CELLULOSE CHEMISTRY AND TECHNOLOGY

EFFECT OF KRAFT PULPING TEMPERATURE AND ALKALINITY ON EUCALYPTUS ECF BLEACHING

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Received August 24, 2015

The effects of eucalyptus kraft pulping conditions on subsequent bleaching were investigated. Three samples of industrial eucalyptus chips underwent kraft pulping with different alkalinities and hexenuronic acid (HexA) content. Pulp was bleached by the sequence OD(EP)DP. Decreasing the cooking temperature reduced phenolic group content and the S:G ratio of residual lignin. Reducing temperature in kraft pulping resulted in better oxygen delignification and had better results whenever low temperatures and lower alkalinities were used. The final pulp brightness was not influenced by cooking temperature or alkalinity. However, viscosity, brightness reversion and chlorine dioxide consumption were influenced by alkalinity. The S:G ratio was greater at higher temperatures. Higher kappa number had better bleachability in Pre-O_2, while samples with higher levels of HexA had lower delta kappa. No correlation was established between phenolic groups and pulp bleachability.

Keywords: oxygen delignification, residual lignin, hexenuronic acids

INTRODUCTION

Different temperatures and alkalinities used in the eucalyptus kraft pulping process affect the chemical composition and structure of unbleached pulps, through producing diverse forms of residual lignin and levels of hexenuronic acid (HexA) in the brownstock. These substances can influence bleaching carried out without molecular chlorine (elemental chlorine free or ECF).[1]

Temperature in kraft pulping has a significant effect on pulp bleachability, which can reduce the consumption of bleaching chemicals to reach a desired brightness and, therefore, production costs.[2] Thus, pulping and bleaching must both be considered when studying the reduction of chemical products in the process.[3] Tran[2] showed that high cooking temperature degraded lignin more, creating more free phenolic hydroxyl groups. Although there are higher alkaline levels at low cooking temperatures, residual lignin was preserved, resulting in lower levels of free phenolic hydroxyl groups and more guaiacyl groups. This fact helps to explain the elevated level of delignification with oxygen and low bleachability for pulp processed at low temperatures[2]. The cooking temperature has a great effect on the phenolic groups; however, in the analysis of these groups, Pinto *et al.*[4] did not establish any relationship between the relative abundance of these units and ease of cooking and bleaching. It is known that lignin content by itself does not determine the performance of wood during the pulping and bleaching steps. The efficiency of these steps is mainly influenced by lignin's structural factors and the syringyl to guaiacyl (S:G) ratio. The S:G ratio determines the consumption of chemical reagents.

High effective alkali concentration in the pulping process makes the oxygen delignification stage more effective, allowing less bleaching reagents to be used.[5] However, during kraft cooking, lignin undergoes many reactions. The formation of carboxylic acid and condensed phenolic hydroxyl groups are among the main alterations that take place in residual lignin. At the end of the pulping process, the residual lignin contains up to three times as many condensed phenolic hydroxyl groups on C-5.[6] These substances are not very reactive in the oxygen bleaching stage (Pre-O_2). The level of phenolic units influences pulp bleachability.[7]

The level of phenolic hydroxyl groups in lignin is also affected by pulping alkalinity. These groups have been shown to make up around 50% of residual lignin in kraft pulp.[8] Cooking conditions that encourage the formation of these functional groups improve pulp bleachability.[1]

In the 1990s, many studies of HexA reactivity were carried out. These studies found out that the pulping processes with high effective alkali concentration resulted in low levels of HexA.[9-11]

HexA is not eliminated in oxygen delignification, which reduces its effectiveness.[12] When this acid is present in pulp, it results in the consumption of reagents, such as chlorine dioxide, which makes the bleaching sequence more expensive.[13] At the final bleaching stage, HexA can cause quality problems, such as brightness reversion and increasing retention of metal ions.[14]

Chlorine dioxide prefers to react with phenolic lignin structures that can form stable radicals, while reactions with non-phenolic lignin and HexA are slower.[15] Removal of oxidized lignin significantly increases the reaction of chlorine dioxide with non-oxidized lignin.[16] It was also observed that chlorine dioxide did not react with HexA itself, only with compounds generated during this stage.[17] The bleachability of eucalyptus kraft pulp can be improved if lower levels of HexA are present in the brownstock.[18]

The objective of this study was to evaluate three cooking temperatures and three alkali loads on kraft pulping of *Eucalyptus spp*., producing different levels of phenolic groups, hexenuronic acids and syringyl-to-guaiacyl ratios, and their effect on pulp bleachability.

EXPERIMENTAL

Three different samples of industrial *Eucalyptus spp.* chips were used to produce fifteen different kraft pulps by conventional cooking in the laboratory. Cooking was performed in a rotary digester. The rotary digester had four electrically heated 1.5-liter-capacity reactors. Each reactor was equipped with a thermometer and pressure gauge. This digester enabled four processes to be carried out at the same time. Chips (100 g o.d.) and the white liquor were inserted into the capsules with water to adjust the liquor-to-wood ratio. The conditions were as follows: 4:1 liquor-to-wood ratio (L/kg), 30% sulfidity, 80 °C initial temperature, 155, 160, and 165 °C final temperature, and 90 min heating-up period. Active alkali (%, as Na_2O) was varied in order to obtain similar degrees of delignification, expressed as kappa number (KN). A series of pulps with different KN was obtained by maintaining similar H-factor and similar alkali load. Another experiment was carried out using 30% sulfidity, an active alkali load of 17, 19, and 21% (as Na_2O), and 4:1 liquor-to-wood ratio. The pulping temperature for this procedure was maintained isothermally at 160 °C for 90 min and included a 90 min heat-up period.

After cooking, the wood chips were removed from the reactor capsules and washed thoroughly with water at room temperature. The pulp was filtered through a 0.2 mm slot screen, dewatered to a consistency of approximately 30%, and then stored in polyethylene bags.

The following parameters were determined for each type of pulp: brightness, kappa number, and HexA. Free phenolic groups were determined and the syringyl-to-guaiacyl ratio (S:G) was measured in the residual lignin of the pulp. KN was analyzed according to the procedure described in standard TAPPI- 236 om-99; and pulp brightness was analyzed according to the procedure described in standard TAPPI- 525 om-92. HexA was determined according to the method proposed by Vuorinen *et al.*[19]

Free phenolic groups

The content of free phenolic hydroxyl groups in the different types of pulp was determined by the periodate oxidation method based on methanol formation. A sample of 350 to 400 mg of pulp was placed in a 20.0 mL test tube with 800 mg of sodium periodate ($NaIO_4$). Then, 7.0 mL of distilled water was added and the tube was shaken until the sodium periodate dissolved completely. After that, 1.0 ml of acetonitrile solution (3.0 mg/mL) was added to the tube as an internal standard. The suspension was homogenized and kept refrigerated at 4 °C for 72 hours and shaken occasionally. The amount of methanol formed was determined by gas chromatography (GC); 1-2 μL of the mixture was injected into the equipment. The GC analysis was carried out at an initial temperature of 80 °C for 20 minutes, an injector temperature of 150°C, a detector temperature of 250 °C, with N_2-carrier gas, and an output of 30 mL/min.

Nitrobenzene oxidation

Samples of pulp with a value corresponding to 50 mg of lignin were passed through a 40 mesh sieve. The samples were transferred to small reactors; 40 mL of 2N NaOH and 2.5 mL of nitrobenzene were added in a nitrogen atmosphere. These reactors were sealed and immersed in an oil bath at 170 °C for two hours. The reactors were shaken occasionally during this time. After the reaction period, they were placed in an ice bath. The reaction product was filtered using a

Whatman qualitative filter and washed with NaOH 2N. The reaction product was transferred to a liquid-liquid extraction flask with 3 x 50 mL of chloroform. The pH of the aqueous phase was adjusted to be between 3 and 4 with concentrated HCl. The aqueous phase was then extracted with dichloromethane (DCM).

One milliliter of 2.6-dimethoxy phenol (0.1093 mmol/mL) was added to the extracted fraction with DCM as an internal standard. Residual water was removed with anhydrous sodium sulfate and evaporated in a vacuum at 40 °C. The residue was dissolved in DCM. A sample of 0.1 mL of *N*,*O*-bis (trimethylsilyl) trifluoroacetamide (BSTFA) of this solution was used for silylation of the sample during one night. After silylation of the sample, the reaction products were analyzed by gas chromatography at the following conditions: initial temperature of 120 °C for 1 minute; 5 °C/minute initial rate up to the final temperature of 250 °C; the maximum temperature was maintained for 10 minutes; 250 °C injector temperature; and 270 °C detector temperature. A SE-30 model column was used. Lignin content was analyzed and S:G ratio was determined by nitrobenzene oxidation using previously reported methods.[20]

Oxygen delignification (O)

Oxygen delignification was carried out in a rotating autoclave with four individual 1.5-liter-capacity reactors. The pulp was mixed with a solution of NaOH (20 kg/t) and H_2O in polyethylene bags at 10% consistency before being put into the reactor. When the temperature reached 95 °C, oxygen (18 kg/t) was injected until 500 kPa pressure was reached. The reaction was maintained for 60 minutes. After 60 minutes, the pressure was released and residual liquor samples were taken for pH analysis. Finally, the pulp was washed with the equivalent of 9 mL of deionized water per gram of over dry (o.d.) pulp.

Bleaching with chlorine dioxide (D), hydrogen peroxide (P) and extraction with hydrogen peroxide (EP)

The pulp was mixed with a solution of chemicals and water in polyethylene bags at 10% consistency and then put into a microwave oven to reach the temperature defined for the bleaching stage. The mixture was kept in a thermostatic bath for a predetermined time. Then, residual liquor samples were taken for pH and analysis of residual bleaching agents. Finally, the pulp was washed with the equivalent of 9 mL of deionized water per gram of o.d. pulp (Table 1).

RESULTS AND DISCUSSION

Eucalyptus is normally cooked to obtain a kappa number (KN) between 15 and 20, which also generates a high level of HexA.[21] In this study, pulp with KN from 13.9 to 20 had HexA levels from 32.3 to 68.5 mmol/kg of pulp, free phenol from 32.7 to 17.1, and S:G ratio from 0.85 to 1.73 (Table 2). A decrease in cooking temperature resulted in lower levels of phenolic groups and S:G ratio, since lower temperatures had longer cooking time. The S:G ratio appears to be the dominant parameter governing the rate and extent of kraft cooking and this dominance appears to be independent of species, genera and growing sites.[22-24]

Table 1
General bleaching conditions

Conditions	Bleaching stages				
	O	D	(EP)	D	P
Consistency (%)	10	10	10	10	10
Time (min)	60	30	60	180	120
Temperature (°C)	95	60	70	70	95
Pressure (kPa)	500	-	-	-	-
NaOH (kg/t)	20	-	10.0	-	8.0
H2SO4 (kg/t)	-	4.0	-		-
O_2 (kg/t)	20	-	-	-	-
ClO_2 (kg/t as Cl_2)	-	Kf=0.18[a]	-	10.0	-
H_2O_2 (kg/t)	-	-	3.0	-	3.0
Final pH	11.5	2.8	12.1	3.9	11.1

[a] Kf = Kappa factor

Figure 1 shows the influence of pulping temperature and alkalinity on the delignification rate in the oxygen stage, as represented by “delta kappa”. Lower temperatures were seen to have greater effect on oxygen delignification (Fig. 1A), even though the pulps initially had lower levels of free phenol and a low S:G ratio in the residual lignin. The pulp in sample "A" had a KN around 16, while samples "B" and "C" had KN around 14. The use of higher alkali load results in higher efficiency of the transformation of 4-*O*- methyl glucuronic acids into HexA's.[25]

Table 2
Characteristics of samples after kraft cooking

Sample	Temperature (°C)	Alkali (%) as Na_2O	Kappa number	HexA mmol/kg	Free phenol	Syringyl/ guayacil ratio
Sample A	155	17	16.6	55.9	27.6	0.85
	160		16.8	45.8	29.0	1.43
	165		16.9	52.6	32.7	1.55
	160	15.5	20	44.9	31.5	1.73
		17	16.8	45.8	29.0	1.43
		19	14.9	33.8	22.3	1.13
Sample B	155	21	14.6	67.3	21.9	0.91
	160		13.9	32.3	25.1	1.00
	165		14.5	43.9	25.5	1.02
	160	17	18.2	51.5	24.0	1.10
		19	16.1	58.9	21.9	0.91
		21	13.9	32.3	18.8	0.88
Sample C	155	21	14.6	41.1	20.9	1.18
	160		14.2	41.3	21.2	1.21
	165		14.6	42.4	22.2	1.27
	160	17	18.3	64.4	23.4	1.22
		19	16.2	68.5	20.9	1.18
		21	14.2	41.3	17.1	0.88

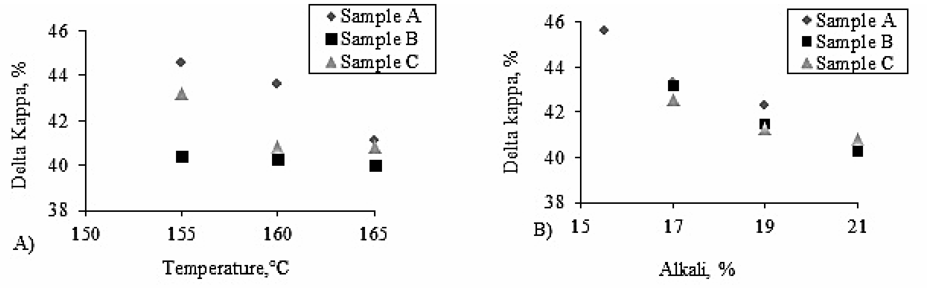

Figure 1: Influence of (A) temperature and (B) alkaline load on cooking and delignification of pulp in the oxygen stage

Conceptually, the structural variations of the residual lignin have an important role in oxygen delignification,[26-28] and the bleachability is generally related to initial KN and the load of sodium hydroxide used in this stage. Higher initial KN presents better bleachability[27] and greater cellulose degradation.[29-30] However, oxygen delignification is influenced by various factors, not only by S:G ratio and phenolic groups, since the KN is not solely made up of lignin.[17]

Decreasing the alkalinity during kraft cooking at 160 °C increased the KN, the levels of phenolic groups, and the S:G ratio (Table 2). According to Pinto *et al.*,[4] reducing the alkali charge when cooking some eucalyptus species increases the S:G ratio because the syringyl lignin has two methoxyl groups in positions 3 and 5 of the aromatic nucleus. Syringyl lignin is known to be more reactive than guaiacyl lignin, which enhances its degradation and removal.[31-32] Previous work[30] could not conclude if the S:G ratio is a dominant parameter governing the ease of delignification of kraft pulps.

Pulps obtained using a lower concentration of alkali in cooking have a greater concentration of organic groups with more reactivity in the residual lignin. The phenolic groups in the residual lignin have a dominant role in delignification with O_2 because the phenolic structures are more reactive than the non-phenolic structures.[26,33] As it has been shown by other authors,[34] the phenolic hydroxyl group content of residual lignin slowly increases during the cooking period. The decrease in alkali used in kraft pulping resulted in greater delignification of pulp in Pre-O_2 (Fig. 1B) since delignification efficiency is highly influenced by initial KN. Higher KN has higher delignification rates and greater selectiveness than pulp with low KN.[35] The results for phenolic hydroxyl groups also suggest that residual lignin is mainly made up of non-conjugated structures that are reduced with the reduction in cooking temperature.[2]

Gomide *et al.*[35] carried out cooking process with different effective alkali levels and obtained eucalyptus pulp with different KNs. They verified that the amount of HexA can vary from 34.7 to 57.9 mmol/kg. This variation is due to different alkali loads used and different uronic acid levels in the wood. In the present study, HexA varied from 32.3 to 68.5 mmol/kg and the same tendency was seen, in which greater alkali charge resulted in pulp with greater levels of HexA acid. This acid causes an increase in consumption of bleaching agents, reduction of brightness, greater brightness reversion, and worse metal removal.[36]

Effect of cooking alkalinity and temperature on brightness in bleaching stages

The brightness result for different bleaching stages in the OD(EP)DP sequence did not have a clear tendency for the effect of cooking alkali, as shown in Table 3. However, there was a notable difference between Samples A, B, and C. A possible explanation was that there were more phenolic groups in brownstock after kraft cooking in Sample A. These groups have an important role in pulp bleachability, and greater alkali load in kraft pulping results in better bleachability of cellulose pulp.[37]

The data in Table 4 shows that it was not possible to establish a clear tendency of the effect of cooking temperature on the different bleaching stages in the OD(EP)DP sequence. Sample A had the greatest number of phenolic groups present in the brownstock after kraft cooking. It had greater reactivity with chlorine dioxide and more efficient bleaching.[38] A study by Gustavsson *et al.*[3] verified that pulp bleachability was more efficient when higher cooking temperatures were used for pulp with low and medium alkaline loads; while for pulp with high alkaline loads, bleachability did not vary. According to Gellerstedt,[39] the desired increase in brightness, which is the goal of bleaching, is unquestionably related to the elimination of lignin compounds. However, Bäckström *et al.*[40] reported an increase in bleachability with a decrease in temperature. Although an increase in cooking temperature improved the selectivity of the process when both [HO^-] and [HS^-] were low. An example of this situation is the cooking carried out with extremely low amounts of chemical reagents. The present study had residual alkali of 9 to 12 g/L.

Residual lignin, HexA content, and lignin-carbohydrate complex content are factors that can explain the differences in pulp bleachability. While there is a relationship between ether β-O-4 structures and bleachability,[3,41] there is no correlation between the phenolic hydroxyl groups in residual lignin in unbleached pulp and bleachability.[42-43] It was not possible to establish a correlation between phenol groups and pulp bleachability in the present study.

Table 3
Pulp brightness in bleaching stages in OD(EP)DP sequence caused by kraft cooking carried out with different alkalinity

Sample	Alkali (%) as Na_2O	O	D_0	(EP)	D	P
		Brightness, % ISO				
Sample A	15.5	51.5	76.9	85.7	89.4	91.9
	17	54.3	77.9	85.3	90.4	91.8
	19	56.7	77.9	85.3	89.6	91.8
Sample B	17	51.3	75.1	84.1	88.6	90.8
	19	51.0	74.7	84.3	88.1	90.5
	21	52.9	74.1	83.5	87.9	90.0
Sample C	17	49.2	73.8	85.5	87.0	89.8
	19	51.0	74.7	84.6	88.1	90.5
	21	51.3	73.3	84.9	86.6	89.5

Table 4
Pulp brightness in bleaching stages in OD(EP)DP sequence caused by kraft cooking carried out at different temperatures

Sample	Temperature (°C)	Brightness, %ISO				
		O	D_0	(EP)	D	P
Sample A	155	55.6	78.7	82.2	89.5	91.9
	160	54.3	77.9	85.3	90.4	91.8
	165	53.6	77.1	84.3	89.2	92.0
Sample B	155	52.9	73.4	83.5	87.9	90.6
	160	52.9	74.3	83.5	87.9	90.0
	165	52.3	74.1	83.3	87.4	89.7
Sample C	155	52.5	74.7	84.5	86.3	89.1
	160	51.3	73.3	84.9	86.6	89.5
	165	50.9	71.0	83.9	86.8	89.1

Table 5
Kappa number of [O and (E+P)] bleaching stages and viscosity of [O, (EP) and P] bleaching stages in OD(E+P)DP sequence caused by kraft cooking carried out with different alkali

Sample	Alkali (%) as Na_2O	Brownstock	O	(EP)	O	(EP)	P
		Kappa number			Viscosity, cP		
Sample A	15.5	20.0	11.4	4.8	34.0	26.2	22.7
	17	16.8	9.7	5.3	29.9	25.8	20.7
	19	14.9	8.1	5.0	23.0	20.9	15.6
Sample B	17	18.2	10.5	4.0	32.2	24.2	18.5
	19	16.1	10.0	5.0	26.9	20.3	14.3
	21	13.9	8.3	3.7	21.3	15.0	13.0
Sample C	17	18.3	10.3	5.4	30.7	26.7	18.1
	19	16.2	10.0	5.0	26.3	18.5	14.9
	21	14.2	8.3	4.1	19.3	15.4	12.4

Effect of cooking alkalinity on Kappa number and viscosity of bleached pulp

Alkali in the brownstock clearly tended to affect the KN result in the O and (EP) stages of the OD(EP)DP sequence. KN diminished after the oxygen delignification stage and after the hydrogen peroxide extraction stage. This shows that KN has a tendency to become similar after the use of the same Kappa factor (0.18) for all of the samples (Table 5), since pulp with higher KN had greater delignification in the oxygen stage.[27] This tendency is sustained because pulp with higher KN has a greater level of phenolic groups and higher S:G ratio (Table 2).

The results reported by Froass *et al.*[42] for softwood suggest that pulp with a higher KN in the residual lignin is more reactive with ClO_2. In their experiments, isolated residual lignin reacted with chlorine. They showed that rather than higher residual lignin KN having less phenolic groups, it had a greater increase in formation of carboxylic acid, which suggests more reactive lignin. Barroca *et al.*[44] also verified that delignification is greater for higher KN in the ClO_2 stage for *Eucalyptus globulus* pulp. Despite the fact that greater cooking temperatures lead to less viscosity and lower yield, authors such as Pascoal Neto *et al.*[37] and Colodette *et al.*[1] verified that a greater amount of residual alkali in the pulp is beneficial to bleachability.

The viscosity result of the different bleaching stages, O, (EP), and P, had a clear tendency of being affected by the alkali in the brownstock. It reduced at each bleaching stage. Samples A, B, and C had different viscosity (Table 5) due to a different alkalinity used in the pulping process. When bleaching conditions are the same for all types of pulp, the difference between them reduces along the sequence.

Effect of cooking temperature on Kappa number and viscosity of bleached pulp

Cooking temperature did not have a clear tendency to affect the KN result in the bleaching stages [O and (EP)] (Table 6). Even though free phenolic groups and the S:G ratio were influenced by temperature, it did not have an effect on the KN of bleached pulp. According to Gustavsson *et al.*,[3] it is believed that free phenol structures are the main site of attack of many bleaching agents, such as O_2 and ClO_2. Despite this, the content of free phenolic hydroxyl groups in the residual lignin in unbleached pulp could not be linked to the bleaching responses in the present study.

According to Daniel *et al.*,[18] the bleachability of cellulose pulp is linked to HexA content in the pulp. HexA increases with active alkali in pulping when it varies from 14 to 17%; when there was more than 17% active alkali in the cooking process, HexA tended to decrease due to greater degradation of xylan chains.

Cooking temperature did not have a clearly defined influence on bleached pulp viscosity (Table 6). The viscosity decreased throughout the bleaching sequence. Different temperatures utilized in the pulping process with the same H factor affect the viscosity of pulp. Higher cooking temperatures have a negative effect on viscosity and bleaching yield.[37]

Effect of alkalinity and temperature on brightness reversion of bleached pulp

The results for brightness reversion have a slight tendency to diminish when more alkali is utilized in the pulping process (Table 7). The sample A had more brightness reversion since it had higher final brightness. Therefore, pulping temperature had no effect on brightness reversion of bleached pulp. Brightness reversion of this bleaching sequence was low because the H_2O_2 utilized in the final stage of the bleaching sequence is an excellent brightness stabilizer.[45]

Table 6
Kappa number of bleaching stages [O and (EP)] and viscosity of bleaching stages [O, (EP) and P] in OD(EP)DP sequence caused by kraft cooking at different temperatures

Sample	Temperature (°C)	Brownstock	O	(EP)	O	(EP)	P
		Kappa number			Viscosity, cP		
Sample A	155	16.6	9.7	5.4	29.1	25.0	18.1
	160	16.8	9.7	5.3	29.9	25.8	20.7
	165	16.9	10.3	4.6	30.4	26.2	19.9
Sample B	155	14.6	8.3	3.7	21.3	15.0	13.0
	160	13.9	8.3	3.7	21.3	15.0	13.0
	165	14.5	8.5	4.0	19.2	13.8	12.1
Sample C	155	14.6	9.7	5.1	25.7	18.3	14.8
	160	14.2	8.3	4.1	19.3	15.4	12.4
	165	14.6	8.7	4.2	18.5	12.4	11.8

Table 7
Brightness reversion and consumption of chlorine dioxide in bleaching

Sample	Alkali (%) as Na_2O	Reversion	Total ClO_2	Temperature (°C)	Reversion	Total ClO_2
Sample A	15.5	2.0	11.6	155	1.8	10.4
	17	1.9	10.4	160	1.9	10.4
	19	1.8	9.3	165	1.7	10.9
Sample B	17	1.4	11.0	155	1.5	9.5
	19	1.6	10.6	160	1.4	9.6
	21	1.5	9.5	165	1.5	9.6
Sample C	17	1.8	10.9	155	1.3	10.4
	19	1.6	10.6	160	1.4	9.5
	21	1.4	9.5	165	1.2	9.8

Effect of alkalinity and temperature on consumption of chlorine dioxide during bleaching

Consumption of ClO_2 reduced slightly when greater amounts of alkali were used in the pulping process (Table 7). Pascoal Neto *et al.*[37] verified that less ClO_2 was consumed in eucalyptus kraft pulp bleaching in sequence $D_0E_1D_1E_2D_2$ as the KN reduced. However, for the same KN, different amounts of chemicals were consumed by different types of pulps, since chemical consumption depends on the HexA, lignin, and oxidizable structure content.[17,36,46] On the other hand, in the present study pulping temperature had no significant effect on ClO_2 consumption in the ECF bleaching sequence. Sevastyanova *et al.*[47] also concluded that the level of HexA in eucalyptus kraft pulp is substantially responsible for ClO_2 consumption, but it was not possible to establish a relationship in the present study, since ClO_2 consumption was similar for all nine samples. This result agrees with the observations of Daniel *et al.*[18]

CONCLUSION

Cooking temperatures and alkaline loads were evaluated for three different bleached eucalyptus samples. Bleaching with oxygen had better results when temperature and alkalinity were lower in kraft cooking. The S:G ratio was greater when higher temperatures were used for the same alkalinity; the S:G ratio was lower when the alkalinity was lower at the same temperature. Higher Kappa numbers had better bleachability in Pre-O_2 stage, while samples with higher levels of HexA had lower delta kappa for this stage. A correlation could not be established between phenolic groups and pulp bleachability. Alkalinity in kraft cooking influenced the Kappa number, viscosity, brightness reversion, and ClO_2 consumption of bleached pulp; however, cooking temperature had no effect on these parameters.

ACKNOWLEDGEMENTS: The authors would like to thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for financial support.

REFERENCES

[1] J. L. Colodette, J. L. Gomide, R. Girard, A. S. Jäskeläinen and D. S. Argyropoulos, *Tappi J.*, **1**, 14 (2002).

[2] A. V. Tran, *Tappi J.*, **1**, 13 (2002).

[3] C. Gustavsson, K. Sjöström and W. A. Al-Dajani, *Nordic Pulp Pap. Res. J.*, **14**, 71 (1999).

[4] P. C. Pinto, D. V. Evtuguin and C. Pascoal Neto, *Ind. Eng. Chem. Res.*, **44**, 9777 (2005).

[5] H. Zou, A. Liukkonen, B. Cole, J. Genco and W. Miller, *Tappi J.*, **83**, 65 (2000).

[6] Z. H. Jiang and D. S. Argyropoulos, *J. Pulp Paper Sci.*, **25**, 25 (1999).

[7] E. P. Maia and J. L. Colodette, *R. Arvore*, **27**, 217 (2003).

[8] D. Lachenal, R. M. Sevellano and J. George, in *Procs. 10th International Symposium on Wood and Pulping Chemistry*, Yokohama, June 7-10, 1999, pp. 354-357.

[9] J. Buchert, A. Teleman, V. Harjunpaa, M. Tenkanen, L. Viikari *et al.*, *Tappi J.*, **78**, 125 (1995).

[10] N. Rawat and T. I. McDonough, in *Procs. TAPPI Pulping Conference*, Montreal, October 25-29, 1998, pp. 883-891.

[11] M. Tenkanen, G. Gellerstedt, T. Vuorinen, A. Teleman, M. Perttula *et al.*, *J. Pulp Paper Sci.*, **25**, 306 (1999).

[12] L. G. Akim, J. L. Colodette and D. S. Argyropoulos, *Can. J. Chem.*, **79**, 201 (2001).

[13] A. Forsström, G. Gellerstedt, P. Jour and J. Li, in *Procs. International Pulp Bleaching Conference*, Stockholm, June 14-16, 2005, pp. 309-312.

[14] O. Sevastyanova, J. Li and G. Gellerstedt, *Nordic Pulp Pap. Res. J.*, **21**, 188 (2006).

[15] D. W. Reeve, in "Pulp Bleaching – Principles and Practice", edited by C. W. Dence and D. W. Reeve, TAPPI Press, 1996, pp. 261-290.

[16] Y. Hamzeh, G. Mortha, D. Lachenal and S. Izadyar, *Polym.-Plast. Technol.*, **47**, 931 (2008).

[17] M. M. Costa and J. L. Colodette, *Braz. J. Chem. Eng.*, **24**, 61 (2007).

[18] A. I. D. Daniel, C. Pascoal Neto, D. V. Evtuguin and A. J. D. Silvestre, *Tappi J.*, **2**, 3 (2003).

[19] T. Vuorinen, J. Burchert, A. Teleman, M. Tenkanen and P. Fagerstrom, in *Procs. International Pulp Bleaching Conference*, Washington, April 14-18, 1996, pp. 43-51.

[20] S. K. Bose, R. C. Francis, M. Govender, T. Bush and A. Spark, *Bioresour. Technol.*, **100**, 1628 (2009).

[21] E. A. K. Pettersson, M. Ragnar and M. E. Lindstöm, *Nordic Pulp Pap. Res. J.*, **17**, 222 (2002).

[22] F. J. B. Gomes, A. G. Gouvea, J. L. Colodette, J. L. Gomide and A. M. M. L. Carvalho, *O Papel*, **69**, 95 (2008).

[23] R. B. Santos, E. A. Capanema, M. Y. Balakshin, H. M. Chang and H. Jameel, *J. Agric. Food Chem.*, **60**, 4923 (2012).

[24] R. B. Santos, E. A. Capanema, M. Y. Balakshin, H. M. Chang and H. Jameel, *BioResources*, **6**, 3623 (2011).

[25] S. C. S. Queiroz, J. L. Gomide, J. L. Coledette and R. C. Oliveira, *R. Árvore*, **28**, 901 (2004).

[26] D. S. Argyropoulos and Y. Liu, *J. Pulp Paper Sci.*, **26**, 107 (2000).

[27] R. Yang, I. Lucian, A. J. Ragauskas and H. Jameel, *J. Wood Chem. Tech.*, **23**, 13 (2003).

[28] V. L. Chiang and M. Funaoka, *Holzforschung*, **42**, 385 (1988).

[29] L. Tao, J. M. Genco, B. J. W. Cole and R. C. Fort Jr., *Tappi J.*, **10**, 29 (2011).

[30] G. Ventorim, E. F. Alves, L. S. Penna and R. C. Francis, *Cellulose Chem. Technol.*, **48**, 365 (2014).

[31] E. Sjoström, "Wood Chemistry: Fundamentals and Applications", Academic Press Inc., 1981, 293 p.

[32] D. Fengel and G. Wegener, "Wood Chemistry: Ultrastructure Reactions", De Gruyter, 1984, 613 p.

[33] E. Johansson and S. Ljunggren, *J. Wood Chem. Technol.*, **14**, 507 (1994).

[34] G. Gellerstedt and E. L. Lindfors, *Holzforschung*, **38**, 151 (1984).

[35] J. L. Gomide, J. L. Colodette, R. C. Oliveira and C. M. Silva, *R. Árvore*, **29**, 129 (2005).

[36] Z.-H. Jiang, B. Van Lierop and R. Berry, *Tappi J.*, **83**, 167 (2000).

[37] C. Pascoal Neto, D. V. Evtuguin, F. P. Furtado and A. P. Mendes Sousa, *Ind. Eng. Chem. Res.*, **41**, 6200 (2002).

[38] D. Lachenal, D. Delmas, Y. Hamzeh, N. Benattar, C. Chirat *et al.*, *Holzforschung*, **66**, 29 (2012).

[39] G. Gellerstedt, in *Procs. 3rd International Colloquium on Eucalyptus Kraft Pulp*, Belo Horizonte, March 4-7, 2005, pp. 1.

[40] M. Bäckström, M. Hägglund and L. Olm, *Pap. Puu.*, **78**, 392 (1996).

[41] G. Gellerstedt and W. Wafa-Al-Dajani, *Holzforschung*, **54**, 609 (2000).

[42] P. M. Froass, A. J. Ragauskas, T. J. Mcdonough and J. E. Jiang, in *Procs. International Pulp Bleaching Conference*, Washington, April 14-18, 1996, pp. 163-170.

[43] B. Van Lierop, Z.-H. Jiang, J. Chen, D. S. Argyropoulos and R. M. Berry, *J. Pulp Paper Sci.*, **26**, 255 (2000).

[44] M. J. M. C. Barroca, R. M. S. Simões and J. A. A. M. Castro, *Appita J.*, **54**, 532 (2001).

[45] P. E. G. Loureiro, D. V. Evtuguin and M. G. V. S. Carvalho, *J. Chem. Technol. Biotechnol.*, **86**, 381 (2011).

[46] J. Buchert, E. Bergnor, G. Lindblad, L. Vikari and M. Ek, *Tappi J.*, **80**, 165 (1997).

[47] O. Sevastyanova, A. Forsström, E. Wackerberg and M. E. Lindström, *Tappi J.*, **11**, 43 (2012).