INFLUENCE OF WOOD PULPING CONDITIONS AND UNBLEACHED PULP COMPOSITION AND STRUCTURE ON THE ECF BLEACHABILITY OF HARDWOOD KRAFT PULPS

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ABSTRACT

The influence of wood pulping conditions and unbleached pulp chemical composition and structure on the ECF (DEDED) bleaching response of *Eucalyptus globulus* kraft pulps was investigated.

When pulping time was varied (kappa number 11.6-17.7) keeping constant other parameters, the total amount of ClO_2 required to fully bleach the pulp (90.5 % brightness) decreased with kappa number decrease. However, the relative amount of oxidant required per kappa number unit reduction, increased (bleachability decreased), showing that ClO_2 oxidizable structures (contributing to kappa number in pulp) became less reactive as their contents in pulp decreased. Such behaviour correlated with an increase of the degree of condensation and decrease of β-O-4 structures content in residual lignin.

When the different pulping parameters were varied individually and pulping time adjusted to have a constant kappa number of 14±0.3, the ClO_2 consumptions to reach 90.5 % brightness varied in the range of 36.5 to 46.9 Kg/ton. The increase in active alkali and sulfidity used in kraft pulping improved bleachability while the pulping temperature (150-170 ºC) didn't affect the bleaching response of pulps. The increase in liquor-to-wood ratio (keeping constant the other pulping parameters) had a detrimental effect on the bleachability. No clear correlation could be established between unbleached pulp brightness and its bleaching response. Overall, the results obtained showed a good correlation between the integral of relative reaction rate constant (H-factor) used in the pulping and pulp bleachability, a low H-factor being beneficial to the bleaching response of pulp. For such unbleached pulps with kappa number 14±0.3, bearing significantly different bleaching responses in general, bleachability was shown to increase as the content of hexenuronic acid increases and residual lignin decreases. No clear correlation could be established between extractives content, lignin structural features and pulp bleachability.

INTRODUCTION

The DEDED bleaching sequence is a typical ECF bleaching sequence and the most widely used worldwide for hardwood kraft pulps (1). Chlorine dioxide is an expensive chemical and, although much less hazardous than chlorine (Cl_2) previously used in bleaching processes, leads to the formation of minor amounts of organochlorine compounds (1). Thus, the reduction of ClO_2 consumption is an important goal of ECF bleached pulp producers.

The conditions used in the pulping do affect the chemical composition and structure of unbleached pulps (2,3) and, therefore, the consumption of bleaching chemicals to reach a desired brightness. Previous studies on the influence of pulping parameters in the bleaching response of kraft pulps were carried out essentially with softwoods and Scandinavian and North American hardwoods and involved both ECF and TCF bleaching sequences (2-7). As far as *Eucalyptus* species are concerned, the information available on this subject is rather scarce (8,9) and not systematic. Some apparent conflict may be observed in such results, assigned essentially to the different type of wood, bleaching processes and experimental design and conditions used.

The bleaching response was related with the chemical composition and structure of unbleached kraft pulp components (2,10-14). Modifications in the residual lignin structure (2,11-13). and hexenuronic acid (HexA) content (2,14) during the alkaline pulping were claimed as responsible for the different bleachability of kraft pulps. Unsaturated lipophilic extractive compounds were also shown to consume bleaching chemicals such as chlorine dioxide (15,16), affecting pulp bleachability.

The aim of this paper is to review our recent investigations (17-22) on the effect of the conditions used in the kraft pulping of *Eucalyptus globulus* wood (constant kappa number of 14±0.3) in the ECF bleachability of pulps and on the establishment of relationships between bleaching response and residual lignin content and structure, HexA and extractives content of unbleached pulp.

MATERIALS AND METHODS

Pulping experiments were carried out with industrial size chips from a 12 years old *E. globulus* clone plantation in 5.8 L forced circulation batch digesters equipped with an external electric heating system and temperature control. The reference pulping conditions were as follows: initial temperature of pulping liquor - 40ºC; time-to-final temperature - 120 min.; final temperature - 160ºC; active alkali charge, AA: 17% (as Na_2O); sulfidity, S: 28%; liquor-to-wood ratio, L/W (volume of liquor (L) / weight of wood (Kg)): 4. In a first series of pulps, only the pulping time was varied, keeping other pulping parameters constant (reference conditions), in order to obtain pulps with variable kappa number. For the remaining series of pulps, pulping parameters/conditions (active alkali charge, sulfidity, temperature, liquor-to-wood ratio) were varied separately, keeping the others constant. In these series pulping time was adjusted in order to have a constant kappa number of 14±0.3 (Table 1).

Bleaching experiments ($D_0E_1D_1E_2D_2$ sequence) were carried out in closed plastic bags introduced in a water bath with temperature control. Standard industrial bleaching conditions were used. The strategy for the distribution of the ClO_2 charge (expressed as “active chlorine”) was as follows: in D_0, a pre-determined ClO_2 charge was used in order to reach a final kappa number ~6 (with no residual ClO_2 at the end of the stage); the remaining ClO_2 charge, pre-determined to achieve 90.5 % brightness in the end of the bleaching sequence, was distributed between D_1 and D_2 stages in proportions of around ~75 and ~25 %. ClO_2 consumption was expressed as weight % of "active chlorine" per dry pulp. ClO_2 in solution was quantified by conventional iodometric titration. The bleaching conditions were as follows: D_0 - 25 min, 50 ºC, pH ≅ 3.0; E_1 - 120 min, 70 ºC, 2.1 % NaOH; D_1 - 240 min, 70 ºC, pH ≅ 3.5; E_2 - 120 min, 70 ºC, 0.6 % NaOH; D_2 - 240 min, 70 ºC, pH≅ 3.5. All stages were carried out at 10% consistency (kg(dry pulp)/kg(suspension)).

The bleaching response or bleachability, defined as the consumption of oxidant normalized to the amount of residual lignin and other oxidizable structures in pulp, was expressed as "(OXE)/ton)/ kappa number" (23) "OXE/ton" stands for oxidation equivalents (Kg of "active chlorine" x 28.20) per ton of unbleached dry pulp; "kappa number" (including the contribution of hexenuronic acid) is the difference between kappa number of pulp entering the bleaching stage or sequence and pulp leaving the bleaching stage or sequence). For practical purposes, the kappa number of fully bleached pulps was assumed as zero.

Chemical analysis of unbleached pulp components was carried out according to previously reported procedures (17-19,24-27). Lipophilic extractives were isolated by dichloromethane extraction and analysed by GC-MS as TMS derivatives. Residual lignins were isolated by mild acidolysis (dioxane/water 9/1, containing HCl 0.2N) (24). The isolation yields were in the range 30-60% (based on Klason lignin content). The lignins were characterised by quantitative ^{13}C NMR (after acetylation) in DMSO-d_6 and by permanganate oxidation followed by GC-MS analysis of the methylated oxidation products (27). HexA and residual lignin were simultaneously quantified by UV spectrophotometry analysis, after pulp dissolution in cadoxen (25). Alternatively, hexenuronic acid was also quantified by the established acid hydrolysis method (26). The brightness of unbleached pulps was measured as the reflectance at 457 nm, according to ISO standard method.

RESULTS AND DISCUSSION

Influence of pulping conditions on bleachability

Variation of pulping time (variable kappa number)

The pulping time was varied, keeping constant other pulping parameters (reference conditions, see Experimental). This allowed the production of pulps with different extents of delignification, kappa number ranging from 17.7 to 11.6. Pulping conditions and results as well as figures of ClO_2 consumption in the bleaching process are shown in Table 1. As expected, the total amount of ClO_2 consumed to reach 90.5% brightness in $D_0E_1D_1E_2D_2$ bleaching sequence decreases as the kappa number of pulps decreases (pulping time increases) (Figure 1). However, when the bleaching response or bleachability, expressed as

Table 1. Conditions and results of kraft pulping (AA: active alkali, S: sulfidity, L/W: liquor-to-wood ratio) (reference pulping conditions and results underlined)

Pulping conditions									
AA, % Na_2O	S, %	T, ºC	L/W, L/Kg	Time, min.	Pulp yield, %	Kappa number	Viscosity, mL/g	Bright-ness, %	ClO_2 consum-ption, %
17	28	160	4	145	56.6	17.7	1445	45.7	4.97
17	28	160	4	150	56.9	17.0	1445	46.6	5.10
17	28	160	4	154	56.2	15.0	1458	47.4	4.40
17	28	160	4	160	55.9	14.7	1400	47.5	4.30
17	28	160	4	165	56.3	14.8	1449	47.6	4.30
<u>17</u>	<u>28</u>	<u>160</u>	<u>4</u>	<u>170</u>	<u>55.5</u>	<u>13.8</u>	<u>1387</u>	<u>47.8</u>	<u>4.10</u>
17	28	160	4	180	55.9	12.5	1345	47.6	4.00
17	28	160	4	195	54.5	12.5	1262	47.6	4.00
17	28	160	4	210	55.1	11.6	1240	48.2	3.90
14	28	160	4	190	56.7	13.7	1500	45.4	4.20
21	28	160	4	145	54.8	13.8	1364	49.5	4.01
24	28	160	4	138	53.8	14.2	1325	49.6	3.65
17	15	160	4	185	55.0	13.9	1251	48.3	4.15
17	21	160	4	175	55.3	13.7	1322	47.4	3.90
17	37	160	4	165	56.9	13.7	1460	46.3	3.65
17	28	150	4	255	56.5	13.7	1427	46.0	3.91
17	28	155	4	197	55.4	13.8	1385	47.3	3.83
17	28	170	4	131	55.8	13.9	1345	47.1	3.88
17	28	160	3.5	170	52.0	14.0	1243	46.8	4.03
17	28	160	5	179	55.7	14.3	1454	46.7	4.29
17	28	160	8	216	54.7	13.7	1476	46.2	4.69

oxidation equivalents (OXE) consumed per kappa number unit reduction (oxidant consumption normalised to the content of lignin and other oxidizable structures) is plotted against the kappa number of unbleached pulp, an increase of this variable (denoting a decrease of bleachability) is observed as the extent of delignification increases (kappa number decrease). Hence, the residual lignin and other oxidizable components remaining in pulp are progressively more resistant to oxidation as their contents in pulp decreases.

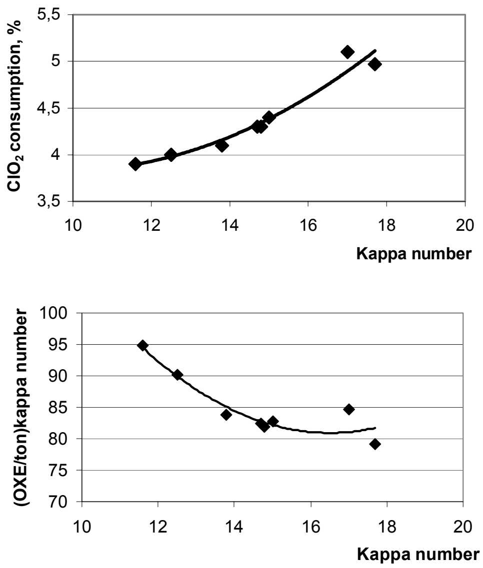

Figure 1. Influence of the kappa number of unbleached pulp on its bleaching response by a DEDED bleaching sequence (90.5 % brightness) (see Table 1 for conditions).

Variation of conventional pulping parameters (constant kappa number)

Four series of pulps were produced by varying separately each one of the following parameters: active alkali (AA), sulfidity (S), temperature (T) and liquor-to-wood ratio (L/W). Other parameters were kept constant at reference values. In each case, the pulping time was adjusted to obtain a constant kappa number of 14±0.3. The pulps were then submitted to the standard ECF DEDED bleaching sequence. The ClO_2 consumptions to fully bleach the pulps (90.5% brightness) ranged from 3.65 to 4.69% (36.5 to 46.9 ton).

The influence of active alkali in the bleachability of unbleached pulp was investigated in the range 14-24% (Table 1). It was found that the bleachability increases remarkably with active alkali (Figure 2). Thus, a high concentration of OH^- and HS^- anions in the pulping liquor is clearly beneficial to the bleaching response of kraft pulp. At low AA (14%), 4.2 % (42.0 Kg/ton of pulp) ClO_2 is consumed to reach 90.5 % brightness, against 3.65% (36.5 Kg/ton of pulp) with AA 24%. This result is in agreement with previous findings which showed that a high residual alkali at the end of the cook is beneficial to bleachability (9). However, the improvement of bleachability with AA is accompanied by a significant decrease of yield (5%) and viscosity (12%) of unbleached pulp (Table 1), which is reflected in the yield and mechanical properties of bleached pulp (results not shown).

As far as sulfidity is concerned, a series of kraft pulps was produced with S ranging between 15 and 37% (Table 1). The amount of OXE consumed per ton of pulp to reach 90.5% brightness, decreases with sulfidity (Figure 2), showing that, at constant active alkali, bleachability is improved when the HS^- / OH^- concentration ratio increases. The use of high sulfidity (37%) allows saving 5.0 kg of ClO_2 per ton of pulp to achieve 90.5 % brightness, 12 % less than with low sulfidity charges (15%) (Table 1). Also, the increase of S leads, as expected, to significant improvements in unbleached pulp yield (3.5%) and pulp viscosity (17%). The use of high sulfidity (up to the highest level investigated, 37 %) is, thus, beneficial from the point of view of the production yield, pulp quality and bleaching chemicals saving.

A series of four pulps was produced by variation of the pulping temperature in the range 150-170 ºC (Table 1). When these pulps were submitted to the bleaching sequence, no significant differences were observed on the corresponding bleaching responses (Figure 2). However, the temperature increase had a slight negative effect in the pulp yield and pulp viscosity (Table 1).

The influence of liquor-to-wood ratio in the bleaching response of unbleached pulps was investigated in the range 3.5-8.0, keeping constant the other pulping parameters (Table 1). The bleachability of pulp drops as the relative proportion of liquor to wood in the pulping reactor increases (Figure 2). Such result

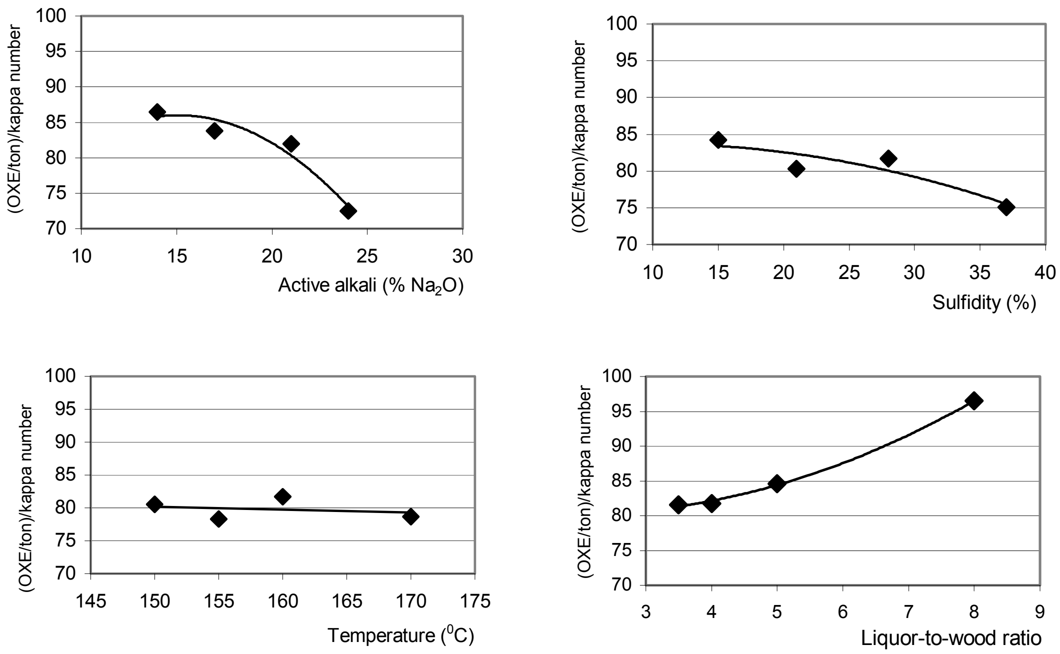

Figure 2. Influence of kraft pulping parameters on the bleaching response of pulps with kappa number 14±0.3 by a DEDED bleaching sequence.

is in agreement with the previously observed behavior of bleaching response with active alkali AA (with constant L/W). When L/W is increased, keeping constant AA, the concentration of OH^- and HS^- anions is lowered, leading to lower bleaching response of pulps. It might be expected that in the presence of higher volumes of liquor, the lower concentration of lignin in the black liquor would be beneficial to bleachability, decreasing the extent of lignin side-reactions in solution (including condensation) and its re-deposition in fibers. However, in the pulping conditions used, this was not observed, certainly because the effect of the lower concentration of reagents is dominant. In fact, when results shown in Figure 2 for AA and L/W are summarized in a single graph (not shown) using concentration in g(Na_2O)/L(liquor), it becomes clear that the alkali concentration is the variable determining bleaching response. The higher alkali concentration obtained with high L/W leads to a decrease of unbleached pulp yield and viscosity, agreeing with results obtained with AA variations (Table 1).

Bleachability and H-Factor

As previously seen (Figure 2), the bleachability (for unbleached pulps with constant kappa number) has a complex dependence on the pulping parameters used to produce the pulp. It would be interesting, from the point of view of industrial practice, to identify a single variable that could be related with bleachability and used in the pulp mil to control chlorine dioxide consumption in the bleaching plant. Vroom (38) proposed a simple kinetic model in which time (t) and temperature (T) are combined in a single variable, in the form of the time integral of the relative rate constant (k_r=k/k_{373}, where k is the rate constant at a given temperature and k_{373} is the rate constant at 373 K)), the so-called H factor. Because the extent of delignification is proportional to H-Factor, this model is widely used to estimate the time and temperature required to attain a desired kappa number in an industrial digester. AA, S and L/W affect pulping time, and, thus, the H factor reflects the variations of all pulping parameters investigated in this work. When the bleachability of kraft pulps with kappa number 14, obtained by variations of AA, S, T and L/W (Table 1), expressed as (OXE/ton)/kappa number is plotted against H-Factor, an interesting tendency is observed: bleachability increases as the H-Factor decreases (Figure 3). From the point of view of bleachability, ECF bleached kraft pulp mills should work with an H-Factor as low as possible. Low H-Factors may be attained by using high active alkali and/or high sulfidity (pulping time, at the same temperature, is reduced (Table 1)). However, high active alkali levels leads to significant pulp yield and pulp viscosity losses (Table 1). On the other hand, high sulfidity levels lead to yield improvements and to better pulp quality (higher viscosity) but to additional problems in the mill, namely equipment corrosion and increased sulfur-based emissions. Optimization of these factors in each particular mill, using H-Factor control, may lead to substantial economic and environmental impact savings.

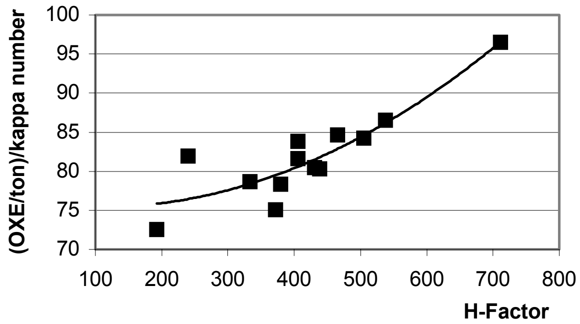

Figure 3. Relationship between ECF bleachability (90.5 % brightness) and H-Factor (unbleached pulps with kappa number 14±0.3, obtained by variation of AA, S, T, L/W - see Table 1 for conditions)

Bleachability and brightness of unbleached pulps

During the bleaching of chemical pulps, after the major the fraction of residual lignin is removed, the last bleaching stages will reduce essentially the content of chromophore structures in the pulps. Consequently, it may be expected that brighter unbleached pulps are easier to bleach. In fact, it was previously observed that kraft pulps produced with variations in active alkaline charge, showed improved brightness and bleaching responses when the alkaline charge was increased (29) (Table 1). However, this is not the case, for example, when pulping is carried out using different sulfidities, keeping

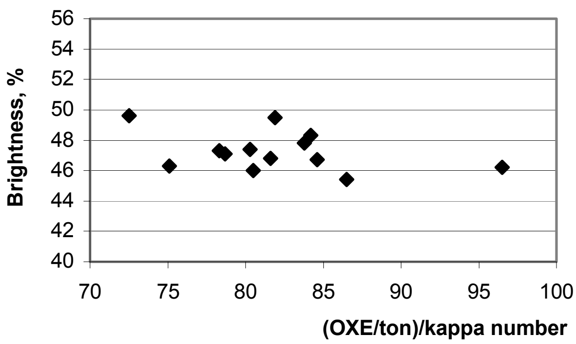

Figure 4. Relationship between the brightness of unbleached pulps (kappa number) 14±0.3 and bleachability by a DEDED bleaching sequence (90.5 % brightness).

constant the active alkali. When sulphidity is increased, the brightness of the unbleached pulp decreases but its ECF bleachability is significantly improved (Table 1). When all the pulps bearing kappa number 14 were considered, although they showed different brightness (45-50%), no correlation could be established between this optical property and the amount of ClO_2 required to reach 90.5 % brightness (Figure 4). In conclusion, at constant kappa number, the ECF bleachability kraft pulps is not necessarily related with the chromophores content of unbleached pulps, expressed as the reflectance of pulp at 457 nm.

Bleachability and chemical composition and structure of kraft pulps

In order to understand the origin of such different bleaching responses, all the unbleached pulps were submitted to detailed chemical and structural analysis, looking essentially to the main and potential ClO_2 consumers: lignin, hexenuronic acid (HexA) and unsaturated lipophilic extractives.

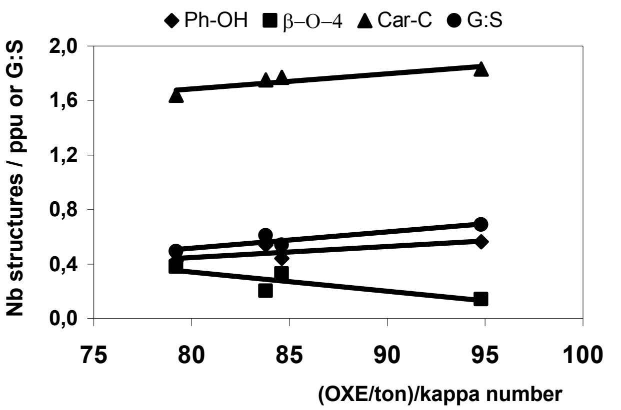

Figure 5. Relationship between bleachability and structural features of residual lignins (determined by ^{13}C NMR) isolated from pulps with kappa number in the range 11.6 to 17.7.

In the case of pulps bearing different kappa numbers, as expected, as the kappa number of pulp was reduced from 17.7 to 11.6, the content of residual lignin as well of extractives decreased; on the other hand, the content of HexA rose as the delignification proceeded in this kappa number range. Residual lignins of these pulps were isolated and characterized by ^{13}C NMR and permanganate oxidation. The observed decrease of bleachability when kappa number was reduced from 17.7 to 11.6 correlated quite well with an increase in the degree of condensation of residual lignin (expressed of the content of aromatic carbons involved in C-C linkages, Car-C) (Figure 5), a decrease of the amount of β-O-4 structures and increase in guaiacyl:syringyl ratio (G:S). The increase of the degree of condensation of lignins when kappa number is lowered was also confirmed by permanganate oxidation analysis. The decrease of bleachability is accompanied by a slight increase in phenolic OH groups (Ph-OH) (Figure 5), suggesting that the abundance of phenolic moieties in residual lignins is not determinant of the bleaching response of pulps.

When pulps with similar kappa number (14±0.3), obtained by variations of pulping parameters, are considered, the situation is much more complex. Residual lignin and HexA are the main contributors to kappa number. The relative importance of these two components to the bleachability was assessed by determining their contents in unbleached pulps. Lignin content for this set of pulps was found to vary

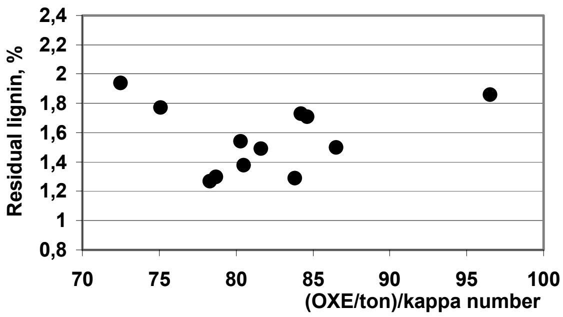

Figure 6. Residual lignin content of pulps with kappa number 14±0.3, bearing different bleachabilities.

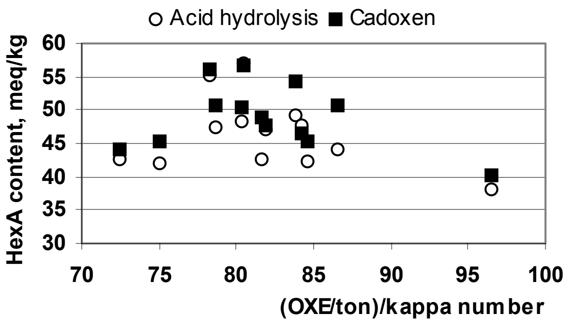

Figure 7. HexA acid content (determined by acid hydrolysis and cadoxen methods) of pulps with kappa number 14±0.3, bearing different bleachabilities.

between 1.3 and 1.9 % while HexA (determined by two alternative methods) were in the range of 40-57 meq/Kg (corresponding to 0.8-0.9%, w/w). When residual lignin is plotted against bleachability expressed as (OXE/ton)/kappa number (Figure 6), at a first glance, no relationship may be established between these two variables. However, if the two points in the left upper corner of the graph (corresponding to the two pulps obtained with extremely high active alkali (24%) or sulphidity (37%) (Table 1)) are not considered in the analysis, a general tendency may be observed: the amount of OXE consumed per kappa number unit decreases as the residual lignin content decreases. Interestingly, when the HexA content is analysed, and, again, the two pulps obtained with extreme conditions are withdrawn, the opposite behaviour is observed (Figure 7). Thus, at constant kappa number, in general, bleachability increases as the ratio lignin content / HexA content decreases. In other words, such result confirms that in equivalent amounts, lignin consumes more ClO_2 than HexA per kappa number unit reduction.

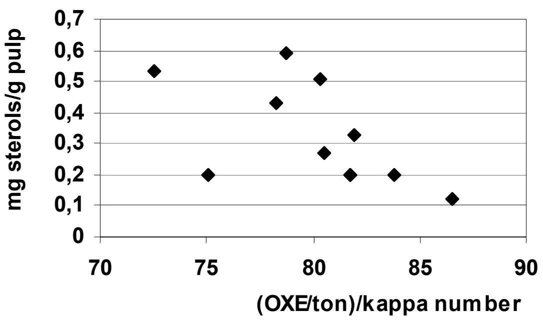

Figure 8. Sterols content of pulps with kappa number 14±0.3, bearing different bleachabilities.

Unsaturated extractives may also contribute to the consumption of chlorine dioxide. In *Eucalyptus globulus* kraft pulps, sterols, namely β-sitosterol, represent the most abundant fraction of lipophilic extractives of kraft pulps (30). In general, if the two extreme pulping conditions (24% AA/28% S and 17% AA/ 37% S) are not considered, the bleachability tends to increase as the content of sterols in pulp increases (Figure 8). This unexpected positive correlation shows that, although unsaturated extractives may consume ClO_2, they do not determine at all the bleaching response of pulp, certainly because of their quite low contents in pulps (0.02-0.06%) when compared to lignin (1.3-1.9%) or HexA (0.8-0.9%).

The intriguing behaviour of the pulps produced with extreme active alkali and sulphidity is not completely understood and will deserve attention in future works.

The quantitative ^{13}C NMR analysis of residual lignins from pulps with kappa number 14±0.3 revealed that the contents of phenolic OH groups and β-O-4 structures as well as the degree of lignin condensation and and guaiacyl to syringyl units ratio (G:S) is practically constant for all the residual lignins (Figure 9). The results from permanganate oxidation also showed that the ratio non-condensed / condensed units in lignin is similar for all the lignins investigated. Hence, for kraft pulps bearing similar kappa numbers, no clear correlation may be established between the residual lignin structural features and the observed ECF bleaching response of corresponding pulps. However, from such results it cannot be concluded that bleachability is independent from the structure of residual lignin. Although the lignin isolation yields are satisfactory and the lignin structural transformations occurring during the isolation procedure are not very significant when compared to enzymatic isolation (results not shown), there is always a fraction of lignin, eventually linked to polysaccharides, which is retained in pulp or is lost during the acidolytic treatment. The structure and composition of this lignin is not known and may certainly contribute to explain the different bleaching responses of pulps.

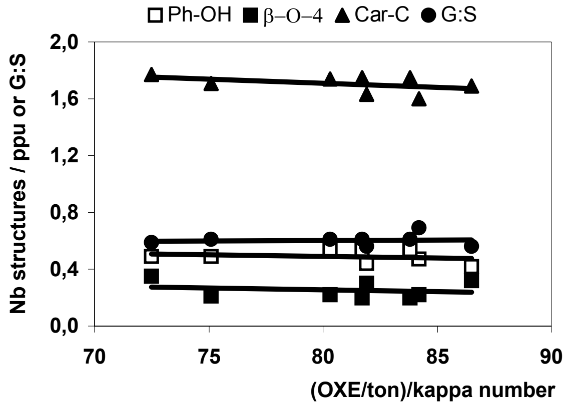

Figure 9. Structural features of residual lignins (determined by ^{13}C NMR) isolated from pulps with kappa number 14±0.3, bearing different bleachabilities.

The criterion used in this work to compare unbleached pulps is kappa number. As previously shown, these pulps have significantly different lignin contents. Since bleachability is determined essentially by lignin content, in future works, in order to assess more adequately the contribution of lignin structure to bleachability, we suggest the using of pulps with similar lignin contents instead of pulps with similar kappa number.

CONCLUSIONS

Pulping parameters affect strongly the bleaching response of *Eucalyptus globulus* kraft pulps in a DEDED sequence.

When the kappa number decreases (pulping time extended) in the range 11.6-17.7, keeping constant other pulping parameters, the amount of ClO_2 required to fully bleach the pulp (90.5 % brightness) decreases. However, the relative amount of oxidation equivalents (OXE) required per kappa number unit reduction, increases (bleachability decreases). This behaviour correlates with the observed increased degree of condensation and decrease of β-O-4 structures in residual lignin.

Pulps with kappa number 14±0.3, produced with variations of active alkali, sulphidity, temperature and liquor-to-wood ratio, show ClO_2 consumptions from 3.65 to 4.69 %, to reach 90.5 % brightness. The best pulp bleaching response, pulp yield and pulp viscosity is obtained for high sulfidity level (37%), keeping other pulping parameters constant at standard levels. Bleachability may be related with the H-Factor used in the pulping. Low H-Factors, obtained by variations in other parameters apart from temperature, afford pulps easier to bleach. This result may have a direct impact on the control strategy of chlorine dioxide consumption in an ECF bleached kraft pulp mill. No relationship could be established between unbleached pulp brightness and its bleachability. The residual lignin content showed to be the key factor determining bleachability. At constant kappa number (uncorrected for HexA), in general, bleachability increases as the ratio lignin / HexA decreases. Unsaturated extractives such as sterols, although they may consume ClO_2, do not play a determinant role in the bleaching response of pulp. No clear correlation could be established between bleachability and β-O-4 structures, phenolic OH groups, guaiacyl to syringyl units ratio (G:S) and degree of condensation of residual lignins. Also, for the pulps investigated, no relationship was observed between the chromophores content of the unbleached pulp and its bleaching response. The absence of correlation between lignin structure and bleachability may be assigned, partially at least, to the lack of representativity of the isolated residual lignins. Additionally, these results may suggest that other chemical structures present in pulps, probably lignin-carbohydrate complexes (wood native or formed during the pulping) or other unknown unsaturated structures, probably issued from carbohydrates, play a key role in the bleaching response of pulps.

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