Fiber diameter, µm	51.93
Lumen diameter, µm	32.96
Fiber wall thickness, µm	9.48

Pulping

Pulp of kappa number 30±1 was produced using 16% effective alkali (expressed as equivalent Na₂O) and a time to maximum temperature of 40 min. This amount of alkali is less than that required by *Pinus patula* (18.5%) and *Pinus maximinoii* (19.1%) to produce pulp of the same kappa number (WRIGHT et al., 1995). Screened pulp yield was 43.7%, which can be considered reasonable for the *Pinus* genus, and is superior to that obtained from *Pinus patula* (41.1%), *Pinus elliotii* (42.5%) and *Pinus taeda* (40.5%) pulped to a kappa number 30±1 (RODRÍGUEZ e TORRES, 1995).

Table 4 presents other unbleached pulp characteristics of the 12-year-old *Pinus tecunumanii*. The HexAs content in the unbleached pulp is similar to that of other softwood kraft pulps. Softwood pulps contain lower amounts of xylans and therefore lower HexAs contents than hardwood pulps. Pulp iron (76.90 mg/kg) and copper (23.76 mg/kg) contents are greater than those found in pulps from other softwood species. Kraft pulp produced from mixtures of *Pinus elliotii* and *Pinus taeda* contained 23 mg Fe/kg and 3.3 mg Cu/kg (SALOMÃO, 2001). The higher values found in the present study may probably have come from the water supply, pulp digester corrosion or a greater soil metals content in the plantation where the samples were collected, which is located in a mining zone.

Oxygen delignification

Oxygen delignification results are presented in Table 5. Delignification was higher in the double (62%) than in the single (41.7%) oxygen stage. These values are within the ranges considered suitable by several authors (POUKKA et al., 1999; SOINIL et al., 1998) for application of a double oxygen stage process for

pine kraft pulp. Single and double stage oxygen delignification exhibited the same selectivity, a property related to the rates of lignin removal and carbohydrate degradation (DENCE e REEVE, 1996). Transition metals play an important role in oxygen delignification since radicals generated in the presence of these metals participate in reactions that degrade both lignin and cellulose. Cellulose depolymerization reactions result in pulp strength loss (SOINIL et al., 1998; BROWN e DAWE, 1996). A greater viscosity loss was observed in the double stage oxygen delignification. Viscosity loss was caused by carbohydrate depolymerization resulting from hydrolysis of β -glycoside bonds. The double stage oxygen delignification produced higher brightness pulp (35.4 %ISO) than the single stage process (29.8 %ISO).

Table 4 – Characteristics of kraft pulp produced from 12-year-old *Pinus tecunumanii*

Quadro 4 – Características da polpa kraft produzida com madeira de *Pinus tecunumanii* aos 12 anos de idade

Parameter	Values
Screened Yield, %	43.7
Effective Alkali, % NaOH	16.0
Kappa number	30
Viscosity, mPa.s	34.0
Brightness, %ISO	34.2
Hexenuronic acid, mmol/kg	33.0
Metals, mg/kg	
	Fe 76
	Cu 23
	Mn 7
	Ca 1036
	Mg 210

Table 6 – Results of bleaching *Pinus tecunumanii* kraft-O pulps to 90% ISO by the ECF sequences ODEoDED, ODEopDED, OODEoDED and OODEopDED

Quadro 6 – Resultados dos branqueamentos da polpa kraft-O 90% ISO de *Pinus tecunumanii* pelas seqüências ODEoDED, ODEopDED, OODEoDED e OODEopDED

Parameters	Sequence			
	ODEoDED	ODEopDED	O/ODEoDED	O/ODEopDED
Brightness, %ISO	90.0	90.1	90.3	90.0
Reversion, %ISO	3.1	3.1	2.6	2.3
Viscosity, mPa.s	15.3	13.8	12.2	11
ClO ₂ as Cl ₂ , kg/o.d.t.	102	87	70	57
H ₂ O ₂ , kg/o.d.t.	-	2	-	2
Bleaching Yield, %	98.2	98.0	97.8	97.0
Total Yield*, %	95.3	95.1	94.1	93.3

* O₂ (Table V) + Bleaching.

Table 5 – Oxygen delignification results (see Table 4 for initial pulp characteristics)

Quadro 5 – Resultados da deslignificação com oxigênio (ver Quadro 4, com a caracterização inicial da polpa)

Results	O-Stage	
	O	OO
Kappa number	17.5	11.4
Viscosity, mPa.s	21.1	14.7
Δ Kappa, %	41.7	62.0
Δ Viscosity, %	37.9	56.8
Selectivity*	1.10	1.09
Brightness, %ISO	29.8	35.4
Yield, %	97.1	96.2

*selectivity = Δ Kappa (%) / Δ Viscosity (%).

Bleaching

It can be seen from the bleaching results shown in Table 6 that the O/ODEopDED sequence required less chlorine dioxide charge than other sequence to produce 90 %ISO brightness pulp. Pulp bleached in these sequences presented the lowest viscosity, although the viscosity (11.0 mPa.s) was still within the limits required by the pulp industry. For pulps produced by the same oxygen delignification process (single versus double stage), the use of hydrogen peroxide in the extraction stage resulted in lower final viscosity. This may have been caused by the presence of transition metals, such as Cu, Fe and Mn, that cause peroxide decomposition and formation of hydroxyl (HO \cdot) and superoxide (O₂ \cdot^-) radicals. Intermediate peroxide decomposition species, including these radicals, do not bleach the pulp but can cause cellulose degradation (JOHNSON, 1994; HOBBS e ABBOT, 1992).

Pulp quality

Figures 1, 2, 3 and 4 present the tensile index, tear index, burst index and tensile energy absorption (TEA) as a function of drainability ($^{\circ}\text{SR}$) for the pulps bleached in the four sequences. Maximum tear index values were reached quickly at low refining levels, implying that little refining is needed to reach high tear strength values. The pulp produced using a single oxygen delignification stage presented higher tensile index, burst index and TEA and was also easier to refine, possibly because this pulp suffered less fiber cell wall damage and less removal of hemicelluloses. Pulps bleached using a peroxide reinforced extraction stage tended to present lower drainability. Peroxide may cause softening of fiber cell walls, resulting in greater compaction during hand sheet formation, which is strongly correlated with the interfiber bond-forming capacity. Tensile strength is controlled by several factors, such as individual fiber strength, fiber length and hand sheet formation and structure. Individual fiber strength is a result of other properties, including the fibrillar angle, cellulose content and fiber structure defects.

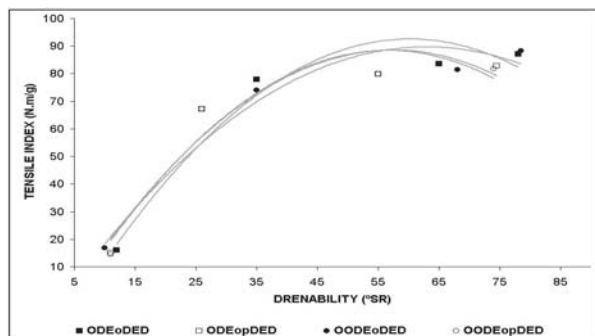


Figure 1 – Tensile strength as a function of drainability.
Figura 1 – Resistência à tração em função da drenabilidade.

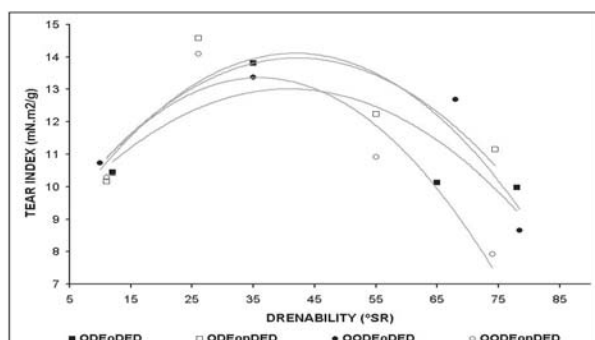


Figure 2 – Tear strength as a function of drainability.
Figura 2 – Resistência ao rasgo em função da drenabilidade.

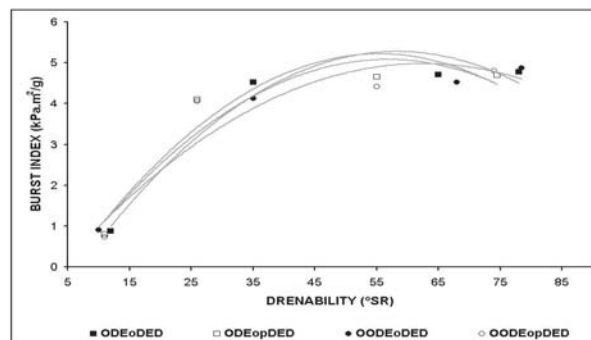


Figure 3 – Burst strength as a function of drainability.
Figura 3 – Resistência ao estouro em função da drenabilidade.

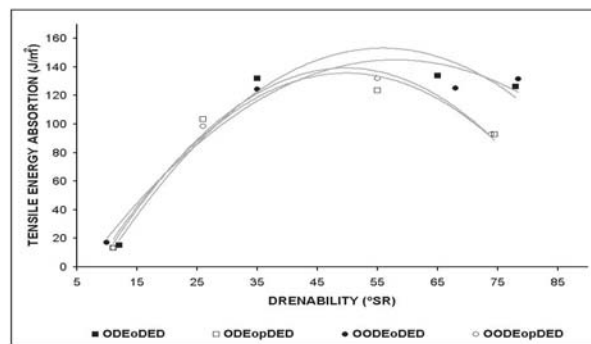


Figure 4 – Tensile energy absorption as a function of drainability.
Figura 4 – Energia de tensão absorvida (TEA) em função da drenabilidade.

CONCLUSIONS

The results obtained in this study demonstrate that *Pinus tecunumanii* (Eguiluz e Perry) wood presents morphological and technological characteristics suitable for production of bleached kraft pulp, making this species an excellent raw material source for the Colombian pulp and paper industry.

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