http://dx.doi.org/10.5935/0100-4042.20140251 *Quim. Nova,* Vol. 37, No. 10, 1646-1649, 2014

Artigo

FINAL CHLORINE DIOXIDE STAGE AT NEAR-NEUTRAL pH FOR BLEACHING EUCALYPTUS PULP

Robisnéa A. Ribeiro[a,*], Fernando J. B. Gomes[a], José N. Floriani[b], Renato A. P. Damásio[a], Iara F. Demuner[a] and Jorge L. Colodette[a]
[a]Departamento de Engenharia Florestal, Universidade Federal de Viçosa, 36570-000 Viçosa – MG, Brasil
[b]White Martins/Praxair, 21730-230 Rio de Janeiro, RJ – Brasil

Recebido em 30/04/2014; aceito em 09/08/2014; publicado na web em 22/09/2014

It is well known that pH is an important parameter for controlling the eucalyptus pulp bleaching when using the final chlorine dioxide stage, since it affects the effectiveness of the process. Recommendations found in the literature for operating are in the 3.5 to 4.0 range. However, in this paper it was shown that final chlorine dioxide has better performance, with significant brightness gain while also preserving pulp quality, when it is operated at near neutral pH. This result can be explained by the generation of sodium bicarbonate *in situ* upon adding carbon dioxide at this stage.

Keywords: eucalyptus; bleaching; buffering; pulp.

INTRODUCTION

Eucalyptus wood has become the most important raw material of bleached market pulp in the world. Bleached eucalyptus kraft pulps are largely used to manufacture tissue and print & writing (P&W) paper grades and lesser for dissolving pulps; it may also be used in mixtures with softwood pulp to improve their strength properties aiming at packaging applications such as multilayer cardboard. For obtaining a high level bleached pulp, some properties should be also controlled such as brightness, i.e., a measure of how much light is reflected by paper under specified conditions. Final brightness and brightness stability requirements are not so strict for tissue (88-90% ISO) but rather important for P&W paper grades (90-92% ISO) since in the latter case these two parameters significantly affects optical brightener agent demand during paper manufacture.[1]

Aiming to attend a demanding consumer market for quality products with lower prices and sustainable practices, it is necessary developing alternative production processes. In this context, alternatives for saving expensive and unfriendly environmental chemical reagents, e.g., chlorine dioxide, are desirable.

Concerning the pulp bleachability, it is not possible that pulp bleaching process to be done in a single stage, being necessary many different chemical stages.[2-4] In the beginning stages the chemicals behave as delignificant agents of the pulp. They have the main function to attack chemically the residual lignin and other undesirable compounds in order to dissolve and eliminate them from the process. Yet in the final stages, the chemicals have the primary function of promoting the pulp brightening to desired brightness levels. In this context, oxidizing reagents must be used in optimum conditions during the whole process, being each reagent applied considered as a single stage. Many different chemical compounds are used in these bleaching stages, such as: chlorine dioxide (D), hydrogen peroxide (P), alkaline extraction (E), and alkaline extraction in combination with hydrogen peroxide pressurized stage (EPO). A bleaching sequence is represented by the abbreviations of the chemical compounds used and should appear in the order which they were applied.

Elemental chlorine was during many years the most popular and effectiveness chemical reagent for bleaching pulp. But, elemental chlorine application has been prohibited in many countries due to environmental and health issues. In this way, the pulp mills have used elemental chlorine free sequences, called ECF; for replacing the elemental chlorine, they have used chlorine dioxide (ClO_2) instead of elemental chlorine. It is the reason of the ClO_2 to be one of the most used bleaching chemical, in spite of to be an expensive compound.

However losses of chlorine dioxide occur during ECF bleaching sequence by side reactions producing chlorite, chlorate, and other inactive chlorine species. These secondary reactions are directly linked to the pH range obtained during the stage with chlorine dioxide.[3,5] These chlorine dioxide sub products are inefficient for pulp bleaching purposes.[6] The optimum pH range of pulp delignification using ClO_2 is 2-3, though the optimum pH brightening of pulp with ClO_2 is 3.5 to 6.0.[3,7-9]

According to Hart and Cornnell[10] the optimum pH for pulp brightening with ClO_2 depends on the charge of chlorine dioxide applied, being very complex to establish a pH that can be labeled optimal. Note that the ClO_2 delignification usually occurs in the first bleaching stage, called the D_0 stage, and bleaching occurs in the later stages of bleaching ClO_2, called stages D_1 e D_2.[7,8,11] A typical bleaching sequence is D_0(EPO)D_1, however, there are longer sequences such as D_0(EPO)D_1ED_2, D_0(EPO)D_1D_2 and D_0(EPO)D_1P. Therefore, the best alternative to optimize the D_1 stage is to operate with the optimal pH for use of chlorine dioxide in order to minimize the formation of chlorite and chlorate.[12]

Studies have shown that the D_1 final stage bleaching allows higher gains in brightness when operated at near neutral pH (5.5 to 6.0) during the bleaching stage.[12-16] Aiming pH control during the process, bleaching plants apply acid and alkaline reagents, e.g., sulfuric acid and sodium hydroxide, respectively. However, the use of NaOH and H_2SO_4 is not convenient to pH control in this range; for example, when high dosages of ClO_2 are applied in the bleaching process, high dosages of NaOH to achieve pH adjustment are necessary; this can be explained due to the large variation between the initial and final pH. The pH decreases due to reactions in the bleaching stage; in this way it is necessary an initial pH range of 11.5 to 12.0, aiming a final pH of 5.5 to 6.0.[17,18] However, the excess alkali at the beginning of chlorine dioxide stage cause its decomposition in chlorate ions.[19-21] Additionally, some authors have also shown an efficiency decrease of chlorine dioxide stage due to chlorate ion generation, which are not effective for pulp bleaching since they do not react with lignin remaining in the pulp (Equation 1).[6,10,14,22,23]

*e-mail: adrianaribeiro_qui@yahoo.com.br

$$2ClO_2 + 2OH^- \rightarrow H_2O + ClO_2^- + ClO_3^- \quad (1)$$

The use of a buffering agent appears as an interesting alternative for controlling the pH near neutral (5.5 to 6.0) because buffering solutions can ensure that the pH is constant throughout the bleaching process maximizing its power.[24] Therefore, the aim of this study was to investigate for the eucalyptus kraft pulp the effect of the use of carbon dioxide (CO_2) in the D_1 stage of the bleaching sequence D_0(EP)D_1, operating at near neutral pH, due to the formation of a buffering system (H_2CO_3/$NaHCO_3$) in the reaction medium. The performance of this system was evaluated for its impact on the chlorine dioxide consumption and pulp quality.

MATERIALS AND METHODS

Materials

A kraft eucalyptus pulp supplied by a Brazilian Pulp Company was used. This sample was collected after oxygen delignification stage (O_2 Stage). The characteristics in the beginning of the experimentation were: brightness equal to 51.8 %ISO; kappa number (residual lignin) equal to11.4; and viscosity equal to 1003 dm^3/kg.

Methods

In order to investigate the effect of using a buffering compound in the final chlorine dioxide bleaching stage, an elemental chlorine free sequence (ECF) D_0(EP)D_1 was performed. The D_0 and EP stages were operated under the same conditions for the reference pulp bleaching sequence, and for the pulp bleaching sequence with CO_2 addition. The first chlorine dioxide stages (D_0) were carried out at 10% consistency, end pH 2.9, 90 °C, 120 minutes, and a kappa factor of 0.2. The EP stages were run at 10% consistency, end pH 11, 75 °C, 90 minutes, and hydrogen peroxide doses of 0.3% by pulp weights. The final dioxide chlorine stages (D_1) were carried out at 10% consistency, 90 °C, and 120 minutes. For the reference treatment (without CO_2 addition and no pH adjustment) variable dosages of chlorine dioxide to achieve the desired brightness were used. The treatment with CO_2 addition as a buffering compound was carried out at end pH 5.5 being used NaOH for controlling the pH, and as well as for the reference variable dosages of chlorine dioxide to achieve the desired brightness were used. In this stage were applied variable dosages of carbon dioxide by bubbling the CO_2 into the pulp during a previously computed time.

The feasibility of using this technology was evaluated by comparing different bleaching conditions, which were conventional bleaching using standard conditions versus optimized application of carbon dioxide (CO_2). The pH desired was achieved by using sodium hydroxide (NaOH). The conditions were established through experiences in the Pulp and Paper Laboratory-UFV. Figure 1 shows a flowchart of the experimental design.

All bleaching stages were carried out in duplicate and inter-stage washings simulated a vacuum filter operating at a dilution factor of two (inlet and outlet consistencies of 2% and 12.5%, respectively). After bleaching stage, pulp was diluted to 0.3% consistency, and hand sheets were formed and dried for 12 hours to 9-10% humidity in an environmentally controlled room (50±2% relative humidity and 23±1 °C). Brightness reversion tests were performed in conformity with Tappi UM 200 method using 10 repetitions (4 h, 105±3°C, 0% relative humidity). Reversion results were expressed as post color number (PCN), in conformity with Tappi TIS 017-10. Pulp kappa number, brightness, and viscosity were determined according to Tappi T236 cm-85, T525 om-92, and T 230 om-94 standard methods, respectively.

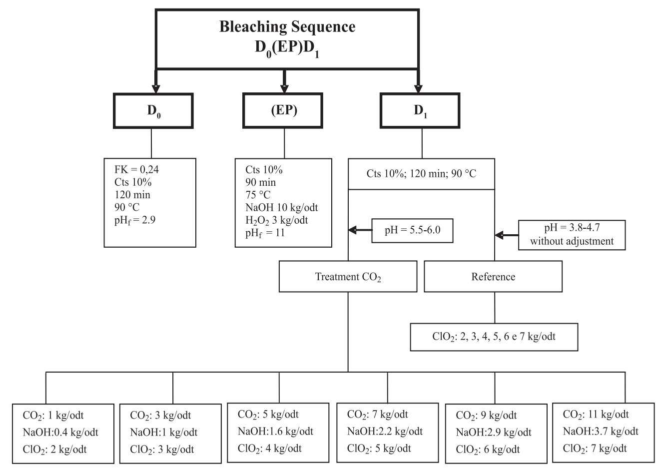

***Figure 1.** Experimental design of the investigation of using ClO_2 near neutral*

RESULTS AND DISCUSSION

Analyzing the performance of the bleaching sequence D_0(EP)D_1 for the brightness of 90% ISO for the reference samples and with the addition of CO_2, it was possible to observe a positive effect of using a buffer agent in the last bleaching stage. The bleaching results are being discussed considering the CO_2 charge applied and its buffering effect, consumption of reagents, bleachability and pulp quality. These results are shown in Table 1 and in Figures 2 to 5.

In Figures 2A and 2B, it is possible to observe the effect of the CO_2 application in the TAC (Total Active Chlorine = ClO_2*2.63 + H_2O_2*2.09) consumption and chlorine dioxide, respectively. The formation of a buffering agent in the reaction medium holding the pH constant during the stage about at 5.5 resulted in a lower consumption of reagents than the reference (Figure 2A). This low consumption of

Table 1. Conditions and results for the bleaching stage D_1 for reference and treated pulp CO_2

Conditions and results in the bleaching stage D_1	Reference						Addition of CO_2					
ClO_2, kg/odt	2	3	4	5	6	7	2	3	4	5	6	7
NaOH, kg/odt	0	0	0	0	0	0	0.4	1	1.6	2.2	2.9	3.7
CO_2, kg/odt	0	0	0	0	0	0	1	3	5	7	9	11
Terminal pH	4.7	4.6	4.4	4.2	4	3.8	5.8	5.8	5.8	5.8	5.9	5.8
Brightness, %ISO	88.1	88.8	89.5	89.7	90	90.7	89	90.2	90.3	91.6	91.8	92
Viscosity, dm^3/kg	817	809	796	790	787	778	791	779	771	770	762	750
PCN	0.46	0.43	0.37	0.3	0.34	0.24	0.37	0.33	0.26	0.24	0.23	0.2

Other conditions: 120 min of time reaction, 10% of consistency, at 90 °C.

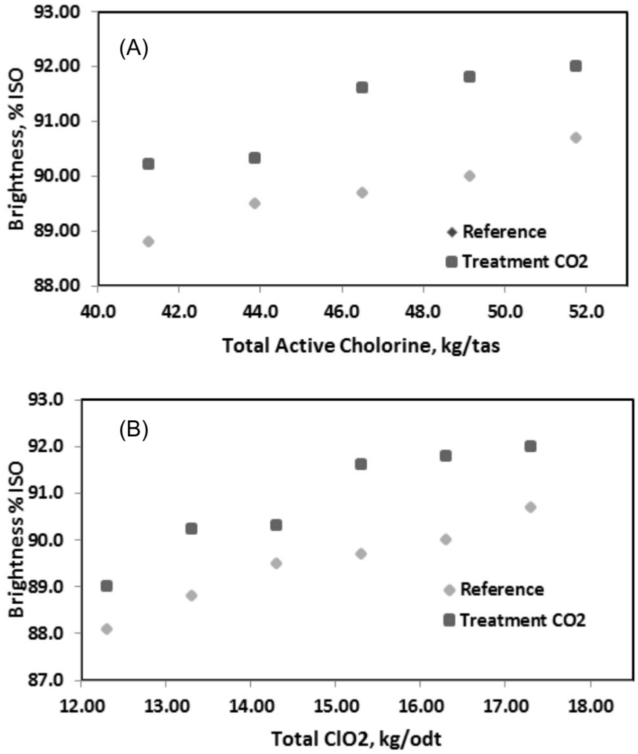

Figure 2. *(A) Amount of total active chlorine, kg/odt necessary to achieve a given brightness, the D_1 stage being conducted at pH 4.0 (reference), and 5.5 (buffered with CO_2); (B) Amount of chlorine dioxide required to reach a brightness of 90% ISO kg /odt; D_1 stage being conducted at pH 4.0 (reference), and 5.5 (buffered with CO_2)*

total active chlorine found in this study can be explained due to low applied chlorine dioxide charge in D_1, since the others stages were operated under the same conditions. It was possible to save 3 kg/odt (oven dry tons) of ClO_2 per ton of bleached pulp when a dosage of 1 kg/odt NaOH and 3 kg/odt of CO_2 was added (Figure 2B). The best performance of the D_1 stage at pH 5.5 to 6.0 can be attributed at the slow regeneration of chlorous acid ($HClO_2$), which is responsible for maximizing the bleaching performance at pH near neutral; the chlorous acid is slowly regenerated from the chlorite ion which reacts oxidizing lignin (equations 2 and 3).[10,20]

$$ClO_2^- + H^+ \rightleftharpoons HClO_2 \quad (2)$$
$$HClO_2 + \text{Lignin} \rightarrow HClO + \text{Oxidized Lignin} \quad (3)$$

In general chlorous acid tends to be reactive, except when it reacts with phenolic lignin, in this case it is produced hypochlorous acid as a product of reduction reaction.[25] It is also observed an equilibrium among hypochlorous acid and chloride ion *versus* chlorine, which is dependent on the pH (Equation 4). Chlorate ion tends to be suppressed due to formation of chloride ions.

$$HClO + Cl^- + H^+ \rightleftharpoons Cl_2 + H_2O \quad (4)$$

If no chloride ion is present in the reaction medium, hypochlorous acid reacts with the chlorous acid promoting the regeneration of the chlorine dioxide (Equation 5).

$$HClO + 2HClO_2 \longrightarrow 2ClO_2 + H_2O + H^+ + Cl^- \quad (5)$$

Many studies have shown that decreasing pH, an increasing in the chlorate ion is observed; this phenomenon is responsible for decreasing the chlorine dioxide oxidative power. On the other hand, increasing pH, there is also a higher formation of chlorite ions, which are responsible for regenerating the chlorine dioxide.[20,24,26]

Another benefit due to buffering in stage D_1 was the improvement of the bleachability of the pulp (Figure 3). It can be seen that the change of pH control technology by employing CO_2 improved the bleachability of the pulp by the sequence D_0(EP)D_1. Bleachability is defined as the number of units of the kappa number removed in bleaching for each kg of active chlorine used in the bleaching process, including all stages.

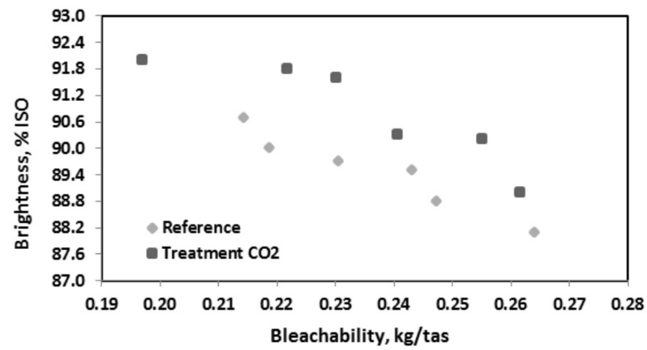

Figure 3. *Bleachability kg/odt a bleached eucalyptus kraft pulp with a sequence D_0(EP)D_1 obtained in different brightness bands, the D_1 stage being conducted at pH 4.0 (reference), and 5.5 (buffered with CO_2)*

The bleached pulp quality was evaluated by the brightness stability and viscosity. The brightness stability was measured by the brightness reversion expressed by the post color number (PCN). High PCN indicates low brightness stability, which can be explained due to leucochromophore groups present in the pulp.[2] Under adverse conditions of moisture and temperature, these groups can be transformed into chromophore groups, returning to its initial structure, causing the pulp yellowing. The Figure 4 exhibits the bleached pulp pH buffered with CO_2 in the D_1 stage, regardless of the dosage, showed a lower PCN than the pulp reference. Therefore, even with a lower ClO_2 dosage required to achieve 90% ISO brightness, pH buffering resulted in the decreasing of the oxidized groups, responsible for the brightness reversion.

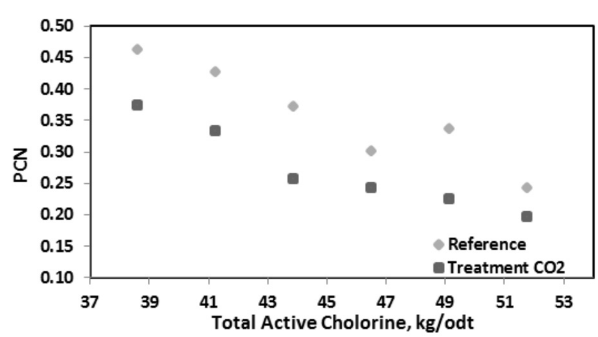

Figure 4. *Brightness stability as measured by post color number (PCN), the pulps bleached by the conventional method (reference), and chlorine dioxide at near neutral pH (buffered with CO_2)*

Bleaching with chlorine dioxide buffered with CO_2 showed slightly negative effect on the viscosity of the bleached pulp compared to conventional bleaching (Figure 5). This fact can be explained due to the intense generation of the hypochlorite acid (HClO) in this pH range, which is the responsible for damaging cellulose chains.[12,27] However, it is important to notice that the process of neutralized bleaching with ClO_2 (addition of CO_2) requires lower dosages of this reagent to achieve desired brightness in relation to the reference process, and hence to the same level of brightness. The pulp viscosities obtained with the new process (779 dm^3/kg), and the reference process (787 dm^3/kg) were close.

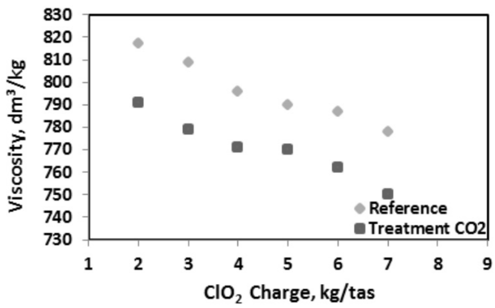

Figure 5. *Final viscosity of the pulps bleached by conventional procedures (reference), and buffered with chlorine dioxide at a pH near neutral (the chlorine dioxide neutralized)*

CONCLUSIONS

It was possible to save 3 kg/odt of ClO_2 per ton of bleached pulp, when a dosage of 1 kg/odt NaOH and 3 kg/odt of CO_2 were used for pulp bleaching aiming 90% ISO brightness. Concerning pulp properties, the results obtained in this paper showed no significant negative effects on pulp quality, being observed a very slight reduction in the final viscosity was observed, which can be explained due to the compounds generated in this pH range; and another positive point of the operating of the D_1 stage in pH near neutral was an improvement in the pulp brightness stability.

AKNOWLEDGMENTS

Funding provided by the Minas Gerais State Research Foundation (FAPEMIG) and from the Brazilian National Council for Science and Technology Development (CNPq) is greatly appreciated.

REFERENCES

1. Gomes, F. J. B.; Colodette, J. L.; Saavedra, S. H. M.; Barbosa, B. M.; Batalha, L. A. R.; *European International Journal of Science and Technology* **2013**, *2*, 207.
2. Jahan, M.; Ni, Y.; He, Z.; *Appita J.* **2010**, *63*, 126.
3. Dence, C. W.; Reeve, D. W.; *Pulp Bleaching: Principles and Practice*; Dence, C. W.; Reeve, D. W., eds.; TAPPI Press: Atlanta, 1996, session IV.8
4. Suess, H. U. In *Ullmann's Encyclopedia of Industrial Chemistry*; Suess, H. U., eds,; Wiley-VCH Verlag GmbH & Co. KGaA, (2006), doi: 10.1002/14356007.a04_191.pub2.
5. Suess, H. U.; *Pulp Bleaching Today*, Walter de Gruyter: Berlin, 2010.
6. Ventorim, G.; Colodette, J. L.; Eiras, K. M.; *Revista O Papel* **2009**, *50*, 39.
7. Pearson, J.; Fletcher, D. E.; Connell, J. D.; *Pulp & Paper* **2000**, *74*, 47.
8. Reid, D. W.; Hinck, M. L.; *Tappi J.* **2003**, *2*, 8.
9. Basta, J.; Andersson, L.; Blom, C.; Forsstrom, A.; Wane, G.; Johansson, N. G.; *Proceedings of the TAPPI Pulping Conference*, Atlanta, 1992.
10. Hart, P.; Connell, D.; *Tappi J.* **2008**, *7*, 3.
11. Basta, J.; Andersson, L.; Blom, C.; Holtinger, L.; Hook, J.; *Appita J.* **1992**, *45*, 29.
12. Jiang, Z. H.; Berry, R.; *Proceedings of the International Pulp Bleaching Conference*, Portland, 2011.
13. Jiang, Z. H.; Richard, R. M.; *International Patent Publication WO/2007/104128*, **2007**.
14. Colodette, J. L.; Mounteer, A. H.; Gomes, F. J. B.; *Proceedings of the International Congress of Chemical Engineering*, Seville, 2012.
15. Earl, P.; Pryke, D.; *Proceedings of the Annual Meeting of the Pulp and Paper Technical Association of Canada*, Canada, 2003; Earl, P.; Pryke, D.; *Proceedings of the Paptac Bleaching Committee*, Montreal, 2005.
16. Milanez, A.; Colodette, J. L.; *Proceedings of the International Pulp Bleaching Conference,* Stockholm, Sweden, 2005.
17. Wartiovaara, I.; *Pap. Puu.* **1982**, *10*, 581.
18. He, Z.; Ni Y.; *J. Pulp Pap. Sci.* **2009**, *35*, 247.
19. Hoige, J.; Bader, H.; *Water. Res.* (1994), doi: 10.1016/0043-1354(94)90118-X.
20. Svenson, D.; Jameel, H.; Chang, H.; Kadla, J. F.; *J. Wood Chem. Technol.* **2006**, *26*, 201.
21. Ni, Y.; Kubes, G. J; Van Heiningen, A. R. P.; *J. Pulp Pap. Sci.* **1993**, *19*, 6.
22. Wafa Al-Dajani, Z. H.; Berry, R.; Van Lierop, B.; *Proceedings of the International Pulp Bleaching Conference*, Montreal, Canada, 2008.
23. Wartiovaara, I.; *Tappi J.* **1986**, *69*, 82.
24. Howard, W.; Strumila, G. B.; *The Bleaching of Pulp*, 3rd ed., TAPPI Press: Atlanta, 1979.
25. Svenson, D. R.; Kadla, J. F.; Chang, H. M.; Jameel, H.; *Can. J. Chem.* **2002**, *80*, 761.
26. Rapson. W. H.; *Tappi J.* **1956**, *39*, 284.
27. Gomes, F. J.; *Dissertação de Mestrado*, Universidade Federal de Viçosa, Brasil, 2010.