

Factors Affecting Bleachability of Eucalypt Pulp

Daniela Correia Martino,* Jorge Luiz Colodette, Teresa Cristina Fonseca Silva, Dalton Longue Júnior, Dayana Mendes Louzada de Paula, and Marco Antônio Bandeira Azevedo

Unbleached and oxygen-prebleached pulps were produced both in industrial and laboratory scale using *Eucalyptus urograndis* woods from two different sites (A and B) as a raw material. Quantitative chemical analysis of wood and pulp was performed, aiming to find a correlation with bleaching performance. Fiber dimensions measurements in wood were also performed. Carbohydrates and lignin composition in wood from A and B were found to be similar, while extractives in acetone presented variations of about 0.5% between wood from site A and B. Laboratory-made unbleached pulps from A and B had brightness varying 0.3% ISO, whereas pulps from industry presented variations over 4% ISO from each other. By virtue of its high unbleached pulp brightness, the industry-made sample A presented a higher bleachability than its sample B counterpart. The higher bleachability of the industry-made sample A was traced to its much higher content of hexenuronic acids (HexA), which was caused by differences in pulping conditions in mill sites A and B.

Keywords: *Eucalyptus*; *Bleachability*; *LoSolids® pulping*, *HexA*

Contact information: *Laboratório de Celulose e Papel, Departamento de Engenharia Florestal, Universidade Federal de Viçosa, Viçosa, MG, 36570-000; Brazil; * Corresponding author: daniela.martino@ufv.br*

INTRODUCTION

The operators of kraft mills face continuing challenges to fulfill the needs of their customers effectively and efficiently. To meet such challenges it is important to understand bleaching performance, which is one of the most expensive steps in the process. Bleachability depends on the chemical composition of wood, the extent of delignification, the conditions and type of pulping process, and the different sequences and operating conditions of bleaching (Duarte and Baptista 2003).

In general, the behavior of the pulp within bleaching is related to chemical features of the wood used as the raw material. Understanding how chemical composition affects pulp bleachability is important for the choice and improvement of clones, optimization of the bleaching process conditions, enhancement of the quality of the product, and reduction of the environmental impact of the pulp and paper industry (Pascoal Neto et al. 2005). Another relevant aspect affecting pulp bleachability is the pulping technology employed and the process variables such as active alkali, sulfidity, maximum temperature, and cooking time. This is because different pulping conditions can cause changes in chemical features of pulp components, such as the nature of the residual lignin, carbohydrate composition of pulp, the soluble lignin content, the amount of lignin-carbohydrate complex, and hexenuronic acids (HexA) present in kraft pulps of hardwoods (Cardoso et al. 2002; Colodette et al. 2002; Duarte and Baptista 2003).

During pulping of hardwood, uronic acids can be converted into HexA via β -elimination of methanol (Teleman *et al.* 1995). HexA content continues to increase after the heating up period, and no degradation of these groups takes place in the course of the pulping process (Chai *et al.* 2001). HexA are detrimental, as they reduce the technical feasibility and cost efficiency of bleaching.

Previous studies showed that pulping parameters drive bleachability when considering the same bleaching sequence (Pascoal Neto *et al.* 2002).

In this work, the same eucalyptus species from two different sites were evaluated in order to attribute the driving factors for bleachability. For this, wood samples were chemically characterized, and their behavior towards laboratory LoSolids[®] pulping was also evaluated. Comparative studies between corresponding industrial and laboratory produced pulps were also done.

EXPERIMENTAL

Hardwood species *Eucalyptus urograndis* wood chips air dried to 20% were collected from two different sites belonging to Brazilian pulp mills, called A and B. Subsequently, they were screened through a 12.5 x 12.5 mm sieve. Mill A is located within the latitude and longitude of 16° 5' 22.9" S, 39° 24' 22.2" W. The annual medium precipitation is 1600 mm, and the Köppen climate classification is Af. Mill B is located at latitude and longitude of 19° 11' 24" S, 42° 29' 43" W. Annual medium precipitation is 1163 mm, and the Köppen climate classification is Aw. Unbleached and oxygen-prebleached pulps produced from the mills A and B were used as references.

Laboratory experiments were carried out using the industrial chips of wood to produce unbleached, oxygen-prebleached, and bleached pulps. Industrial unbleached pulps and oxygen-prebleached pulps were also used to produce laboratory bleached kraft pulps. At the end, three types of laboratory bleached pulps from each wood were produced: one from industrial oxygen-prebleached pulp (1), one from industrial unbleached pulp (2), and one from the laboratory process (3). Figure 1 represents the scheme of the work.

Wood Characterization

Wood chemical analyses were run on sawdust, which was screened according to the TAPPI T257 cm-85 standard procedure. Wood basic density (CM-46:92), total extractives (T264 cm-97), extractives in ethanol/toluene (T204 cm-97), acetone extractives (T280 pm-99), acid insoluble lignin (T222 om-98), acid soluble lignin (UM 250), metals (T266 om-94), lignin syringyl/guaiacyl (S/G) ratio (Chen 1992), sugar composition (Wallis *et al.* 1996), total uronic acids (Scott 1979), and acetyl groups (Solár *et al.* 1987) were evaluated.

The fraction of glucose present in the glucomanan was calculated from the content of mannose, using the glucose/mannose ratio of 1:1 as previously reported, (Sjöström 1993). The cellulose content was calculated by the difference between total glucose and glucose in glucomanan. The hemicellulose content was calculated from the sum of xylose, galactose, mannose, arabinose, uronic acids, acetyl groups, and the fraction of glucans attached to it.

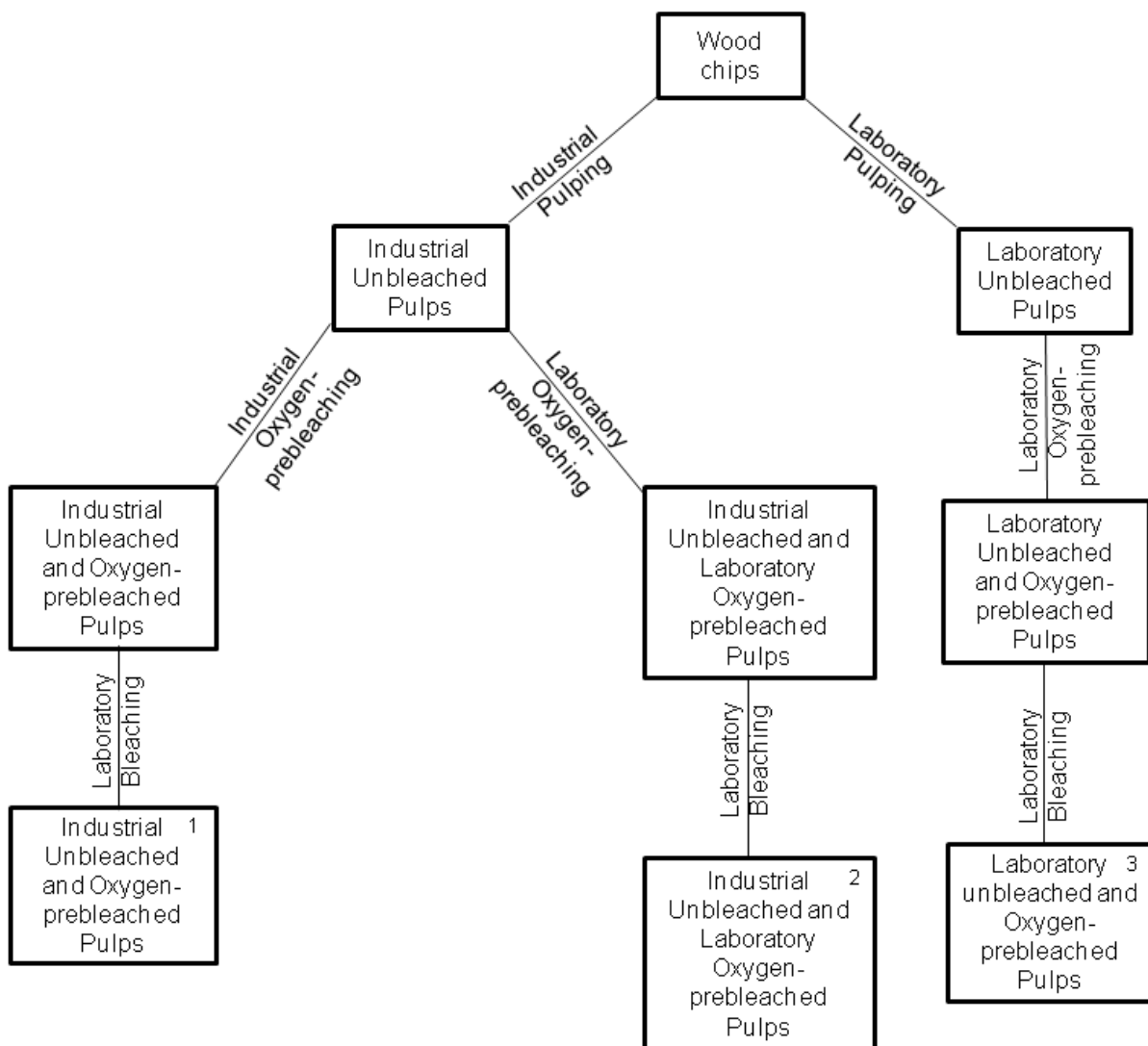


Fig. 1. Scheme of work comprising industrial and laboratory steps

The fibers measurements were made in a calibrated optical microscope Image-Pro Plus. For each sample 100 fibers were measured, both for the estimation of the lengths as to the diameter. Lumen diameter and cell wall thickness were also determined.

Pulping

Kraft cooking was performed in 5 replicates using 500 g of absolutely air dried wood chips, aiming to achieve a kappa number of 17 ± 0.5 . The cooking system was equipped with a MK digester model 1/K409 with a capacity of 7 L, heated by electronic controls connected to a computer and equipped with a manometer, heat exchanger, and circulation pump. The digester was connected to a set of heated and pressurized accumulator vessels, which enabled the injection split of cooking liquor.

Before cooking, the wood chips were steamed at 100°C for 20 min. The conditions used in cooking were the same for both pulps and are described in Table 1 (Pimenta 2006).

Table 1. Cooking Conditions

Parameters	Impregnation Zone	Upper Cooking Zone	Lower Cooking Zone
Time to temperature (min)	15	15	-
Time at temperature (min)	30	60	120
Temperature (°C)	110	155	156
Alkaline division, % of total EA*	50	30	20
Liquor/wood	4/1	4/1	4/1
Sulfidity, %	28.7	28.7	28.7

*EA: Effective alkali

The following procedures were used for unbleached and bleached pulps according to TAPPI (2001): forming handsheets (T218 sp-97), brightness (T452 om-98), kappa number (T236 om-85), viscosity (T230 om-94), and metals (T266 om-94). Carbohydrates composition and S/G ratio were determined as previously described for wood. The screening yield and the rejects content were determined gravimetrically, and the hexenuronic acids content was determined according to Vuorinen *et al.* (1996).

Pulp Oxygen-prebleaching and Bleaching

Oxygen-prebleaching of unbleached pulps and bleaching were achieved using the same conditions for all pulps (Table 2). The bleaching sequence performed was D*(EP)D. The oxygen-prebleaching was carried out in a Mark V (*Quantum Technologies Inc.*) reactor/mixer, for which no MgSO₄ was added.

Table 2. Oxygen-prebleaching and Bleaching Conditions

Conditions	Stages			
	O	D*	(EP)	D
Consistency, %	10	10	10	10
Temperature, °C	100	90	80	75
Time, min	60	120	60	120
Pressure, kPa	600	-	-	-
O ₂ , kg/t	20	-	-	-
Kappa factor	-	0.16	-	-
Final pH	-	3.0	-	4.5
ClO ₂ , kg/t	-	-	-	10
H ₂ SO ₄ , kg/t	-	*	-	*
H ₂ O ₂ , kg/t	-	-	3	-
NaOH, kg/t	20	*	10	*

* Acid or base addition for pH adjustment.

Variations in viscosity and kappa number were calculated based on the value of these parameters before and after the studied stages. The selectivity of the determined stage was calculated by dividing the kappa drop (Δ kappa) by the viscosity drop (Δ viscosity). Bleachability was calculated by dividing Δ kappa in the bleaching process by total active chlorine consumption (TAC) to achieve an ISO brightness of 90%.

RESULTS AND DISCUSSION

Wood Characterization

Fiber dimensions

Table 3 shows the dimensions of the wood fibers for both wood samples A and B. There were no significant differences between the samples in terms of length, width, and lumen diameter. The wall thickness showed a significant difference that can affect the consumption of effective alkali, as discussed later.

Table 3. Dimension Characteristics of Wood Fibers of *Eucalyptus* spp.

Parameters	Woods			
	A		B	
	Average	CV, %	Average	CV, %
Length, mm	1.0a	17.8	1.1a	13.2
Width, μ m	21.5a	17.2	21.7a	18.7
Lumen diameter, μ m	13.9a	25.4	14.6a	26.6
Wall thickness, μ m	3.8a	26.8	3.6b	20.7

The average values followed by the same letter indicated no significant differences by the “t” test at 5% probability ($p < 0.05$).

Physical-chemical characterization

Characterization of the wood samples A and B was performed according to their basic and apparent densities and also their chemical composition (Table 4). Similar results were found between basic and apparent densities. The basic densities of the woods A and B were 480 kg/m³ and 473 kg/m³, respectively, and these results are in accordance with the values practiced by the pulp mills which have prioritized the use of wood with basic density close to 500 kg/m³, with a tendency to slightly lower values (Gomide et al 2005).

Carbohydrate and lignin composition of both wood samples was also quite similar. Glucans represented almost 50% of the chemical constitution for both woods, as expected. Xylans comprise the main hemicellulose of hardwoods and, not surprisingly, it contributed almost 18% to the wood composition (xylan + uronic acids + acetyl groups). Mannans comprised the smallest fraction of the wood carbohydrates. The woods showed a variation in the cellulose and hemicelluloses content of only 0.5% and 0.4%, respectively. Wood extractives measurements revealed different contents depending on the solvent used. When ethanol/toluene was used, the quantities were similar. However, the extractives soluble in acetone and the total extractives of the wood from mill A were higher than the wood of mill B, which is expected since acetone is highly effective in removing fatty acids, resins, and gums.

The insoluble and soluble lignins showed variations of 0.5 % between the wood samples. The frequency of syringyl structures (S) was 2.5 to 3.0 times higher than the guaiacyl structures (G). S/G values are in agreement for eucalyptus species and were similar to values reported earlier (Gomide *et al.* 2005; Mokfienski *et al.* 2008). Higher syringyl lignins have higher content of uncondensed β -O-4 coupling, indicating a lower degree of condensation. Thus, lignins that contain higher S/G ratio are, in general, easier to delignify during kraft cooking because they are less condensed (Gomide *et al.* 2005; Gomes *et al.* 2008; Santos *et al.* 2010).

Table 4. Physical-chemical Analysis of *Eucalyptus* spp. Woods

Parameters	Woods		
	A	B	
Basic density, kg/m ³	480	473	
Apparent density, kg/m ³	183	179	
Cellulose*, %	47.6	48.1	
Hemicelluloses**, %	21.5	21.1	
Glucose, %	48.8	49.2	
Xylose, %	11.8	11.6	
Galactose, %	0.9	1.0	
Mannose, %	1.2	1.1	
Arabinose, %	0.2	0.3	
Uronic acids, %	4.0	4.0	
Acetyl groups, %	2.2	2.0	
Extractives, %	Acetone	1.6	1.1
	Ethanol/toluene	2.6	2.6
	Totals	3.7	3.5
Lignin, %	Insoluble	24.8	25.3
	Soluble	4.7	4.2
	Total	29.5	29.5
	S/G ratio	3.0	2.5
Metals, mg/kg	Cu	1.4	1.2
	Fe	9.9	8.5
	Ca	491	356
	Mg	123	183
	K	469	371

All results are average of two replicates

*Cellulose = total glucose – glucose from glucomannans (1/1); ** include the glucans that constitutes the hemicelluloses; Hemicelluloses: xylose + mannose + galactose + arabinose + glucose (glucomanan) + uronic acids + acetyl groups.

Interestingly, there is a wide variation in the metals content of the studied woods (Table 4). Among the inorganic components measured in the wood, the iron reacts with oxygen compounds used in pulp bleaching (oxygen, hydrogen peroxide, and ozone), reducing its effectiveness and increasing the consumption of chemical reagents (Colodette *et al.* 2002). The greatest difference in metal content between A and B was found for iron (Fe) and magnesium (Mg). Wood from mill A showed 16.5% higher Fe content compared to mill B and 49% lower Mg content. The majority of the

metals present in the pulping process are derived from wood used in the process, and the content of these materials varies with the tree source (Jemaa *et al.* 1999; Alen 2000; Arpalahti *et al.* 2000; Silva *et al.* 2002).

Pulping

Table 5 displays the results of cooking performed in the laboratory and industry to produce unbleached pulps. Wood A showed effective alkali demand slightly higher than wood B (variation of 0.5%) and, consequently, lower yield. Wood A also showed higher extractives soluble in acetone, which cause higher consumption of chemicals, resulting in more drastic pulping conditions and lower pulp yield, as well as some breakdown of cellulose.

Table 5. Characteristics of Unbleached Pulps

Parameters	Industrial		Laboratorial	
	A	B	A	B
EA, %	-	-	19.5	19.0
Screening yield, %	-	-	52.0	52.7
Kappa number	16.8	16.4	17.2	17.1
Brightness, % ISO	36.9	32.7	38.2	37.9
HexA ¹ , mmol/kg	63.3	55.4	61.2	56.7
Viscosity, dm ³ /kg	1343	1205	1407	1357
Fe, mg/kg	306	46.1	26.5	197
Mg, mg/kg	695	212	847	811
S/G ratio	1.4	1.3	1.4	1.4

¹ HexA = hexenuronic acids

Higher effective alkali demand for wood A may also be related to its higher thickness presented by its chips (4.4 mm) compared to the chips of wood B (3.8 mm). The higher the chips thickness, the more difficult the impregnation of the cooking liquor, which makes it necessary to use a higher concentration of alkali to achieve the same delignification degree that was achieved when thinner chips are used (Queiroz *et al.* 2004). The greater wall thickness presented by the fibers of wood A (3.8 µm) compared to fibers of wood B (3.6 µm) is also a reasonable explanation that must be considered when dealing with chips impregnation.

Industrial cooking of woods A and B resulted in pulps with kappa numbers of 16.8 and 16.4, respectively, (Table 5), which means that their delignification degrees were similar to those obtained in the laboratory where kappa numbers of 17.2 and 17.1 (Table 5) were achieved for wood samples A and B, respectively. Hexenuronic acids and residual lignin contribute to the kappa number (Li and Gellerstedt 1997; Costa and Colodette 2007). It was found a consumption of 8.4 to 8.6 equivalents of KMnO₄/mol HexAs, and therefore one kappa number unit was found to be equivalent to about 11.9 mmol of HexAs /kg of pulp (Gellerstedt and Li 1996; Devenyns *et al.* 1997; Li and

Gellerstedt 1997). Devenyns *et al.* (1997) presented a value of 10.0 mmol of HexAs /kg of pulp (10.0 mmol of HexA contribute to 1 kappa unit). In this study, we considered 10.0 mmol of HexAs to calculate the HexA fraction that contributes to the kappa number. Comparing unbleached industrial pulps, the brightness difference was 4.2% ISO, being higher for pulp A. When comparing the brightness of the unbleached laboratory pulp, this difference was 0.3% ISO, also higher for the pulp A. This behavior can be explained by the higher fraction of hexenuronic acids present in industrial (6.3) and laboratory-made (6.1) pulps A and, consequently, the lower fraction of lignin in the pulps of greater brightness. The results of industrial and laboratory pulps of the wood A have shown a difference of brightness of 1.3% ISO, being higher for the pulp produced in the laboratory. When pulp from wood B was analyzed comparing laboratory and industrial process, a surprisingly brightness variation of 5.2% ISO was observed, with better results for laboratorial pulp. Such discrepant variation of brightness in pulps from the same source indicates possible differences during industrial and laboratory cooking. Brightness difference between industrial and laboratorial unbleached pulp was found to be 1.3% ISO. The lower difference between industrial process of wood A and B may be attributed to better industrial process control of industry A than industry B. In both cases, however, laboratory-made pulps presented the highest brightness.

For example, the use of black liquor to complete the liquor/wood ratio, which is typical of industrial operation, was not performed in laboratorial tests. Moreover, careful selection of chips has been done in laboratorial scale, which is not possible for industrial operations. Differences in the viscosity of pulp was also noticed among industrial pulps (11.5%), being higher for the pulp of wood A. Laboratorial pulps had less than 4% viscosity variation, but pulp from wood A had higher viscosity. Such variations among industrial pulps may be due to process variables. For instance, comparing the industrial and laboratorial pulps A, the variation in the viscosity was approximately 5%, and between industrial and laboratorial pulps B, this variation was 12.6%. In the case of pulps from the same site (industrial A and laboratorial A or industrial B and laboratorial B) the difference of the viscosity is likely attributed to conditions employed in the industrial and laboratorial pulping process. Both industrial and laboratorial unbleached pulps showed similar S/G ratio values, which means that this variable probably will not influence the bleachability (Table 5).

Pulp Oxygen-prebleaching and Bleaching

Oxygen-prebleaching

Unbleached industrial and laboratory pulps under oxygen-prebleaching provided the results presented in Fig. 2. Comparisons were made between mills A and B: 1) industrial oxygen-prebleached pulps; 2) industrial unbleached pulps and oxygen-prebleached in the laboratory; 3) unbleached pulps produced and oxygen-prebleached in the laboratory.

Industrial oxygen-prebleached pulp A showed the highest brightness (62.2 % ISO) when compared to the other pulps (Fig. 2). This behavior may be due to the presence of the major fraction of hexenuronic acids and, consequently, a smaller fraction of lignin that comprise the kappa number of this pulp. An important observation is that the brightness of the industrial unbleached pulp A (36.9 % ISO – Table 5), was higher than that of the unbleached industrial pulp B (32.7 % ISO – Table 5).

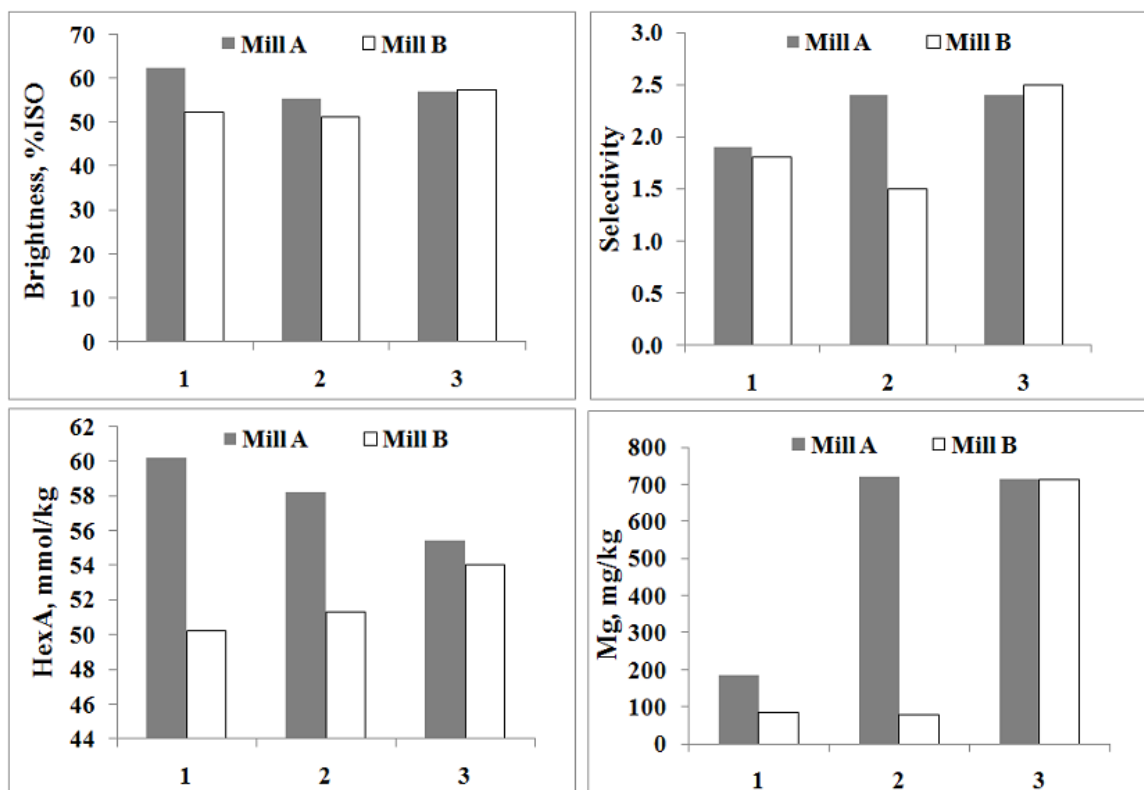


Fig. 2. Brightness, selectivity, hexenuronic acids, and magnesium of the delignified pulps. 1) Industrial oxygen-bleached pulps; 2) Industrial unbleached pulps and oxygen-bleached in the laboratory, and 3) Unbleached pulps produced and oxygen-bleached in the laboratory

The selectivity was calculated based on the Δ kappa and Δ viscosity. In general, the pulps with higher selectivity were those produced and oxygen-bleached in the laboratory A and B (3) and the industrial unbleached and oxygen-bleached laboratory A (2) samples. These pulps also showed higher magnesium content, which positively affects the viscosity through fiber protection effect and, consequently, the selectivity.

Bleaching

The bleaching sequence D*(EP)D was applied to all six pulps under the same conditions, and the results are presented in Fig. 3. Comparisons were made between mills A and B: 1) industrial oxygen-bleached pulps; 2) industrial unbleached pulps and oxygen-bleached in the laboratory; 3) unbleached pulps produced and oxygen-bleached in the laboratory. The industrial pulps were collected respecting the residence time of the equipment in factories units A and B.

Higher selectivity was observed for the pulps from mill A, whereas the hexenuronic acids content were higher for the pulps from mill B (Fig. 3). HexA consumes bleaching chemicals, causing an increase in their ability to chelate metals, and consequently, greater brightness reversion. However, there are indications that HexA may protect xylans against terminal depolymerization reactions, so its presence in the pulp preserves the yield in alkaline steps.

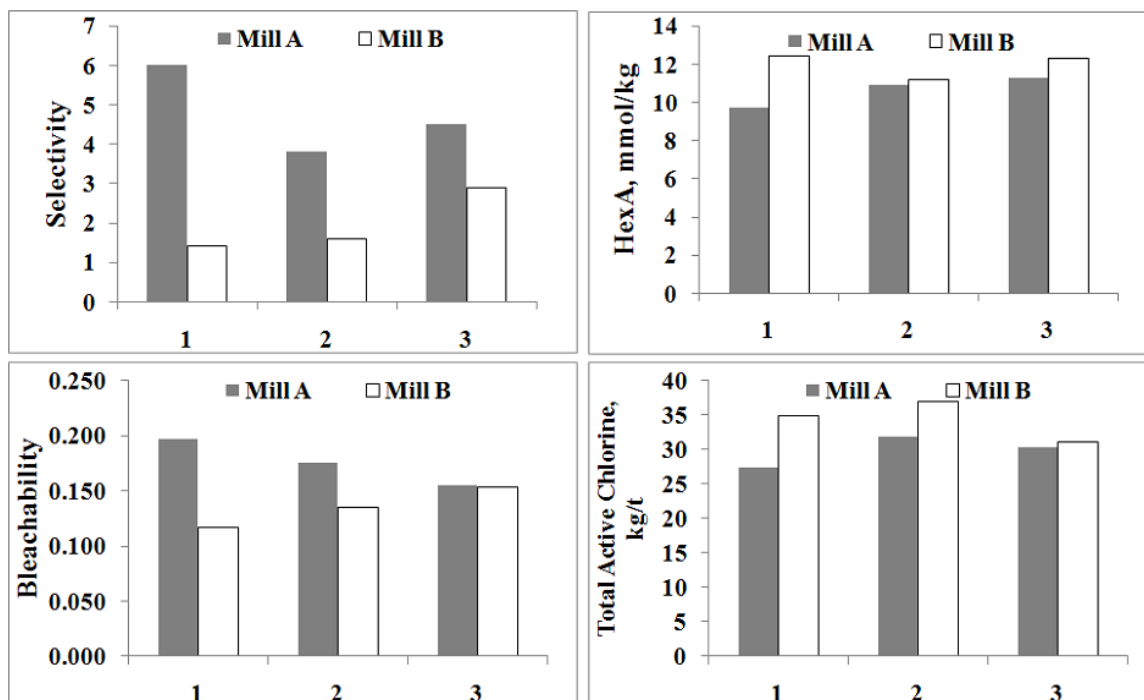


Fig. 3. Selectivity, hexenuronic acids, bleachability, and total active chlorine of the bleached pulps. 1) Industrial oxygen-bleached pulps; 2) Industrial unbleached pulps and oxygen-bleached in the laboratory; and 3) Unbleached pulps produced and oxygen-bleached in the laboratory.

Bleachability can be defined as the ease with which a determined pulp can be bleached. In this study it was calculated by considering the variation of kappa number (after oxygen delignification and after EP stage) and the total active chlorine consumption. Industrial oxygen-bleached pulp A showed the highest bleachability (0.197 Δ kappa/kg TAC), whereas the industrial oxygen-bleached pulp B showed the lowest bleachability (0.117 Δ kappa/kg TAC), which can be explained by its greater brightness after oxygen-bleaching (62.2 % ISO – Fig. 2) and by the lower consumption of total active chlorine (27.4 kg/ton - Fig. 3).

It is worth noting that industrial unbleached pulp A which originated industrial oxygen-bleached pulp A, showed higher initial brightness (36.9 % ISO – Table 5), compared to industrial unbleached pulp B (32.7 % ISO – Table 5), which originated from the industrial oxygen-bleached pulp B, and this behavior was maintained throughout the sequence.

Regardless of being cooked in the laboratory or in the mill, no significant effect was observed in the oxygen-bleaching stage performance for pulps originating from mills A and B.

The pulps produced in the laboratory showed similar bleachability, being 0.155 Δ kappa/kg TAC for the pulp A and 0.154 Δ kappa/kg TAC for the pulp B (Fig. 3). Despite the wide variation of iron content of the woods (Table 4), this variation did not affect the pulp bleachability. For instance, the laboratory-made pulps showed similar bleachability. In general, the consumption of total active chlorine ranged from 27.4 to 37.0 kg/ton of pulp.

CONCLUSIONS

1. Laboratory cooked and oxygen-prebleached pulps from chips collected in mills A and B showed similar bleachabilities, indicating no effect of wood in this parameter.
2. Unbleached pulps collected in mills A and B that were oxygen-prebleached in the laboratory showed highest bleachability for mill A, indicating an effect of cooking on bleachability; this same trend was maintained when the pulps were collected after the oxygen-prebleached stage in the mills.
3. The higher brightness of the unbleached pulp collected in mill A explains its higher bleachability in relation to that collected in mill B.
4. The higher brightness of the pulp from mill A in relation to that of mill B at a given kappa number is explained by the higher HexA/lignin ratio present in the former.

ACKNOWLEDGMENTS

We would like to thank the Universidade Federal de Viçosa and the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) for the scholarship granted.

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Article submitted: January 20, 2012; Peer review completed: June 16, 2012; Revised version received and accepted: December 19, 2012; Final corrections received: January 18, 2013; Published: January 22, 2013.