

Artigos

The performance of *Acacia mearnsii* De Wild for kraft pulping

Performance da madeira de *Acacia mearnsii* De Wild para polpação kraft

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ABSTRACT

The growing worldwide interest in pulp produced from *Acacia mearnsii* encourages studies that prove its propensity and efficiency for this purpose. Thus, the objective of this work was to evaluate the performance of *Acacia mearnsii* to produce kraft pulp, under different pulping conditions. Wood samples from seed production areas (SPA) and clones were evaluated. Kraft pulping was performed at constant H-factor (1363), and the active alkali varied from 14% to 24%. The wood density of clone and SPA samples was approximately 0.544 g/cm³. The chemical analysis revealed that the content of extractives, lignin, and carbohydrates was 4.67%, 16.66%, and 77.02%, respectively. The optimal pulping condition was obtained with active alkali of 14%, where kappa number was 16; screened pulp yield was 57%. The results show that *Acacia mearnsii* is an outstanding source of short fibers to produce kraft pulp.

Keywords: Pulp yield; Wood chemistry; Wood properties

RESUMO

O crescente interesse mundial na polpa celulósica produzida a partir da madeira de *Acacia mearnsii* incentiva estudos que comprovem sua propensão e eficiência para esse fim. Dessa forma, o objetivo deste estudo foi avaliar as propriedades físico-químicas da madeira de *Acacia mearnsii*, bem como avaliar seu desempenho na produção de celulose kraft, sob diferentes condições de cozimento. Amostras de madeiras das áreas de produção de sementes (APS) e clones foram avaliados. A polpação kraft foi realizada com fator H constante (1363) e álcali ativo variando de 14% a 24%. A densidade básica das madeiras de clone e APS não diferiram estatisticamente (0,544 g/cm³). A análise química revelou que o conteúdo médio (clone e APS) de extrativos, lignina e carboidratos foi de 4,67%, 16,66% e 77,02%, respectivamente. A condição de polpação mais eficiente foi obtida com álcali ativo de 14%, número kappa 16 e rendimento depurado de 57%. De acordo com os resultados, a madeira de *Acacia mearnsii* apresentou grande potencial para ser utilizada como fonte de fibra curta na obtenção de polpa celulósica pelo processo kraft.

Palavras-chave: Rendimento de celulose; Química da madeira; Propriedades da madeira

1 INTRODUCTION

The growing demand of the pulp market across the globe has motivated researches in this field. According to the annual report from *Indústria Brasileira de Árvores* “Brazilian Tree Industry”, in 2019, Brazil was pointed as the second largest pulp producer in the world, and the largest exporter of cellulose pulp in the world market, with US\$ 1.7 billion ahead of the second-place exporter (INDÚSTRIA BRASILEIRA DE ÁRVORES, 2020).

Wood is currently the main source of fibers for the pulp and paper industry, and different sources (species) have been continuously evaluated for this purpose. Fortunately, planted forests are extremely abundant in Brazil and have shown great results in terms of quality and productivity due to the advanced technologies in genetic engineering, cultivation techniques and precision forestry.

Acacia mearnsii De Wild is a leguminous of the Clade Mimosoideae that shows good adaptability in humid, cold, and relatively hot climate regions (EMBRAPA, 2016). The species is popularly known in Brazil as “acácia-negra”, and the wood reveals several silvicultural and technological qualities, such as low lignin content, high carbohydrate contents, and a medium-to-high wood density. Currently, *Acacia mearnsii* is mainly

used for the extraction of tannin from its bark, and the timber is destined to products with low added value, such as power generation (HIGA *et al.*, 1999; BECK-PAY, 2012).

After the tannin extraction, the wood is considered a byproduct and it is either used for power generation as firewood and/or charcoal, or exported to Asian countries where it is mainly used for pulp production. Yet, *Acacia mearnsii* is very little used for pulp in Brazil, even considering the wide range of lignocellulosic materials that kraft pulping process uses and could benefit from.

The genus *Acacia mearnsii* has a medium-to-high wood density and low lignin content (BROWN; KO, 1997), which are important parameters for the pulping process that could lead to a lower wood consumption and less use of chemicals in the pulping and bleaching processes (MOKFIENSKI *et al.*, 2008; GOMIDE; FANTUZZI NETO; REGAZZI, 2010). This wood has been reported as a good feedstock for tissue paper due to its anatomical elements with lower mechanical resistance when compared to the genus *Eucalyptus* (SANTOS; ANJOS; SIMÕES, 2005).

The use of a widely cultivated species combined with the possibility of obtaining pulp with high quality must arouse the worldwide interest in using this raw material for the pulp and paper manufacture, which could add value to the Brazilian plantations.

Given the industrial potential of *Acacia mearnsii* for the pulp and paper industry, the present study aimed to evaluate the chemical and physical properties of *Acacia mearnsii* wood samples collected from seed production areas (SPA) and clones and its performance to the production of kraft pulp.

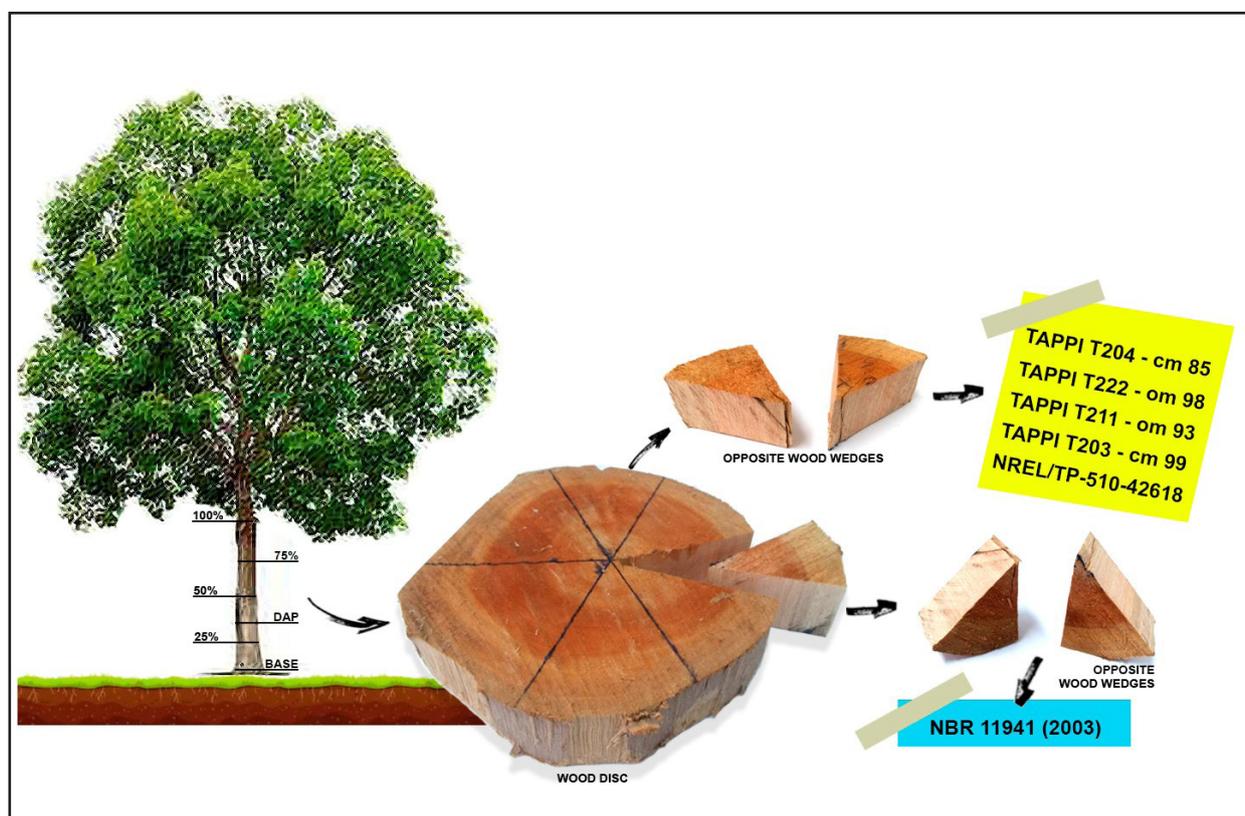
2 MATERIAL AND METHODS

2.1 Wood preparation and characterization

The present study evaluated wood samples of *Acacia mearnsii* De Wild from commercial plantations in Cristal, State of Rio Grande do Sul, Brazil. Ten representative

trees were studied, five from the seed production area (SPA) and five clones, both ~ 7 years old. The trees were randomly selected in the plantations, observing its vigor and sanitary state (absence of apparent diseases). The trees were harvested, and wood discs were taken at the base, 25, 50, 75, and 100% of the commercial height. After air-drying, the discs were sectioned according to the quartering method, where two opposite wood wedges of each disc were selected for chemical analysis and the other two were used to determine the basic wood density (Figure 1).

Figure 1 – Diagram of wood sampling of *Acacia mearnsii*



Source: Authors (2017)

Wood samples were prepared according to TAPPI Standard Test Method T 264 om-88 "Preparation of wood for chemical analysis". All measurements were performed in triplicate and the procedures used for characterization of the *Acacia mearnsii* samples are listed in Table 1.

Table 1 – Analyses performed to characterize *Acacia mearnsii* wood samples

Parameter	Method
Basic density	ABNT NBR 11941 (2003)*
Ash content	TAPPI T211 om-93**
Extractives content	TAPPI T204 cm-85
Klason lignin	TAPPI T222 om-98
Carbohydrates	NREL/TP-510-42618
Alpha-cellulose	TAPPI T203 cm-99
S/G ratio	Oxidation with nitrobenzene***
Functional groups	FTIR****

Source: Authors (2017)

In where: *NBR = Norma Brasileira; **TAPPI = Technical Association of the Pulp and Paper Industry; ***Determined through the Syringaldehyde/Vanilin ratio and corrected to S/G ratio; ** **FTIR = Fourier-transform infrared spectroscopy.

2.2 Kraft pulping

Commercial wood chips obtained from SPA were subjected to kraft pulping. The cooks were performed in a REGMED AUE/20 rotary digester with four 1-L reactor cells, which is electrically heated and equipped with a thermometer and pressure gauge, allowing four cooks in a single batch, using 200 g of OD (oven-dried) wood chips.

Sodium hydroxide 98% (NaOH) and sodium sulfide tetrahydrate 50% (Na₂S) were used for the preparation of the white liquor. The pulping conditions are shown in Table 2. In order to access the *Acacia mearnsii* pulpability, the active alkali (AA) was varied while the other pulping conditions were kept constant.

Table 2 – Pulping conditions

Parameter	Condition
Maximum temperature	170 °C
Time to temperature	70 minutes
Time at temperature	80 minutes
Liquor/Wood Ratio	4/1
Sulfidity	25%
Active Alkali	14, 16, 18, 20, 22, and 24 %

Source: Authors (2017)

After the pulping, a sample of the generated black liquor was collected to determine the pH, and then, neutralized and stored. Pulped chips were placed in a stainless-steel box with a 100-mesh screen, washed thoroughly with water, and disintegrated. Screening was carried out in Somerville laboratory equipment for the separation of pulp and rejects. The material retained on the plate (rejects) was collected, oven-dried at 105°C, and its weight was recorded before and after for determining the percentage of rejects. The pulp was centrifuged to ~ 30% consistency and weighted to obtain the pulp yield, and then stored for further characterization. The characterization of pulp and black liquor generated was performed according to the methods shown in Table 3.

Table 3 – Analytical methods used for brown pulp and black liquor characterization

Parameter	Method
Total pulp yield	Gravimetric
Screened pulp yield	Gravimetric
Rejects yield	Gravimetric
pH of black liquor	pH meter
Kappa Number	TAPPI T 236 – om 85

Source: Authors (2017)

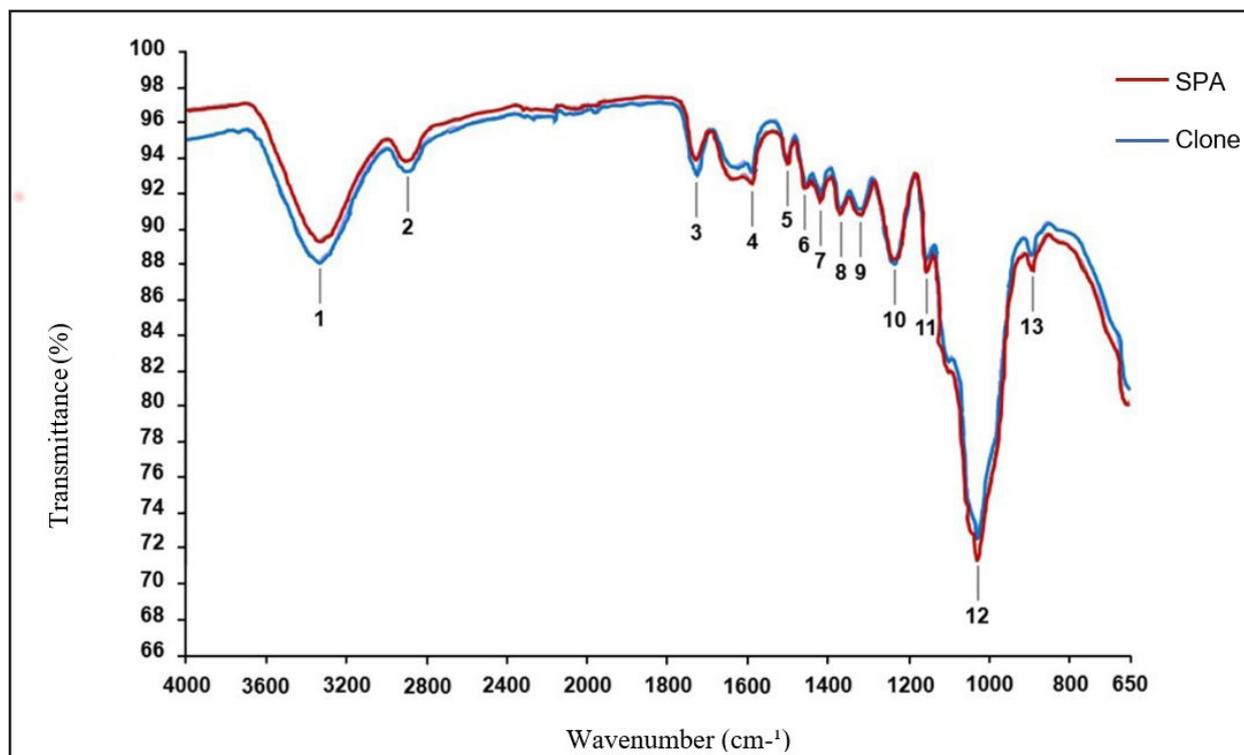
The results were submitted to analysis of variance (ANOVA) to verify the existence or not of significant difference between the means of chemical properties of clone wood and SPA, at a significance level of 5%.

3 RESULTS AND DISCUSSION

3.1 Chemical composition of woods

Clone and SPA samples of *Acacia mearnsii* showed similar chemical properties with respect to functional groups, as can be seen in the FTIR spectra (Figure 2).

Figure 2 – FTIR spectra of clone and SPA *Acacia mearnsii* samples



Source: Authors (2017)

Very few differences were observed in the spectra; for instance, at 3,336.99 cm^{-1} (peak 1), the transmittance of the clone sample was slightly greater than the SPA sample. This peak is characterized by O-H bonds of alcohols, phenols and acids (XING; WANG; LI, 2015).

Typical wood “fingerprints” peaks are observed from 1,800 to 800 cm^{-1} (PANDEY, 1999; COLOM *et al.*, 2003; PANDEY; PITMAN, 2003; BODIRLAU; TEACA, 2009). In Figure 2, these peaks are numbered from 3 to 13, which refer to the functional groups of the main constituents: cellulose, hemicelluloses and lignin. Notably, FTIR spectra do not show reasonable difference between the two *Acacia mearnsii* samples.

The similarity between clone and SPA samples was also confirmed by chemical analysis and basic wood density (Table 4). The samples investigated in this work showed higher basic wood density (0.544 g/cm^3) than the *Acacia mearnsii* samples studied by Segura, Zanão and Silva (2010) (0.516 g/cm^3). Gomide *et al.* (2004) reported

that raw materials with density $\sim 0.500 \text{ g/cm}^3$ are ideal for the pulp and paper industry, indicating that *Acacia mearnsii* is suitable for the pulping process.

Table 4 – Chemical analysis and basic wood density of *Acacia mearnsii* samples

Parameter	Clone	SPA
Ash (%)	0.34 a	0.36 a
Extractives (%)	4.83 a	4.50 a
Klason lignin (%)	16.20 a	17.12 a
Carbohydrates (%)	77.91a	76.13 a
Alfa-cellulose (%)	46.30 a	46.36 a
S/G ratio*	2.69 a	2.93 b
Basic wood density (g/cm^3)	0.544 a	0.544 a

Source: Authors (2017)

In where: Means followed by the same letter, in the rows, do not differ statistically from each other by the 95% probability Tukey test; *S/G: syringil:guaiacil ratio.

The ash content ($\sim 0.35\%$) is within the expected range for this species, as described by Brown and Ko (1997) and Furtado *et al.* (2015). Ash negatively affects the pulping process even in low amounts. According to Cardoso *et al.* (2001), woods with low ash are preferable in the pulp production, because its accumulation over the process causes scaling and equipment corrosion, leading to production losses and shorter lifetime of equipment.

The extractives content ($\sim 4.67\%$) is high, which may negatively affect the kraft pulping process. These wood compounds increase the chemical demand and may cause corrosion of equipment, especially by the acidic extractives and the ones that form complexes with metallic material (INSTITUTO DE PESQUISAS TECNOLÓGICAS DO ESTADO DE SÃO PAULO, 1988).

The Klason lignin content in *Acacia mearnsii* is quite variable. Sansígolo, Busnardo and Gonzaga (1986) has reported 18.28%, Rizaluddin *et al.* (2015), 20.3%, Marinho *et al.* (2017), 19.7%, and Rachwal *et al.* (2007), from 14.17% to 17.95%. The content obtained in this work was $\sim 16.66\%$. Raw materials with low lignin content

are ideal to the pulping process since they require less chemicals and hence facilitate both pulping and bleaching processes.

Lignin is a polymer biosynthesized by coupling three major phenylpropanoid (C6–C3) units, namely, sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol forming syringylpropane (S), guaiacylpropane (G), and p-hydroxyphenylpropane (H) units in lignin (LIN; DENCE, 1992). It is worth mentioning that the wood performance over chemical pulping is also related to the type of lignin: higher levels of S in relation to G units are favorable (SIXTA, 2006). The S/G ratios found in this work (2.69 and 2.93 for clone and SPA samples, respectively) are similar to eucalyptus samples. Manders (1987) stated that hardwoods have an average S/G ratio of 2.3 to 3.3, although there is a large variation, depending on the species evaluated.

Carbohydrate contents (~ 77.02%) are close to typical commercial hardwoods used for pulp production, such as *Eucalyptus grandis* (73.15%) (SARTO; SANSIGOLO, 2010) and eucalyptus clones (76.6%) (TRUGILHO *et al.*, 2005). These high levels of carbohydrates greatly influence the enhancement of pulp yield in the pulping process.

The alpha-cellulose content (~ 46%) is similar to eucalyptus used in the industry. Sá (2014) reported values of 43 to 47.7% for *Eucalyptus sp.*; Santos *et al.* (2016) observed 50.85% for *Eucalyptus urograndis*, whereas Costa *et al.* (1997) found 41.5, 45.7, and 41.4% for *Eucalyptus urophylla*, *Eucalyptus citriodora* and *Eucalyptus pellita*, respectively. Sá (2014) stated that the gravimetric method for the determination of alpha-cellulose may overestimate its content; thus, the monomeric sugar units were determined (Table 5). It is important to mention that typical correction factors are applied to convert the monomeric units into their anhydrous forms. The factor for pentoses (xylose and arabinose) is 0.88 and for hexoses (glucose, galactose, and mannose) is 0.9 (FERREIRA *et al.*, 2006; SÁ, 2014).

Table 5 – Monomeric sugars and carbohydrates of *Acacia mearnsii* samples determined by HPLC

Monomeric sugar (%)	Clone	SPA	Carbohydrates (%)	Clone	SPA
Mannose	3.36	3.26	Mannan	3.02	2.93
Galactose	3.72	3.42	Galactan	3.34	3.07
Glucose	51.75	49.76	Glucan	46.57	44.78
Xylose	10.13	10.24	Xylan	8.91	9.01
Arabinose	2.19	2.24	Arabinan	1.40	1.97
Hemicelluloses *	19.40	19.16	Hemicelluloses *	16.67	16.98

Source: Authors (2017)

In where: *The hemicelluloses content is a sum the monomeric sugars and their respective carbohydrates. The glucose from the glucomannans, acetyl groups and uronic acids were not considered.

Glucose is the monomeric sugar that builds up the most abundant wood compound (cellulose), and for *Acacia mearnsii*, this was the highest content among the evaluated sugars. Lower values were observed by Takahashi, Nakagawa-Izumi and Ohi (2010) for *Acacia mangium* (43.6%) and by Tanifuji *et al.* (2011) for *Acacia mearnsii* (41.15% of glucan). However, according to Sjöström (1993), a small fraction of glucose is present in the glucomannans (a type of hemicellulose), since its content depends on the species and can vary from 2 to 5% of the dry weight of the wood; thus, the evaluated glucan was not considered as pure cellulose.

Xylan is the main hemicellulose of hardwoods (MOKFIENSKI *et al.*, 2008; SÁ, 2014); hence, the xylose was the second most abundant monomeric sugar after glucose (~ 10%). The xylan content found in the present investigation (~ 8.96%) is lower than the content reported in the literature. Tanifuji *et al.* (2011) and Rizaluddin *et al.* (2015) found 14.9 and 17.1%, respectively; whereas Takahashi, Nakagawa-Izumi and Ohi (2010) obtained 11.1% of xylose and Pinto, Evtuguin and Pascoal Neto (2005), 10% for *Acacia mangium*. In addition, Gomide, Fantuzzi Neto and Leite (2004),

when studying different eucalyptus clones, found glucan contents varying from 44.5 to 50%, while xylans varied from 10.8 to 13.2%, values slightly higher than the ones obtained in this work.

The other sugars greatly differed from eucalyptus. A eucalyptus clone evaluated by Ferreira *et al.* (2006), showed arabinan, mannan and galactan contents of 0.5, 1.6 and 1.2%, respectively. Tanifuji *et al.* (2011) found 0.1, 1.6, and 2.3% for the same sugars in *Acacia mearnsii*. Furthermore, Lourenço *et al.* (2008) observed values of 1.1 to 2.2% of arabinose, 4 to 5% of mannose, and ~1% of galactose in *Acacia melanoxylon*.

According to Costa (2011), since cellulose is the main compound in pulp its content in the wood determines alone, or together with hemicelluloses, important parameters such as pulp yield and strength. The yield may be affected by hemicelluloses because they are more easily degraded under the alkaline condition of kraft pulping than cellulose. Thus, wood with high hemicelluloses and low cellulose contents will result in lower yields, especially when high effective alkali is applied.

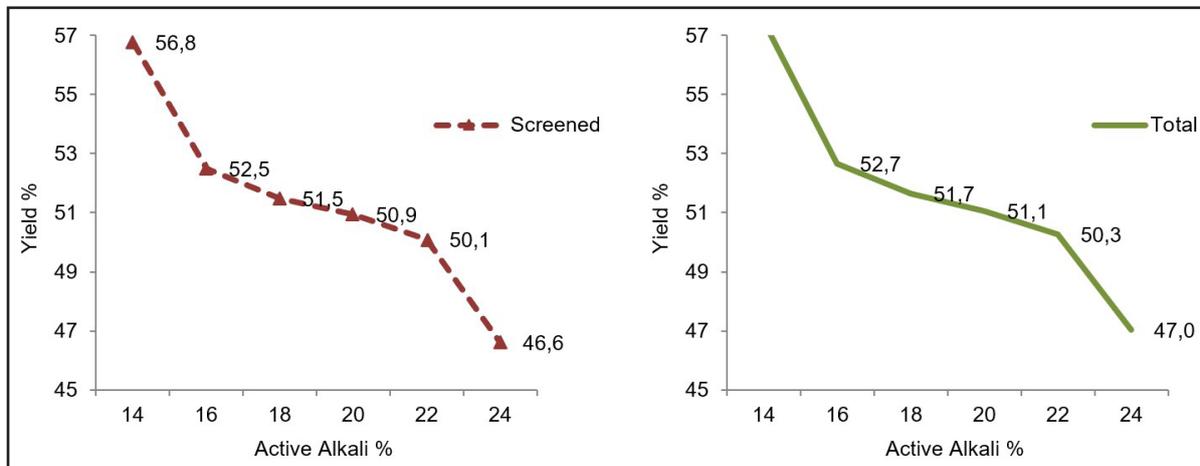
3.2 Kraft pulping

The chemical analysis and basic wood density of clone and SPA samples showed that both are very similar. Therefore, only wood chips from SPA were used to perform the kraft pulping.

Under the established pulping conditions, *Acacia mearnsii* showed a good performance over the kraft pulping. Figures 3 and 4 depict the yields (total and screened), and kappa number, respectively.

Wood is the main cost of a pulp mill (SIXTA, 2006); thus, pulp yield is possibly a decisive economic factor. Therefore, it is important that the pulping conditions are optimal to reach maximum yield, leading to a cost-effective and viable process.

Figure 3 – Total and screened yields of *Acacia mearnsii* pulps as a function of active alkali load



Source: Authors (2017)

Figure 3 shows that the yield decreases as the active alkali is increased. The highest pulp yield (total yield of ~ 57% and screened yield of ~ 56%) was achieved when AA of 14% was applied, which was the lowest alkali charge studied. On the other hand, the lowest yield was obtained when the highest AA (24%) was applied (total yield of ~ 47% and screened yield of ~ 46%). According to Klock *et al.* (2013), when cooking temperature and time are kept constant and the active alkali (AA) is increased, lower yields, residual lignin, and rejects are obtained. The ions OH^- and HS^- besides degrading lignin also degrade some of the carbohydrates, especially those of low molecular weight (ALMEIDA ; SILVA JÚNIOR, 2004); which explains the lower pulp yields when higher AA were applied. Despite the decrease in pulp yield, *Acacia mearnsii* showed a satisfactory pulp yield, regardless of the active alkali applied.

In this study, high pulping yields were found for *Acacia mearnsii* wood when compared to values reported in the literature for the same species. Marinho *et al.* (2017) produced pulp from *Acacia mearnsii* and obtained a yield of 47.62% and kappa number of 12.4 by the kraft process with 20% of AA and 25% of sulfidity. As shown in Figures 3 and 4, when the active alkali load of 20% was applied to the *Acacia mearnsii* wood, the pulp yield was 50.1% and kappa number was 13.7.

Muneri (1997) compared pulp yield of pulps produced from *Acacia mearnsii* (323 kg/m³) and from *Eucalyptus grandis* (224 kg/m³), and found that *Acacia mearnsii* achieved superior yields. According to Chan (2015), the high yields obtained by *Acacia mearnsii* combined to its fibers dimensions show that this biomass is highly adequate for pulp production. The authors added that the acacia fibers are similar to *Eucalyptus* spp fibers in regard of length and width.

The high pulp yields (total and screened) obtained in this study (Figure 3) can be explained by the high carbohydrate content in the wood (Table 4), which was preserved when low AA was applied (14 to 18%). *Acacia mearnsii* showed superior pulp yields when compared to *Eucalyptus* sp that was evaluated by Colodette *et al.* (2002) and Trugilho *et al.* (2005). The formers obtained screened yield of 47.5% and kappa number of 18, whereas the others obtained a total pulp yield of 54.3% and kappa number of 16.3.

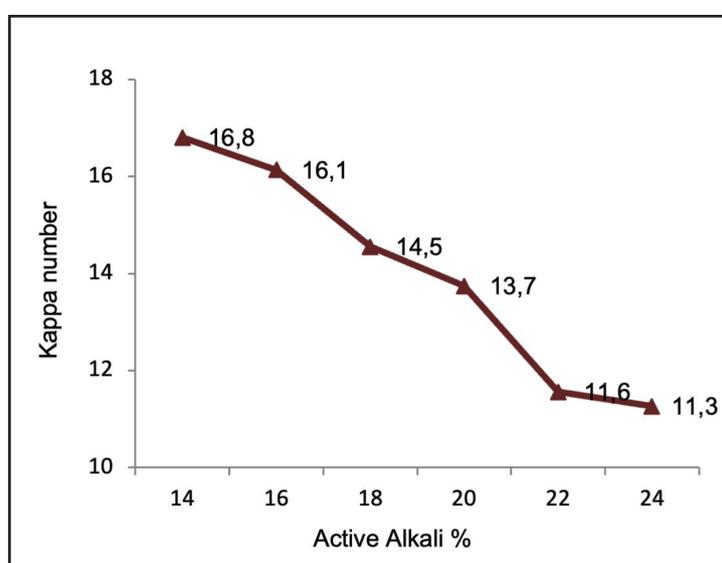
Other factors that contributed to the low demand of alkali are the low lignin content and high S/G ratio (Table 4). According to Foelkel (2008) and Marinho *et al.* (2017), *Acacia mearnsii* wood, has on average 20% of lignin and high S/G ratio. In addition, Pereira *et al.* (1994) studied the influence of S/G ratio on alkali demand over the kraft pulping process, and the authors identified that the higher the S/G ratio, the lower is the alkali demand, since S is more reactive and more susceptible to degradation by the ions OH⁻ and HS⁻ than G units.

The good performance of *Acacia mearnsii* over the kraft pulping was also confirmed by the greater lignin removal during process; i.e. low kappa numbers were achieved (Figure 4), as kappa number indicates the amount of residual lignin present in the pulp. Thus, the lower its value, the lower it is the lignin content in the pulp, consequently, bleaching will be easier and more economical (GOMES *et al.*, 2008).

Figure 4 shows that the kappa number decreased as the AA increased. The kappa number of bleaching grade pulps in Brazil typically varies from 16 to 18 (CORREIA; D'ANGELO; SILVA JUNIOR, 2019), which was achieved in this study (16.7) when low alkali charge (AA = 14%) was applied. The lowest kappa number observed was 11.26

(AA = 24%), with a screened yield of 46.6%. In addition, it was possible to produce pulp with kappa number of 11.5 when high alkali charge was applied (AA = 22%), and yet, the yield was satisfactory (screened yield of 50.1%). However, when the active alkali varied from 22 to 24%, an inexpressive kappa number reduction (from 11.6 to 11.3) was observed, and the screened yield decreased from 50.1 to 46.6%. Thus, one can infer that AA at 22% is the optimal alkali charge for *Acacia mearnsii* when the objective is the maximum removal of lignin over the kraft pulping, and still obtain a good yield.

Figure 4 – Kappa number of *Acacia mearnsii* pulps as a function of active alkali load



Source: Authors (2017)

It is important to mention that the low lignin content and high S/G ratio are determining factors for the low content of residual lignin in the pulps (SIXTA, 2006; BARBOSA; MALTHA; SILVA, 2008).

Although the pulp yield and the kappa numbers obtained in this study are suitable for the pulp and paper industry, there are other parameters inherent to the pulping process that should be evaluated, such as the rejects and pH of the black liquor (Table 6). Rejects are oversized materials that did not pass through the plate during the screening performed after the pulping process. These materials consist mainly of undercooked wood chips, knots, barks and impurities (BIERMANN, 1996; SIXTA, 2006).

Table 6 – Pulping rejects and pH of the black liquor

Active alkali (%)	Rejects (%)	pH
14	0.2	10.79
16	0.1	11.18
18	0.1	11.37
20	0.1	11.20
22	0.1	11.17
24	0.4	11.15

Source: Authors (2017)

The wood chips used for pulping in laboratories are usually more homogeneous than commercial wood chips because of the manual screening (removal of knots, barks, impurities, and over, and undersized chips). Thus, since the *Acacia mearnsii* chips used in this investigation were obtained from a wood yard, and no further screening was performed, the percentage of rejects is representative of the industrial process. Brazilian pulp mills work with percentage of rejects of ~ 0.5% for kappa number of 16-18, which is higher than the amount observed for *Acacia mearnsii*.

Besides pulp yield and pulp quality, the properties of generated black liquor must be taken into consideration. This process stream is composed of residual inorganic chemicals, various wood extractives and degradation products from delignification reactions and fragmentation of carbohydrates (SINGH; ANAYA, 2007). Typically, the kraft black liquor is combusted in a recovery boiler to retrieve the original chemicals (NaOH and Na₂S) with concomitant production of steam and power from the dissolved organics.

There was no major difference between the cooks on the regard of pH. Silva Junior and Brito (2008) pointed out that at the end of kraft pulping the pH varies from 10 to 12, which was observed in this study. Moreover Biermann (1996) stated that pH should be kept relatively high, to avoid lignin reprecipitation, which can negatively affect the bleaching process.

4 CONCLUSIONS

Acacia mearnsii clone and SPA wood samples showed basic density of ~ 0.544 g/cm³, which is considered a suitable density for the pulp and paper industry. The chemical analysis showed low lignin content (~ 16.7%), high S/G ratio (~ 2.8), low ash content (~ 0.35%) and high carbohydrates content (~ 77%).

The best result of active alkaline charge was 14%, which resulted in high screened pulp yield (~ 57%) and a satisfactory kappa number (16.7). In addition, this condition generated low rejects (0.2%).

Overall, *Acacia mearnsii* is an outstanding source of short fibers for pulp manufacture based on the wood quality and technological parameters evaluated in this work.

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