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EFFECT OF RESIDUAL EFFECTIVE ALKALI ON EUCALYPTUS KRAFT PULP YIELD AND CHEMISTRY

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EFFECT OF RESIDUAL EFFECTIVE ALKALI ON EUCALYPTUS KRAFT PULP YIELD AND CHEMISTRY

HIGHLIGHTS

The low-REA cooks showed higher pulp yield, xylan yield, cellulose yield and viscosity.

The lignin-HexA free screen yields were about similar in the kappa range of 18-26.

The low-REA cooks required about 20% less EA than high-REA ones to achieve the kappa.

Among the various woods, *E. globulus* was the easiest to delignify.

ABSTRACT

The impact of residual effective alkali (REA) and pulp delignification degree on Eucalyptus kraft pulp yield and chemistry was investigated. In this study four types of eucalypt clones were evaluated. The eucalypt woods were cooked to kappa numbers of 14 ± 1, 18 ± 1, 22 ± 1 and 26 ± 1 using two different ranges of REA, namely: low-REA (1-2 g·L^{-1}) and high-REA (8-9 g·L^{-1}). In general, the low-REA cooks lead to pulps of higher yield, viscosity and xylans content and lower brightness and hexenuronic acid (HexA) content, in relation to the high-REA cooks. In addition, the low-REA cooks required about 20% less effective alkali to achieve the target kappa, in spite of demanding about 50% more H-factor. Similar trends were observed for the other woods and kappa values evaluated, but the level of gains varied substantially among woods and delignification degrees. Among the various woods, *E. globulus* was the easiest to delignify. There was a trend of higher brown pulp yield for the cooks terminated at higher kappa in the range of 14-26, but the lignin-HexA free screen yields were about similar in the kappa range of 18-26 for a given wood type.

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INTRODUCTION

Kraft pulping is the most widely used process for production of chemical pulps (Gullichsen & Fogelholm, 2000). Wood chips are treated with a strong alkaline solution composed mainly of HO^- and HS^- ions, at temperatures about 150 – 170 °C (Pinto, et al., 2005). Several process parameters influence the chemistry and efficiency of alkaline delignification, including time/temperature (H-factor), effective alkali charge (EA), sulfidity, etc. These parameters affect the characteristics of the resulting pulp regarding the nature and content of its main components, namely: cellulose, hemicelluloses and lignin (Colodette et al., 2002).

During the kraft process, wood delignification is accompanied by simultaneous and undesirable dissolution of carbohydrates mainly by alkaline hydrolysis and sequential elimination of the terminal reducing end groups (Nieminen et al., 2014). Hemicelluloses are more susceptible to alkaline hydrolysis than cellulose due to their low degree of polymerization, amorphous state, and accessibility to the pulping liquor. Therefore, the loss of hemicelluloses is responsible for a significant part of the total yield loss observed during Kraft pulping (Clark, 1985; Sjöström, 1993). The main hardwoods hemicellulose is the O-acetyl-4-O-methylglucuronoxylan (Hutterer et al., 2016).

Increment in pulp yield is a major goal of a chemical process, since it allows increased mill throughput and reduced specific wood consumption. For this purpose, the main approaches to meet such goal are: retarding or avoiding the carbohydrate degradation reactions, increasing delignification rate, and enhancing the mass transfer phenomenon during cooking (Colodette and Gomes, 2014). In this context, lowering the residual effective alkali (REA) at end of cook appears as an interesting alternative to enhance kraft pulping performance, since allows a higher pulp yield by xylan precipitation onto the fibers (Goyal, 2017; Pinto et al., 2005). Currently the REA varies between 4- 18 g·L^{-1} for various mills. However, the range of 7-9 g·L^{-1} is more common. For some mills the REA target can be lowered without affecting the operation of evaporator and the recovery boiler (Goyal, 2017).

Kraft cooking at low-REA presents certain economic advantages because the low EA demand implies less causticizing load, thus decreasing costs in the recovery cycle (Goyal, 2017; Hansson and Hartler 1969; Hanna et al.1998). On the other hand, there are some drawbacks. Cooking at low-REA demands higher H-factors, which can be provided by either increasing the cooking reaction time or the temperature. However, the increase in temperature results in larger steam consumption and therefore is economically disadvantageous (Nesselrodt, et. al., 2015).

Another issue related to low-REA cooking is the potential risk of lignin precipitation, which may have considerable consequences in the bleaching costs and in the pulps bleachability as well as in the black liquor management due its increased viscosity with consequent system (Goyal, 2017; Hansson and Hartler 1969; Hanna et al.1998). However, Goyal (2017) showed that the cooking with low-REA did not show any appreciable difference of bleachability of the pulps, between pulps cooked with low-REA compared to high-REA pulps, and always results in higher pulp yield at a given delignification degree. Based on these results, a range of REA is recommended no loss on bleaching and with satisfactory pulp yield. Therefore, when considering low-REA cook one must balance the benefits and drawbacks.

Another important aspect linked to the increment in pulp yield is the kappa number itself. A very old cooking rule states that terminating a cook at high kappa number results in high pulp yield (Segura et al., 2016; MacLeod, 2007). Although this rule is very true when comparing total pulping yields, it is not so reliable for comparing to screened yields. Yield comparisons at different kappa numbers are usually not fair unless the results are compared at fixed REA and only lignin and HexA-free screen yield (Lignin HexA- free screen yield) be considered. Fair cooking yield comparison shall be done with the screened yield and not total yield because rejects are not fibers and they are usually discarded or very poorly reused in subsequent pulping cycles. In addition, if bleached pulp grades are sought after, one must compare the screen yields discounting their contents of lignin and HexA, the so-called lignin and HexA-free screened yield. This is necessary because during bleaching both lignin and HexA are largely removed and their weight shall not be accounted for in the yield measurements.

Besides, it is of paramount importance that cooking results be compared at similar REA, otherwise the yield results are meaningless (Colodette and Gomes, 2014). The only way to meet these constraints is by playing with both effective alkali charge and cooking time-temperature (H-factor) so that at the end of the cook, different kappa numbers are achieved at similar REA. This is exactly what was done in this study and it is a novelty in relation to previous studies.

In addition, wood type can also substantially affect pulp yield, as well as quality of the brown pulp, because *Eucalyptus* wood-fiber characteristics may vary substantially among the various species and clones as well as with age (Magaton et al., 2009). Thus, the pulping can affect in different way its composition, like as residual lignin nature, pulp carbohydrate composition, and the contents of alkali-leachable lignin and HexA present in hardwood kraft pulps (Colodette, 2002). Therefore, in this study was used four different types of *Eucalyptus*

wood, typically used in pulp manufacture, for the greater reliability of the results obtained.

In this context, the objective of this study was to evaluate the impact of low and high residual effective alkali (1-2 and 8-9 g·L^{-1} NaOH), and pulp degree of delignification (kappa number 14-26) on the performance of kraft cooking *Eucalyptus* woods typically used in pulp manufacture.

MATERIAL AND METHODS

The feedstock consisted of wood chips from *E. urophylla* x *E. grandis* hybrid, seven year old, grown in Brazil, and wood chips from *E. nitens* and *E. globulus*, sixteen years old, *E nitens* x *E. globulus* hybrid, twelve years old, all grown in Chile. The chips were classified according and air-dried conditioned SCAN-CN 40:94 standard procedure, dried to about 15% moisture, and stored for further use. A fraction of the air-dried accepts were used to evaluate the wood chemical composition. The chips were converted into sawdust in a knife-mill (Willey Co, USA), classified according to TAPPI T257cm-85 standard and air-dried to ~10% moisture.

The chemical composition was carried out on extractive-free wood sawdust (T280 pm-99). The content of acid-soluble lignin (Goldschmid, 1971), acid-insoluble lignin (T222 om-98), lignin syringyl/guaiacyl ratio (Lin and Dence, 1992), ash content (Tappi 211 om-93), sugars content (Wallis et al., 1996), total uronic acid (Scott 1979) and acetyl groups (Solár et al., 1987) were quantified. The wood basic density was measured according to SCAN-CM46:92 standard procedures.

The kraft cooking of the four *Eucalyptus* woods was performed in duplicate in a 7-L MK digester with 500 g of chips, oven dry (od) equivalent. The cooks were carried out with a liquor/wood ratio of 4 L:1 kg, 30% sulfidity, maximum temperature of 165 °C, 70-min time-to-temperature and variable effective alkali charge and time-at-temperature to meet the kappa number targets of 14±1, 18±1, 22±1 and 26±1 and the low (1-2 g·L^{-1} NaOH) and high (8-9 g·L^{-1} NaOH) residual effective alkali (REA) for the various woods. By varying the time at the maximum temperature of 165 °C (H-factor) and the EA charge applied, using the trial-and-error technique, it was possible to meet the desired REA ranges at given kappa numbers. At the end of each cook, the chips were discharged and disintegrated in a 20-L hydrapulper at 2% consistency, washed and screened in an equipment (Voith Co., Germany) garnished with a flat screened of 0.2 mm slots, and at the end of this stage the rejects were collected. The screened pulps were analyzed for extractives content (TAPPI T280 pm-99), ash content (TAPPI T-211 om-93), kappa number (TAPPI T236 cm-85), HexA content (TAPPI T282 pm-07), viscosity (SCAN-CM 15:99), pentosans (TAPPI T280 om-99), sugar composition (SCAN- CM 71:09) and brightness (ISO 2470). From the

values of kappa number and HexA, the corrected kappa number values (only lignin) were determined according to the procedure described by Li and Gellerstedst (1997). The black liquor was analyzed for residual effective alkali (SCAN-N 33:94).

RESULTS

Basic density and chemical composition of wood

Basic density and chemical composition of the various *Eucalyptus* woods investigated in this study are presented in Table 1.

Kraft pulping

Impact of REA, kappa number and wood type on EA charge and H-factor requirements

The values of H-factor and EA charge required to achieve kappa numbers of 14-26, with low-REA and high-REA, for the four wood types are show in Figure 1.

TABLE 1 Basic density and chemical composition of Eucalyptus wood.

Wood trait	E. nitens x E. globulus hybrid	E. nitens	E. globulus	E. urophylla x E. grandis hybrid
Basic density (kg·m^{-3})	493	521	562	452
Ash, (%)	0.31	0.21	0.31	0.26
Extractives in acetone (%)	1.9	1.5	2.2	1.3
Acid-insoluble lignin (%)	20.6	20.7	19.5	24.0
Acid-soluble lignin (%)	5.6	5.0	5.2	4.1
Total lignin (%)	26.2	25.7	24.7	28.1
Lignin S/G ratio	4.7	3.4	4.8	2.9
Acetyl Groups (%)	2.5	2.3	2.3	2.1
Total uronic acids (%)	2.7	3.1	2.5	2.8
Glucans (%)	48	49	52.0	52.1
Xylans (%)	16.2	16.7	14.2	11.6
Galactans (%)	0.9	0.9	1.4	1.3
Mannans (%)	1.2	1.4	1.0	0.8
Arabinans, (%)	0.3	0.2	0.3	0.2
Total Sugar (%)	66.6	68.2	68.9	66
Cellulose^a (%)	46.8	47.6	51.0	51.3
Hemicelluloses^b (%)	25.0	26.0	22.7	19.6

Cellulose^a = total glucans – glucans from glucomannans (1/1); hemicelluloses^b = xylans + mannans + galactans + arabinans + 2x glucans from glucomannans) + uronic acids + acetyl groups.
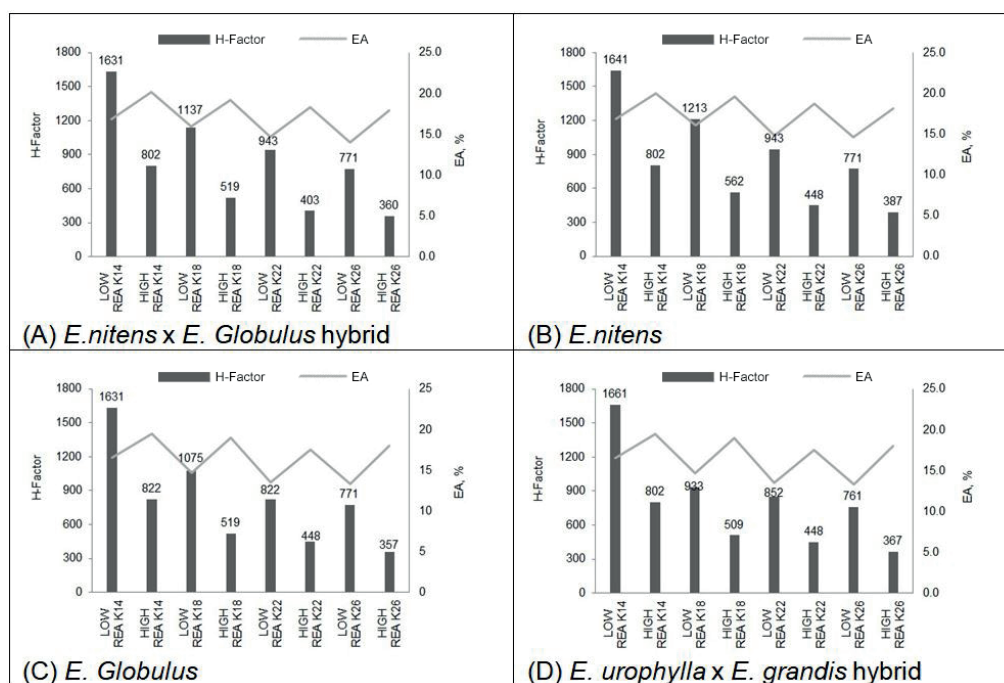
FIGURE 1 Effect of low and high residual effective alkali and kappa number variations on effective alkali charge and H factor requirements in kraft pulping of four *Eucalyptus* woods.

Impact of REA, kappa number and wood type on lignin-HexA free pulp screen yield

By considering pulps of different kappa numbers and similar REA, it was possible to investigate the impact of kappa number on lignin-HexA free screen yield and establish why different kappa numbers produce different yields (Table 2).

Impact of REA, kappa number and wood type on brown pulp chemical and physical compositions

The brown pulp chemical and physical characteristics are reported in Figure 2, Figure 3 and Table 3. The brown pulp xylan content refer to the xylan backbone only.

DISCUSSION

Wood density and chemical composition

Basic densities were very different among the samples. The highest and lowest measured densities were for *E. globulus* (562 kg·m⁻³) and *E. urophylla* x *E. grandis* hybrid (452 kg·m⁻³), respectively. These density values are typical of *Eucalyptus* woods used in pulp manufacture in South America (Gomide et al, 2005). The acetone extractive contents varied in the range of 1.3-2.2%, with maximum and minimum values for *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively. In general, these levels of extractives may be considered low compared to other tropical hardwoods (Gomide et
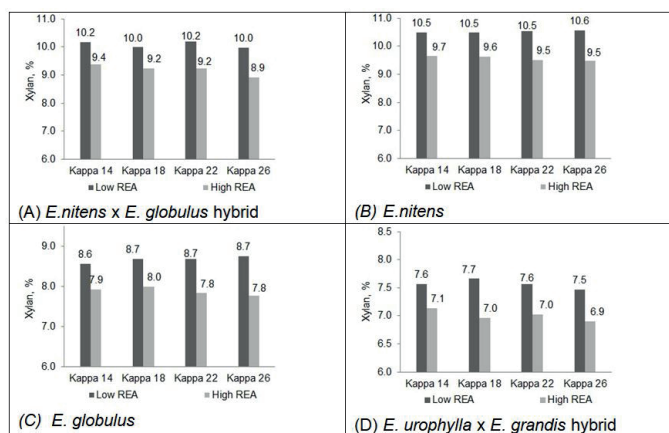

FIGURE 2 Effect of low and high REA and kappa number variations on pulp xylan backbone contents in kraft pulping of four *Eucalypt* woods.

TABLE 2 Effect of kappa number on screened yield and lignin HexA-free yields in low-REA and high-REA kraft pulping of four *Eucalypt* woods.

Parameter and Results								
E. nitens x *E. globulus* hybrid								
Kappa Number	14		18		22		26	
REA (g·L⁻¹)	1.0	8.2	1.2	8.1	1.0	8.3	1.1	8.0
Black liquor (pH)	12.1	12.8	12.1	12.7	12.2	12.8	12.1	12.8
Screen yield (%)	51.7	50.8	52.7	51.6	53.1	51.7	53.1	51.1
[a]Lig-HexA Free Screen Yield (%)	50.3	49.4	50.9	49.9	51.0	49.7	50.6	48.8
Reject (%)	0.0	0.2	1.3	1.2	2.6	3.0	4.0	4.5
[b]Δ due to decrease REA	0.9	1.0	1.3	1.8				
E. nitens								
Kappa Number	14		18		22		26	
REA (g·L⁻¹)	1.3	8.0	1.0	8.9	1.0	9.0	1.0	8.4
Black liquor (pH)	12.1	12.7	12.1	12.8	12.2	12.8	12.2	12.8
Screen yield, %	52.2	51.4	54.1	53.0	54.9	53.5	54.6	52.8
[a]Lig-HexA Free Screen Yield (%)	50.9	50.0	52.4	51.3	52.8	51.4	52.1	50.4
Reject (%)	0.1	0.3	0.3	0.4	1.1	1.1	2.8	3.0
[b]Δ due to decrease REA	0.9	1.1	1.4	1.7				
E. globulus								
Kappa Number	14		18		22		26	
REA (g·L⁻¹)	1.3	8.2	1.2	8.1	1.0	8.5	1.0	8.7
Black liquor (pH)	12.2	12.7	12.1	12.7	12.1	12.8	12.1	12.8
Screen yield (%)	53.9	53.0	54.8	53.7	55.1	53.7	54.9	53.2
[a]Lig-HexA Free Screen Yield (%)	52.4	51.6	52.9	51.9	52.9	51.6	52.3	50.7
Reject (%)	0.1	0.3	1.5	1.2	3.0	3.2	3.8	4.4
[b]Δ due to decreased REA	0.9	1.0	1.3	1.6				
E. urophylla x *grandis* hybrid								
Kappa Number	14		18		22		26	
REA (g·L⁻¹)	2.0	9.0	1.8	9.0	1.0	8.3	1.1	9.0
Black liquor (pH)	12.1	12.8	12.1	12.7	12.1	12.7	12.1	12.8
Screen yield (%)	52.5	52.0	53.7	52.7	54.3	52.9	54.3	52.4
[a]Lig-HexA Free Screen Yield (%)	51.1	50.6	51.9	51.0	52.2	50.8	51.8	50.0
Reject (%)	0.0	0.2	0.4	0.6	1.2	1.5	2.1	2.3
[b]Δ due to decreased REA	0.5	0.9	1.3	1.8				

[a]Lignin-HexA Free Screen Yield = Screen yield – (lignin yield + HexA yield). [b]Δ Lignin-HexA Free Screen Yield due to decrease REA..
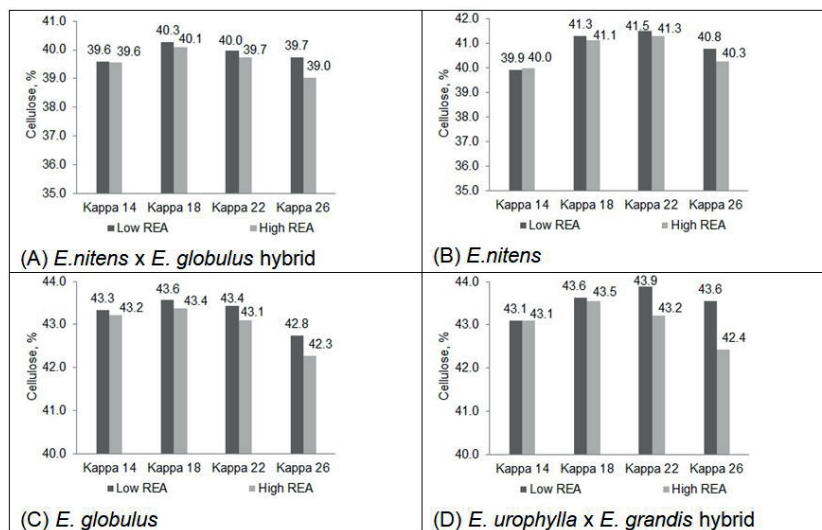

FIGURE 3 Effect of low and high REA and kappa number variations on pulp cellulose contents in kraft pulping of four eucalypt woods.

TABLE 3 Contents of lignin, HexA and MeGlcA and physical characteristic of unbleached pulps, viscosity and brightness, derived from cooks to kappa numbers of 14-26 at low-REA and high-REA of four *Eucalyptus* wood species.

Parameter and Results								
E. nitens x *E. globulus* hybrid								
Kappa Number	14		18		22		26	
Residual Effective Alkali (g·L^{-1})	1.0	8.2	1.2	8.1	1.0	8.3	1.1	8.0
[a]Lignin content (%)	1.2	1.3	2.0	1.9	2.7	2.6	3.4	3.2
HexA content (mmol·kg^{-1})	63	68	58	62	49	57	41	54
MeGlcA (%)	1.1	0.9	1.3	1.1	1.6	1.4	1.9	1.6
Viscosity (dm^3·kg^{-1})	1059	990	1189	1096	1280	1181	1389	1270
Brightness (%ISO)	33.0	35.6	30.4	34.1	29.2	32.9	28.4	32
E. nitens								
Kappa Number	14		18		22		26	
Residual Effective Alkali (g·L^{-1})	1.3	8.0	1.0	8.9	1.0	9.0	1.0	8.4
[a]Lignin content (%)	1.3	1.2	2.0	1.9	2,7	2.6	3.3	3.2
HexA content (mmol·kg^{-1})	61	67	57	60	50	55	46	53
MeGlcA (%)	1.0	0.8	1.2	1.0	1.4	1.2	1.6	1.3
Viscosity (dm^3·kg^{-1})	1035	967	1191	1100	1292	1176	1400	1280
Brightness (%ISO)	33.4	37.8	31.3	36.2	30.4	34.8	29.9	34.3
E. globulus								
Kappa Number	14		18		22		26	
Residual Effective Alkali (g·L^{-1})	1.3	8.2	1.2	8.1	1.0	8.5	1.0	8.7
[a]Lignin content (%)	1.4	1.3	2.0	1.9	2.7	2.6	3.4	3.2
HexA content (mmol·kg^{-1})	54	58	51	55	45	53	40	51
MeGlcA (%)	1.1	0.9	1.3	1.0	1.5	1.2	1.6	1.4
Viscosity (dm^3·kg^{-1})	1090	1034	1184	1110	1309	1190	1425	1277
Brightness (%ISO)	29.3	31.9	28.0	31.4	26.7	28.5	24.8	27.7
E. urophylla x *grandis* hybrid								
Kappa Number	14		18		22		26	
Residual Effective Alkali (g·L^{-1})	2.0	9.0	1.8	9.0	1.0	8.3	1.1	9.0
[a]Lignin content (%)	1.3	1.1	1.9	1.8	2.6	2.5	3.4	3.1
HexA content (mmol·kg^{-1})	66	74	63	66	55	66	41	63
MeGlcA (%)	0.9	0.8	1.2	1.0	1.4	1.2	1.6	1.4
Viscosity (dm^3·kg^{-1})	1009	963	1180	1130	1311	1240	1400	1330
Brightness (%ISO)	34.8	37.4	32.9	36.8	31.2	35.7	29.9	34.2

[a]Lignin content = 0.15 x (k – 0.086 x CHexA), where k is the kappa number, and CHexA is HexA content in mmol·kg^{-1} (Li & Gellerstedt,1997)

al, 2005). The ash content, which corresponds to the wood inorganic materials, was similar for *E. nitens* x *E. globulus* hybrid, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, with value of 0.3%, while for *E. nitens*, the ash content was slightly smaller, with value of 0.2%. Total carbohydrate content ranged from 66% to 69%, with glucan and xylan as the major components. There were slight variations in the contents of arabinans, galactans and mannans among the various wood species but overall the contents of these sugars were irrelevant, which is positive given their low stability throughout kraft cooking. Glucans content varied in the range of 48-52% with the higher values for *E. globulus* and the hybrid of *E. grandis* x *E. urophylla*. The xylan contents varied in the range of 11.6-16.7% with higher values for *E. nitens* and the hybrid of *E. globulus* x *E. nitens*. Similar trends have been reported elsewhere (Magaton et al., 2006; Pinto et al., 2005). Total wood lignin content varied from 24% to 28% with the lowest value for *E. globulus* and the highest for *E. urophylla* x *E. grandis* hybrid. The lower content of lignin in *E. globulus* compared to others wood has been reported elsewhere (Santos et al., 2012; Pinto et al., 2005; Rencoret et al., 2007; Magaton et al., 2006). The low wood lignin content is quite favorable for bleached pulp production because it reduces wood and chemical demand, which are the most relevant production costs components (Gomide 2005; Pinto et al., 2005; Rencoret et al., 2007). The wood contents of acetyl (2.1-2.5%) and uronic acid (2.5-3.1%) groups were in the range of values reported elsewhere (Magaton et al., 2009). More acetyl groups were found in the woods containing more xylans as should have been expected. However, this trend was not observed for the uronic acids. In fact, the *E. urophylla* x *E. grandis* hybrid wood, which contained only 11.6% xylans, presented 2.8% of uronic acid groups, while the *E. nitens* x *E. globulus* hybrid had 16.2%

xylans and only 2.7% uronic acids. The cellulose (46.8-51.3%) and hemicelluloses (19.6-26%) contents were very different among the various wood samples. The highest and lowest cellulose contents were measured for *E. urophylla* x *E. grandis* hybrid (51.3%) and *E. nitens* x *E. globulus* hybrid (46.8%), respectively. For hemicelluloses content, the highest and lowest values were measured for *E. nitens* (26%) and *E. urophylla* x *E. grandis* hybrid (19.6%), respectively.

Kraft pulping

Impact of REA, kappa number and wood type on EA charge and H-factor requirements

It is observed that the EA charge and H-factor were largely influenced by the target REA, with higher H-factors and low EA charge requirements for the low-REA cooks and the opposite for the high-REA cooks. Kraft cooking at low-REA presents certain economic advantages because the low EA demand implies less causticizing load, thus decreasing costs in the recovery cycle. In addition, cooking with low EA tend to preserve carbohydrates during cooking with potential yield and pulp viscosity gains (Pinto et. al., 2005). On the other hand, cooking at low-REA demands higher H-factors, which can be provided by either increasing the cooking reaction time or the temperature. In a mill scale, the natural choice would be increasing the temperature because the increase in reaction time would decrease mill throughput. The increase in temperature results in larger steam consumption and therefore is economically disadvantageous. Therefore, when considering low-REA cook one must balance the cost savings due to reduced causticizing load against the increase in steam consumption or the increase in reaction time (Nesselrodt, et. al., 2015). This is a difficult calculation to be mendeadly when we consider the different needs of mills. For some mills the REA target can be lowered without affecting the cost the operation of evaporation, the recovery boiler and mill throughput. For example, for some mills, the lower white liquor requirement, hence, an energy savings in lime kiln, is a positive factor if recovery boiler limited. This can permit the increase in reaction time can be possible without change about costs.

In average, considering all four woods, the low-REA cooks required about 20% less effective alkali to achieve the target kappa in relation to the high-REA cooks. For example, for the *E. urophylla* x *E. grandis* hybrid wood, the low-REA cooks allowed for EA charge savings of 26 and 15% for kappa numbers 26 and 14, respectively, in relation to the high-REA cooks. However,

low-REA cooks demanded, in average, about 50% more H-factor in relation to the high-REA cooks, considering all four *Eucalyptus* woods and kappa number values. The maximum and minimum H-factor increases due to low-REA cooks were 57% and 45% for *E. nitens* x *E. globulus* hybrid cooked at kappa 22 and 18, respectively. In addition, in the kappa number range investigated, 14-26, the EA charge and H-factor requirements tend to decrease as the reduction of delignification degree. No significant effect of wood type was observed on EA charge and H-factor requirements for a given REA and kappa number value.

Impact of REA, kappa number and wood type on lignin-HexA free pulp screen yield

In order to compare pulping screed yield at different kappa numbers, the REA at the end of the cooks must be similar and only lignin and HexA-free screen yield must be considered. The only way to meet these constraints is by playing with both effective alkali charge and cooking time-temperature (H-factor) so that at the end of the cook, different kappa numbers are achieved at similar REA. This is exactly what was done in this study.

Various studies have indicated that higher brown pulp screen yields are obtained when cooking is terminated at higher kappa numbers (Segura et al., 2016; Colodette and Gomes, 2014; Colodette et al., 2007). This trend was also found in our study, except for kappa number 26, due to high reject content, as can be seen in Table 2. However, if one considers the lignin-and HexA-free screen yield (bleached yield), this trend is not so clear. The results presented in Table 2 show that the lignin-HexA free screen yield tend to remain similar with increasing kappa number, regardless of raw material and REA, except for the kappa number 14 pulp that showed lower yields in relation to those of kappa 18-26 pulps. For example, for *E. urophylla* x *E. grandis* hybrid cooked at low-REA, the lignin- and HexA-free yields were of 51.1, 51.9, 52.2 and 51.8% for kappa numbers of 14, 18, 22 and 26, respectively. Thus, the removal of lignin is the main cause of yield decrease in the kappa range of 18-26. For the kappa number 26, the reject content increased in relation to other kappa numbers, this is explaining the decreasing of the yield.

According to Santiago (2008), a decreasing in the effective alkali charge leads to increased pulping yield and selectivity thereof. This behavior was notable in this paper, since an increase maximum of 1.8% in the lignin- and HexA-free pulp screen yield was achieved at kappa number 26 for the low-REA cook, for both hybrids of *E.*

nitens x *E. globulus* and *E. urophylla* x *E. grandis* woods. For kappa number 18, more commonly required by mill, a smaller yield gains were achieved in the order of 1.0% for *E. nitens* x *E. globulus* hybrid, 1.1% for *E. nitens*, 1.0% for *E. globulus* and 0.9% for *E. urophylla* x *E. grandis* hybrid (Table 2). The cooking with low residual effective alkali results higher yield, likely due to improved preservation of hemicelluloses and/or partial precipitation of dissolved xylans onto the fibers (Santiago and Neto, 2008; Colodette, et al., 2002).

As the pulping conditions, among woods, were very similar for a fixed kappa number, yield comparisons among the various woods is fair and possible. The maximum values of lignin-HexA free screen yields were 52.9, 52.8, 52.2 and 51.0% from *E. globulus* (kappa number 18), *E. nitens*, *E. urophylla* x *grandis* hybrid, *E. nitens* x *E. globulus* hybrid (kappa number 22), respectively. It is worth noting that at the high-REA the same yield trends among the various woods was observed, except the absolute yield values were in general lower. *E. globulus* gave the highest yields and the *E. globulus* x *E. nitens* hybrid the lowest. The relative content of lignin in wood certainly contribute to different pulping performances of different *Eucalyptus* species, and, the differences observed between *E. globulus* and *E. nitens* x *E. globulus* hybrid are clearly related to this factor (Table 1). Also, it is worth noting that, despite there is the potential risk of lignin precipitation at low-REA cooking, that did not occur in this study, since the black liquor pH was about 12.2. According to Gomes (2001), at normal cooking conditions, the lignin precipitation occurs in pH lower that 12, being considerable in pH 9.5 In addition, the low-REA cooks can positively impact on other black liquor properties, with energy savings in black liquor evaporation due to high ratio organic to inorganic present in black liquor (Goyal, 2017; Hanna, 1998; Hanson and Hartler, 1969).

Impact of REA, kappa number and wood type on brown pulp chemical and physical compositions

The two main components of brown pulps are cellulose and hemicelluloses, with lignin and HexA representing a very small fraction of the pulp on a weight basis. The xylans are synonym of hemicelluloses in *Eucalyptus* kraft pulp. The contents of xylan backbone in the original woods were 16.2, 16.7, 14.2 and 11.6 % for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively (Table 1). The xylan backbone contents in the brown pulps produced in different kappa numbers at low-REA and

high-REA, on wood weight, varied from 8.9-10.2, 9.5-10.6, 7.8-8.7, 6.9-7.7% for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively. Hence, it is clear that the xylans retained in the pulp correlates to the original xylan backbone content present in the wood. Significant amounts of the xylan backbone were lost across kraft cooking, with the effect being more significant for the high-REA cooks. The xylan backbone loss across pulping, for the various kappa numbers and wood types, represented from 3.9% to 6.2% (wood basis) for low-REA cooks and from 4.5% to 7.3% (wood basis) for the high-REA cooks. In the low-REA cooks, considering all four kappa values, the relative xylan losses were 38, 37, 39 and 35%, respectively, for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid. In the high-REA cooks, the relative xylan losses were about 5% higher being 43, 43, 44 and 40%, respectively, for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid. No significant effect of kappa number value was observed on xylan retention for a given REA value, regardless of wood type. For example, for the *E. globulus* wood cooked at low-REA, the increase of kappa number from 14 to 26 resulted xylan losses of 39%, in both cases. Similar trends were observed for the other wood types. No effect on xylan removal in different kappa numbers, for the various *Eucalyptus* woods are explained by the REA, which was carefully kept constant. On the other hand, when the focus is to analyze the effect of REA, the low-REA cooks led to smaller xylans losses, suggesting that effective alkali charge play a key role in the stability and retention of this polysaccharide during the pulping process. Previous works concerning the impact low-REA cooks on carbohydrate dissolution of unbleached pulp have demonstrated significantly increased both total yield and viscosity, for similar kappa number, which was mainly attributed to higher carbohydrates retention, especially xylan (Santiago, 2008; Achrén et al., 1998).

The contents of cellulose in the original woods were 46.8, 47.6, 51.0 and 51.3 % for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively (Table 1). The cellulose contents in the brown pulps produced in different kappa numbers at low-REA and high-REA, on wood weight, varied from 39.0-40.3, 39.9-41.5, 42.3-43.6 and 42.4-43.9% for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively. Hence, it is clear that the cellulose retained in the pulp correlates to the original cellulose content present in the wood. A smaller amount of the cellulose was lost across

kraft cooking when compared to loss of xylan backbone, with the effect being more significant for the high-REA cooks. The cellulose loss across pulping, for the various kappa numbers and wood types, represented from 6.7% to 7.8% (wood basis) for low-REA cooks and from 7.0% to 8.3% (wood basis) for the high-REA cooks. In the low-REA cooks, considering all four kappa values, the relative cellulose losses were 15.0, 14.1, 15.3 and 15.1%, respectively, for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid. In the high-REA cooks, the relative cellulose losses were in average 0.6% higher being 15.4, 14.7, 15.7 and 16.2%, respectively, for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid. No significant effect of kappa number value was observed on cellulose retention for a given REA value, regardless of wood type, except for kappa number 26. For example, for the *E. globulus* wood cooked at low-REA, the increase of kappa number from 14 to 26 resulted cellulose losses of 15.1 and 16.1%, respectively. Similar trends were observed for the other wood types. The no effect on cellulose removal in different kappa numbers, for the various *Eucalyptus* woods are explained by the fixed REA, which was carefully kept constant. Already the difference found for kappa number 26 can be explained due to higher amount of reject obtained in the cooking. On the other hand, when the focus is to analyze the effect of REA, the low-REA cooks led to smaller celluloses losses, suggesting that effective alkali charge play a key role in the stability and retention of this polysaccharide during the pulping process. The higher cellulose loss in the high-REA cooks is explained by enhanced secondary peeling reactions in the presence of higher alkali concentration. In addition to xylans and cellulose, *Eucalyptus* brown pulp contains minor quantities of lignin, HexA and MeGlcA.

The lignin contents in the brown pulp produced in different kappa numbers and at low-REA and high-REA was calculated according to Li & Gellerstedt (1997). Higher amounts of the lignin were obtained for the low-REA cooks. The lignin content for the various kappa numbers and the four wood types, represented from 1.4% to 3.4% for low-REA cooks and from 1.1% to 3.1% for the high-REA cooks. As expected, the lignin content trends to increase as the kappa number increases in the range of 14-26. For example, for the *E. globulus* wood cooked at low-REA, the increase of kappa number from 14 to 26 resulted lignin content increase of 1.4 to 3.4%. Similar trends were observed for the other wood types. In general, no significant effect of wood type was observed on lignin content for a given REA and

kappa number value, except to *E. globulus* that present the higher values of lignin, since HexA content was the smallest. The effect on lignin content at low and high cooks, for the various *Eucalyptus* woods and different kappa numbers are explained by lignin precipitation (Colodette, 2002). On the other hand, when the focus is to analyze the effect of kappa number and wood type on lignin content, there are clear trend that the increase of the kappa number lead to increases lignin content regardless of wood. However, the lignin content at kappa number fixed, to a given wood type, depends of HexA content formed during pulping (Magaton et al., 2008).

Higher amounts of the HexA were obtained for the high-REA cooks. The HexA content for the various kappa numbers and the four wood types, represented from 40 to 66 mmol·kg^{-1} for low-REA cooks and from 51 to 74 mmol·kg^{-1} for the high-REA cooks. In the kappa number range investigated, the HexA content increases as delignification proceeds. For example, for the *E. globulus* wood cooked at low-REA, the increase of kappa number from 14 to 26 resulted HexA decrease of 54 to 40 mmol·kg^{-1}. Similar trends were observed for the other wood types. In general, no significant effect of wood type was observed on HexA content for a given REA and kappa number value, except to *E. globulus* that present the lower values of HexA. The smaller HexA content found in low-REA cooks in relation to high-REA cooks can be associated to decrease of the reactions rate HexA formation, since the EA charge is smaller to achieve target REA and the rate of formation/degradation of HexA was shown to depend essentially on HO^{-} (Gomide 2005; Hutterer et al., 2017). On the other hand, HexA content in pulps increased along the kraft pulping process due to adjusted the pulping time to obtain a target kappa number, while keeping the other pulping parameters at partially constant levels (Bergnor-Gidnert et al., 1998). The smaller amount of HexA in *E. globulus* in relation the others *Eucalyptus* species can be due to varying contents of 4-O-methyl- glucuronoxylans among species that influences the amount of HexA formed (Magaton et al., 2008).

The most of the uronic acids groups, present in hardwood, are 4-0-methylglycouronic acid group (MeGlcAs). Therefore, it was assumed in this study, that the uronic acid quantified in the pulp are all 4-0-methylglycouronic acid group (MeGlcA). Higher amounts of the MeGlcA were obtained for the low-REA cooks. The MeGlcA content for the various kappa numbers and the four wood types, represented from 1.1 to 1.9% for low-REA cooks and from 0.8 to 1.3% for the high-REA cooks. In the kappa number range investigated,

as kappa number decreases, the MeGlcA also decreases. For example, for the *E. globulus* wood cooked at low-REA, the increase of kappa number from 14 to 26 resulted MeGlcA increase of 1.1 to 1.6%. Similar trends were observed for the other wood types. In general, no significant effect of wood type was observed on MeGlcA content for a given REA and kappa number value, except to *E. nitens* x *E. globulus* hybrid that presented values slightly higher to kappa numbers 22 and 26. The higher MeGlcA content found in low-REA cooks in relation to high-REA cooks can be associated to smaller xylans losses and decreased formation rate of HexA, since the MeGlcA are the precursors of HexA (Gomes et al., 2014; Magaton, 2008). On the other hand, MeGlcA content in pulps increased as the kappa number increases due to adjusted the pulping time (decreasing of H-factor) to obtain a target kappa number, while keeping the other pulping parameters at partially constant levels (Monrroy et al., 2008). The higher amount of MeGlcA in *E. nitens* x *E. globulus* hybrid in relation the others *Eucalyptus* species can be due to varying contents of 4-O-methyl-glucuranoxilanas among species that influences the remaining amount of MeGlcA in pulp (Magaton et al., 2008).

A clear tendency of viscosity improvement in pulps from low-REA cooks was observed, representing relative estimated viscosity gains of 93 $dm^3 \cdot kg^{-1}$ for *E. nitens* x *E. globulus* hybrid, 91 $dm^3 \cdot kg^{-1}$ for *E. nitens*, 74 $dm^3 \cdot kg^{-1}$ for *E. globulus* and 50 $dm^3 \cdot kg^{-1}$ for *E. urophylla* x *E. grandis* hybrid in relation to pulps from high-REA cooks, when cooked to kappa number 18. The viscosity gains increase as the kappa number increases. For example, considering all four woods, the pulps cooked to kappa number 26 from low-REA cooks had the viscosity gains of about 120 $dm^3 \cdot kg^{-1}$. In the kappa number range investigated, 14-26, the viscosity loss increases as the kappa number decreases (delignification increases). For example, for the *E. globulus* wood cooked at low-REA, the decrease of kappa number from 26 to 14 resulted viscosity decrease of 1425 to 1090 $dm^3 \cdot kg^{-1}$. Similar trends were observed for the other wood types. In general, no significant effect of wood type was observed on viscosity for a given REA and kappa number value. The higher viscosity values found in pulps from low-REA cooks in relation to high-REA cooks is associated to higher preservation of cellulose due to possible decrease of alkaline hydrolysis reactions and consequently the secondary peeling reactions in the cellulose chains (Santiago, 2008; Santiago and Neto, 2008). On the other hand, viscosity in pulps decreased along the kraft pulping process due to higher degradation of the carbohydrate

chains (Gomide et al., 2011). Similar viscosity values found among the four wood types, for a given REA and kappa number value, can be due to keeping the pulping parameters at partially constant levels.

A negative impact on pulp brightness was caused by the decrease of REA concentration in the pulping process. For example, for the *E. globulus* wood cooked in kappa number 18, the cooks at low-REA in relation to high-REA resulted brightness decrease of 31.4 to 28 % ISO. As expected, in the kappa number range investigated, 14-26, the brightness increases as delignification proceeds. For example, the decrease of kappa number from 26 to 14 for the *E. globulus* wood cooked at low-REA, resulted brightness increase of 24.8 to 29.3% ISO. Similar trends were observed for the other wood types. Significant effects of wood type were observed on brightness for a given REA and kappa number value, manly for *E. urophylla* x *E. grandis* hybrid (32.9% ISO) and *E. globulus* (28% ISO) that present the higher and the smaller brightness, respectively, for brown pulps produced in kappa numbers 18 and at low-REA. The smaller brightness obtained in pulps from low-REA cooks in relation to high-REA cooks can be explained by the decrease in the content of aliphatic hydroxyl groups and the carboxyl groups in the residual lignin (Colodette et al., 2002). It was reported by Aurell and Hartler (1965) as well, that a low residual alkali concentration in the cook gives rise to pulps with a low brightness due to a formation of chromophoric structures in the lignin. Also, Hartler and Norrström (1969) demonstrated that applying a high H-factor to reach a given kappa number is accompanied by a low residual amount of β-O-4 structures in the residual lignin. On the other hand, brightness in pulps decreased as the reduction of delignification degree due to higher amount of residual lignin in the pulp (Gustavsson, 2006). The different brightness values found among the wood types studied, to a given REA and kappa number value can be explained by HexA and lignin content that composing the kappa number (Costa and Colodette, 2007).

CONCLUSIONS

This study investigates the effect of residual effective alkali (low and high) and pulp degree of delignification (kappa 14-26) on the performance of kraft cooking of four Eucalyptus woods. Regardless of wood type, low-REA cooks required about 20% less effective alkali than high-REA ones to achieve the target kappa values. Among the various woods, *E. globulus* was the easiest to delignify. There was a trend to higher brown

pulp screen yields for the cooks terminated at higher kappa number, in the range of 14-26, but the lignin-HexA free screen yields were about similar in the kappa range of 18-26. At 18±1 kappa, the low-REA cooks showed higher pulp yield (1.0%), xylan yield (0.8%), cellulose yield (0.2%) and viscosity (90 dm^3·kg^{-1}), in relation to the high-REA ones. There was a trend for higher preservation of pulp MeGlcA and lower formation of HexA in the low-REA cooks, with the opposite occurring for the high-REA ones. Low-REA cooks produced pulps of lower brightness.

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