Evaluation of bleachability on pine and eucalyptus kraft pulps

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Abstract

In recent decades, the pulp industry has been changing and improving its manufacturing processes in order to enhance production capacity, product quality and environmental performance. The aim of this study was to evaluate the bleachability effect on the efficient washing and alkaline leaching in eucalyptus and pine Kraft pulp using three different bleaching sequences: AD(EP)D, A/D(EP)DP and D_{HT}(EP)DP. This study was carried out in two stages. In the first part, the optimum conditions for pulp bleaching in order to achieve a brightness of 90% ISO were established. The second step was a comparative study between the pulp that received alkaline leaching and efficient washing with reference pulp (without treatment). For the discussion of the results the brightness, viscosity, kappa number and HexA in pulp were analyzed. The three sequences studied reached the desired brightness, but the sequence AD (EP) D has been obtained a lower reagent consumption for the same brightness. In the three sequences studied, the efficient washing of the pulp after oxygen delignification has contributed significantly to the removal of dissolved organic and inorganic material in the pulp and the alkaline leaching decreased significantly the pulp kappa number due to a higher pulp delignification and bleachability.

Keywords: bleachability, alkaline leaching, efficient washing

Introduction

In recent decades, the pulp industry has been changing and improving its manufacturing processes in order to enhance production capacity, product quality and environmental performance. The presence of dissolved organic and inorganic material in the pulp after washing hampers the efficient operation of the bleaching process, mainly due to a higher consumption of chemicals and the consequent increase of color and chemical (COD) and biological (BOD) oxygen demand from industrial plant effluent. The alkaline leaching pulp has as a purpose to remove lignin trapped on the cellulose fibers, resulting in a lower kappa number and lower reagent consumption in the next stage. In alkaline delignification certain amount of carbohydrate is also dissolved and it gives as result a decrease in pulp yield.

The pulp washing in bleaching removes dissolved organic and inorganic materials that provide suitable conditions for the subsequent bleaching stage minimizing disturbances and reducing the consumption of reagents. (FRASSÃO, T. V., 2008). The best possible washing result is obtained when clean water is applied for all washing steps, typically, the pulp washing is done in a countercurrent system, where clean water is applied at the end of the wash and the filtrate is reused in the previous steps, moving in counter current to the input side of the cellulose in the system.

Studies on alkaline leaching of the pulp after the oxygen delignification stage, showed that an increase in the alkali charge and temperature provides greater reductions in kappa number and viscosity. (DENCE E REEVE, 1996).

According to authors Li, J. and MacLeod, J. M. (1992), large amounts of residual lignin can be removed from the Kraft pulp by the alkaline leaching of appropriate process conditions. According to these authors, the amount of removed lignin increased with high concentrations of NaOH and high temperatures. The oxygen-free alkaline leaching did not affect cellulose at temperatures up to 100 º C, but there was an increase in the extraction of hemicelluloses as we increased the concentration of NaOH.

At high pH, the lignin reacts with the alkali, especially at high temperatures. The fibers are swollen in alkaline conditions, a favorable lignin transfer occurring out of the fibers (VILPPONEN, A. 1987).

The aim of this study was to evaluate the bleachability effect on efficient washing and alkaline leaching in eucalyptus and pine Kraft pulp using three different bleaching sequences: AD(EP)D, A/D(EP)DP and D_{HT}(EP)DP.

Experimental

Thirteen different cellulose pulps from oxygen delignification stage were used: eleven eucalyptus pulps (1 to 11) and two pine pulps (12 and 13). The initial characterization of the pulps is shown in Table 1.

Table 1: Initial characterization of cellulose pulps

Pulps	Brightness (% ISO)	Kappa N^o	Viscosity (dm^3/kg)	Hexa's (mmol/Kg)	COD (Kg O_2/odt)
1	62.7	9.5	1037	49.7	5.5
2	60.9	10.4	1095	57.3	8.1
3	54.7	10.5	1077	58.3	92
4	51.5	9.3	1004	44.4	6.5
5	44.7	9.3	944	45.0	10.9
6	51.3	7.9	741	22.5	1.7
7	58.1	9.8	1034	52.9	8.0
8	59.7	9.9	961	53.3	5.4
9	61.8	10.5	1116	55.7	25.5
10	59.9	10.8	1215	49.0	25.5
11	62.1	9.9	997	46.7	23.6
12	43.0	9.8	956	22.9	23.8
13	32.9	10.4	701	13.2	4.8

This study was carried out in two stages. In the first part, the optimum conditions for pulp bleaching in order to achieve a brightness of 90% ISO were established. The second step was a comparative study between the pulp that received alkaline leaching and efficient washing with reference pulp (without treatment).

The pulps from oxygen delignification stage were washed efficiently with 50 m3 of distilled water per ton of dry pulp. After efficient washing was performed leaching alkaline (treatment with NaOH). This stage was carried in polyethylene bags with samples of known weights of pulps, the following conditions: 90 min, 90^{o}C, 10% consistency and 20 kg/odt of NaOH. After hand mixing, the material was heated in a microwave oven until the temperature of treatment is reached and transferred to a steam bath equipped with a thermostat, which was maintained at a specified time.

Three bleaching sequences were utilized: AD(EP)D (sequence 1), A/D(EP)DP (sequence 2) and DHT(EP)DP (sequence 3). The conditions of the initial stage of bleaching can be observed in Table 2:

Table 2: Operating conditions of the initial stages of bleaching

Conditions	A	D	D_{HT}
Time, min	120	15	120
Temperature, °C	95	85	95
Consistency, %	10	10	10
H_2SO_4, kg/odt.	*	-	*
NaOH, kg/odt.	20.0	*	-
Kappa Factor	-	0.20	0.20

* Variable dosage for pH adjustment.

For sequences 1 and 3, the pulp was washed with 9 m^3 of distilled water after the reaction, in a form to simulate industrial washing. The pulp of the sequence 2 was not washed after the acid stage and then chlorine dioxide (A/D) is added immediately, after this stage, the pulp was washed with distilled water to 9 m^3.

The conditions used for extraction with peroxide (EP) (sequences 1, 2 and 3), chlorine dioxide bleaching end (sequences 1, 2 and 3) and bleaching with hydrogen peroxide end (after 2 and 3) are presented in Table 3:

Table 3: Conditions used in the sequences 1, 2 and 3

Conditions	**(EP)**	**D**	**P**
Time, min	90	120	60
Temperature, °C	85	80	90
Consistency, %	10	10	10
H_2SO_4, kg/odt.	-	1.0	-
NaOH, kg/odt	10.0	-	6.0
H_2O_2, kg/odt.	3.0	-	2.0
ClO_2, kg/odt	-	*	-
$MgSO_4$, kg/odt	-	-	3.0

*Variable dosage to achieve the desired brightness.

At the end of the reaction time of each stage, the pulp was washed with distilled water, a ratio of 9 m3 of distilled water per ton of dry pulp.

The performance of each stage was evaluated based on the kappa number, viscosity, HexA's and pulp brightness.

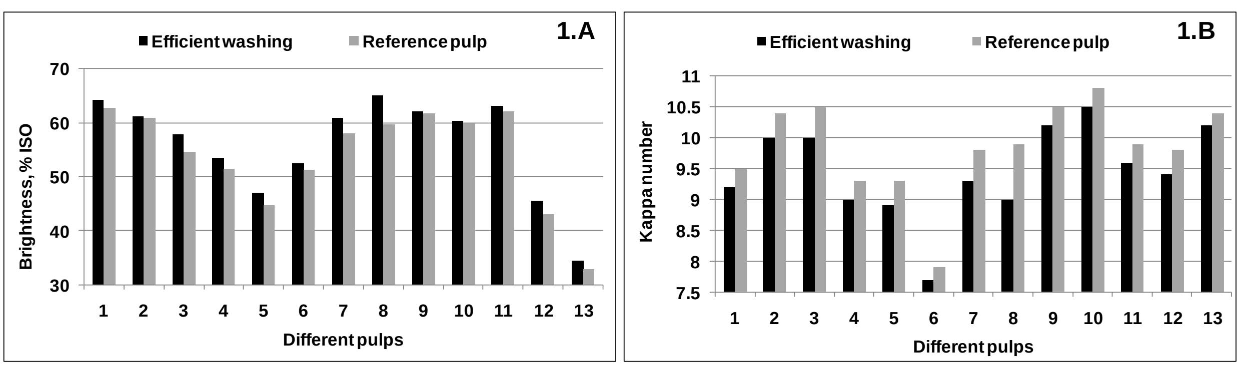
The analysis of kappa number, pulp brightness and viscosity were measured by the TAPPI method (1999). The HexA's in the pulp were measured by the procedure established by Vuorinen et al. (1996). The analyses of COD of the effluents were measured according to the procedure CPPA H3.

Results and Discussion

Bleaching Pre

Effect of pulp washing efficiency

The pulps from the pre O_2 were washed with 50m^3 of water per ton of dry pulp to remove as much organic and inorganic materials dissolved in the pulp after the pre - O_2. In Figure 1 we can observe the effect of the degree of washing when compared with the reference pulps (washed with 9m^3 of water per ton of dry pulp - pulp pre O_2).



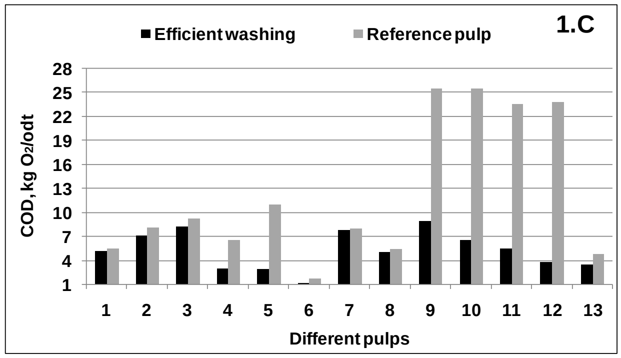


Figure 1: Effect of efficient washing of pulp cellulose: 1.The effect on brightness; 1.B The effect on the kappa number; 1.C The effect on COD.

The efficient of the washing of the pulps provided a small gain in brightness in the pulp and consequently a decrease in kappa number, this occurred due to a higher removal of organic material present in the pulps (Figure 1.C). The greater the amount of organic compounds contained in the liquor, the higher oxygen consumption and the higher the COD.

According PIOTTO (2003), an efficient washing of brown pulp reduces the consumption of oxidant in the bleaching. If before the first bleaching stage, will reduce the load of organic compounds, resulting in decreased concentrations of AOX, BOD and COD of the effluent.

The dissolved material that goes with the pulp to the stage of delignification and / or bleaching can damage the delignification or bleaching, and also increase the consumption of bleaching chemical, as lower final brightness of pulp or low resistance of this. (TRINDADE, H. de S., 2003).

Effect of alkaline leaching

After washing with water efficient, the pulps passed through an alkaline treatment. Figure 2 shows the effect of alkaline leaching compared with the reference pulps.

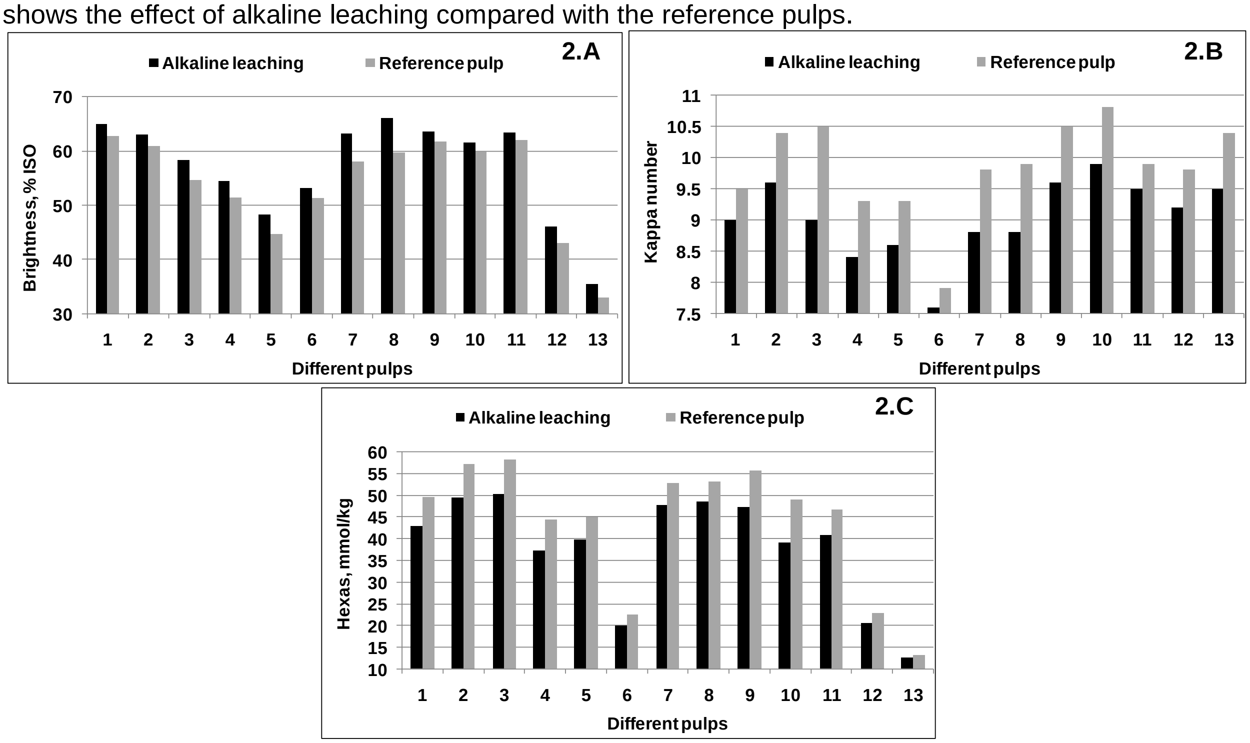


Figure 2: Effect of alkaline leaching of pulps: 2.A The effect on brightness; 2.B The effect on kappa number; 2.C The effect on HexA's content.

Pulps which received treatment with alkali showed a higher brightness and lower kappa number compared to the reference Pulps. This is explained by the fact that the alkali remove certain amount of lignin in the pulp. In a study conducted by Li, J. and MacLeod, J. M. (1993) it was observed that the leaching of alkaline Kraft pulp cellulose provided a higher reduction of the kappa number in the leached when compared to the reference pulp. The amount of lignin removed was 25-31% higher in the pulp leached.

The content of HexA is also diminished with the alkaline leaching, being the kappa number consequently reduced, as part of the kappa number composed of HexA's.

In strong alkaline solution and high temperatures, the HexA's decompose slowly (VENTORIM, 2004).

Bleaching

The Pulps that received efficient washing and treated with alkali were then bleached, using three different sequences: AD(EP)D (sequence 1), A /D(EP)DP (sequence 2) and D_{HT}(EP)DP (sequence 3). Figure 3 shows the profiles of brightness, kappa number and content of HexA's during the first bleaching stage by the three studied sequences.

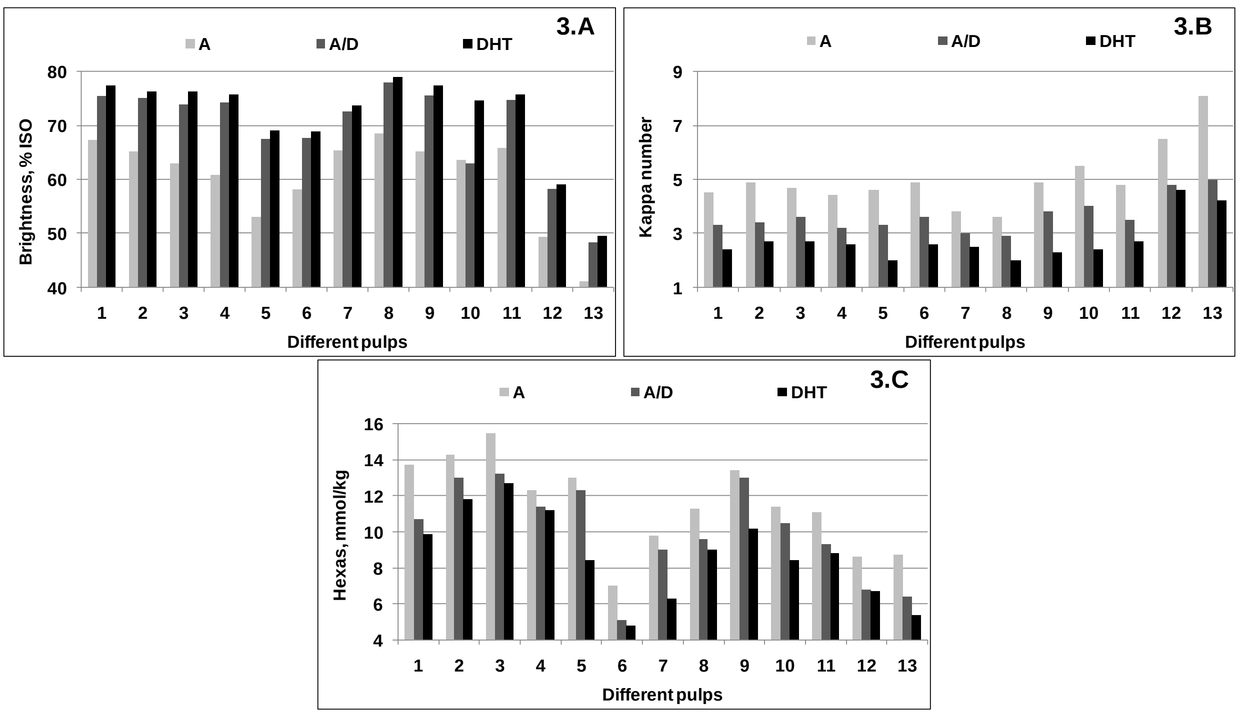


Figure 3: Initial stage of bleaching by the three sequences studied. 3.A Profile the brightness; 3.B Profile kappa number, 3C Profile HexA content's.

It is noted in Figure 3 that the brightness values of the pulps conducted by following D_{HT} showed is higher than the other brightness values of other bleaching sequences, and hence the pulps conducted by the following D_{HT} had a lower kappa number. This can be explained by the chlorine dioxide at high temperatures degrade lignin in pulps.

In relation the HexA's content in pulps it is observed that the initial stage of bleaching D_{HT} promoted a greater reduction of HexA's, followed by the stages A/D and A, respectively. The chlorine dioxide stage has a higher reaction rate with the HexA's than the stage of acid hydrolysis (VENTORIM, 2004), although the chlorine dioxide does not react with HexA's, but only the chlorine and hypochlorous acid that are generated in stage chlorine dioxide.

The amount of HexA's in pine pulps (pulp 12 and 13) is smaller than in the eucalyptus pulps (pulps 1 to 11). The hardwood kraft pulps contain more hexenuronic acids groups of the long fiber produced by the same type of pulping (JIANG et al., 2000), since hardwood contain more than 4-O-metilglicuronoxilana, which is the precursor of hexenuronic acids.

The rate of hydrolysis of hexenuronic acids increases nine times with the increase of reaction temperature from 80 to 100°C (Shimizu, 1981, quoted by JIANG et al., 2000). However, hydrolysis in acidic medium, even when intensified (1h/110°C/pH3.5), does not result in complete degradation of hexenuronic acids in kraft pulps.

Total active chlorine dosage at the end of bleaching

All three studied sequences reached a desired brightness of 90.0 + or- 0.5% ISO. Figure 4 shows the consumption of total active chlorine (CAT, kg / odt) of each sequence over bleaching.

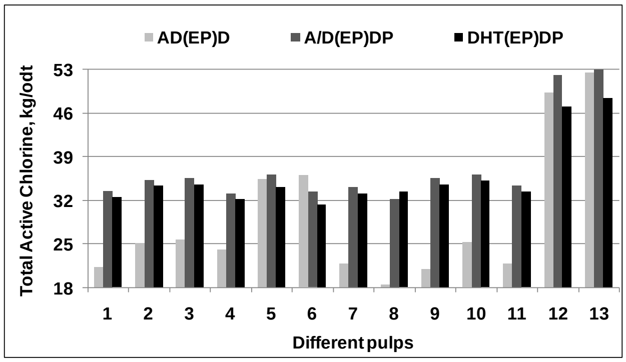


Figure 4: CAT * used in the bleaching of pulps by three different sequences.
* CAT: ClO2 (as chlorine) + 2.09*H2O2

The sequence showed that a lower dose of CAT was the sequence AD(EP)D, followed by sequences D_{HT}(EP)DP and A/D(EP)DP, respectively This result was probably due to the absence of the final stage P in the sequence 1; and shows the positive effect of an intermediate washing, which made the dosage of CAT was lower without affecting the final brightness of pulp of eucalyptus. As for the pine pulps (pulps 12 and 13), we see that the sequence 1 was not what obtained the lower charge of CAT, evidencing that for pulps of pine, short sequences of bleaching are not the most recommended.

Effect of final viscosity in the three sequences studied:

The final viscosity of each studied bleaching sequence was evaluated and a comparison between them was made by Figure 5.

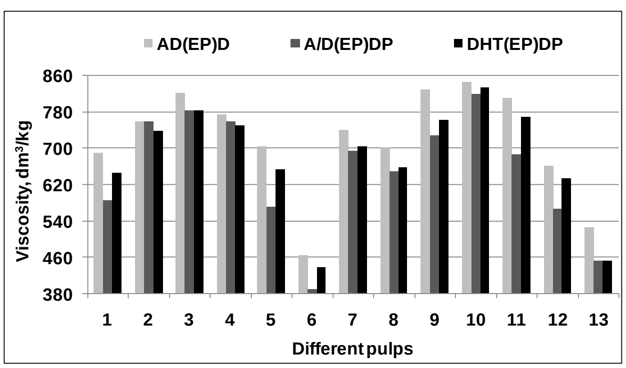


Figure 5: Evaluation of the final viscosity of the pulps studied by the three bleaching sequences.

The viscosity values of Eucalyptus pulps (pulps 1 to 11) were higher than those of pine pulps (pulps 12 and 13), because of lower initial viscosity of the pulp of pine and the major loss of pulp viscosity Pine for bleaching in the pulp of eucalyptus. The higher losses in the case of pine are explained by a higher demand for chlorine dioxide to achieve the brightness of 90% ISO.

The final viscosity of the pulps conducted by the AD(EP)D sequence were higher than the viscosities of other sequences, this fact can be explained by lower demand of reagents in sequence 1, showing a lower carbohydrate degradation in this sequence.

Conclusions

- The efficiently washed pulps had a lower COD (kg/odt) than the reference pulps; efficient washing has resulted in pulps that are cleaner and easier to bleach.
- The alkali treatment efficiently reduced the kappa number of the pulp and led to a small reduction in the HexA's content of pulp compared to the reference pulps.
- The pulps conducted by the initial stage of D_{HT} bleaching resulted in pulps with higher brightness levels and lower levels of HexA's.
- The AD(EP)D sequence had a lower reagent consumption for the same brightness and a final viscosity higher than the other studied sequences.

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