# Impact of Sulfidity on the Kraft Pulping of *Eucalyptus*

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This study aimed to evaluate the influence of white liquor sulfidity on the efficiency of the kraft pulping process. For this study, *Eucalyptus* spp. chips were used. Laboratory cooking with variable sulfidity levels (0 to 40% at 5% intervals) was conducted under previously optimized conditions, aiming to obtain pulp with a Kappa number of 18 ± 0.9 and residual effective alkali between 9 and 12 $g \cdot L^{-1}$. At the end of each cook, Kappa number, solids generation, specific wood, and alkali consumption were evaluated. The sulfidity variation in white liquor influenced all analyzed parameters, and concerning the specific wood consumption, a distinct behavior was observed for the low sulfidity (S ≤ 19.52%) and high sulfidity regions (S > 19.52%). Based on the obtained results, the production of eucalyptus kraft pulp with white liquor sulfidity of approximately 20% is recommended.

*Keywords: Sodium sulfide; Obtainment of pulp; Kraft pulp; Soda process*

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## INTRODUCTION

In pulping chemical processes, the basic objective is the production of pulps with the dissolution of lignin, with the lowest possible damage to carbohydrates and to the process yield (Gomide 1979). Such processes are classified according to the pH and may be acidic or alkaline.

Alkaline chemical processes consist of wood chips treated with a strong alkaline solution called white liquor. Among these, there are soda and kraft processes. The kraft process is the most used by the pulp industry since the 1930s (Gomide 1979; Silva Júnior 1994; Silva 2001; Toucini 2013; Almeida 2014).

According to Rydholm (1965), in the kraft process, sodium sulfide is obtained by the transformation of sodium sulfate in the recovery boiler. Fresh sodium sulfate is added to the black liquor to recompose the process' alkaline charge.

Depending on the high charge of alkali, the pH at the beginning of kraft cooking is approximately 14, which makes more than half of sulfur be in ionized state as $S_2^-$. In the course of the process, $OH^-$ ion is gradually consumed by wood components. $S_2^-$ is hydrolyzed in $HS^-$ and $OH^-$, which will also react with the wood. At the end of cooking, almost all of the $S_2^-$ has been hydrolyzed to hydrosulfide ($HS^-$) and hydroxyl ($OH^-$) (Rydholm 1965). Therefore, it is desirable that at the end of cooking, the black liquor pH is between 10 and 12 (Vasconcelos 2005).

The sodium sulfide concentration present in the cooking liquor is expressed as sulfidity. Sulfidity is the ratio between the sodium sulfide concentration and active alkali used (Toucini 2013). According to Carvalho (1999), several studies show that in industries using eucalyptus, 20 to 30% of sulfidity is used. This value is greatly influenced by factors

such as the used raw material, cooking conditions, and recovery costs of black liquor. Silva (2001), report that the sodium sulfide charge in the range of 0 to 20% results in a significant decrease in pulp viscosity.

Pulping processes are influenced, in addition to the reagents' concentration, by factors such as time and temperature used (Toucini 2013). Cooking duration depends on the desired delignification level, which is usually expressed as the Kappa number.

The kraft process is highly used because it produces a high quality of processed pulp, especially regarding its bleachability and physical-mechanical properties. However, pulp characteristics may change according to some process variables, such as applied alkaline charge, delignification time, and temperature, among others (Silva Júnior 1994).

Another positive aspect of introducing sodium sulfide into the cooking liquor is the efficiency improvement of the chemical reagents' recovery system and the process energy generation (Gomide *et al*. 1980). According to Carvalho (1999), when keeping the effective alkali charge fixed, liquors with greater sulfidity reduce the reagents' recovery costs.

However, the kraft pulping process shows some disadvantages, among which include low yield (wood conversion into pulp), high investment for the implementation of pulp production mills, high production cost, and the generation of odorific gases (Gomide *et al*. 1987; Silva Jr. 1994, 1997; Almeida 2014).

The poor odor characteristic of the kraft pulp industry is due to the formation of total reduced sulfur (TRS) compounds during cooking (Gomide *et al*. 1987). Such compounds are corrosive and noticeable at low concentrations, which can cause serious discomfort problems to communities adjacent to pulp mills (Foglio 1991; Vieira 2013). Although in recent years several innovations have been introduced in the pulp production industries, such as the use of more efficient recovery boilers with combustion stability and low emission of polluting gases (Tran and Vakkilainen 2012), not even the most modern modified pulping processes have been able to eliminate TRS emissions (Silva *et al*. 2002).

The best alternative to the TRS emission reduction would be changes in the pulping process focused on reducing the cooking liquor sulfidity because the advantages of sulfidity use from 20% are marginal for short-fiber woods (Grace *et al*. 1989). The best way for the full elimination of odorous compounds would be the complete removal of sulfur compounds from the kraft process, reversing it back into the soda process (Silva Júnior 1994; Almeida 2014).

Studies aimed at the full removal of sodium sulfide from the cooking liquor have gained interest in the pulp industry again due to the possibility of generating recovered lignin of higher added value due to the absence of sulfur in its structure. According to Foelkel (2016), the lignin obtained from kraft black liquor is not pure, as it contains contaminations such as sulfur. These compounds make its application unfeasible to noble and valuable products, such as carbon fiber. The soda process is presented as a feasible alternative to industrial plants that intent to obtain sulfur-free pulp and/or black liquor, and can be economically feasible, even penalizing the properties of the produced pulp.

Although the effects of the sodium sulfide addition in the cooking liquor have been the subject of studies in the past, especially in the 1960s and 1970s, still, there have been few specific studies for species of *Eucalyptus* spp. genus, and especially in extended cooking and at low temperature. As an example, the review study conducted by Kleppe (1970) can be mentioned, and it still remains as one of the most quoted regarding the sulfidity variation in hardwoods. In this study, the author presents data obtained from birch wood cooking for pulps with kappa number 25, where 5, 10, 15, 25, and 40% sulfidity levels were used in the white liquor. It was concluded that the use of sodium sulfide

concentration in liquor below 15% significantly penalizes the process yield. However, in the cited study there were some gaps in the sulfidity ranges used, such as the values 20 and 30%. The fact that not all values were analyzed makes it impossible to carry out an accurate mathematical adjustment of potential models, especially in the sulfidity range classified as optimum by other authors (Grace *et al*. 1989; Carvalho 1999; Silva 2001).

Table 1 shows some recent studies involving the sulfidity variation in hardwood pulping processes.

**Table 1.** Some Studies Involving the Sulfidity Variation in Hardwood Pulping Processes

| Authors | Species | Sulfidity, % | Alkaline charge | Kappa number |
|---|---|---|---|---|
| Silva (2001) | *Eucalyptus* spp. | 15[a], 20[a], 28[a], 33 | 16.3% as NaOH [d] | 17 ± 0.5 |
| Yoon *et al*. (2001) | 6 espécies de folhosas[b] | 10, 20, 30 | 16.0% [c] | 10.0 – 50.0 |
| Silva *et al*. (2002) | *Eucalyptus* spp. | 20, 25, 30, 35 | 16.3% as NaOH [d] | 16.9 – 20.9 |
| Pascoal Neto *et al*. (2003) | *Eucalyptus globulus* | 15, 21, 28, 37 | 17.0% as $Na_2O$[c] | 14.0 ± 0.3 |
| Rahmati *et al.* (2007) | *E. camaldulensis* | 20, 30, 40 | 19.0 – 25.0% as NaOH [c] | 19.9 – 34.4 |
| Olm *et al*. (2009) | Birch | 35, 50, 80, 100 | 17.5 – 19.5% [d] | 14.0 – 26.0 |
| Rosli *et al.* (2009) | *Acacia mangium* | 15, 20, 25, 30 | 13.0 – 23.0% as Na2O [c] | 10.5 – 44.6 |
| Santos *et al*. (2016) | *E. urophylla* x *E. grandis* | 0[a], 5[a], 10[a], 15[a], 20[a], 25[a] | 17.4% as NaOH [c] | 6.5 – 9.4 |
| Lombardi and Luiz (2017) | Mix de eucalipto e pinus | 26, 34 | Variável | 18.0 |

[a] – Cooking with addittive;
[b] - Aspen, Bass, Birch, Maple, Oak, and Sweet gum; [c] -active alkali; [d] – effective álcali

Table 1 shows that most studies have sought to optimize sulfidity in kraft cooking and not necessarily to understand the sulfidity effect in alkaline pulping processes. In addition, there have been few studies considering *Eucalyptus* wood, which is currently the main source of bleached hardwood kraft pulps. It is also noted that most of the studies were conducted with variable kappa number (in some studies for unbleachable pulps) and/or using some type of chemical additive.

Therefore, this study aims to evaluate the influence of white liquor sulfidity on the efficiency of the alkaline pulping process of *Eucalyptus* spp. wood in a constant delignification level (kappa number 18 ± 0.9), analyzing the quality of the obtained pulp and making it possible to determine the optimal process conditions, proposing an updated analysis on this topic. The research was conducted with the purpose of providing a foundation for future studies and/or industries in the sector that intend to change the sulfidity used in the pulping process, especially regarding the potential for obtaining kraft lignin with low sulfur content recovered from black liquor – biorefinery concept.

## EXPERIMENTAL

### Materials

For the present study, industrial chips of *Eucalyptus* spp. collected in the chip cell of an industrial plant located in Brazil, State of São Paulo, were used. The chips were air dried and later screened with a laboratory screener. A thickness fraction of 4 mm to 6 mm was used in the experiments.

### Technological Characterization of the Material

*Chips basic and apparent density*

Chips' basic and apparent densities were determined, and the results were expressed as the arithmetic average of repetitions. The determination of the chips' basic density followed the maximum moisture content method as per NBR 11941 (2003). The chips' apparent density was determined by the volumetric method, calculated by the ratio between the chips dry mass necessary to complete the volume of a 2-L beaker.

*Chemical characterization*

Chips were sampled and prepared according to the TAPPI T257 om 85 (1985) standard. Ash contents as per TAPPI T211 om-91 (1991), extractives according to TAPPI T204 cm-07 (2007), and total lignin (Segura 2012) were determined. All analyses were performed in triplicate.

In addition to these parameters, holocellulose content was calculated as follows,

$$Hc = 100 - (Ex + Lt) \quad (1)$$

where *Hc* is holocellulose content (%), *Ex* is total extractives content (%), and *Lt* is total lignin content (%).

### Pulping Processes

Conventional cooks were conducted in triplicate in a rotary autoclave (Regmed AU/E – 20 model; Regmed Ind. Técnica de Precisão Ltda, Osasco, Brazil) that contained eight individualized stainless-steel capsules with a capacity of 450 mL each. Conventional cooking with a total time of 240 min was performed (60 + 180 min). Alkaline charge and maximum temperature were adjusted to obtain pulp with a Kappa number 18 ± 0.9 and black liquor with residual effective alkali between 9 to 12 $g.L^{-1}$ (as NaOH).

Nine different sulfidity levels were considered, namely 0, 5, 10, 15, 20, 25, 30, 35 and 40%. In each cooking, the equivalent to 65 g of dry chips and a liquor to wood ratio of 4:1 were used. At the end of each cooking, the liquor of each capsule was collected, and the pulp was washed with running water.

### Methods

*Pulp analyses*

After washing, the pulp was disaggregated and weighed to determine the global yield for the pulping process as the ratio between pulp dry mass and chip dry mass. Subsequently, the pulp was purified in a laboratory purifier with a 0.2 mm slot. Rejects were collected on the screen surface and dried in autoclave at 105 ± 2 °C for determining the screened yield as dry mass of screened pulp per chip dry mass and the rejects yield as the ratio between rejects dry mass per chip dry mass.

In the screened pulp, the Kappa number according to TAPPI T236 om-99 (1999), and viscosity according to TAPPI T230 om-07 (2007) were determined. From the parameters described, the pulping process selectivity and specific wood consumption were determined using Eqs. 2 and 3,

$$Sel = \frac{\text{Visc}}{\text{K}} \quad (2)$$

$$WSC = \frac{1}{BD \cdot SY} \quad (3)$$

where *Sel* is the selectivity, *Visc* is the viscosity of pulp ($cm^3.g^{-1}$), *WSC* is specific wood consumption ($m^3.od\ t^{-1}$), *BD* is basic density ($g.cm^{-3}$), and *SY* is screened yield (in decimal).

*Black liquor analysis*

The black liquor collected at the end of each cooking was analyzed for the final pH according to SCAN N33:94 (1994), residual effective alkali concentration, $g.L^{-1}$ NaOH base as per SCAN N33:94 (1994), and residual sulfidity (%) according to SCAN N33:94 (1994). From the obtained results, the effective alkali consumed in the pulping process, the effective alkali consumed per pulp ton produced and the solid generated per oven-dry pulp ton produced were calculated according to Eqs. 4 to 6,

$$EAC = EAA - REA \quad (4)$$

$$EAC' = \frac{EAC \times LW}{SY} \quad (5)$$

$$Solids = \frac{(1-GY)+AA}{SY} \quad (6)$$

where *EAC* is effective alkali consumed by cooking ($g.L^{-1}$ as NaOH ), *EAA* is effective alkali applied ($g.L^{-1}$ as NaOH ), *REA* is residual effective alkali ($g.L^{-1}$ as NaOH ), *EAC'* is effective alkali consumed per oven-dry pulp ($kg.od\ t^{-1}$), *LW* is the liquor to wood ratio ($L.kg^{-1}$), *SY* is screened yield (in decimal), *Solids* is the tons solids generated per oven-dry pulp ton ($tons.\ od\ t^{-1}$), *GY* is global yield (in decimal), and *AA* is active alkali applied (in decimal).

*Data analysis*

The results presented with the material technological characterization represent the arithmetic averages of each parameter, and its standard deviations and coefficients of variation. Variables related to pulping processes were subjected to the analysis of variance (ANOVA) at 1% of significance and polynomial regression when relevant. The best model for each variable was chosen through coefficient of determination statistics ($R^2$) (Statgraphics 18® Centurion, Statgraphics Technology, Inc., The Plains, VA, USA).

## RESULTS AND DISCUSSION

### Technological Characterization of the Material

*Chips' basic and apparent density*

The value obtained from the basic density for the *Eucalyptus* spp. material that was used in this study was 0.477 $g.cm^{-3}$. The used value was within the density range adopted by the Brazilian pulp industries. The industries have prioritized eucalyptus clones with

basic densities close to 0.500 g·cm$^{-3}$ with a tendency towards slightly lower densities (Gomide *et al*. 2005).

Regarding the apparent density, the result of 0.176 g.cm$^{-3}$ obtained in this study was consistent with that reported by other authors. Vivian (2015), in a study with *E. grandis* × *E. urophylla* hybrid at 5 years old, reported 0.167 g·cm$^{-3}$ of apparent density and Bonfatti Júnior (2014) found 0.183 g·cm$^{-3}$ of apparent density for hybrid of the same genus at 6 years old.

*Chemical characterization*

Total extractive (3.53%), total lignin (26.4%), and holocellulose values (70.1%) were consistent with those mentioned in the literature. For example, in a study conducted with 75 clones of *Eucalyptus* spp. of commercial cutting age, Fantuzzi Neto (2012) observed an average content of extractives of 3.08%, lignin average content of 27.3%, and on average 69.6% holocellulose content. Gomide *et al.* (2005), working with 10 samples of eucalyptus clones at cutting age and from different places of Brazil, observed extractives content between 3.0 and 4.5%, total lignin content between 27.5 and 30.5%, and holocellulose content between 64.9 and 69.9%. The material under study showed 0.27% of ash content, a value lower than that mentioned by Fengel and Wegener (1989), who stated approximately 0.5% ash content in wood.

Based on the technological characterization results, the material used in this study can be considered representative among the materials used on an industrial scale in Brazil used in the production of bleached pulp of eucalyptus.

## Pulping Processes

Table 2 shows cooking results in the form of averages and analysis of variance. The ANOVA for the Kappa number showed no significant difference, *i.e.*, the obtained results ratify the analytical error admitted by the standard, which is 5% according to TAPPI T236 om-99 (1999). The delignification level achieved at the end of cooking influences several properties including the obtained pulp resistance and process yield (Rydholm 1965; Carvalho 1999). Therefore, it is important that this parameter is kept constant between the different treatments to ensure that the other analyzed variables are not influenced by the delignification intensity.

Almeida (2014) conducted *Eucalyptus* spp. wood cooking using 0 and 30% sulfidity and reported that when obtaining pulp with kappa number 18, the cooking with no addition of sodium sulfide resulted in a higher concentration of residual alkali in black liquor. In contrast, Ribeiro *et al.* (2018) evidenced in their study the importance of maintaining the residual effective alkali concentration within a given range, in order to prevent other properties of the pulp from becoming affected, such as viscosity and concentration of hexenuronic acids. Therefore, in this study, the range from 9 to 12 g/L was adopted, which reflects the industrial reality. An 8.1% of coefficient of variation was obtained among the residual effective alkali results. It was observed that the analysis of variance was significant at the level of 1% probability. Given that the standard SCAN N33:94 (1994) was used in this study for determining such parameter, the analytical error was 4.8%.

At the end of cooking, the alkali charge present in black liquor should be sufficient to keep the pH above 12 (Carvalho 1999). In this study, a pH average value of 12.54 ± 0.14 was observed to avoid problems with lignin re-precipitation over the pulp (Table 2).

**Table 2.** Average of the Results Obtained in Cooking and Summary of Analysis of Variance

| Parameter | Sulfidity (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 |
| Kappa number $^{ns}$ | 18.5 | 18.1 | 17.9 | 18.3 | 18.4 | 18.2 | 18.4 | 18.0 | 18.5 |
| Max. temperature (ºC) * | 165 | 160 | 156 | 154 | 153 | 152 | 151 | 151 | 150 |
| EAA (% as NaOH) * | 20.0 | 19.5 | 18.5 | 17.0 | 17.0 | 16.5 | 16.5 | 16.5 | 16.5 |
| H-factor * | 1645 | 1270 | 900 | 755 | 691 | 632 | 580 | 580 | 530 |
| Global yield (%) * | 51.4 | 53.5 | 53.3 | 55.2 | 56.4 | 56.2 | 56.7 | 56.7 | 56.8 |
| Rejects yield (%) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Screened yield (%) * | 51.4 | 53.5 | 53.3 | 55.2 | 56.4 | 56.2 | 56.7 | 56.7 | 56.8 |
| WSC ($m^3$. od $t^{-1}$) * | 4.08 | 3.92 | 3.93 | 3,.80 | 3.72 | 3.73 | 3.70 | 3.70 | 3.69 |
| Viscosity ($cm^3$. $g^{-1}$) * | 875 | 1026 | 1109 | 1126 | 1200 | 1200 | 1276 | 1331 | 1208 |
| Selectivity * | 47.4 | 56.6 | 62.1 | 61.5 | 65.2 | 66.1 | 69.4 | 73.9 | 65.4 |
| REA (g. $L^{-1}$ as NaOH) * | 9.3 | 11.1 | 10.6 | 10.9 | 9.4 | 9.4 | 10.7 | 10.9 | 11.5 |
| EAC' (kg. od $t^{-1}$) * | 181 | 153 | 146 | 121 | 129 | 124 | 114 | 112 | 108 |
| Final pH * | 12.6 | 12.7 | 12.6 | 12.6 | 12.5 | 12.6 | 12.5 | 12.3 | 12.7 |
| Solids (tons.od $t^{-1}$ ) * | 1.34 | 1.24 | 1.24 | 1.14 | 1.11 | 1.11 | 1.11 | 1.12 | 1.13 |
| * - Significant at the level of 1% probability ($p < 0.01$); $^{ns}$ – non-significant ($p \geq 0.01$) | | | | | | | | | |

To meet the assumptions proposed for the development of this study, variable pulping conditions were used for each treatment. This was directly reflected on the pulping process yield. It is noteworthy that in all treatments the rejects generation was not obtained, so the global and screened pulp yields were equal, as shown in Table 2.

The results obtained in this study developed with *Eucalyptus* spp. wood (Table 2), were similar to those obtained by Rosli *et al.* (2009), which when evaluating the pulping condition effects in *Acacia mangium* wood, obtained pulp with kappa number 18 ± 0.9 while using 15 and 30% sulfidity. However, the condition with lower sulfidity required lower active alkali charge, higher temperature, and shorter time to achieve the same delignification level, resulting in lower process yield and pulp with lower physical-mechanical resistances.

Pulping yield influences other parameters, such as the specific wood consumption. The WSC in this study was generated only considering the yield achieved in each cooking, as obtained by Segura (2015), not considering the losses in subsequent processes.

**Table 3.** Models Adjusted for WSC, Correlation Results Obtained, and the Analysis of Variance

| Parameter | Model | Range of Sulfidity | *a* | *b* | $R^2$ |
|---|---|---|---|---|---|
| WSC | $Y = a + bx$ | $0 \leq S \leq 20$ | 4.058 | -0.0169 | 0.9067* |
| | | $20 \leq S \leq 40$ | 3.762 | -0.0018 | 0.1753$^{ns}$ |
| *Y* - specific wood consumption ($m^3$.od $t^{-1}$); *x* - white liquor sulfidity (%); $R^2$ - correlation coefficient of equations; * - significant analysis of variance at the probability level of 1% ($p < 0.01$); $^{ns}$ - non-significant analysis of variance ($p \geq 0.01$) | | | | | |

Because the result of the ANOVA for the specific wood consumption was significant at the level of 1% probability (Table 2), the mathematical models shown in Fig. 1 and Table 3 were adjusted. Two trends were noticed for this parameter, behaving differently between the low (0 to 20%) and high sulfidity processes (20 to 40%).

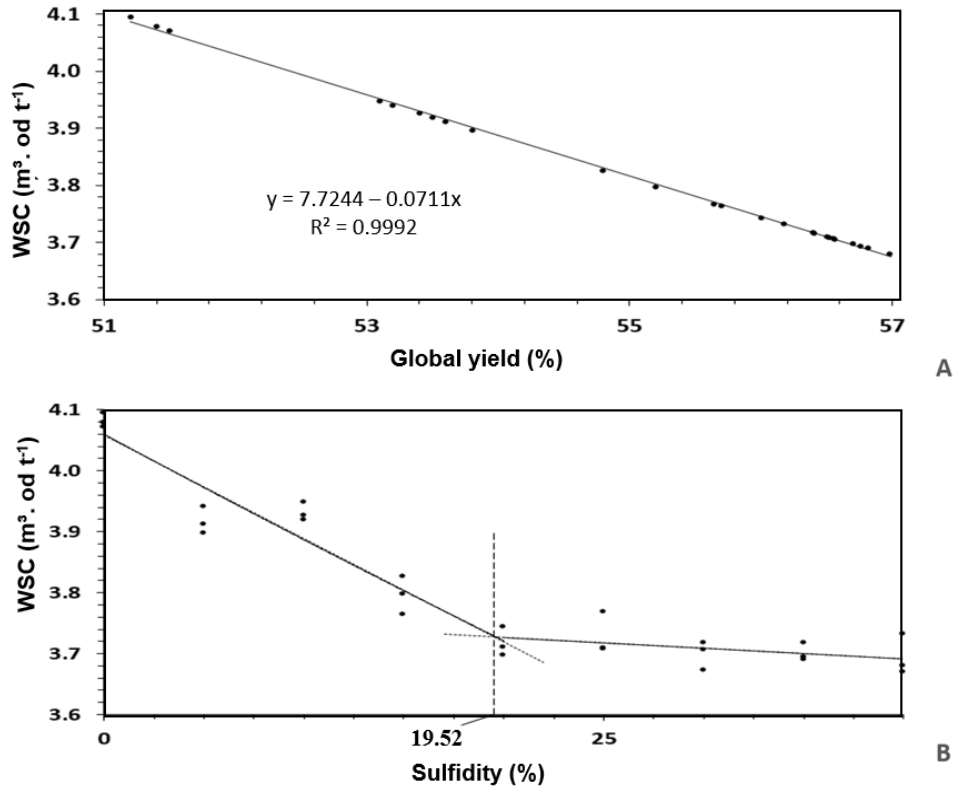


**Fig. 1.** (a) Ratio between screened pulp yield and specific wood consumption and (b) WSC according to the white liquor sulfidity level

Although the ANOVA of high sulfidity data ($S \leq 20$) was not significant at 1% probability (Table 3), the model was adjusted to obtain the intersection point of lines. The intersection point was at 19.5% of sulfidity, which is equivalent to the specific consumption of 3.73 $m^3$ of wood to obtain 1 oven-dry pulp ton. This result confirms the observation of Grace *et al.* (1989), which stated for hardwoods the use of sulfidity in white liquor greater than 20% can result in negligible gains.

In treatments where sulfidity levels below 20% were used, the highest specific wood consumption (4.08 $m^3$.od $t^{-1}$) was obtained in the treatment with no addition of sodium sulfide in white liquor (S = 0%). This was the highest specific wood consumption obtained in this study. In the range of 20 to 40% sulfidity, the average consumption of 3.71 ± 0.03 $m^3$ of wood for each oven-dry ton of produced pulp was observed.

The strategy adopted in this study to achieve the established levels of Kappa number and REA follows industrial standards. The standards correspond to a change in the alkaline charge applied and/or at the maximum cooking time, given that the change in the white liquor sulfidity changes the kinetics of kraft delignification.

Silva *et al.* (2002) and Rahmati *et al.* (2007), in studies involving different sulfidity levels in wood cooking of species of the *Eucalyptus* spp. genus, report that it is not possible

to maintain the other cooking conditions constant and achieve the same delignification level of the pulps obtained when this parameter (sulfidity) is changed. Pascoal Neto *et al*. (2003), chose to keep the temperature constant and change the cooking time when pulping *Eucalyptus globulus* wood with variable levels of sulfidity (15, 21, 28 and 37%), to obtain pulp with kappa number 14.0 ± 0.3. However, the strategy adopted in the cited work is often not practicable on an industrial scale, since changing the retention time of reactors can alter or influence the daily production of a plant. Therefore, the cooking temperature variation directly reflects in the H-factor, a ratio between cooking time and temperature, required in each treatment. In this study, the cooking times were kept constant for all treatments, hence the H-factor variation observed was only due to the variation in the maximum temperature used.

The analysis of variance results of alkali charge parameters and H-factor were significant at 1% probability (Table 2). Therefore, mathematical models were adjusted to investigate the behavior of these parameters when varying the white liquor sulfidity.

The models adjusted for effective alkali applied and H-factor are shown in Fig. 2. It is possible to note that the applied alkali levels and H-factor tended to show less variation from 20% of sulfidity. Among the evaluated sulfidity levels, the soda process ($S$ = 0%) was the treatment that required the highest alkaline charge (20%) and highest H-factor (1645) to achieve the established delignification level (Kappa number 18 ± 0.9).

The sulfidity percentage to be used in white liquor is a parameter determined by the industrial project. The industrial project is variable according to the desired product, the environmental restrictions on the total reduced sulfur emissions of the region where the plant is installed, or even the burning capacity of lime kiln. In the pulp industries in Brazil, the white liquor sulfidity level ranges from 25 to 35% (Lombardi and Luiz 2017).

Sulfidity reduction to levels lower than those defined in the project specifications of industrial plants can result in negative impacts on the chemical recovery area and utilities of a pulp mill. The considerable increase in H-factor can result in increased steam consumption to favor the increase in the required temperature and the higher demand for alkali can generate overload in the caustification stage of white liquor.

The sulfidity level to be used in the cooking operation is directly reflected in the recovery costs of black liquor. The lower level of initial sulfidity results in a higher amount of sodium hydroxide in white liquor, which may require a greater overload of the white liquor caustification system (Grace *et al*. 1989; Carvalho 1999). Caustification is the process step where white liquor sodium hydroxide is recovered through the burning of lime mud in the kiln (Tran and Vakkilainen 2012). The sulfidity content used in the pulping process is directly related to the production of lime mud, given that lower sulfidity implies higher sodium carbonate content in green liquor and higher oil consumption in lime kiln (Lombardi and Luiz 2017).

The kinetics change of the pulping process, expressed by the need to vary the pulping conditions (temperature/H-factor and alkali charge) in each sulfidity level of white liquor, can be confirmed by the consumption profile analysis of chemical reagents throughout the cooking.

In this study, the sodium sulfide consumption in pulping processes is discussed based on the percentage of sulfidity remaining in black liquor. The lingering sulfidity in black liquor is directly related to the consumed and residual sodium sulfide concentrations in each treatment.

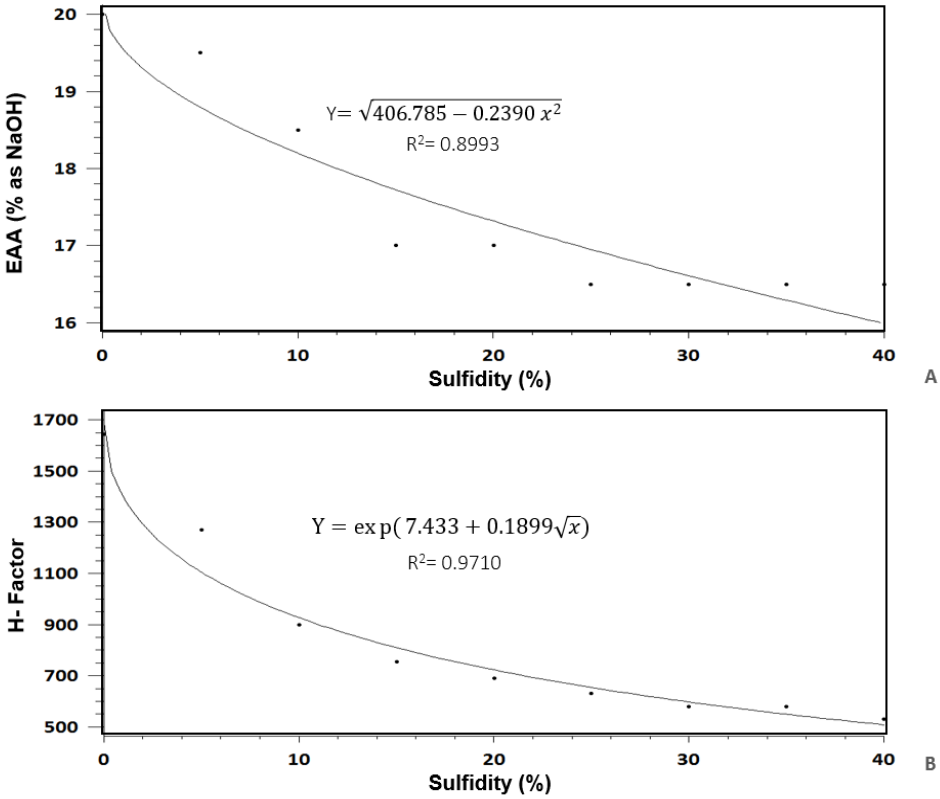


**Fig. 2.** (a) EAA and (b) H-Factor depending on the white liquor sulfidity level

The analysis of variance of residual sulfidity variables and specific alkali consumption showed significant results at 1% probability (Table 2), deeming it necessary to investigate the behavior of these parameters when varying the sulfidity of cooking liquor. In Fig. 3, the models are adjusted for sulfidity content in black liquor and in Fig. 4 the models are adjusted for specific consumption of effective alkali.

As verified in Fig. 3, in treatments with 0, 5, 10, and 15% of initial sulfidity, all sodium sulfide was consumed throughout the pulping processes, resulting in 0% sulfidity in black liquor.

Brannvall (2017), mentions that several studies from the 1940s to 1960s reported that high concentrations of sodium sulfide are more important in the initial and main stages of the pulping process, with little and/or no effect in the final delignification stage. Therefore, the results found in this study open a path for future studies on the kinetics of sodium sulfide consumption throughout the pulping process, mainly for sulfidity levels below 20%.

The specific consumption of effective alkali (Fig. 4) was increased for treatments with low levels of white liquor sulfidity (S < 19.52%), as well as the residual sulfidity content.

The model generated for specific alkali consumption (Fig. 4) observed that when using sulfidity in white liquor below 19.52%, a trend of significant increase of effective alkali consumption is noted.

The kinetics change in the pulping process observed by changes in specific alkali and wood consumption may reflect directly on the preservation of hemicelluloses, and such

a trend can be verified by the integrity level of carbohydrates in brown pulps (Almeida 2003; Rahmati *et al.* 2007).

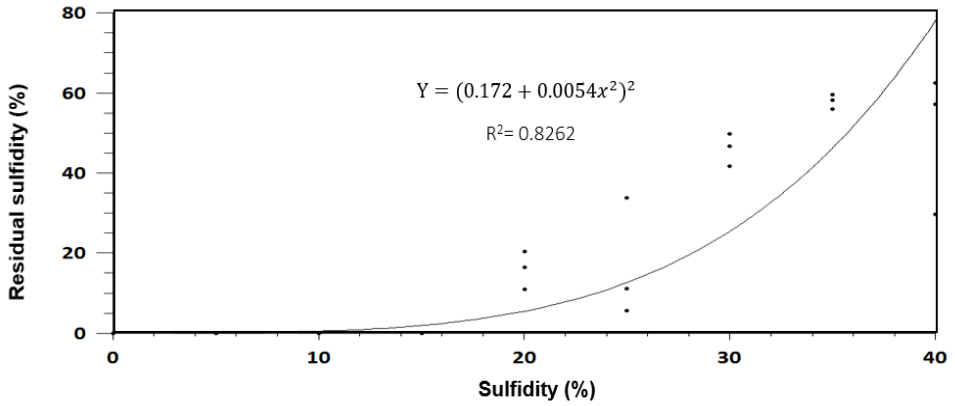


**Fig. 3.** Residual sulfidity depending on the white liquor sulfidity level

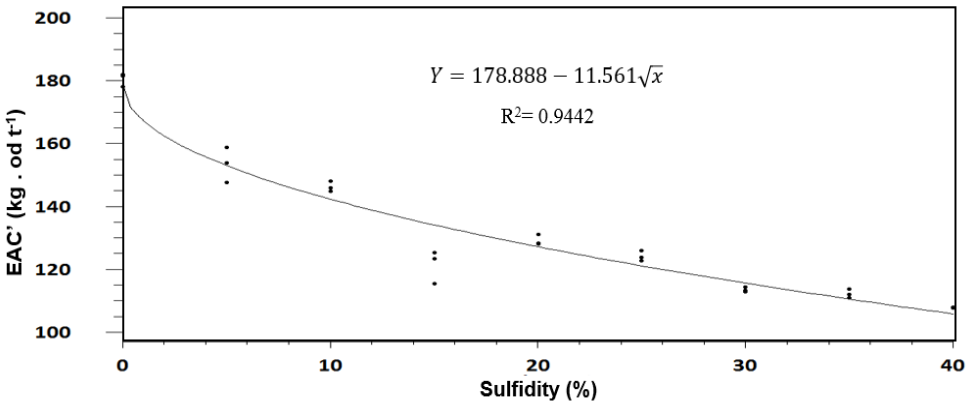


**Fig. 4.** EAC' depending on the white liquor sulfidity level

As previously reported, the specific wood consumption and alkali among the treatments used in this study showed significant differences, which directly reflects on carbohydrate degradation. As in all treatments, the Kappa number remained within the pre-established range. The variation in selectivity observed in Table 2 was solely due to the pulp's viscosity.

The integrity of carbohydrates is also related to the solids content generated in black liquor, and as a result, the greater the degradation of carbohydrates throughout the pulping process. The greater the amount of organic matter present in black liquor, the consequently higher solids content will be sent to the recovery boiler. Mathematical models were adjusted to verify the effect of sulfidity variation in black liquor on the pulping process selectivity and solids content generated in black liquor. The obtained equations are shown in Fig. 5.

The model generated for selectivity (Fig. 5a) observed that a process using white liquor with 19.5% sulfidity will show a selectivity of approximately 64.

The treatment with 0% sulfidity was the least selective among all treatments evaluated in this study, with a selectivity of 47.4. Selectivity is a parameter calculated from viscosity; therefore, it was observed that the full removal of sodium sulfide from white

liquor can impair the carbohydrates integrity and may result in pulps with lower physical-mechanical resistance when compared to other treatments.

Ban and Lucia (2003) mention several authors who reported that the greater the sulfidity in the liquor, the better the delignification rates of wood, and the better the pulping process selectivity. By contrast, Olm *et al.* (2009), in a study using high levels of sulfidity (35 to 100%) in the birch wood pulping process, when obtaining pulp with kappa number 17 and applying 19.5% effective alkali, observed that the process viscosity increased while the liquor sulfidity level increased, although the process yield had no significant change. Viscosity and selectivity results obtained in this study differ from those presented by the authors mentioned above. Table 2 shows that it is possible to note a decrease trend in viscosity after 35% sulfidity, evidencing that a greater selectivity of the *Eucalyptus* spp. wood pulping process is found in this range.

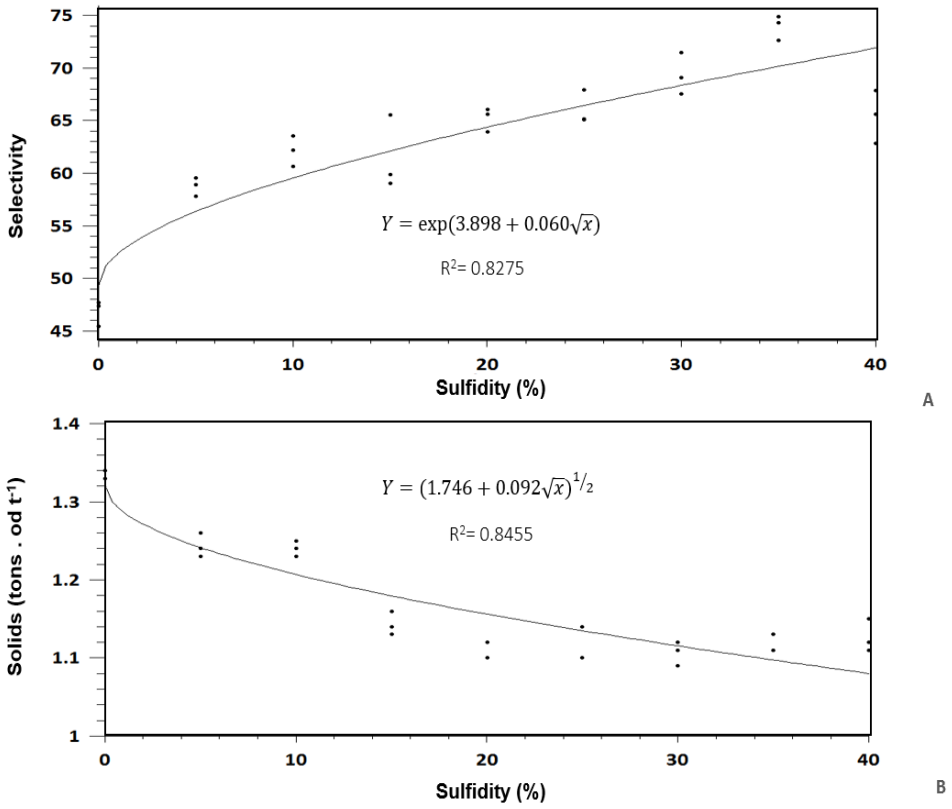


**Fig. 5.** (a) Selectivity and (b) solids generated depending on the white liquor sulfidity level

The solids generation is related to the pulping process yield and alkaline charge applied. The pulping process with no addition of sodium sulfide ($S$ = 0%) was the one that resulted in a greater amount of starting solids to obtain a ton of brown pulp (1.34 tons. od $t^{-1}$). In this case, the highest alkali charge was used and the lowest yield among all treatments conducted in this study was obtained. The cooking with high levels of initial sulfidity ($S$ > 19.52%), which required lower alkali charge and showed higher yields, generated a lower number of solids (Fig. 5b).

## Impact Analysis of Sodium Sulfide Concentration on the Pulping Process

In this study, the influence of sodium sulfide concentration variation on white liquor was verified on several important parameters for the pulping process. The impact of sulfidity on three realities were chosen, namely: 1) $S$ = 0%, comprising the full removal of sodium sulfide from cooking liquor, *i.e.*, soda pulping process; 2) $S$ = 19.52%, sulfidity level optimized in this study for the specific wood consumption; and 3) $S$ = 32%, percentage of sulfidity characteristic of modern Brazilian pulp mills.

Table 4 shows the estimated values from the equations generated in this study for the analyzed parameters.

**Table 4.** Estimated Values for Each Studied Parameter

| Parameter | Sulfidity (%) | | |
|---|---|---|---|
| | 0.00 | 19.52 | 32.00 |
| WSC ($m^3$. od $t^{-1}$) | 4.06 | 3.73 | 3.71 |
| EAA (% as NaOH) | 20.2 | 17.8 | 12.7 |
| H-Factor | 1690 | 730 | 577 |
| Residual sulfidity (%) | 0.0 | 5.0 | 32.7 |
| Effective alkali consumed (kg. od $t^{-1}$) | 179 | 128 | 113 |
| Selectivity | 49.3 | 64.2 | 69.3 |
| Solids generated (tons.od $t^{-1}$) | 1.30 | 1.16 | 1.11 |

The absence of sodium sulfide in white liquor generated significant changes in the process and quality of the produced pulp and is also considered a more viable alternative for production processes with low or even no atmospheric emission of sulfur reduced compounds (TRS).

In Brazil, in the past, a few industrial plants used the soda process for the production of bleached eucalyptus kraft pulp. This process gave rise to pulps with low brightness and resistance, and consequently lower commercial value. Additionally, as observed in this study, the industrial process yield was lower, leading to a higher specific wood consumption; and these two associated factors provide a lower potential of financial results in these industrial plants.

On the other hand, when considering the possibility of recovered lignin production, soda pulping processes of eucalyptus chips may be an interesting alternative in the production of high-purity lignin, which can eventually compensate for the loss of quality of the kraft pulp.

Yoon *et al*. (2000) reported that the TRS generation is inversely proportional to the white liquor sulfidity and the pulp kappa number. Therefore, while maintaining the constant kappa number, the reduction of TRS emission can be achieved by reducing the liquor sulfidity. As reported before, the increase in white liquor sulfidity above 19.52% does not incur a significant impact on the specific wood consumption. Therefore, in locations where there are environmental restrictions on the emission of TRS, the reduction of cooking liquor sulfidity can be presented as an operational possibility. From the results obtained in this study, it is noted that the decrease in white liquor sulfidity, for example, from 32 to 19.52% results in 84.7% less residual sulfidity in black liquor.

When analyzing the impact of sulfidity reduction in a plant that was designed to use 32% sulfidity to 19.52%, results obtained in this study observed that the solids

generated were not affected. However, an overload may occur in the caustification and chemical recovery stages because the process will require the application of 40.2% more effective alkali, H-factor 26.52% higher, and consume 13.3% more effective alkali.

## CONCLUSIONS

1. Based on the results of this study, it can be stated that the optimal sulfidity level for the bleached pulp production of eucalyptus is approximately 20% when having the specific wood consumption as the definition parameter.
2. The sulfidity variation in white liquor influences the entire pulping process based on the employed conditions and the results obtained. Treatments with low sulfidity content in white liquor showed higher specific consumption of effective alkali.
3. This study reopens the discussion on the need to use high sulfidity levels in pulping processes with hardwoods, especially *Eucalyptus* spp. woods.
4. Also, it provides support for future studies on the TRS quantification and determination of sulfur concentration in lignin recovered from black liquor, mainly for low sulfidity levels in white liquor ($S \leq 20\%$).

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## REFERENCES CITED

Almeida, D. P. (2014). *Polpação Soda com Aditivos e Cinética de Deslignificação Kraft [Soda Pulping with Additives and Kraft Pulping Kinetics]*, Ph.D. Dissertation, Universidade Federal de Viçosa, Viçosa, Brazil.

Almeida, F. S. (2003). *Influência da Carga Alcalina no Processo de Polpação Lo-Solids® para Madeira de Eucalipto [The Influence of Alkali Charge on Lo-Solids® Pulping Process for Eucalyptus Woods]*, Master's Thesis, Universidade de São Paulo, Piracicaba, Brazil.

Ban, W., and Lucia, L.A. (2003)." Enhancing kraft pulping through unconventional, higher sulfide-containing pretreatment liquors – A review," *Tappi Journal* 2(3), 1-26. (https://projects.ncsu.edu/project/dsargyro/documents/TAPPIGLREVIEW2003.pdf,), Acessed 21 March 2020.

Bonfatti Júnior, E. A. (2014). *Deslignificação com Oxigênio para Polpa Kraft com Alto Número Kappa [Oxygen Delignification for Kraft Pulp with High Kappa Number]*, Master's Thesis, Universidade de São Paulo, Piracicaba, Brazil.

Brannvall, E. (2017). "Limits of delignification in kraft cooking," *BioResources* 12(1), 2081-2107. DOI: 10.15376/biores.12.1.Brannvall

Carvalho, M. G. V. S. (1999). *Efeito Das Variáveis De Cozimento Nas Características Químicas de Pastas Kraft de Eucalyptus Globulus [Effect Cooking's Variable on the*

*Chemical Characteristics of Eucalyptus globulus Kraft Pulp]*, Doctoral Thesis, Universidade de Coimbra, Coimbra, Portugal.

Fantuzzi Neto, H. (2012). *Qualidade Da Madeira De Eucalipto Para Produção De Celulose Kraft[Wood Quality of Eucalyptus for Kraft Pulp Production]*, Doctoral Thesis, Universidade Federal de Viçosa, Viçosa, Brazil.

Fengel, D., and Wegener, G. (1989). *Wood: Chemistry, Ultrastructure, Reactions.* Walter de Gruyter, Berlin, Germany.

Foelkel, C. E. B. (2016). "As biorrefinarias integradas no setor Brasileiro de fabricação de celulose e papel de Eucalipto [Integrated biorefineries at the Brazilian pulp and Eucalyptus paper manufacturing sector]," *Eucalyptus Online Book & Newsletter*, (http://www.eucalyptus.com.br/), Accessed 20 July 2019.

Foglio, D. (1991). "Novas tecnologias em fábricas de celulose de tipo kraft [New technologies in kraft pulp mills]," in*: 24 Congresso Anual de Celulose e Papel [24th Annual Pulp and Paper Meetig]*, ABTCP - Associação Brasileira Técnica de Celulose e Papel [Brazilian Pulp and Paper Technical Association], São Paulo, Brazil, pp. 1011-1020.

Gomide, J. L. (1979). *Polpa de Celulose: Química dos Processos Alcalinos de Polpação [Pulp: Chemistry of Alkaline Pulping Processes*], Universidade Federal de Viçosa, Viçosa, Brazil.

Gomide, J. L., Colodette, J. L., Oliveira, R. C. d., and Silva, C. M. (2005). "Caracterização tecnológica, para produção de celulose, da nova geração de clones de *Eucalyptus* do Brasil [Technological characterization of the new generation of *Eucalyptus* clones in Brazil for kraft pulp prodution]," *Revista Árvore* 9, 129–137. DOI: 10.1590/S0100-67622005000100014

Gomide, J. L., Oliveira, R. C., and Colodette, J. L. (1980). "Produção de polpa kraft de eucalipto, com adição de antraquinona [Production of eucalyptus kraft pulp, with antraquinone]," *Revista Árvore* 4, 203-214.

Gomide, J. L., Vivone, R. R., and Marques, A. R. (1987). "Utilização do processo soda/antraquinona para produção de celulose branqueável de *Eucalyptus* spp. [Use of the soda/antraquinone process for the production of bleached cellulose from *Eucalytus* spp.]," in: *Congresso Anual de Celulose e Papel [Annual Pulp and Paper Meetig]*, ABCP- Associação Brasileira de Celulose e Papel [Brazilian Pulp and Paper Association], São Paulo, Brazil, pp. 35-42.

Grace, T. M., Leopold, B., and Malcolm, E. W. (1989). *Pulp and Paper Manufacture Vol. 5 – Alkaline Pulping*, TAPPI Press/CPPA, Atlanta, GA, USA.

Kleppe, P. J. (1970). "Kraft pulping," *TAPPI Journal* 53 (1), 35-47.

Lombardi, L. R., and Luiz, A. C. (2017). "Avaliação da sulfidez do licor branco na qualidade da celulose kraft [Evaluation of white liquor sulfidity on kraft pulp quality]," *O Papel* 78(7), 76–80.

NBR 11941:2003 (2003). "Madeira: Determinação da densidade básica [Wood: Basic density determination]," Associação Brasileira de Normas Técnicas [Brazilian Association of Techmical Standards], São Paulo, SP, Brazil.

Olm, L., Tormund, D., and Lundqvist, F. (2009). "High sulphidity kraft pulping," *Nordic Pulp and Paper Research Journal* 24 (4), 433-439. DOI: 10.3183/npprj-2009-24-04-p433-439

Pascoal Neto, C., Eytuguin, D. V., Daniel, A. I. D., Silvestre, F. P., Furtado, P., Mendes Souza, P. (2003). "Influence of wood pulping conditions and unbleached pulp composition and structure on the ECF bleachability of hardwood kraft pulps," in: *I*th

*International Colloquium on Eucalyptus Pulp*, Universidade Federal de Viçosa, Viçosa, Brazil, 12 p. (http://www.eucalyptus.com.br/icep01/carlos_pascoal_neto.pdf), Accessed 21 March 2020.

Rahmati, H., Navace-Ardeh, S., and Aminian, H. (2007). "Influence of sulfidity and active alkali on the proprieties of pulp produced *Eucalyptus camaldulensis*," *J. Plant Sci*. 2(6), 600-606. DOI: 10.3923/jps.2007.600.606

Ribeiro, R. A., Colodette, J. L., and Vaz Júnior, S. (2018). "Effect of residual effective alkali on eucalyptus kraft pulp yield and chemistry," *Cerne* 24 (4), 408-419. DOI: 10.1590/01047760201824042593

Rosli, W. D. W., Mazlan, I., and Law, K. N. (2009). "Effects of kraft pulping variables on pulp and paper properties of *Acacia mangium* kraft pulp," *Chem. Technol.* 43(3), 9-15. (http://www.cellulosechemtechnol.ro/pdf/CCT1-3-2009/p.9-15.pdf), Accessed 20 July 2019.

Rydholm, S. A. (1965). *Pulping Processes*, Wiley Interscience, New York, NY, USA.

SCAN N 33:94 (1994). "Residual alkali (hydroxide ion content), in black liquor," Scandinavian Standard, Stockholm, Sweden.

Santos, R., Mello Júnior, J. A., Caraschi, J. C., Ventorim, G., and Pereira, F. A. (2016). "Polpação kraft e kraft/AQ da madeira pré-hidrolisada de híbrido de *Eucalyptus urophylla* x *grandis* [Kraft and kraft/AQ pulping from prehidrolyzed wood of hybrid *Eucalyptus urophylla* x *grandis*]," *Ciência Florestal* 26(4), 1281-1290. DOI: 10.5902/1980509825148

https://tspace.library.utoronto.ca/bitstream/1807/32881/1/Saturnino_Daniel_M_201206_PhD_thesis.pdf, Accessed 21 March 2020.

Segura, T. E. S. (2012). *Avaliação das Madeiras de Eucalyptus grandis X Eucalyptus urophylla E Acacia mearnsii para a Produção de Celulose Kraft pelos Processos Convencional e Lo-Solids ® [Evaluation of the Woods of Eucalyptus grandis X Eucalyptus urophilla and Acacia mearnsii for the Kraft Pulp Production on Conventional and Lo-Solids ® Pulping Processes]*, Master's Thesis, Universidade de São Paulo, Piracicaba, Brazil.

Segura, T. E. S. (2015). *Avaliação das Madeiras de Corymbia citriodora, Corymbia torelliana e Seus Híbridos Visando à Produção de Celulose Kraft Branqueada [Evaluationof the Woods of Corymbia citriodora, Corymbia tolerianna and Their Hybrids for Bleached Kraft Pulp Production]*, Doctoral Thesis, Universidade de São Paulo, Piracicaba, Brazil.

Silva, F. J., Gomide, J. L., Colodette, J. L., and Oliveira Filho, A. C. (2002). "Efeito da redução da sulfidez com adição de antraquinona nas emissões poluentes e na qualidade da polpa kraft de eucalipto [Effect of reducing sulfidity with the addition of antraquinone on pollutants emission and on eucalyptus kraft pulp's quality]," *O Papel* 62(2), 77-87.

Silva, F. J. (2001). *Impactos da Sulfidez e Adição de Antraquinona nas Emissões de Metilmercaptana, Nas Características E Na Branqueabilidade De Polpas Kraft De Eucalyptus [Impacts of the Sulfidity and Addition of Anthraquinone on Methylmercaptan Emission and on the Charcasteristics and Bleachability of Kraft Pulps of Eucalyptus spp.]*, Master's Thesis, Universidade Federal de Viçosa, Viçosa, Brazil.

Silva Júnior, F. G. (1997). *Polpação Kraft do Eucalipto com Adição de Antraquinona, Polissulfetos e Surfactante [Kraft Pulping of Eucalyptus with Antraquinone,*

*Polissulfide and Surfactant]*, Ph.D. Dissertation, Universidade Estadual de Campinas, Campinas, Brazil.

Silva Júnior, F. G. (1994). *Conversão do Processo Kraft em Soda DDA (sal Disódico de 1,4–di–hidro-9-10-di-hidroxiantraceno) para Madeira de Eucalipto [Conversion of the Kraft Process in Soda-DDA(Di-Sodium Salt of 1,4-Dihidro-9,10-Dihydroxianthracene for Eucapyptus]*, Master's Thesis, Universidade de São Paulo, Piracicaba, Brazil.

TAPPI T204 cm-07 (2007). "Solvent extractives of wood and pulp," TAPPI Press, Atlanta, GA, USA.

TAPPI T211 om-91 (1991). "Ash in wood, pulp, paper and paperboard: Combustion at 525ºC," TAPPI Press, Atlanta, GA, USA.

TAPPI T230 om-07 (2007). "Viscosity of pulp (capillary viscometer method)," TAPPI Press, Atlanta, GA, USA.

TAPPI T236 om-99 (1999). "Kappa number of pulp," TAPPI Press, Atlanta, GA, USA.

TAPPI T257 om-85. (1985). "Sampling and preparing wood for analysis," TAPPI Press, Atlanta, GA, USA.

Toucini, R. (2013). "Processos de polpação, lavagem, depuração e secagem da polpa [Pulping processes, pulp's washing, screening and drying]," in: *Celulose,* Senai/SP, São Paulo, Brazil, pp. 59-126.

Tran, H., and Vakkilainen, E. (2012). "The kraft chemical recovery process," TAPPI Kraft Recover Course, St. Petersburg, FL, USA, pp. 1-8.

Vasconcelos, F. S. B. (2005). *Avaliação do Processo Superbatch$^{TM}$ de Polpação de Pinus taeda [Evaluation of the Superbatch$^{TM}$ Pulping Process for Pinus taeda]*, Master's Thesis, Universidade de São Paulo, Piracicaba, Brazil.

Vieira, M. M. (2013). *Abordagem de Procedimentos Legais para o Controle de Incômodos Olfativos [Approach to Legal Procedures for the Control of Olfactory Disasters]*, Master's Thesis, Universidade Federal de Santa Catarina, Florianópolis, Brazil.

Vivian, M. A. (2015). *Aumento da Eficiência do Processo Kraft de Polpação a Partir de Pré-Tratamento de Cavacos de Madeira de Eucalipto [Increase of the Kraft Pulping Process Efficiency from Pretreatment of Eucalyptus Wood Chips]*, Ph.D. Dissertation, Universidade de São Paulo, Piracicaba, Brazil.

Yoon, S. H., Chai, X. S., Zhu, J. Y., Li, J., and Malcolm, E. W. (2001). "In-digester reduction of organic sulfur compounds in kraft pulping," *Advances in Environmental Research* 5(1), 91-98. DOI: 10.1016/S1093-0191(00)00045-9

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