

Thorough Characterization of Tropical Pine Species for Kraft Pulp Production

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ABSTRACT

This study was conducted to evaluate the wood technological characteristics of *Pinus maximinoi*, *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea* and their potential for producing bleached kraft pulp. Samples of *Pinus taeda* wood were used as reference material. For all species wood chips were used for the technological characterization, pulping, bleaching process analysis and pulp properties. The results showed that the different species presented similar wood characteristics, with some highlights for *Pinus taeda* wood, with a slightly higher basic density (0.422 g/cm³) and lower extractives content (3.54 %). In the cooking process, the highest screened yields were observed for *Pinus taeda* (46.9 %) and *Pinus maximinoi* (47.2 %). Regarding the bleaching process, *Pinus taeda* showed the highest viscosity (817 cm³/g) and greater selectivity (0.158). For physical-mechanical properties, the kraft pulps showed similar results, with the exception of tear index, where *Pinus taeda* presented the best performance, which may have been positively influenced by the higher percentage of xylans found for the cellulosic pulp of this species. However, in general, the results showed that all four species of *Pinus* presented characteristics very suitable for production of bleached kraft pulp, with emphasis on *Pinus taeda* and *Pinus maximinoi* species.

Key-words: *Pinus*; wood quality; kraft pulp.

INTRODUCTION

Brazil is the second largest pulp producer in the world, reaching 22.5 million tons of production in 2021, which is based on two main genus, *Pinus* and *Eucalyptus*. The total area of planted trees in 2021 was 9.93 million hectares, being only 19.4 % of *Pinus* species, which are concentrated mainly in the Southern region of the country (88.9 %), in the states of Paraná and Santa Catarina, due to the edaphoclimatic conditions and the location of the main processing centers for this type of wood [1].

Pine wood (softwood) is the main raw material for the long fiber kraft pulp production in Brazil, which is mostly intended for the production of papers that demand high properties of strength, such as packaging (corrugated paper, cardboard and sack kraft) as well as for absorbent products (fluff pulp) [2].

The arrival of the coronavirus pandemic in 2020 changed the habit of people around the world, the growth in delivery and e-commerce for instance, led to an increase of 3.9 % in packaging paper demand in 2021, where the domestic market was the main focus on paper sales [1]. Thus, in order to keep up with this growing market, a greater amount of softwood kraft pulp is needed, increasing the production and the planted area of *Pinus*.

Among the most planted species of *Pinus* in Brazil, the one that stands out is *Pinus taeda* L., cultivated mainly in southern region, due to better adaptation to the climatic conditions of this region. However, there are other species of *Pinus*, such as the tropical ones, with great potential for use, representing a possibility of increasing the planted area with pine in the national territory, in addition to the southern region of Brazil.

Several species of tropical pines may be cited, such as *Pinus maximinoi*, *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea*, for example. *Pinus maximinoi* is naturally present from Mexico to Nicaragua and has shown a remarkable difference in growth and wood quality for pulp production [3]. *Pinus caribaea* var. *hondurensis* also occurs in Central America, from Nicaragua, Honduras, Mexico, Guatemala and Belize, and *Pinus caribaea* var. *caribaea* is from Cuban region. Both species require more tropical, frost-free climatic conditions for their fast growing [4]. These species have been showing an interesting potential for pulp mills, since they develop reasonably well in other regions and maintain a good quality of the kraft pulp generated [2, 5, 6, 7].

However, to operationally incorporate and consolidate species such as these as producers of wood for pulp and paper industry, further studies are needed to demonstrate their performance from the process to the final product. Therefore, this study was conducted to evaluate the wood technological characteristics of *Pinus maximinoi*, *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea* and the potential of these species for producing high quality bleached kraft pulp.

MATERIAL AND METHODS

Wood Samples

Wood samples of *Pinus maximinoi*, *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea* from 13-year-old trees were used. These wood samples were compared to the wood of *Pinus taeda* species at the same age, since it is the most used species for the softwood kraft pulp production in Brazil. *Pinus maximinoi* and *Pinus taeda* material were collected from plantation areas located in Telêmaco Borba city in the state of Paraná, at 24° 11' 15" (S) latitude and 50° 30' 58" (O) longitude, 24° 24' 16" (S) latitude and 50° 33' 19" (O) longitude, respectively. *Pinus caribaea* var. *hondurensis* was collected in the Jaguariaíva city, Paraná state, at 24° 15' 48" (S) latitude and 49° 55' 56" (O) longitude, and *Pinus caribaea* var. *caribaea* was collected in Ventania, also Paraná state, at 24° 0' 54" (S) latitude and 50° 12' 19" (O) longitude.

Five trees of each evaluated pine species, with DBH (Diameter at Breast Height – 1.3 m) and heights corresponding to the average population, were harvested and removed four 100 cm long parts, at the base, 33, 66 and 100 % of commercial height. The wood pine samples were processed into chips through a laboratory chipper and later classified according to the SCAN-CM 40:1 standard procedure, where the chips retained in the two intermediate sieves, 13 mm and 7 mm in diameter, were considered accepted and were selected for further laboratory analysis.

Wood Characterization

The wood basic density was determined from a disc removed at DBH according to SCAN CM-46:92 standard procedures. For quantitative chemical analysis of the chips, sawdust samples were obtained from them, classified in 40 and 60 mesh sieves, placed in a room with constant relative humidity and temperature (50 % and 23 °C, respectively). The performed analysis included the total extractives content (TAPPI T 204 cm-17), insoluble lignin (TAPPI T 222 om-97), soluble lignin (TAPPI UM 250) and inorganic ash (TAPPI T 211 om-16). The carbohydrates content was determined by a high-performance liquid chromatography (HPLC) using the modified TAPPI T 249 cm-09 standard.

Pulping Process

The pulping process was carried out in a lab digester aiming a kappa number of 30±5% by varying the alkaline charge to reach the target kappa number. Pulping conditions were: 30 % sulfidity, 4.5 L/kg liquor/wood ratio. Trials were performed in triplicate for each studied sample. Pulping conditions are shown in Table I.

Table I. Conditions used for the pulping process.

Pulping Stage	Time to temperature, min	Time at temperature, min	Temperature, °C
Pre-steaming	10	20	100
Impregnation	15	45	138
Pulping	20	124	166.2

After the pulping trial, the chips were discharged from the reactors and washed extensively with water at room temperature. The cooked chips were defibrated in a lab hydropulper and the resulting pulp screened through a 0.25 mm slotted lab flat screen. After dewatering, all samples were analyzed, being determined the kappa number (TAPPI T 236 om-13), screened yield, rejects content and pulp viscosity (TAPPI T 230 om-13). It was used a production indicator “Specific Wood Consumption” (SWC) which was calculated to evaluate the performance of each wood sample for pulp production. The SWC, m³ ton⁻¹ of pulp, was calculated according to the Equation 1. This production indicator is inversely proportional to the basic wood density, kg m⁻³(BD) and the screened yield, % (SY). The 0.9 factor that appears in the numerator of the equation is the conversion factor for air dry ton (ADT), considering the pulp with 10 % moisture.

$$SWC = \frac{1}{(BD \times SY)} \times 0,9 \quad \text{Equation 1}$$

where:

SWC = wood specific consumption, m³/o.d. metric ton

BD = basic density, g/cm³

SY = screened yield (as a fraction)

The black liquors generated were also evaluated, determining the residual effective alkali (SCAN N2:88), black liquor pH (NBR 9251) and solids content (TAPPI T 650 om-15).

Oxygen Delignification and Bleaching

Brownstock pulps were oxygen delignified in double-stage (O/O) and later bleached with a D₀ (EOP) D₁ P sequence to a target brightness of 90 % ISO. General bleaching conditions are shown in Table II, the ClO₂ and H₂O₂ consumptions are described in the results section.

Table II. Bleaching conditions for each stage.

Bleaching Conditions	Sequence				
	O/O	D ₀	(EOP)	D ₁	P
Consistency, %	10/10	11	11	11	11
Time, min	30/60	15	100	93	90
Temperature, °C	90/100	80	84	72	80
Pressure, kPa	1000/500	-	200	-	-
Bleaching Reagents					
NaOH, kg/a.d. ton	35.0/0	-	11.5	-	2.3 - 4.0
O ₂ , kg/a.d. ton	25.0/0	-	3.5	-	-
MgSO ₄ , kg/a.d. ton	3.33/0	-	-	-	-
H ₂ SO ₄ , kg/a.d. ton	-	-	-	-	-
Final pH	11,8	3,2	11,1	3,9	10,8

¹NaOH = sodium hydroxide; O₂ = oxygen; MgSO₄ = magnesium sulfate; ClO₂ = chlorine dioxide; H₂O₂ = hydrogen peroxide.

After each bleaching stage, pulp brightness was determined (TAPPI T 527 om-13) and at the final bleaching stage, the kappa number (TAPPI T 236 om-13) and intrinsic pulp viscosity (TAPPI T 230 om-13) were determined. Brightness reversion was also measured in the bleached pulp (TAPPI UM 200).

The efficiency and selectivity of oxygen delignification process was determined according to Equations 2 and 3, respectively.

$$Efficiency = \left(\frac{kappa\ number\ decrease}{initial\ kappa\ number} \right) * 100 \quad \text{Equation 2}$$

$$Selectivity = \frac{kappa\ number\ decrease}{viscosity\ decrease, cm^3/g} \quad \text{Equation 3}$$

The bleachability has been defined as the Equations 4 and 5, for efficiency and selectivity, respectively. For Total Active Chlorine it was used Equation 6. The factors 2.63 and 2.09 are simple conversions of ClO₂ and H₂O₂ into active Cl₂ based on their oxidation equivalents.

$$Efficiency = \frac{kappa\ number\ decrease}{initial\ kappa\ number} \quad \text{Equation 4}$$

$$Selectivity = \frac{kappa\ number\ decrease}{Total\ Active\ Chlorine} \quad \text{Equation 5}$$

$$Total\ Active\ Chlorine\ (TAC) = (ClO_2 \times 2.63) + (H_2O_2 \times 2.09) \quad \text{Equation 6}$$

Tracheid Morphology and Chemical Characterization of Bleached Pulps

The morphological analysis of the kraft pulps were performed using the Valmet Fiber Image Analyzer (Valmet FS5) (TAPPI T 271 om-12 and ISO 16065-N). This equipment applies image analysis to perform tracheid measurement. The carbohydrates content of bleached pulps was determined by a high-performance liquid chromatography (HPLC) using the modified TAPPI T 249 cm-09 standard. The hexenuronic acids (HexA) were quantified according to TAPPI T 282 pm-07.

Beating and Physical-Mechanical Properties of Bleached Pulps

The bleached pulps were beaten in a PFI mill laboratory, according to TAPPI standard T 248 sp-15, at varying rotation: 0, 1500, 3000, 5000 and 7000 rpm. Handsheet samples for the physical-mechanical tests (Table III), with approximate weight (grammage) of 60 g/m², were obtained in a conventional laboratory sheet former according to TAPPI Standard Test Methods (TAPPI T 205 sp-12).

Table III. Parameters determined in bleached and beaten pulps.

Parameter	TAPPI Standard Test Method
Tensile index	T 494 om-13 “Tensile properties of paper and paperboard (using constant rate of elongation apparatus)”
Burst index	T 403 om-15 “Bursting strength of paper”
Tear index	T 414 om-12 “Internal tearing resistance of paper (Elmendorf-type method)”
Bulk	T 411 om-15 “Thickness (caliper) of paper, paperboard, and combined board”

Data Analysis

Statistical analyses were carried out in Minitab software (version 21.1.0.0) using the 5 % significance level for variance analysis. In this case, the hypotheses tested were: H₀: all means are equal, i.e., there is no significant difference between treatments, and H_a: there is at least an average statically distinct from the others. When significant difference was detected between treatments, the Tukey test was used at 5 % of significance.

RESULTS AND DISCUSSION

Wood characterization

The results of wood characterization, basic density and chemical composition, for *Pinus taeda*, *Pinus maximinoi*, *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea* are shown in Table IV.

Table IV. Wood characterizations.

Parameter	PTA	PMA	PHO	PCA
Basic density, g/cm ³	0.422 a	0.415 a	0.399 a	0.395 a
Total extractives content, %	3.54 b	3.96 b	4.60 a	4.75 a
Total lignin content, %	27.74 a	27.71 a	27.96 a	28.01 a
Ash content, %	0.15 ab	0.14 ab	0.08 b	0.22 a
Holocellulose content, %	66.51 a	65.40 a	66.22 a	65.22 a

¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*. ²Different letters between the columns indicate a significant difference in the Tukey test at 5 % of probability.

Basic density is by far one of the most significant wood characteristics for kraft pulp use and production, variable of easy and quick determination, which is correlated with the morphological features of the wood [8, 9] and with the physical-mechanical properties of the final product [10]. Fiber dimensions are important indicators of wood's potential for pulp and paper manufacturing. Denser woods tend to have fibers with greater length, what is an important factor related to the tensile strength of papers, for example [11].

The basic density influences the performance of pulping process, concerning the digester productivity and kraft pulp quality [12]. Among many reasons, it can be considered as one of the main parameters to evaluate the wood quality, aiming its use as raw material for the production of kraft pulp [13].

Pinus taeda showed the highest wood basic density, followed by *Pinus maximinoi*, *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea*. The variation between all species was not statistically significant. The wood basic density of *Pinus maximinoi* is compliant with a study that reported 0.399 g/cm³ for a 14 years old *Pinus maximinoi* wood [2]. Few references are found for *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea*. A basic density of 0.431 g/cm³ for *Pinus caribaea* var. *hondurensis* at 18 years old [14], 0.339 g/cm³ for *Pinus caribaea* var. *caribaea* at 6.5 years old [15] and 0.374 g/cm³ at 17 years old [4], were reported in other studies.

For pulping, wood with lower extractives and lignin content is preferred as this greatly reduces the cost of chemicals used for its removal. One of the main objectives of the pulping process is the removal of lignin content, therefore, low levels facilitate the cooking and delignification process, contributing to a lower degradation of tracheids and higher yields, consequently. High extractives levels are also undesirable in the pulping process as they can cause “pitch”, incrustations in industrial equipment, in addition to being deposited in the cellulosic pulp and consume more alkali in the wood cooking process.

Extractives content was found to differ between species, *Pinus caribaea* var. *caribaea* and *Pinus caribaea* var. *hondurensis* showed higher extractives contents compared to the other analyzed species. For lignin content no significant difference was noted, also the lignin contents found in the study are in agreement with the expected values for conifers (28 % to 30 %) [16]. For extractives content, *Pinus maximinoi* follows the pattern reported in other studies, 3.5% [17] and 4.5% [2]. For *Pinus caribaea* var. *hondurensis*, extractives content of 4.71 % for trees with 6.5 years old [15] and 7.39 % for 18 years old [14] were observed.

The expected range for ash content for coniferous wood is 0.10 % to 1.0 % [18], therefore all species in this study were within the mentioned range. Cellulose content was found to be higher for *Pinus caribaea* var. *caribaea*, followed by *Pinus taeda*, *Pinus caribaea* var. *hondurensis* and *Pinus maximinoi*. Regarding to holocellulose, a value of 70.03 % was reported for *Pinus caribaea* var. *hondurensis* [15]. For *Pinus maximinoi* wood, similar values were found, 64.5 % [2] and 67.7 % [17]. The holocellulose content can be correlated with the total carbohydrate content present in the wood, thus positively correlating with the yield of the pulping process.

Pulping process

Table V shows the pulping parameters for all species analyzed, it is possible to observe that *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea* consumed more active alkali than the other species. The higher extractives content for these two species may have been one of the reasons that required a greater amount of alkaline charge. Lignin and extractives consume great part of the alkali charge in the first minutes of cooking, when pulping reaches the maximum temperature the delignification can be hampered by the lack of alkali.

Table V. Pulping parameters.

Parameter	PTA	PMA	PHO	PCA
H-factor	1529	1530	1529	1511
Active alkali, % NaOH on wood	21.0	21.1	21.5	21.5
Kappa number	30.3	29.5	29.6	29.5

¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*.

The pulping results obtained at variable conditions to reach the target kappa number are presented in Table VI. *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea* presented the lowest yields, besides the lower basic density, the cooking process for these two species consumed more active alkali, what may have interfered the yield results and the low pulp viscosity value of *Pinus caribaea* var. *hondurensis* (Table VII). Similar screened yields were found for *Pinus taeda* and *Pinus maximinoi* with 14 years old, 47.4% and 47.5%, respectively [2]. For 11 years old trees, total yields of 45.76% for *Pinus taeda* and 45.26% for *Pinus maximinoi* were reached in other study [19].

The species showed similar black liquor solids content. This variable is important once the solids burning capacity in the recovery boiler can determine the industrial production capacity in a pulp and paper mill, if no others restrictions are applied, as steam consumption and wood chip feeding.

Table VI. Pulping results.

Parameter	PTA	PMA	PHO	PCA
Total yield, %	47.0 a	47.3 a	46.0 b	46.1 b
Reject content, %	0.07 a	0.05 a	0.05 a	0.09 a
Screened yield, %	46.9 a	47.2 a	45.9 b	46.0 b
Black liquor solids, %	15.8 a	16.9 a	16.4 a	16.1 a

¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*. ²Different letters between the columns indicate a significant difference in the Tukey test at 5 % of probability.

For pulp viscosities, *Pinus taeda* and *Pinus maximinoi* demanded less alkaline charge in the cooking process, what may have led to higher pulp viscosity values. The highest value of HexA concentration observed was 27.3 mmol/kg for *Pinus taeda*, this behavior may be related to the greater presence of xylans found in the pulp from this species, once in the kraft pulping process the hexenuronic acids (HexA) are formed by elimination of methoxyl from the reaction of 4-O-methyl- α -D-glucuronic acid groups with alkali [20].

Pinus taeda and *Pinus maximinoi* wood showed lower specific wood consumption compared to *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea*. The SWC results show the significant impact of wood density, where the lowest values were obtained for the densest woods and the woods that delivered the highest pulping yields. Lower SWC reflects in lower wood costs for pulp production, since to reach the same amount of pulp, less wood volume would be necessary.

Other authors highlight the importance of specific wood consumption [21], who statement that wood with low density can result in higher specific consumption, which is a disadvantage for the company, especially if there is a limitation in the supply of raw materials. Wood is one of the main elements in the composition of pulp production costs in the world, representing around 40% of this amount [22].

Table VII. Pulp characterization.

Parameter	PTA	PMA	PHO	PCA
Intrinsic viscosity, cm³/g	1124 c	1130 b	1080 d	1143 a
Hexenuronic acids (HexA), mmol/kg	27,3 a	21,1 b	21,0 b	21,7 b
Specific wood consumption, m³/odt	4.55 b	4.59 b	4.91 a	4.95 a

¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*. ²Different letters between the columns indicate a significant difference in the Tukey test at 5 % of probability.

Oxygen delignification

In order to remove the residual lignin from pulp an oxygen delignification is required before the bleaching process. This stage makes it possible to interrupt the cooking process at higher kappa numbers, enhancing yield gains, since oxygen delignification is more selective than the cooking process [23]. The oxygen delignification results for the four wood species evaluated are shown in Table VIII.

Regarding the brightness parameter, the results showed a tendency for slightly higher values for pulps with lower kappa numbers (*Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea*). However, it is important to emphasize, that these two higher brightness in this study, resulted in lower pulp intrinsic viscosities after delignification and greater chemical costs in the cooking process.

The oxygen delignification process can be evaluated through its efficiency and selectivity, which are determining factors in the performance analysis of this stage. The oxygen stage presents low selectivity in relation to other oxidizing processes, resulting in high degradation of the cellulose, consequently reducing the viscosity of the pulp [24]. Among the evaluated species, *Pinus maximinoi* presented the highest selectivity, where oxygen

attacked the lignin more than carbohydrates, preserving viscosity, however, this species showed the lowest efficiency. Another highlight is the low selectivity of *Pinus caribaea* var. *caribaea*, approximately 30.9 % smaller when compared to *Pinus maximinoi*.

Table VIII. Oxygen delignification.

Parameter	PTA	PMA	PHO	PCA
Kappa Number	13.8 a	13.6 ab	12.7 b	12.6 b
Brightness, % ISO	35.7 b	34.4 b	41.2 a	36.1 b
Intrinsic Viscosity, cm³/g	925 b	951 a	889 d	896 c
Efficiency, Δk/kf	54,5	53,9	57,1	57,3
Selectivity, Δk/Δv	0,083	0,089	0,088	0,068

¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*. ²Different letters between the columns indicate a significant difference in the Tukey test at 5 % of probability.

Bleached pulp

Bleaching is a chemical process, which aims to remove color in pulps derived from residual lignin or other colored impurities, maintain cellulose chain length and brighten the fibers. Between the important variables for monitoring the steps in the bleaching process are viscosity and brightness, the results of these variables for the four species evaluated can be found in Table IX.

Table IX. Bleached pulp characterization.

Parameter	PTA	PMA	PHO	PCA
Final Brightness, % ISO	91.0 a	89.6 b	91.3 a	89.7 b
Brightness Reversion, % ISO	4.8 a	1.1 d	3.4 b	2.3 c
Final Intrinsic Viscosity, cm³/g	817 a	798 c	756 d	805 b
ClO₂, kg/a.d. ton	27.0	28.0	26.0	26.0
H₂O₂, kg/a.d. ton	6.5	7.0	6.5	6.5
Total Active Chlorine (TAC), %	84.6	88.3	82.0	82.0
Efficiency, Δk/kf	33.5	26.2	30.8	24.2
Selectivity, Δk/TAC	0.158	0.148	0.150	0.148

¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*. ²Different letters between the columns indicate a significant difference in the Tukey test at 5 % of probability.

Concerning the pulp intrinsic viscosity, *Pinus caribaea* var. *hondurensis* presented the lowest value among the four species, however all the other three species showed very similar values, showing that *Pinus taeda* and *Pinus maximinoi* kept their good performance, with lower carbohydrate degradation along the process.

Regarding the final bleached brightness of the pulps, the results were very similar, all above the brightness practiced in the industry for bleached softwood pulp (89 % ISO). Nevertheless, it is possible to observe a trend towards better performance of *Pinus taeda* and *Pinus caribaea* var. *hondurensis*, with the highest brightness value.

For brightness reversion, the highest value found for *Pinus taeda* may be correlated with the highest xylan content present in this pulp (Table VII). Once, the 4-O-methylglucuronic acids from xylan chains are the precursors of hexenuronic acids (HexA), created under alkaline cooking conditions. This hexenuronic acid is known to be one of the contributing factors in brightness reversion [25, 26]. Carbonyl groups and lignin residues can also be involved in the brightness reversion reactions [27].

Total active chlorine consumption was lower for *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea*, however, the greater efficiency and selectivity of the bleaching process were observed for *Pinus*

taeda. Consumptions of 20.78 kg/a.d.ton for ClO₂, 10.7 kg/a.d.ton for H₂O₂, and final viscosity around 603 dm³/kg, in the bleaching of *Pinus taeda* and *Pinus maximinoi* pulp were observed in another study [2].

Morphological and chemical characterization of bleached pulp

Tracheid morphological parameters varied between species and contrary to what was expected, woods with higher densities did not result in tracheids with greater morphological properties (*coarseness* and tracheid length). However, the number of tracheids found, followed the trend observed in the other properties, where woods with greater *coarseness* had the lowest number of tracheids per milligram (Table X).

Table X. Morphological and chemical bleached pulp characterization.

Parameter	PTA	PMA	PHO	PCA
Coarseness, mg/m	0.269 d	0.333 c	0.382 a	0.358 b
Tracheid length, mm	2.385 d	2.859 c	3.090 b	3.199 a
Tracheid width, µm	25.17 d	28.63 c	29.33 b	30.20 a
Number of fibers/mg ISO, 1/mg	2812 a	2254 b	1096 d	2055 c
Glucose content, %	78.9 b	83.9 a	82.2 ab	78.8 b
Hemicellulose content, %	15.9 a	14.1 b	14.3 b	14.6 b
• Xylan content, %	8.50 a	6.73 c	7.10 bc	7.50 b
• Mannan content, %	6.48 ab	6.58 a	6.41 b	6.18 c
• Galactan content, %	0.28 b	0.31 b	0.31 b	0.45 a
• Arabinan content, %	0.60 a	0.52 bc	0.50 c	0.55 b

¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*. ²Different letters between the columns indicate a significant difference in the Tukey test at 5 % of probability.

The tracheids morphology is one of the factors that interfere in the performance of the physical-mechanical properties of pulp and paper. The relative cell wall thickness is reflected in the *coarseness* property [28], therefore, analyzing the results of this property in this study, *Pinus caribaea* var. *hondurensis* presented the highest value and *Pinus taeda* the lowest one. Tracheids with higher *coarseness* tend to produce an open, absorbent, bulky sheet, resulting in high tearing resistance and low burst and tensile strength [10]. Also, in paper production, more energy is needed to refine this type of tracheids, with higher *coarseness*. On the other hand, tracheids with low *coarseness* (thin cell walls) are likely to produce dense well-formed paper, once the cell walls collapse more easily into ribbons during sheet formation [28].

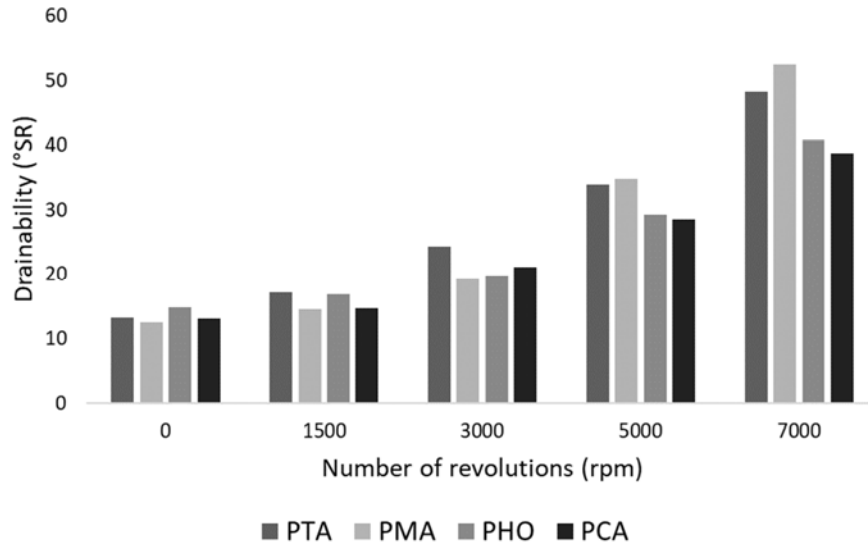
Regarding the tracheid length, a minimum value is required for interfiber bonding, being proportional to strength properties, as the tear one [10]. *Pinus caribaea* var. *caribaea* presented the highest tracheid length, approximately 34 % higher than the lowest value observed for *Pinus taeda*. Fiber distribution, as mentioned before, correlates inversely well with *coarseness*, where *Pinus taeda* showed the greatest amount. A large number of fibers may contribute to a better formation, smoothness and opacity of the paper, as it promotes greater intertwining of the fibers, which also positively interferes with better tensile and burst properties. However, excess number of fibers can result in drainage problems on the fourdrinier and higher steam consumption in drying section.

For carbohydrate composition, *Pinus maximinoi* showed the greatest value for glucose and *Pinus taeda* the highest values for hemicelluloses, especially xylans content. Hemicelluloses are important components in the performance of physical-mechanical tests, as they help in the refining stage.

Physical-mechanical test results

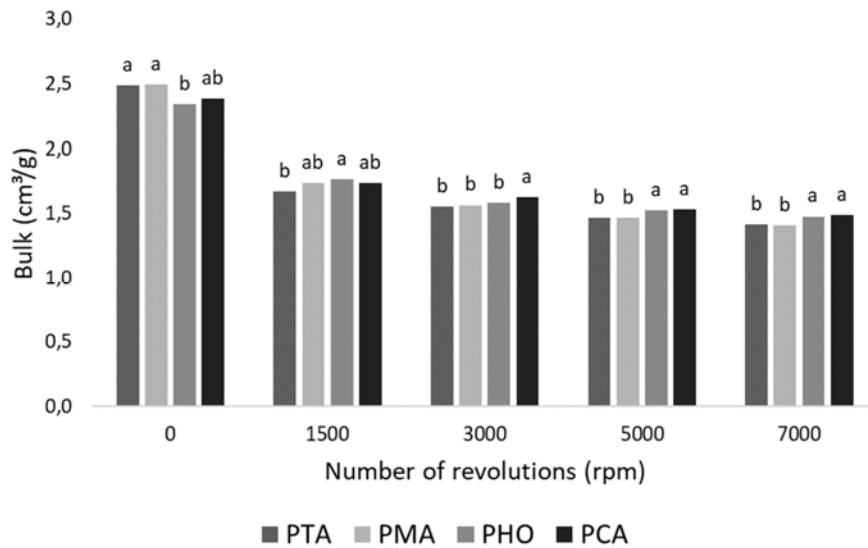
Among the physical-mechanical properties (Figure 1), as expected, the drainability (Schopper Riegler degrees) increased as the revolution number got higher. The four species had similar refining behaviors, however, *Pinus taeda* and *Pinus maximinoi* showed a slightly trend to refine faster and better than the others in final revolutions.

Comparing the material, despite the slightly statistically difference, the four species showed similar behavior for bulk (Figure 2) and burst index (Figure 3) properties. As mentioned before, the tracheids cell wall thickness in the bleached pulps were very similar, what may have helped to reflect these alike performances. Nonetheless, slightly low values were observed for *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea* for tensile index (Figure 4) and a different behavior had been noticed for tear index (Figure 5), where *Pinus taeda* showed higher values after refining. Analyzing the morphological and chemical properties of these materials, it is possible to observe that there was no significant difference in the tracheids wall thickness, however, *Pinus taeda* presented higher hemicelluloses contents, mainly xylans, which contribute to the refining process [29] and may have positively influenced the development of this mechanical property, raising the values for this species. The xylans content was 26.3 %, 19.7 % and 13.3 % higher for *Pinus taeda* when compared to *Pinus maximinoi*, *Pinus caribaea* var. *hondurensis* and *Pinus caribaea* var. *caribaea*, respectively.



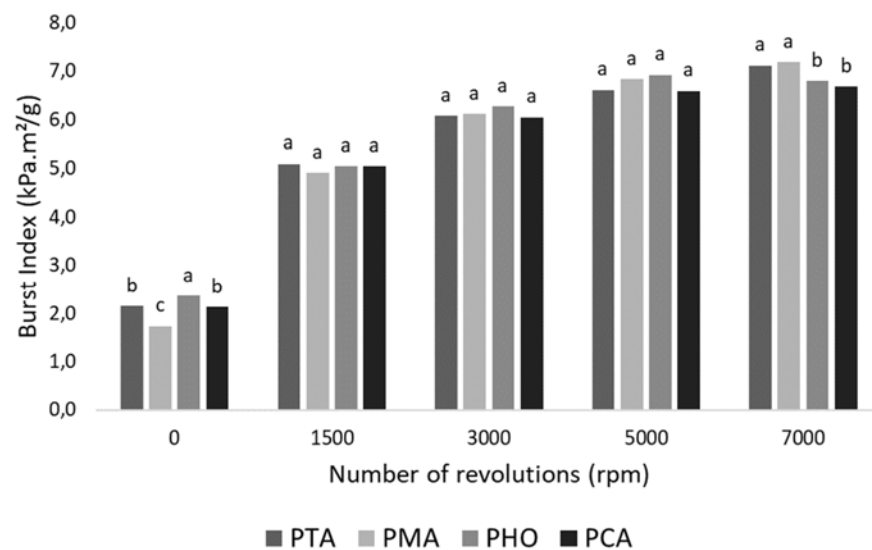
PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*.

Figure 1. Drainability of bleached pulp.



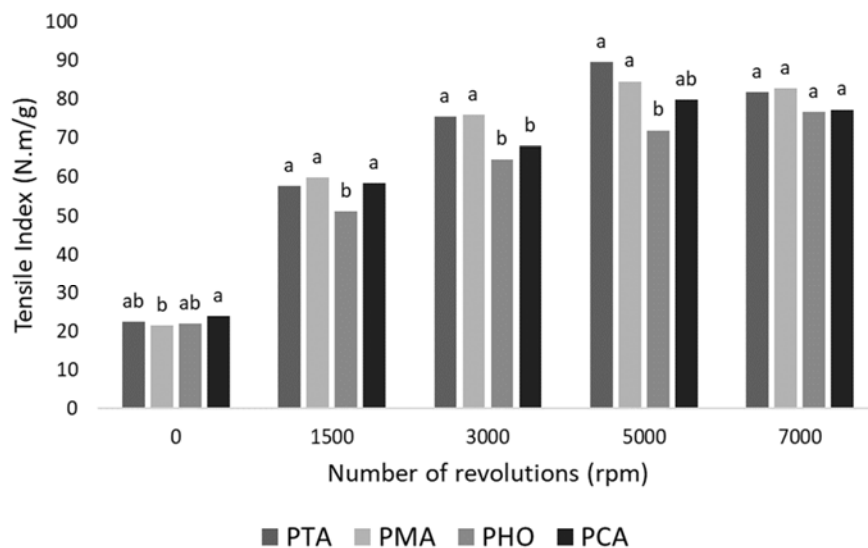
¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*. ²Different letters between the columns indicate a significant difference in the Tukey test at 5 % of probability.

Figure 2. Bulk of bleached pulp.



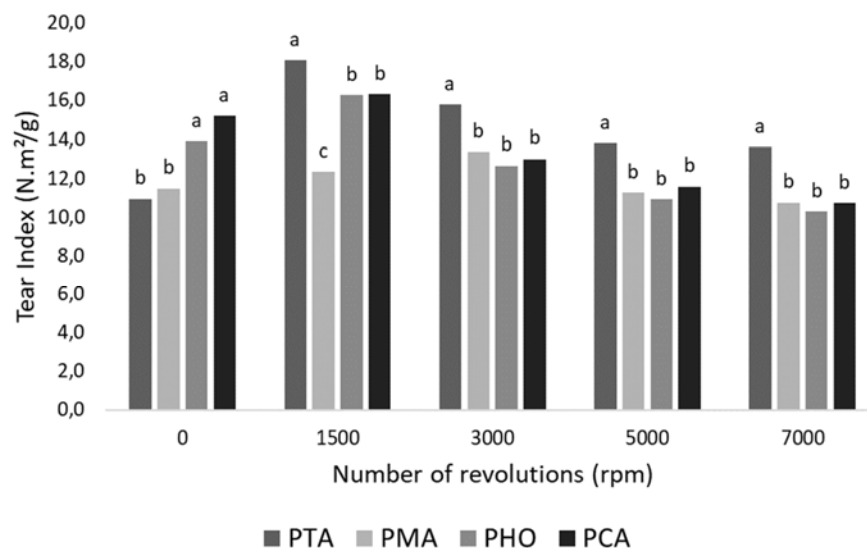
¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*. ²Different letters between the columns indicate a significant difference in the Tukey test at 5 % of probability.

Figure 3. Burst Index of bleached pulp.



¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*. ²Different letters between the columns indicate a significant difference in the Tukey test at 5 % of probability.

Figure 4. Tensile Index of bleached pulp.



¹PTA: *Pinus taeda*; PMA: *Pinus maximinoi*; PHO: *Pinus caribaea* var. *hondurensis*; PCA: *Pinus caribaea* var. *caribaea*. ²Different letters between the columns indicate a significant difference in the Tukey test at 5 % of probability.

Figure 5. Tear Index of bleached pulp.

CONCLUSIONS

The results analysis allows to conclude that the technological characteristics of *Pinus taeda* and *Pinus maximinoi* wood are very similar, resulting in good performances in pulping process with higher yields and also in the development of the physical-mechanical properties of bleached kraft pulp.

Pinus caribaea var. *hondurensis* and *Pinus caribaea* var. *caribaea* showed slightly lower results when compared to *Pinus taeda*, with higher consumption of reagents in the pulping process, lower screened yield and final viscosity of bleached kraft pulp. *Pinus maximinoi* showed the highest selectivity in the oxygen delignification process and *Pinus taeda* in the bleaching process.

Despite showing better anatomical characteristics, the physical-mechanical properties of these species were not superior to *Pinus taeda*. The higher content of xylans in the *Pinus taeda* bleached kraft pulp favored the refining stage, reaching better values mainly for the tear index of this material when compared to the others.

However, in general, all four species of *Pinus* presented morphological and technological characteristics very suitable for production of bleached kraft pulp, making these species excellent raw materials for pulp and paper industry.

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