The effects of temperature, alkali charge and additives in the oxygen delignification in high kappa number eucalyptus pulp kraft

Efeitos da temperatura, da carga alcalina e dos aditivos na deslignificação com oxigênio para polpa kraft de eucalipto com alto número kappa

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Resumo

O objetivo desse trabalho foi avaliar o efeito da temperatura, da carga alcalina e dos aditivos antraquinona e etanol na deslignificação com oxigênio para polpa kraft de *Eucalyptus grandis* vs. *Eucalyptus urophylla* com alto número kappa e teor de rejeitos. Para a produção da polpa celulósica foi o cozimento kraft convencional com carga alcalina de 13%, sulfidez de 25% além do fator H de 580. Para a redução do teor de rejeitos, a polpa foi submetida a duas passagens por moinho desfibrador. A deslignificação com oxigênio ocorreu em média consistência (10%) e pressão de oxigênio de 5 kgf·cm⁻² além do delineamento combinando quatro cargas alcalinas (15, 30, 45 e 60 kg·t⁻¹) e quatro temperaturas (80, 100, 120 e 140°C). A avaliação do efeito dos aditivos foi feita com a aplicação de 0,05% de antraquinona e etanol separadamente do mesmo modo os tratamentos sem aditivo como testemunhas. O número kappa da polpa marrom produzida foi de 63,9 com 8,7% de rejeitos. A comparação entre os fatores de carga alcalina e de temperatura mostram que o primeiro é mais influente no processo de deslignificação com oxigênio. Contudo, é aumentando-se a temperatura que foi possível reduzir o kappa com menor queda na seletividade. Além disso, a temperatura atua como agente ativador das reações do processo, visto que para qualquer carga aplicada, a concentração de álcali residual diminui com o aumento da temperatura. Não houve grandes quedas no rendimento com os aumentos de carga de álcali e temperatura. Simultaneamente, a transformação dos rejeitos em polpa garantiu manutenção do rendimento. A adição de antraquinona não mostrou ganhos no rendimento assim como na redução do número kappa, porém, tornou o processo mais seletivo. A adição de etanol mostrou resultados positivos em termos de redução de número kappa e de rejeitos como também o aumento do rendimento. O total de sólidos gerados não sofreu influência significativa da ação dos aditivos.

Palavras-chave: Antraquinona, Etanol, Seletividade, Eficiência, Celulose.

Abstract

The purpose of this paper was to evaluate the effect of temperature, alkali charge, anthraquinone and ethanol additives in oxygen delignification for kraft pulp of *Eucalyptus grandis* vs. *Eucalyptus urophylla* with high kappa number and rejects content. In pulp production, the conventional kraft cooking was used with 13% alkaline charge, 25% sulfidity, in addition to H factor of 580. To reduce the rejects content, the pulp was subjected to two passages through the disc refiner. The oxygen delignification occurred in medium consistency (10%) and oxygen pressure of 5 kgf·cm⁻², in addition to the delignification with the combination of four alkaline charges (15, 30, 45 and 60 kg·t⁻¹) and four temperatures (80, 100, 120 and 140°C). The additives effect evaluation was made with 0.05% of anthraquinone and ethanol separately, just like the treatments with no additives as a reference. The brown pulp kappa number produced was 63.9 with 8.7% of rejects content. The comparison between the alkaline charge and temperature factors shows that the first is more influential in the oxygen delignification process. However, by increasing the temperature it was possible to reduce the kappa number with lower drop in selectivity. In addition, the temperature is the activating agent of the process reactions, given that for any alkaline charge applied, the residual alkali concentration decreases with the temperature increase. Also, there was no great drop in yield with the increased alkali charge and temperature. Simultaneously, the conversion of rejects into pulp ensured the yield maintenance. The anthraquinone addition showed no gains in the yield and in the kappa number results, but the process became more selective. The addition of ethanol showed positive results in terms of kappa number and rejects reduction, and also an increased yield. The total of solids generated had no significant influence of additives action.

Keywords: Anthraquinone, Ethanol, Selectivity, Efficiency, Cellulose.

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INTRODUCTION

The oxygen delignification is a technology established in the pulp production industries (AGARWAL et al., 1999; SALVADOR, 2000). This process is in part considered as a continuation of the pulping alkaline processes and, somehow, as the first step in the bleaching process. However, the best way to classify it would be as a bridge between the pulping and bleaching processes.

The oxygen delignification is the removal of part of the residual lignin of kraft cooking through the pulp reaction with oxygen and sodium hydroxide, using the temperature as an activating element. In this reaction the free-lignin structures are fragmented by the oxygen action, resulting in higher solubility and easy reduction of this compound (ALA-KAILA; REILAMA, 2001).

The first industrial facility of oxygen delignification was in South Africa in 1971 (ALLEN et al., 2005; BOUCHARD et al., 2003; SIXTA et al., 2006) and in the following decade, the use of oxygen in alkaline extraction stages began to be marketed (REEVE, 1996).

The motivations for the application of oxygen in the pulps delignification have changed over time. In the 70s, it was necessary to close the washing water circuits and perform its recovery for costs reduction. After that, this became a partial or total replacement of chlorine or chlorine dioxide stages by non-chlorinated reagents (CARTER et al., 1997). The environmental, technical and economic benefits of oxygen delignification include low demand of chemical reagents in the subsequent stages of bleaching, greater brightness with a lower amount of reagents, less rejects content, water consumption and effluents production (MCDONOUGH, 1995; SIXTA et al., 2006; COLODETTE et al., 2007).

Figure 1 shows a simplified flowchart of oxygen delignification and Table 1 shows some typical conditions in the oxygen delignification in the industrial environment.

Figure 1. Oxygen delignification flowchart (SUSILO; BENNINGTON, 2007).

Figura 1. Fluxograma da deslignificação com oxigênio (SUSILO; BENNINGTON, 2007).

Table 1. Typical conditions in the oxygen delignification for industrial environment (MCDONOUGH, 1996).

Tabela 1. Condições típicas da deslignificação com oxigênio no meio industrial (MCDONOUGH, 1996).

Operational Conditions	Average Consistency	High Consistency
Pulp consistency, %	10 – 14	25 - 34
Reaction time, min	50 – 60	30 - 45
Reaction temperature, °C	70 – 105	100 - 115
Alkaline charge, kg·t ⁻¹	18 – 28	18 - 23
Oxygen load, kg·t ⁻¹	20 – 24	15 - 24

The oxygen delignification with high kappa number pulps allows removing large amounts of residual lignin present in pulp (VENSON et al., 2015); however, its implementation requires planning, since its effectiveness is limited: approximately 50% of delignification (FRIGIERI, 2016; SILVA, 2010). If the delignification is higher, there is a serious degradation of the carbohydrate fraction

of pulp, resulting in the deterioration of the pulp viscosity and mechanical strength properties (MCDONOUGH, 1996, GIACOMIN, 2015).

The reactions that degrade cellulose can be divided in two categories: the random oxidative cleavage reaction of the chain, which may occur at any point along the macromolecule and the peeling reaction in the terminal units of cellulose chains (SJÖSTRÖM, 1981). Although both reactions may occur during the oxygen delignification, the random cleavage of the chain is the one that causes more damage to pulp, while the peeling reaction is responsible for the loss of yield in the process.

According to Colodette et al. (1993) the drop in viscosity of the pulp that was subjected to oxygen delignification comes from the presence of free radicals produced by the oxygen reaction along with lignin phenolic hydroxylic groups (JI et al., 2009). These radicals degrade the pulp carbohydrates by oxidation, culminating in the oxidative cleavage of the polysaccharide chain into smaller units (COLODETTE; MARTINO, 2015). This problem can be minimized with the use of two-stage oxygen delignification, in addition to the use of chemical additives that neutralize the effects of free radicals.

Magnesium sulfate is considered a typical additive of oxygen delignification and is used on industrial scale. However, other additives have been investigated aiming to improve the process selectivity. Examples of that are the alcohols such as methanol and ethanol that possibly act as capturers of free radicals (*scavengers*) (RABELO, 2006; VENSON et al., 2015).

Considered as the first really effective additive and with practical value in the soda or kraft process of pulping (GOMIDE, 1980), the anthraquinone has been quite present in the pulp and paper industries and has opened new technological opportunities, such as the improvement in the pulp quality, increase in the alkaline pulping process yield, and also the possibility of sulfur reduction in the cooking liquor (LIEBERGOTT; VAN LIEROP, 1981). When used in the oxygen delignification, it provided an increase in the pulp viscosity and reduction in the production total costs (SILVA, 2010).

Studies on the oxygen delignification of eucalyptus pulp have been conducted with low kappa number pulp, approximately 18. However, little is known when the initial kappa number of pulp is high. For this reason, this research had the purpose of evaluating the influence of temperature, alkaline charge, and anthraquinone and ethanol additives in the oxygen delignification of eucalyptus kraft pulps with high kappa number and rejects contents.

MATERIAL AND METHODS

kraft Pulping

For conducting oxygen delignification trials, pulps obtained by the conventional kraft process were obtained. The raw material for the cooking were industrial wood chips of *Eucalyptus grandis* x *Eucalyptus urophylla* hybrids with thickness from 4 to 6 mm. Twenty cookings were performed in a forced circulation digester and electric heating with two stainless steel vassels, with a capacity of ten liters and 1200 g of wood chips in each. The purpose was to obtain pulp with kappa number 65 ± 2 . The cooking conditions are described in Table 2.

Table 2. Cooking conditions.

Tabela 2. Condições dos cozimentos.

Parameters	Conditions
Alkaline charge (NaOH base) (%)	13
Sulfidity (%)	25
Heating time (min)	60
Time at maximum temperature (min)	30
Maximum temperature (°C)	170
H Factor	580
Wood chips dry mass (g)	1200
Liquor/wood ratio (dm ³ ·kg ⁻¹)	4/1

After cooking the pulps were washed with water until the full removal of the residual black liquor. The washed pulps passed twice through a laboratory disks refiner, with 5 mm opening and 3450 rpm rotation to disaggregate and reduce the rejects content. Then they were centrifuged, disaggregated, homogenized in a single sample and stored in polyethylene bags and kept under refrigeration at 4 ± 2 °C.

Oxygen delignification

The oxygen delignification was performed in a rotating electronic autoclave with electric heating and 20 liters volume, comprising four individual tubes of one liter each. Pulp samples with 80 g a.s. each were placed into the reactor in medium consistency and heated up to the predetermined temperatures. With the set temperature achieved and under constant mixing, oxygen was injected. After the reaction, the system was depressurized and, in addition to the pulps, 30 mL of samples of the residual filtrate were collected for analysis. Pulps were washed with the equivalent to 9 m³ of distilled water per ton of absolutely dry pulp.

The experimental design used was fully randomized in a factorial arrangement. The involved factors were temperature (80, 100, 120 and 140 °C), alkaline charge (15, 30, 45 and 60 kg · t⁻¹) and additives (no additive, 0.05% of anthraquinone and 0.05% of ethanol, in relation to the pulp dry mass). The combination of these three factors comprised 48 treatments with three repetitions each.

For all the combinations with the three factors (temperature x alkaline charge x additives), the conditions of reaction time, oxygen pressure and consistency were constant, which were respectively 60 minutes, 5 kgf · cm⁻² and 10%.

In the case of the treatments with addition of anthraquinone, the oxygen injection occurred after half an hour when the system had reached the maximum temperature, so that the substance accomplished its function. In each treatment, the obtained pulp was analyzed on the basis of the parameters shown in Table 3.

Table 3. Determined parameters in brown and pre-bleached pulps.

Tabela 3. Parâmetros determinados nas polpas marrons e pré-branqueadas.

Parameter	Standard/Procedure
Gross yield	Ratio between mass a.s. of pulp before and after the process
Depurated yield	Ratio between mass a.s. of screened pulp before and after the process
Rejects content	Ratio between mass a.s. of rejects (material retained in sieves with gap of 0.2 mm of laboratory depurator) and the pulp mass a.s. before the process
kappa Number*	TAPPI - T236 om-99 (TAPPI, 1999)

*Determined with the rejects-free pulp.

The process selectivity and the solids content generated per ton of pulp were calculated according to the equations 1 and 2.

$$S = \frac{K_f}{SY} \quad (1)$$

Equation 1. S is equivalent to the process selectivity; K_f is the final kappa number and SY the screened yield in percentage.

$$tss/adt = \frac{(1 - TY) + CAA}{SY} \times 0,9 \quad (2)$$

Equation 2. tss/adt is equivalent to the solids content generated per ton of pulp in t · tsa⁻¹; TY is the total yield in percentage; CAA corresponds to the alkaline charge applied in decimal; SY is the screened yield in percentage and 0.9 refers to the absolutely dry pulp conversion factor to tsa (air-dried-ton) considering the pulp with 10% humidity.

In the filtrated samples the final pH and the residual alkaline concentration were determined according to the SCAN-N 2:28 standard (SCAN, 1988) (equation 3); to the difference between the applied alkaline charge and the residual alkaline concentration, the NaOH consumption was applied (equation 4).

$$CAR (kg \cdot t^{-1}) = \frac{1000}{C} \times CAR(g \cdot L^{-1}) \quad (3)$$

Equation 3: Therefore 1000 is the grams correction factor to kilogram; C is equivalent to the pulp consistency in percentage, and CAR is the residual alkaline concentration in kilogram per ton.

$$NaOH \text{ consumption } (\%) = \frac{CAA - CAR}{CAA} \times 100 \quad (4)$$

Equation 4: CAA corresponds to the alkaline charge applied in decimal; CAR is the residual alkaline concentration in kilogram per ton.

Data analysis

The Bartlett test was used in the statistical analysis and the variance homogeneity was noticed. After this step, the variance analysis and the Tukey test were conducted when comparing the averages to the level of 5% significance (95% of confidence).

RESULTS AND DISCUSSION

kraft Pulping

In the kraft cooking process the total yield was 62.9% with rejects content of 8.7%. The brown pulp kappa number obtained was 63.9. The residual active alkali at the end of the process was $6.0 \text{ g} \cdot \text{L}^{-1}$ and the total of solids generated was $0.83 \text{ t} \cdot \text{t}_{\text{sa}}^{-1}$. In summary, 20.6 kg of brown pulp were produced in 18 cooking. The results obtained during the pulping stage may be considered typical if we refer to eucalyptus chips processed by conventional batch cooking.

Oxygen delignification

Table 4 shows the average among the three repetitions of all treatments for each analyzed parameter.

The treatment with 140°C and alkaline charge of $60 \text{ kg} \cdot \text{t}^{-1}$ with ethanol promoted the lowest kappa number and less rejects content. However, taking into account these conditions, but with no additive, there was a greater solids content generated and lower screened yield. We point out that the lower kappa number found corresponds to a delignification rate of 54.2%, i.e., the percentage is above what is considered safe to maintain the integrity of pulp polysaccharides (MCDONOUGH, 1996, GIACOMIN, 2015).

The best selectivity was found in milder conditions of temperature (80°C) and alkaline charge ($15 \text{ kg} \cdot \text{t}^{-1}$), in addition to the presence of anthraquinone. According to Ventorim et al. (2006) pulps with higher kappa number show a higher initial viscosity and, typically, lose viscosity on oxygen delignification easier than with lower kappa number. However, the lowest selectivities found in this research were not inferior to the lowest selectivities seen by the aforementioned authors, who worked with lower kappa number pulps.

Oxygen delignification: features of pulp

Table 5 shows the effect on the pulp parameters with variations of temperature, alkaline charge and additives in the oxygen delignification.

It was possible to verify the kappa number reduction both by the temperature increase and by the applied alkaline charge, also followed by the selectivity drop and rejects content reduction. And in the screened yield, only one reduction was observed with the temperature increase, while the alkaline charge did not show significant influence for this parameter.

Through the rejects content drop it is possible to view the oxygen delignification efficiency in the conversion of rejects into pulp, especially when observing the temperature action. This new pulp produced from the rejects feeds the screened yield and promotes the maintenance of these parameters, also in the most intense conditions.

The oxygen delignification applied to $60 \text{ kg} \cdot \text{t}^{-1}$ of NaOH promoted greater reduction of kappa number, and also lower rejects content in all tested temperatures. The increased temperature used in the oxygen delignification caused a reduction of kappa number in all alkaline charges applied. The greater reduction of this parameter was observed with the temperature at 140°C .

The results obtained with the parameters variation show that an increase in the alkaline charge of 15 to $60 \text{ kg} \cdot \text{t}^{-1}$ has reduced the kappa number in 22.9 units concerning the brown pulp. This efficiency gain, regardless of the temperature, indicates that the alkaline charge is the most important variable to improve the oxygen delignification efficiency. Such behavior was not identified by Venson (2008), who concluded that the delignification efficiency is more sensitive to the temperature than to the alkaline charge.

The temperature provided selectivity similar to the alkaline charge, and this was superior only in the lower temperature. The more selective treatments of $15 \text{ kg} \cdot \text{t}^{-1}$ were considered in the alkaline charge. These mild conditions showed a higher kappa number and rejects content. Featuring a greater delignification, the charge of $60 \text{ kg} \cdot \text{t}^{-1}$ also resulted in a substantial drop in selectivity. The high increases in temperature represent considerable reductions in the kappa number without great drops in selectivity.

Table 4. Average results for all treatments.

Tabela 4. Resultados médios de todos tratamentos realizados.

Temperature (°C)	Charge (kg·t ⁻¹)	Additive	NK	SY	TR	SEL	TS	PF	AAR	CN
80	15	SEM	56.15	86.68	8.70	0.65	0.07	8.35	0.00	100.00
		AQ	61.07	83.88	8.68	0.73	0.11	8.69	0.00	100.00
		ET	53.64	86.66	8.62	0.62	0.07	6.31	0.00	100.00
	30	SEM	49.62	85.91	7.34	0.58	0.11	11.15	0.10	96.67
		AQ	58.51	87.22	7.58	0.67	0.09	10.61	0.20	93.33
		ET	48.15	85.38	7.15	0.56	0.12	10.61	0.20	93.33
	45	SEM	48.85	88.67	6.45	0.55	0.11	12.03	1.09	75.70
		AQ	53.25	87.52	7.43	0.61	0.11	11.41	1.27	71.85
		ET	43.18	87.80	6.21	0.49	0.12	11.73	1.40	68.89
	60	SEM	48.16	90.94	5.48	0.53	0.11	12.72	2.22	58.74
		AQ	51.93	88.25	6.63	0.59	0.13	12.25	2.53	57.78
		ET	42.70	89.10	4.57	0.48	0.14	12.53	2.30	61.67
100	15	SEM	54.36	85.80	8.42	0.63	0.09	8.26	0.00	100.00
		AQ	61.46	88.62	8.36	0.69	0.05	8.67	0.00	100.00
		ET	53.20	88.28	8.19	0.60	0.06	7.76	0.00	100.00
	30	SEM	47.03	84.50	7.13	0.56	0.13	9.14	0.00	100.00
		AQ	57.80	85.45	7.50	0.68	0.12	9.87	0.00	100.00
		ET	47.09	84.79	6.97	0.56	0.13	8.91	0.00	100.00
	45	SEM	45.53	85.37	6.34	0.53	0.15	11.35	0.36	92.00
		AQ	51.86	85.66	7.10	0.61	0.14	11.63	0.70	84.44
		ET	42.22	85.25	6.12	0.49	0.14	11.78	0.40	91.11
	60	SEM	40.35	85.43	5.35	0.47	0.28	12.34	0.94	84.28
		AQ	51.70	85.81	6.51	0.60	0.16	12.13	1.80	70.00
		ET	34.47	87.70	4.35	0.39	0.16	12.12	1.50	75.00
120	15	SEM	54.05	84.72	8.42	0.64	0.10	7.99	0.00	100.00
		AQ	60.80	86.70	8.47	0.70	0.07	8.41	0.00	100.00
		ET	52.72	86.84	8.15	0.61	0.08	7.80	0.00	100.00
	30	SEM	49.96	84.11	5.86	0.56	0.15	9.12	0.00	100.00
		AQ	54.91	87.86	7.12	0.62	0.09	9.22	0.00	100.00
		ET	46.46	86.40	6.75	0.54	0.11	9.10	0.00	100.00
	45	SEM	45.29	84.20	6.90	0.54	0.16	9.84	0.00	100.00
		AQ	51.78	83.49	6.73	0.62	0.17	10.36	0.20	95.56
		ET	42.16	85.50	5.86	0.49	0.15	9.52	0.00	100.00
	60	SEM	35.17	83.75	5.24	0.42	0.20	10.53	0.19	96.83
		AQ	47.04	83.33	6.11	0.56	0.20	11.75	0.90	85.00
		ET	32.35	85.74	3.65	0.38	0.19	11.48	0.48	92.06
140	15	SEM	53.14	83.94	8.25	0.63	0.11	7.87	0.00	100.00
		AQ	60.80	86.12	8.32	0.71	0.08	8.34	0.00	100.00
		ET	51.42	85.45	8.12	0.60	0.09	7.81	0.00	100.00
	30	SEM	45.37	87.05	6.82	0.52	0.11	9.09	0.00	100.00
		AQ	53.50	84.18	6.98	0.64	0.14	9.41	0.00	100.00
		ET	44.36	86.53	6.27	0.51	0.12	9.26	0.00	100.00
	45	SEM	44.59	84.46	5.69	0.53	0.17	9.46	0.00	100.00
		AQ	49.92	84.92	6.29	0.59	0.16	9.96	0.00	100.00
		ET	41.51	87.00	5.37	0.48	0.14	9.59	0.00	100.00
	60	SEM	33.84	83.27	4.47	0.41	0.22	10.59	0.13	97.78
		AQ	44.74	83.44	5.71	0.54	0.20	11.63	0.70	88.33
		ET	29.25	85.05	3.28	0.34	0.21	11.32	0.37	93.78

NK: kappa Number; SY: screened yield (%); TR: rejects content (%); SEL: selectivity; TS: tss/adt and t-tsa- I; PF: final pH; AAR: residual active alkali (g·L⁻¹); CN: NaOH consumption (%), SEM: no additives; ET: with ethanol; AQ: with anthraquinone.

Table 5. Average results of pulp analysis.**Tabela 5.** Resultados médios das análises da polpa celulósica.

Factors		NK	SY	TR	SEL	TS
Temperature, °C	80	56.07a	86.14a	8.39a	0.59a	0.09d
	90	49.98b	85.78a	6.96b	0.53b	0.12c
	100	46.68c	85.90a	6.37c	0.51c	0.14b
	120	40.97d	85.98a	5.11d	0.41d	0.17a
Charge, kg.t ⁻¹	15	51.26a	87.33a	7.07a	0.54a	0.11c
	30	48.92b	86.14b	6.86b	0.52b	0.13b
	45	47.47c	85.22c	6.60c	0.51c	0.14a
	60	46.03d	85.11c	6.30d	0.50d	0.14a
Additives	Sem	46.77b	85.54b	6.67b	0.50b	0.13a
	AQ	54.44a	85.77b	7.22a	0.58a	0.13a
	ET	44.05c	86.52a	6.22c	0.47c	0.13a

NK: kappa number; SY: screened yield (%); TR: rejects content (%); SEL: selectivity; TS: tss/adt and t-tsa⁻¹; SEM: no additives; ET: with ethanol; AQ: with anthraquinone. The different letters in the same column and factor indicate a significant difference by Tukey test with 5% significance.

In general, the results show that an improvement in delignification cannot be sought, either by the temperature increase or alkaline charge increase, without impairing the selectivity process. This loss of selectivity is extensively reported in the literature, being an intrinsic feature of oxygen delignification and representing the main problem of this process (AKIM et al., 2001; GIACOMIN, 2015; MCDONOUGH, 1996; VENTORIM et al. 2006).

As well as the black liquor, the residual filtrate of oxygen delignification also has as a destination the recovery boiler. The solids generation in delignification needs attention for not becoming a bottleneck in the pulp production. In this research, the alkaline charge and temperature factors had an important role, and the first was more influential. The increased alkaline charge also increases the delignification, which is directly proportional to the reduction of rejects and opposite to the screened yield.

On the application of anthraquinone and ethanol there were significant changes in the kappa number. Anthraquinone impaired the delignification, because the treatment with no additive showed a kappa number of 7.67, which is lower than the number using anthraquinone. And ethanol promoted a reduction of more than 10 points when compared to the anthraquinone treatment and 2.72 when compared to the treatment with no additive.

Concerning the yield there was no significant difference between the treatment with no additive and with anthraquinone, however, the addition of ethanol promoted the 1% increase in the screened yield.

As previously seen, concerning the temperature and alkaline charge factors, the reduction in the rejects content feeds the screened yield, given that this process converts the rejects into pulp. In the delignification efficiency, the best results for the rejects content were obtained from the addition of ethanol, reflecting in a greater screened yield.

The total of solids generated by ton of delignified pulp suffered no significant influence on the use of additives, producing 0.13 t · tsa⁻¹ for all applied additives.

Table 6 shows the presence of interactions between the factors according to ANOVA with 5% probability (0.01 ≤ p < 0.05) for the pulp features.

Table 6. Presence of factors interactions in the pulp features.**Tabela 6.** Presença de interações dos fatores nas características da polpa.

Interaction	NK	SY	TR	SEL	TS
Temperature x Charge	sg	sg	sg	sg	sg
Temperature x Additive	sg	sg	ns	sg	sg
Charge x Additive	sg	ns	sg	sg	ns
Temperature x Charge x Additive	sg	ns	sg	sg	sg

NK: kappa number; SY: screened yield (%); TR: rejects content (%); SEL: selectivity; TS: tss/adt and t-tsa⁻¹; sg: significant interaction at 5% probability (0.01 ≤ p < 0.05); ns: non-significant interaction at 5% probability (0.01 ≤ p < 0.05).

In addition to the individual response of each factor, factorial experiments also provided the interaction between the factors. This type of experiment checks if the differences in the levels response of one of the factors are similar or different in each of the levels of the other factor (PERECIN; CARGNELUTTI FILHO; 2008). In this study, for the significant interactions, the variations caused in each parameter by one factor along with the variation of another were similar, and despite significant, interactions were little informative.

In kappa number and rejects content, the treatments effect was improved with the increased alkaline charge and temperature, in addition to the presence of ethanol. Selectivity is improved in lower alkaline charges and temperatures, and in the presence of anthraquinone. The total of solids generated is growing in the higher alkaline charges and temperatures; however, when there is interaction with the additive factor, its production is reduced.

Oxygen delignification: features of the residual filtrate

As well as in cooking, the lignin precipitation at the end of the oxygen delignification is undesirable. In the pulping process the control parameter is the residual alkali and for the delignification it is the residual filtrate pH.

According to Rabelo (2006) and Suess (2010), the delignification in strongly alkaline conditions is necessary, because a significant part of the reaction with oxygen occurs in pH above 12. The pH over 10 at the end of delignification is recommended because a lower pH at the end allows the lignin precipitation (BACKA; RAGNAR, 2003; RAGNAR; BACKA, 2005).

In addition to the pH in the filtrate, the residual alkaline concentration and the NaOH consumption are parameters that also help in the process adjustment. The analysis averages of the residual filtrate, considering each parameter within each independent factor, can be seen in Table 7.

Table 7. Average results of residual filtrate analysis.

Tabela 7. Resultados médios das análises do filtrado residual.

Factors		Final pH	AAR g·L ⁻¹	NaOH Consumption (%)
Temperature, °C	80	10.70a	0.94a	81.50c
	100	10.32b	0.47b	91.40b
	120	9.59c	0.15c	97.45a
	140	9.52c	0.10d	98.32a
Charge, kg·t ⁻¹	15	8.02d	0.00c	100.00a
	30	9.62c	0.04c	98.61b
	45	10.72b	0.45b	89.96c
	60	11.78a	1.17a	80.10d
Additives	Without	9.99b	0.31c	93.88a
	Anthraquinone	10.27a	0.52a	90.39c
	Ethanol	9.85c	0.42b	92.24b

Different letters for the same parameter indicate significant difference by Tukey test, with 5% significance.

For the temperature of 80 °C the NaOH consumption was the lowest during the reaction. Considering the charge factor in the final pH results of the filtrate and the residual alkaline concentration in the liquor, these indicated that the other charges were sufficient to prevent the lignin precipitation, except the charge of 15 kg·t⁻¹.

The greater NaOH charge applied (60 kg·t⁻¹) resulted in a higher final pH and with higher concentration of residual alkaline, a situation that was also found by Venson (2008). Considering the influence of temperatures such as 120°C and 140°C in treatments, greater uses of alkali were obtained, and therefore, the lowest final pH and lowest amounts of residual alkali in filtrates. These results serve as an indicative of the temperature influence on the delignification rate, and that there is no sufficient presence of sodium hydroxide without an activating element to complete the reaction.

Treatments with anthraquinone showed better maintenance of final pH, greater residual alkaline concentration and lower alkaline charge consumption than the conditions with no additives and with ethanol. Considering the alkaline charge consumption, additive-free treatments were superior because the presence of ethanol caused a substantial drop in final pH. This fact was also found by Venson (2008).

Interactions were also identified among all factors in the residual filtrate characterization parameters according to ANOVA with 5% probability ($0.01 \leq p < 0.05$). As occurred with the pulp features, the interactions were little informative, because the effect of one factor, any of the three, was similar in the variation of other factors.

Considering the factors interactions, the final pH increases with the applied charge, and this behavior is potentiated when there is anthraquinone, and decreases when the temperature is increased. The residual alkaline concentration is lower in the highest temperatures and in the lowest alkaline charge, and this also occurs with the final pH. The presence of anthraquinone allows a higher residual active alkali, except when the charge is $15 \text{ kg} \cdot \text{t}^{-1}$. This charge is insufficient at any temperature and additive, with no remaining residual active alkali.

NaOH consumption is greater with higher temperatures and lower with alkaline charges. When the interaction with the additive factor is analyzed, in the presence of anthraquinone and ethanol, the alkali consumption is lower.

CONCLUSIONS

The results found in this study allow concluding that processing the pulp with rejects until the oxygen delignification results in a slight economic advantage. Given that the rejects are converted into pulp, they offset the screened yield drop.

The alkaline charge shows an influence in the oxygen delignification that is greater than the temperature. However, the temperature increases provide increases in the delignification efficiency. Temperature increases cause lower loss in selectivity than the increases in alkaline charge.

The anthraquinone addition provided greater selectivity, but with no gains in other parameters. Ethanol provided improvements in the oxygen delignification in several senses. First there was an increased efficiency of delignification and reduction of rejects, increasing 1% the screened yield. Therefore, the use of ethanol is, in fact, very suitable for pulps with high residual lignin content, given that the kappa number reduction was significant and the yield increased.

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