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POST-O_2 *EUCALYPTUS* PULP IN A/D(EP)DP BLEACHING SEQUENCE WASHED WITH RECIRCULATION OF THE ALKALINE FILTRATE

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Circuit closure in the pulp manufacturing process may mitigate water scarcity. This work aimed to analyse the feasibility of reusing the alkaline filtrate (carryover) from the (EP) stage of producing hardwood pulp in the A/D(EP)DP bleaching sequence. Pulp from *Eucalyptus grandis* and *Eucalyptus grandis* × *Eucalyptus urophylla* wood and the alkaline effluent from (EP) bleaching stage were collected in a pulp mill. Bleaching was conducted both without this effluent (as a control) and with 15 kg odt^{-1} of the alkaline filtrate from the (EP) stage. The consumption of reagents during bleaching and the chemical, physical, mechanical and optical pulp properties were evaluated. The alkaline filtrate increased the pulp kappa number from 1.4 to 2.2 with a fixed reagent dosage. The consumption of chlorine dioxide, sulfuric acid and the brightness reversion were 13.7, 17.3 and 20.1% higher in treatments using carryover, respectively to achieve a brightness level of 89 ± 0.2% ISO in the bleaching process. The viscosity, hemicelluloses content and the pulp properties did not vary between these two treatments. The adoption of effluent recirculation should consider the environmental and economic gain of reducing the water consumption and the negative effect of pulp chemical changes and the increase in reagent consumption.

Keywords: Circuit closure, pulp mill, pulp properties, wastewater, wood

INTRODUCTION

Water consumption in agriculture, industry and home use increases the scarcity of water resource (Semertzidis et al. 2018). In Brazil, the Federal Law 9433 of 1997 determines the rates for water use and discharge in industries. The pulp and paper industry demands large quantities of water and generates large volumes of effluents.

The optimisation of water use in pulp mills should be prioritised on bleaching, as this stage generates 50% of the factories effluents (Kansal et al. 2008, Kamali & Khodaparast 2015). Circuit closure reduces water use; however, the effect of this operation on reagent consumption, equipment wear and final product quality should be evaluated (Frigieri et al. 2015, Frigieri et al. 2016, Masrol et al. 2018).

The pH of the alkaline bleach filtrate is similar to that of the black liquor evaporated and burned in the recovery boiler (Kamali & Khodaparast 2015) and can be recirculated in the recovery cycle of chemical reagents (Huber et al. 2014). In addition, alkaline filtrate recirculation improves the performance of the effluent treatment plant, reducing the chemical oxygen demand load, the color and toxicity of the effluent to be treated. However, this technique requires evaporators to support the volume increase, as well as systems for washing the brown and delignified pulp with O_2 to avoid increasing the consumption of chemical reagents in the subsequent bleaching stages.

The objective of this study was to evaluate the reuse of the alkaline extraction EP filtrate in the wash after the Post-O_2 stage, considering the consumption of bleaching reagents and the final quality of the cellulose pulp.

MATERIALS AND METHODS

Sample collection and characterization

Samples of pulp delignified with O_2 (post-O_2) and the alkaline effluent filtered after the (EP) stage in an ECF bleaching sequence were collected at a *Eucalyptus grandis* and *Eucalyptus grandis* × *Eucalyptus urophylla* kraft pulp mill.

Bleaching

The pulp samples were bleached using the A/D(EP)DP sequence. The sequence consists of an acid stage followed by chlorine dioxide without intermediate washing of the pulp, "A/D"; alkaline extraction enhanced with hydrogen peroxide, "(EP)"; one stage with chlorine dioxide, "D" and followed by another with hydrogen peroxide, "P".

The addition of an organic load of 15 kg odt^{-1} of the alkaline (EP) filtrate after the post-O_2 stage to the pulp simulated the recirculation of the filtrate. This value is normal in kraft pulp mills.

Bleaching conditions were adjusted to reach 89 ± 0.2% ISO brightness without interference from organic matter in the control sequence (Table 1). These bleaching conditions dosage were also used in the pulp with an organic load of 15 kg odt^{-1} of the alkaline filtrate from the (EP) stage.

The dosage of chlorine dioxide and sulfuric acid in the second bleaching evaluation were set in order for the pulp both with and without the organic load of 15 kg odt^{-1} of the alkaline (EP) filtrate to reach 89 ± 0.2% ISO.

Evaluation of pulp quality

Brightness, kappa number, brightness reversion, viscosity, hemicellulose and hexenuronic acid contents, organic alloys, sodium, potassium, calcium, magnesium, ashes and extractives were determined in pulp samples. The pulps were refined and a graph with the number of revolutions in relation to the tensile index was prepared. The tear index, burst index, opacity, drainability and refinability were generated as functions of the tensile index (Table 2). Each test was replicated five times.

Table 1 Bleaching conditions used in the experiment

Stages	A	D	(EP)	D	P
Consistency (%)	10	10	10	10	10
Temperature (°C)	95	85	95	80	80
Time (min)	120	20	40	90	90
Kappa factor	-	0.26	-	-	-
ClO_2^- (kg odt^{-1})	-	-	-	10	-
NaOH (kg odt^{-1})	-	7	10	-	2.5
H_2O_2 (kg odt^{-1})	-	-	5	-	5
H_2SO_4 (kg odt^{-1})	5	-	-	-	-
Final pH	-	3.0	11.5–12	4.0–4.5	10.5–11

Table 2 Procedures used in the cellulosic pulp characterization

Procedure	Standard
Sheet preparation	T205 sp-06
Kappa number	TAPPI – 236
Brightness	T452 om-08
Brightness reversion	TAPPI um-200
Hemicellulose	T249 cm-85
Viscosity	Capillary viscometer method
Hexenuronic acids	Vuorinen et al. (1996)
Organic Alogens (OX)	PTS – RH:012/90 (1990)
Extractives in dichloromethane and ethyl acetate	T203 om-94
Metal content	TAPPI – 266
Tensile index	T494 om-06
Tear index	T414 om-04
Burst index	T403 om-02
Opacity	T1214 sp-07
Refinability	T248 sp-08
Drainability (Freeness)	T227 om-09

Statistical analysis

The values for cellulose pulp chemical characteristics were submitted for the homogeneity of variances (Bartlett's test at 5% significance) and normality (Shapiro-Wilk test at 5% significance) analysis.

A statistical analysis of the model identity was performed to evaluate whether the physical, mechanical and optical characteristics of the control pulp and of that with 15 kg odt^{-1}, as a function of refining, could be adjusted in a model at 5% significance.

RESULTS

Alkaline filtrate (carryover) recirculation and chemical reagent consumption

The addition of alkaline filtrate altered the pulp bleaching, with a fixed dosage. The kappa number was higher and the brightness lower for the pulp produced using this alkaline filtrate. It was necessary to increase the bleaching reagent consumption to revert this problem (Table 3).

Pulp chemical properties after bleaching

The use of the alkaline filtrate altered the chemical properties of the cellulose pulp, increasing the brightness reversion and some minerals, but it did not affect the extractive content, hexenuronic acids and hemicellulose (Table 4).

Physical-mechanical properties of the pulp after bleaching

The carryover did not affect the physical-mechanical and optical properties of the pulp. Therefore, for these properties; only one model could be used to describe the refining level (Figure1).

Table 3 Kappa number, brightness and reagent consumption during bleaching in cellulose pulp with and without carryover addition

Parameter	Control	Carryover (15 kg odt^{-1})
With fixed reagent dosage		
Kappa number after (EP) stage	1.40	2.20
Brightness (EP) stage	76.90	76.10
Final brightness	88.80	87.20
With variable dosage to reach final brightness of 89 ± 0.2% ISO		
Kappa number	1.60	1.90
ClO_2^- (kg odt^{-1}) consumed	13.59	15.44
H_2SO_4 (kg odt^{-1}) consumed	15.00	17.60
Final brightness	88.80	88.90

Table 4 Brightness reversion, chemical characteristics and mineral content of the cellulose pulp with or without carryover addition

Bleaching	Control	Carryover (15 kg odt^{-1})
Brightness reversion (% ISO)	1.79a	2.15b
Viscosity (cP)	11.94a	11.50a
OX (gCl^- t^{-1})	54.20a	74.10b
Extractives in dichloromethane and ethyl acetate	0.06a	0.06a
Hexenuronic acids (mmol kg^{-1})	3.16a	2.62a
Hemicellulose (%)	17.10a	16.30a
Na^+ (mg L^{-1})	0.088a	0.051b
K^+ (mg L^{-1})	0.013a	0.018a
Mg^{2+} (mg L^{-1})	0.011a	0.036b
Ca^{2+} (mg L^{-1})	0.14a	0.11a
Fe^{2+} (mg L^{-1})	0.007a	0.009a
Mn^{2+} (mg L^{-1})	0.003a	0.001a

Means with the same letter are not significantly different at 0.05 level.

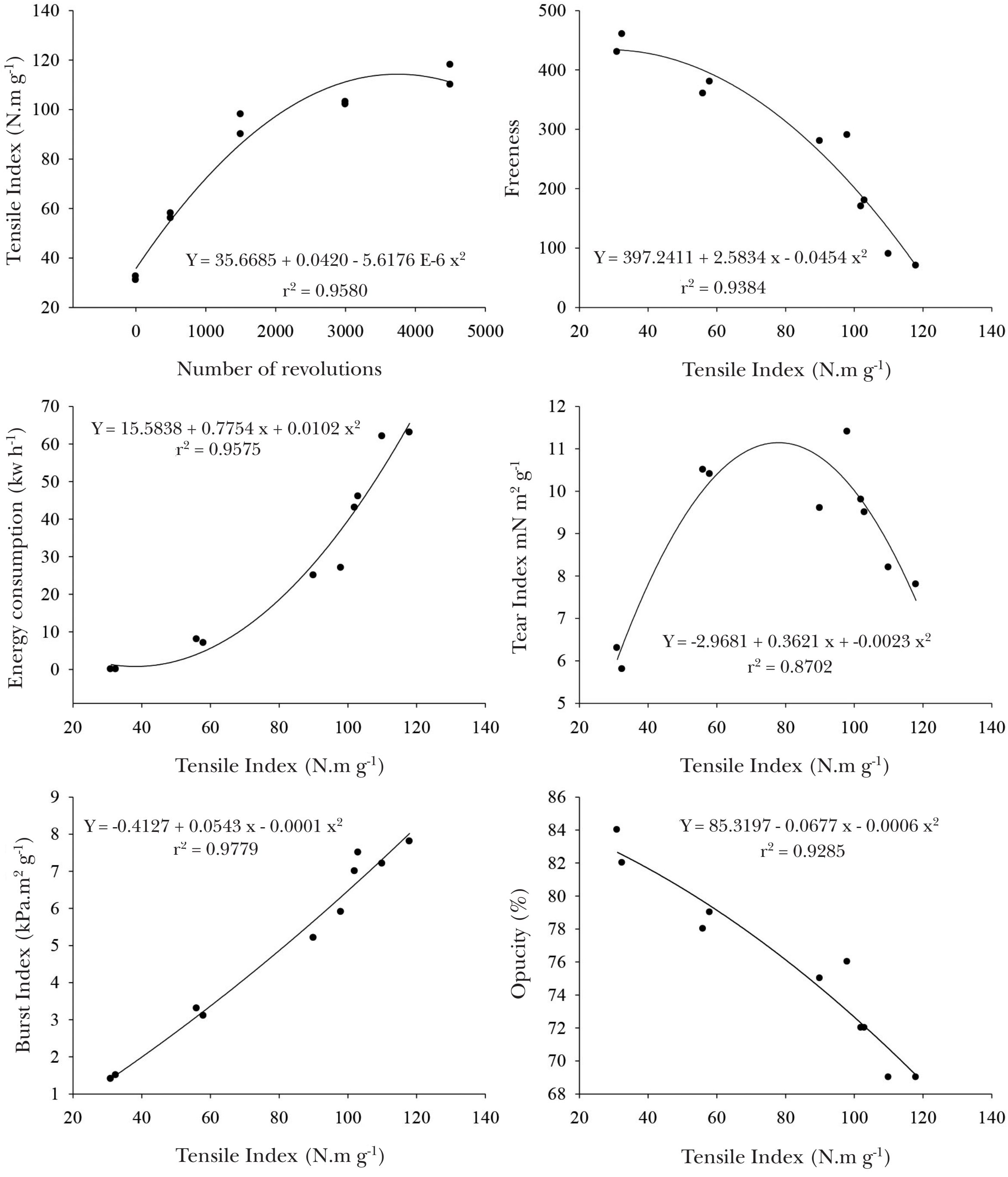

Figure 1 Tension index, refinability, tear index and bursting strength of refined pulp with or without carryover

DISCUSSION

Alkaline filtrate (carryover) recirculation and chemical reagent consumption

The higher kappa number and lower brightness for the pulp with 15 kg odt^{-1} of the alkaline filtrate (carryover) indicates a higher concentration of chromophoric compounds in the cellulose pulp. The filtrate recirculation returned the residual lignin and extractives to the system (Sixta 2006, He et al. 2018). The increased in the compounds oxidised by permanganate and resulted in a kappa number of 2.2 and final brightness of 87.2% ISO.

The higher H_2SO_4 load in the acid hydrolysis stage A (Table 1) of the pulps in relation to the control sequence was due to the carryover alkalinity (Sixta 2006). The increased in pH negatively impacted the chlorine dioxide stage and increased its consumption (Sevastyanova et al. 2012, Ferraz & Ventorim 2018). It was caused by the chlorite (ClO_2^-) formation in pH 4.0 and reducing the delignification rate of chlorine dioxide. The minimum chemical reagent loss in stage D occured at a pH between 3.0–4.0. At pH below 2.0, chlorate formation (ClO_3^-) was favored, which also damaged the dioxidation stage (Dence & Reeve 1996).

The higher chlorine dioxide load (12%) in the second D stage using carryover to reach final brightness of 89 ± 0.2% ISO increased the consumption of chemical reagents, and thus increased the bleaching costs (Brogdon 2015, Sarto et al. 2015). Circuit closure might have more advantageous for hardwood pulps compared to conifers, because the last group had more resistant lignin and resinous extractives (Brogdon 2015). Negative effects of the recirculation of the alkaline filtrate could be adjusted with a greater amount of chemical reagents to remove the organic compounds from returning to the system and affected the final pulp brightness.

Pulp chemical properties after bleaching

The alteration of the pulp chemical properties increased the brightness reversion of the bleached pulp by 20.1% as compared to the control with the addition of 15 kg odt^{-1} of the alkaline filtrate, this can be explained by a higher amount of leuco-chromophore compounds remaining in the pulp after bleaching. The similar extractive and hexenuronic acid content were compounds which contributed to the brightness reversion (Nie et al. 2015) between treatments. It indicated that the brightness reversion might be associated with other leuco-chromophore compounds, such as hydroxylated carboxylic acid (Maltha et al. 2011).

The higher organic alogens (OX) concentration of the pulp, increased by 36.7% compared to the control with the addition of the carryover, was due to the increased ClO_2^- consumption during bleaching. These values were still acceptable for ECF pulp (< 200 $gCl^- t^{-1}$) as those below 30 $gCl^- t^{-1}$ of OX were suitable for ECF light processes (Sixta 2006).

Similar viscosity and hemicellulose content with the use of carryover were important because viscosity indirectly affected the polymerization degree of the pulp and hemicelluloses improved the pulp refining, increasing its swelling and the fiber flexibility due to hydrophilic groups (Biermann 1996). These parameters must remain constant to avoid the reduction of pulp strength and its refinability.

The carryover increased the potassium and magnesium contents in the bleached pulp by 41% and 225% respectively, reduced the sodium by 42% and had no effect on calcium, iron, manganese and potassium; implying that carryover minerals were impregnated in the cellulose pulp during effluent recirculation. The increase of minerals reduced the pulp quality and caused incrustations in the equipment (Huber et al. 2014).

Physical-mechanical pulp properties after bleaching

The similar values of the physico-mechanical properties for the same refining level in the pulps with or without carryover suggested that the fiber integrity and the connection between them were not affected by carryover recirculation (Gharehkhania et al. 2015). A high chlorine dioxide consumption during bleaching might degrade the pulp (Favaro et al. 2014), as reported for *Eucalyptus camaldulensis* and *Acacia mangium* (Karin et al. 2011). However, it did not occur in the current treatments, indicating that the increased carryover load during bleaching did not affect the fiber morphology and its interactions, which could be explained by the low increase in reagent loading due to the addition of the carryover.

The increase of the tensile index and bursting strength throughout the refining, and an increase in the tear index followed by a decrease, indicated that fiber bonding had increased and its subsequent degradation during this process. Refining increased the number of fiber connections in one stage but also degraded them in a later stage; the tensile index and bursting strength were related to the connection between the fibers, whereas the tear index was related to fiber morphology (Gharehkhania et al. 2015). The tear index was reduced at lower refining levels in softwood pulps, as reported for *Pinus massoniana* and China fir (Chen et al. 2016). This index in hardwood pulps increased at the first refining level due to the increase in the number of connections and decreased at higher levels due to fiber degradation (Gharehkhania et al. 2015), as reported for *Corymbia citriodora* (Severo et al.

2013) and *Eucalyptus grandis* × *Eucalyptus urophylla* (Zanuncio et al. 2016).

The decrease in opacity caused by the increased refining indicated that light passed through the paper more easily. The volume of voids in the pulp without refining was larger and the light passed through the space and fiber wall resulting in diffraction and dissipation. These spaces were scarce in the refined pulps, so the light crossed only the cell wall with lower diffraction (Biermann 1996). The opacity reduction with the refining increment was reported for grass (Andrade & Colodette 2016), softwood (Chen et al 2016, 2017) and hardwood (Zanuncio et al. 2016, Pupo et al. 2019) pulps.

CONCLUSION

Effluent recirculation with a fixed reagent dosage increased the kappa number and decreased the pulp brightness, which suggested a higher chlorine dioxide and sulfuric acid load was necessary in order to reach 89 ± 0.2% ISO. The addition of 15 kg odt^{-1} of the carryover increased the consumption of ClO_2^- and sulfuric acid by 13.7% and 17.3% respectively. The main effects of the carryover in bleached pulp were an increase in OX content, brightness reversion and calcium content. The carryover recirculation did not affect the viscosity, hemicellulose and hexenuronic acid contents or the physical-mechanical and optical properties of the refined pulp. Effluent recirculation should consider environmental and economic gains from water use, increased reagent consumption in bleaching and chemical changes in the cellulose pulp.

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