Hexenuronic acid contents of Eucalyptus globulus kraft pulps: Variation with pulping conditions and effect on ECF bleachability

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ABSTRACT: This study investigates the effect of pulping time and process parameters on the content of hexenuronic acid (HexA) in *Eucalyptus globulus* kraft pulps. Under selected standard pulping conditions, the amount of HexA in pulps increases during cooking. This behavior, significantly different from that of softwood pulps, is tentatively attributed to the milder conditions used in the pulping or to topochemical effects rather than to differences in the chemical structure of the glucuronoxylans from hardwoods and softwoods. We found that, for the same kappa number (14, obtained by adjusting pulping time), the HexA content decreases when active alkali increases from 17% to 24% and increases with sulfidity in the range 15%-28%. A decrease in the HexA content occurs when the temperature rises from 150°C to 170°C and when liquor-to-wood ratio increases from 4 to 8. The variations observed are determined by two simultaneously occurring processes: HexA formation and degradation or dissolution with xylans. When the unbleached pulps with kappa number 14 were fully bleached by a DEDED sequence, we observed a general increase in chlorine dioxide consumption as the HexA of the unbleached pulp decreases.

Application: The results of this research can be used in the control of hexenuronic acid formation in hardwood kraft pulp mills.

Under the conditions used in kraft pulping of wood, 4-*O*-methylglucuronic acid in glucuronoxylans is partially converted into hexenuronic acid (HexA) moieties by elimination of methanol [1]. These unsaturated structures increase the consumption of bleaching chemicals (ozone, chlorine dioxide, and peracids), decrease the brightness stability of pulps, and may also contribute to the formation and deposition of oxalic acid in the bleaching equipment [2]. Therefore, monitoring the HexA contents of unbleached pulps is an important goal, with potential benefits for the quality of bleached pulp and mill economy and management.

As HexA is formed during the pulping, it may be simultaneously degraded in the alkaline medium or partially eliminated as a result of xylan dissolution [3]. Hence, the content of HexA in unbleached alkaline pulps is the result of two competitive processes: formation and degradation. In the case of kraft pulping of softwoods, HexA is formed essentially during the initial pulping stages (rise to temperature). At the final cooking temperature its content in pulps decreases continuously with time due to alkaline degradation and xylan dissolution [3-5]. Previous studies looked at the influence of kraft pulping parameters on the formation and degradation of HexA for softwoods [3, 5]. Those showed that the rate of degradation of HexA increases with the concentration of hydroxide and hydrogen sulfide anions. The increase in pulping temperature leads to lower HexA contents in pulp. However, as far as hardwoods are concerned, the literature on this topic is less abundant and it is particularly scarce for *Eucalyptus globulus* [6-8]. Additionally, although it is known that HexA may consume bleaching chemicals, such as chlorine dioxide, the impact of HexA on the bleaching response of *E. globulus* kraft pulps has not yet been assessed.

In this study we investigated how pulping time (degree of delignification) and pulping parameters (active alkali, sulfidity, temperature, and liquor-to-wood ratio) affect the amount of HexA in *E. globulus* kraft pulps and how HexA content affects elemental chlorine free (ECF) bleachability of pulps.

EXPERIMENTAL

The pulping experiments used industrial size chips from a 12-year-old *E. globulus* clone plantation, using a 2-L forced circulation batch digester equipped with an external electric heating system and temperature control. In the case where the complete separation of fibers did not occur, the pulp or partially delignified wood was submitted to mechanical fiber separation in a disc refiner. All pulps were then thoroughly washed until the filtrate was neutral. The standard pulping conditions were temperature-160 °C; time-to-temperature-120 min; active alkali (AA)-17% (as Na_2O); sulfidity (S)-28%; liquor-to-wood ratio (L/W)-4. In experiments in which we varied pulping parameters, we changed each parameter individually, while keeping the others at standard levels. The kappa number was determined by the TAPPI standard method and was not corrected for the HexA content of pulp. Pulping conditions and results are summarized in **Table I**.

Bleachability was assessed by submitting pulps to a $D_0E_1D_2E_2D_2$ bleaching sequence. Bleaching experiments (D and E stages) 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 to use a pre-determined ClO_2 charge in the D_0 stage, allowing the pulp to reach a kappa number of about 6 (with no residual ClO_2). The remaining ClO_2 charge, pre-determined to achieve 90.5% brightness in the end of the bleaching sequence (with no residual ClO_2), was distributed between the D_1 and D_2 stages in proportions of about 75% and about 25%, respectively.

PULPING CONDITIONS							
AA, % Na_2O	S, %	T, °C	L/W, L/kg	TIME, min.	PULP YIELD, %	PENTOSAN CONTENT, %	KAPPA NUMBER
17	28	160	4	145	56.6	14.3	17.7
17	28	160	4	150	56.9	14.7	17.0
17	28	160	4	170	55.5	14.1	13.8
17	28	160	4	210	55.1	13.0	11.6
14	28	160	4	190	56.7	14.7	13.7
21	28	160	4	145	54.8	13.8	13.8
24	28	160	4	138	53.8	12.7	14.2
17	15	160	4	185	55.0	13.9	13.9
17	21	160	4	175	55.3	14.1	13.7
17	37	160	4	165	56.9	16.2	13.7
17	28	150	4	255	56.5	15.2	13.7
17	28	155	4	197	55.4	13.3	13.8
17	28	170	4	131	55.8	13.0	13.9
17	28	160	3.5	170	52.0	15.2	14.0
17	28	160	5	179	55.7	15.1	14.3
17	28	160	8	216	54.7	16.7	13.7

I. Pulping conditions and results (AA: active alkali, S: sulfidity, L/W: liquor-to-wood ratio)

	MOLAR PROPORTIONS, % ((nb acid units/nb xylose units) x 100)				
CONDITIONS	Spruce		*Eucalyptus globulus*		
SAMPLES	MeGlcA	HexA	MeGlcA	Gal-MeGlcA*	HexA
Intial xylan	14.7	0	11.9	4.4	0
100°C (heating-up period)	16.0	0	11.7	5.3	0
160°C, 0 min	10.5	6.2	7.8	3.6	5.8
160°C, 20 min	4.5	8.6	Tr	Tr	8.8

*4-*O*-Methylglucuronic acid substituted at *O*-2 with galactose

II. Results of ^{1}H NMR analysis of uronic acids contents of* Eucalyptus globulus *and spruce xylans submitted to chemical treatment simulating kraft cooking conditions (0.88 M NaOH+0.33 M Na_2S, 160 °C).

HexA in unbleached pulps were quantified by acid hydrolysis followed by UV spectrophotometric analysis of the furan derivatives, giving a band at 245 nm (acid hydrolysis method) [9]. The acid hydrolysis treatment of pulp was carried out in a 300 mL Parr Reactor equipped with an external heating system, mechanical stirring, and temperature control. Analyses were carried out at least in triplicate. We also used a new, alternative method to quatify HexA that involves the dissolution of pulp in cadoxen and simultaneous UV spectrophotometric analysis of HexA and residual lignin [10]. The analyses of HexA by this new method, hereafter designated as the cadoxen method, were at least duplicated. Pentosans were quantified by the established bromide/bromate method [11].

Xylans from acid chlorite delignified *E. globulus* and spruce woods (holocellulose) were extracted with aqueous 5% KOH and precipitated in ethanol, according to a published methodology [11]. The xylans (without previous purification) were submitted to a chemical treatment simulating the kraft pulping conditions, using 50 mL stainless steel autoclaves with Teflon liner, containing 50 mg of xylan and 5 mL of white liquor (0.88 M NaOH+0.33 M Na_2S). Autoclaves were placed in an electric oven at room temperature and heated at 1°C/min until the final temperature (160°C) was reached. After reaction, xylan was precipitated by acidification of the liquor, dissolved in H_2O and analyzed by ^{1}H NMR (internal standard sodium 3-(trimethylsilyl)propionate-d_4) using published conditions [12]. We calculated the relative molar proportions of HexA, 4-O-methyl-α-D-glucuronic acid (MeGlcA), and 4-O-methyl-α-D-glucuronic acid substituted at *O*-2 with α-D-galactose (Gal-MeGlcA) using the ratio between the integral of the corresponding anomeric protons resonances and the integral of the anomeric proton resonance of internal anhydroxylose units (**Fig. 1**, **Table II**).

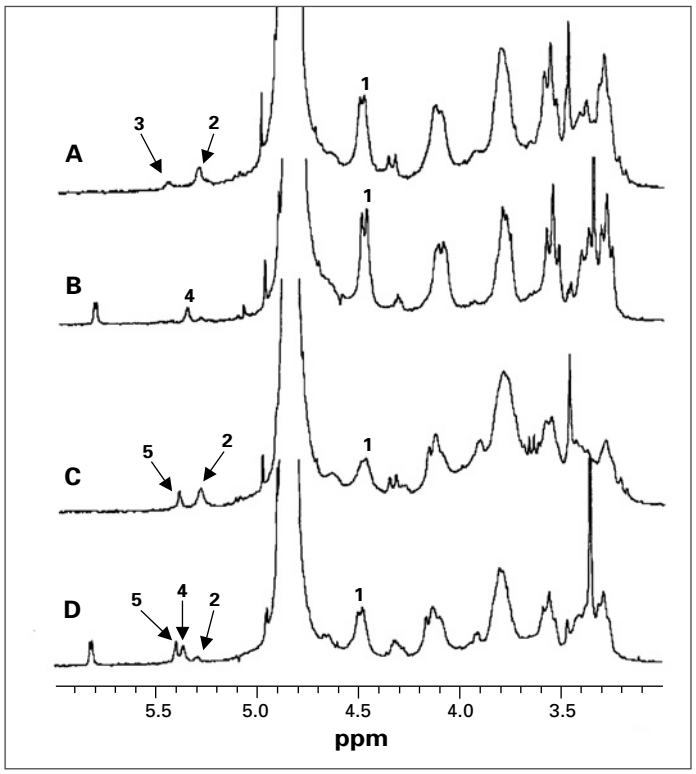
RESULTS AND DISCUSSION

Variation of HexA content with degree of pulp delignification

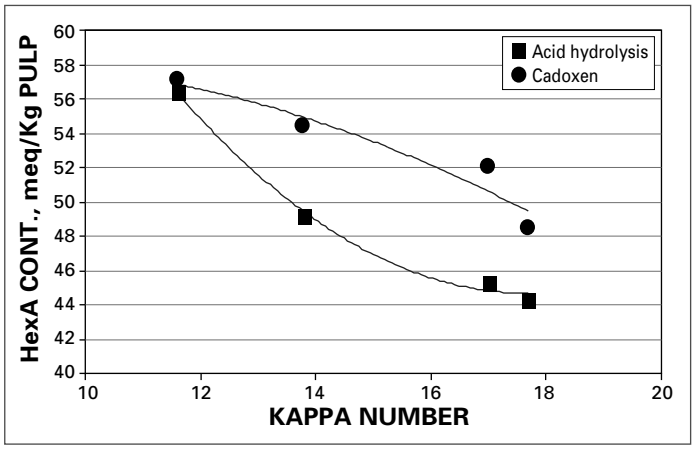
We produced pulps with kappa numbers in the 17.7-11.6 range by varying the pulping time between 145 and 210 min, while keeping the other pulping parameters at standard levels (Table I). In the kappa number range investigated, the HexA content determined by the acid hydrolysis method increases as delignification proceeds (**Fig. 2**). This tendency was confirmed by the cadoxen method. The lower HexA content obtained by the acid hydrolysis method, when compared to the cadoxen method, may be attributed to the incomplete HexA hydrolysis [10].

This HexA content profile, in apparent conflict with previous results published for softwoods [3-5], prompted us to investigate the HexA behavior from the early stages of the kraft pulping of *E. globulus*.

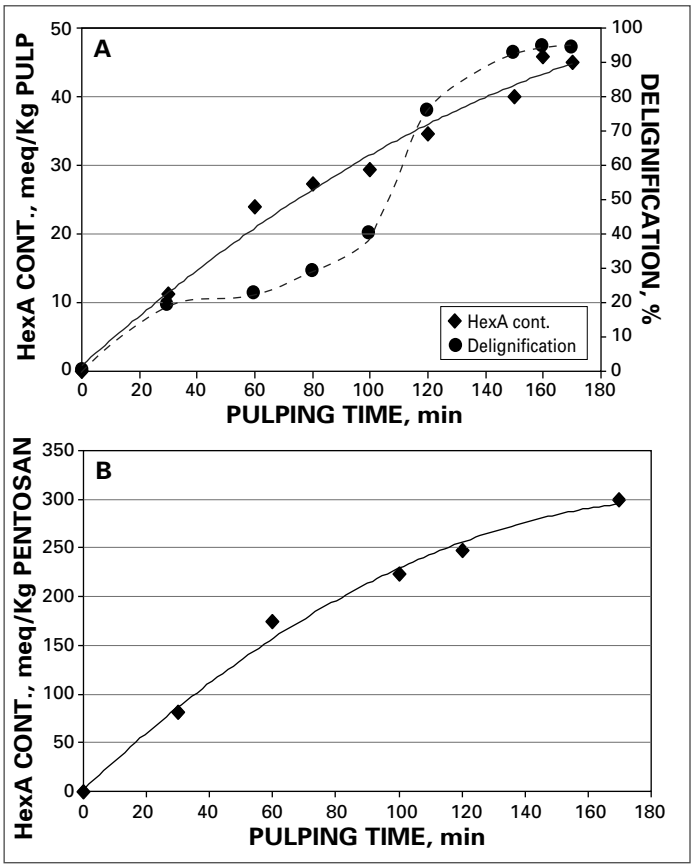
A series of pulps with different degrees of delignification was produced, representing the three kinetic phases of pulping: initial, bulk, and residual phases. The contents of HexA in partially delignified wood (samples from early stages of delignification) and pulps were determined by the acid hydrolysis method, involving the quantification of furan derivatives in the hydrolysate by UV analysis at 245 nm. In the case of the high lignin content samples, we expected that degraded residual lignin leached during the acidic treatment [13] may contribute to the absorption at 245 nm and to the measured HexA content. Even taking into account the interference of degraded lignin in HexA analysis, our results clearly show that the content of HexA in pulp increases with pulping time, until delignification reaches 95% (**Fig. 3A**). When the HexA content was expressed on a pulp pentosan content basis (meq/kg pentosan) (**Fig. 3B**), the same general behavior was observed, showing a clear enrichment of HexA moieties in the xylan remaining in the pulp. Hence, such results confirm that the kinetic pattern of HexA formation/degradation in *E. globulus* is significantly different from that of softwoods. The rate of HexA formation



1. ^{1}H NMR spectra of xylans from Eucalyptus globulus and spruce woods submitted to chemical treatment simulating kraft cooking conditions. A: initial Eucalyptus globulus xylan; B: Eucalyptus globulus xylan submitted to alkaline treatment (160ºC, 20 min); C: initial spruce xylan; D: spruce xylan submitted to alkaline treatment (160°C, 20 min). 1: H-1 of internal Xyl; 2: H-1 of MeGlcA; 3: H-1 of MeGlcA in Gal-MeGlcA moieties; 4: H-1 of HexA; 5: H-1 in Ara.



2. Influence of kappa number on the HexA content of Eucalyptus globulus kraft pulps (see Table 1 for pulping conditions).

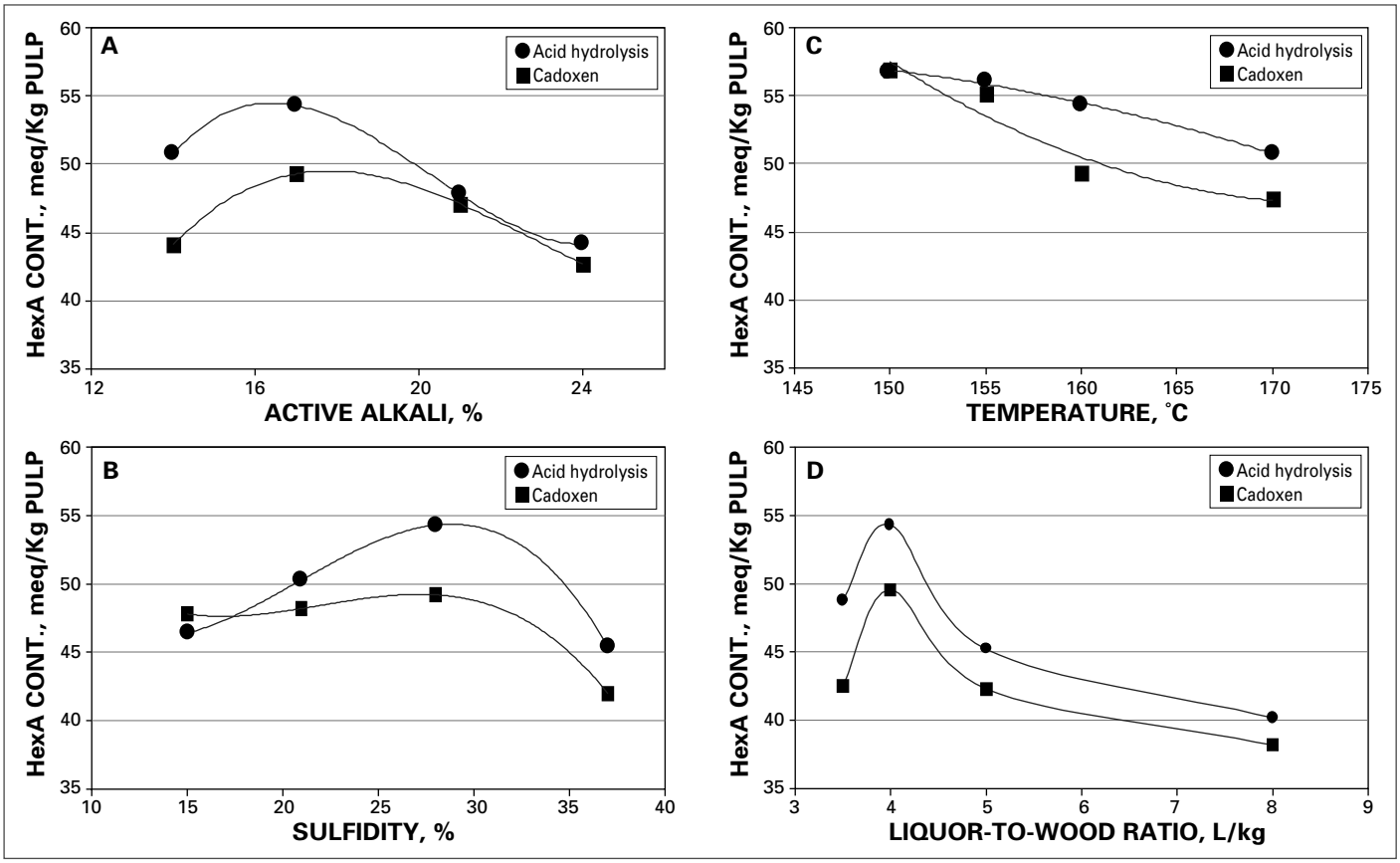


3. Effect of pulping time on the degree of delignification and HexA content of Eucalyptus globulus kraft pulps reported as meq/kg of pulp (A) and as meq/kg of pentosan in pulp (B) (active alkali: 15%, sulfidity: 28%, temperature: 160° C, time-to-temperature: 120 min, liquor-to-wood-ratio: 4)

should be higher than the rate of degradation, until the residual phase is reached.

Aiming to understand such different behavior, we investigated the influence of structural differences between xylans from *E. globulus* and from softwoods in the formation and degradation of HexA in alkaline media. Recently, we have shown that glucuronoxylan from *E. globulus* has a peculiar structure. It is a (2-*O*-α-D-galactopyranosyl-4-*O*-methyl-α-D-glucurono)-D-xylan with a xylan backbone branched at *O*-2 with short side chains composed by terminal 4-*O*-methyl-α-D-glucuronic acid (MeGlcA) (ca. 2/3) and 4-*O*-methyl-α-D-glucuronic acid substituted at *O*-2 with α-galactose (Gal-MeGlcA) (ca. 1/3) [12].

The xylans extracted from *E. globulus* (galactoglucuronoxylan) and spruce (arabinoglucuronoxylan) woods were submitted to a chemical treatment simulating kraft pulping conditions and then analyzed by ^{1}H NMR (Fig. 1, Table II). Although a significant part of the xylan (30%-80%) is dissolved (depending on the extent of treatment) and cannot be recovered by precipitation, some conclusions may be drawn from this study (Table II). During the initial heating period (100ºC, 75 min after the heating started), no HexA was detected in both recovered xylans. However, when the temperature reaches 160ºC, about 40% of the uronic acids in the recovered spruce xylan are converted to HexA. In the case of eucalypt, HexA represents about 35% of total uronic acids. MeGlcA and Gal-MeGlcA are converted into HexA in similar proportions. Surprisingly, when the treatment is prolonged by 20 min at 160ºC, all the glucuronic acid moieties (as MeGlcA or as Gal-MeGlcA) in the insoluble *E. globulus* xylan are converted into HexA, while in the case of spruce xylan, 35% of uronic acids still remain as MeGlcA. Since HexA in softwoods form quickly in the early stages of delignification and are



4. Influence of pulping parameters on the HexA content of Eucalyptus globulus kraft pulps at constant kappa number of 14±0.3 (see Table 1 for pulping conditions).

degraded as delignification proceeds, while in *E. globulus*, HexA content increases during pulping, it could be expected that spruce xylan MeGlcA is more readily converted into HexA than the corresponding counterparts in *E. globulus* xylan.

Against our expectations, MeGlcA in spruce xylan seems to be more resistant to the alkaline β-elimination of methanol leading to the formation of HexA, than glucuronic acid in *E. globulus* xylan. At the end of the treatment (160ºC, 20 min), both xylans have the same level of HexA, but spruce xylan, unlike *E. globulus* xylan, still has some MeGlcA that can be potentially converted into HexA. This suggests that the differences observed in the HexA formation/degradation profile during *E. globulus* and softwood kraft pulping cannot be attributed due to differences in the chemical structure of corresponding xylans. It may be tentatively attributed to the milder conditions (effective alkali and temperature) used in *E. globulus* pulping. The rate of formation/degradation of HexA was shown to depend essentially on OH^- and HS^- concentration [3]. The lower effective alkali in pulping liquors of hardwoods, when compared to softwoods, may explain the predominance of HexA formation over degradation as pulping progresses. Additionally, the contribution of topochemical specificities (accessibility of lignin and polysaccharides by pulping chemicals in cell walls) of hardwoods and softwoods cannot be excluded. Both propositions need further investigation.

Almost simultaneously with our work, Chai et al. [14] have reported results for HexA formation/degradation profiles in the kraft pulping of different hardwoods, similar to what we found for *E. globulus*.

Variation of HexA contents with pulping parameters

In order to investigate the influence of pulping parameters on HexA contents of kraft pulps, four series of pulps were produced by varying separately the active alkali (AA), sulfidity (S), temperature, and liquor-to-wood ratio (L/W), keeping the other parameters constant at standard levels (Table I). In each case, we adjusted the pulping time to obtain a constant kappa number of 14±0.3.

Our investigation looked at the influence of active alkali (AA) in HexA content of pulp in the range of 14%-24%. Previous studies with softwood kraft pulps [5] showed that higher alkali concentration in the pulping liquor, at constant kappa number, resulted in a lower amount of HexA in pulp. With *E. globulus*, this behavior is only partially observed (**Fig. 4A**). The HexA content of pulps increases when AA goes from 14% to 17%. For AA higher than 17%, the HexA content decreases. This result suggests that, probably, in the last stages of pulping, for AA between 14% and 17%, the rate of HexA formation is still higher than degradation, while for higher AA, HexA degradation or dissolution dominates over formation. Pentosan analysis (Table I) shows that the content of xylans in pulps decreases as AA increases, thus explaining, partially at least, the decrease of HexA content in pulps obtained with high AA. However, we cannot exclude the possible contribution of the lower pulping time when high AA is used (at 24% AA, 52 min less than at 14% AA) to the

decrease in HexA content (HexA content increases with time, see discussion above).

A series of kraft pulps were produced with sulfidities of 15% to 37%. The HexA content of pulps rose slightly with sulfidity in the range of 15%-28%, then decreased significantly at a sulfidity of 37% (**Figure 4B**). We tentatively attribute this complex behavior to the simultaneous variation of OH^- and HS^- concentrations and pulping time. The degradation of HexA is highly determined by OH^-, rather than by HS^- concentration [3]. For this set of pulps, the absolute OH^- concentration decreases as sulfidity rises (constant active alkali) while pulping time decreases. So, for lower sulfidity (15%-28%), the slight increase in HexA content is probably attributable to the reduction in HexA degradation (due to the decrease in OH^- concentration). For high sulfidity, the observed decrease in pulping time (at 37% S, 20 min less than with 15% S) may be the determinant in the lower HexA content. This is supported by the higher xylan content of pulp obtained with 37% S, as shown by a pentosan content 2% (based o.d. pulp) higher than that of other pulps from this series (Table I), suggesting a lower degree of conversion of MeGlcA (or GalMeGlcA) into HexA.

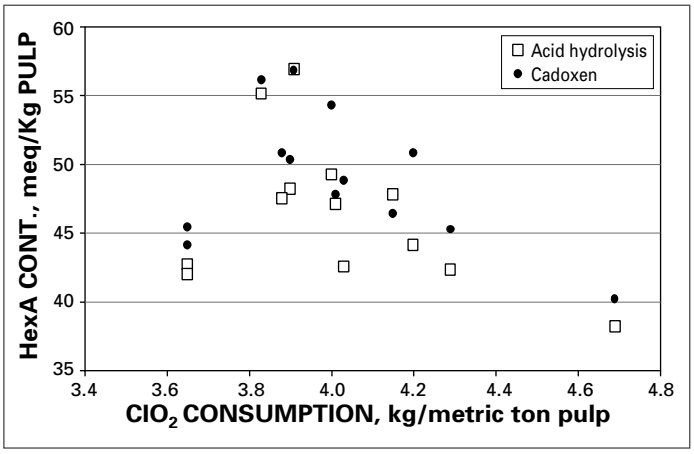
The pulping temperature was previously shown to increase the rate of degradation of HexA [3] in softwood kraft pulps. To investigate the effect of temperature on HexA contents of *E. globulus* kraft pulps, we produced a series of four pulps by varying the pulping temperature in the range 150ºC -170ºC. The content of HexA decreases as pulping temperature is increased (**Fig. 4C**), probably due to an increase of the extent of alkaline degradation reactions over HexA formation and due to xylan dissolution, as shown by the lower pentosan content of pulps (Table I). However, again, the contribution of the reduced pulping time (Table I) (lower HexA formation) to the lower content of HexA in pulps produced at higher temperature cannot be excluded.

Figure 4D shows the profile of HexA content of pulps obtained with different liquor-to-wood ratios (L/W). HexA content increases from L/W 3.5 to L/W 4.0 and then, a decrease is observed for higher L/W. We varied L/W and kept AA constant (expressed on a wood basis), so that OH^- and HS^- concentration is diminished in the pulping solution as L/W rises. Thus, the observed complex variation of HexA with L/W should be essentially determined by OH^- concentration. Because the rate of HexA is primarily determined by OH^- concentration, the significant decrease of HexA content is certainly attributable to the lower alkali in the pulping liquor, particularly for L/W higher than 4.

The HexA profiles determined by the acid hydrolysis and cadoxen methods, are quite similar, reinforcing the validity of data obtained.

Influence of HexA contents on the ECF bleachability of pulps

The pulps produced by variation of pulping parameters (active alkali, sulfidity, temperature, and liquor-to-wood ratio, Table I), having kappa number 14±0.3 and HexA content in the range 38-57 meq/kg (determined by the acid hydrolysis method) were submitted to a $D_0E_1D_1E_2D_2$ bleaching sequence. The ClO_2 consumed to fully bleach the pulps (90.5% brightness) varied between 3.6 and 4.7 kg/metric ton of pulp, showing that the different pulping parameters investigated strongly affect the bleachability of the pulp.



5. Relationship between HexA content of unbleached pulp and the amount of ClO_2 required to reach 90.5 % brightness in DEDED bleaching sequence, for the series of pulps with kappa number 14±0.3.

When the HexA content is plotted against the ClO_2 consumption (**Fig. 5**), apparently we see no correlation between bleachability and HexA content of unbleached pulp. That changes if we do not consider in this analysis the two points on the left lower corner of the figure, corresponding to unbleached pulps obtained with extreme conditions of active alkali (AA: 24%, S: 28%, T: 160ºC, L/W: 4) or sulfidity (AA: 17%, S: 37%, T: 160ºC, L/W: 4). Then we see a general trend to increase the chlorine dioxide consumption to fully bleach the pulp as the HexA content decreases. Because residual lignin and HexA affect kappa number, such behavior suggests that, at a constant kappa number, the unbleached pulp becomes harder to bleach as the "residual lignin content/HexA content" ratio increases. However, since that behavior is not observed for the full range of kraft pulping conditions used, such generalizations are tentative.

CONCLUSIONS

The content of HexA in *E. globulus* kraft pulps increased along the kraft pulping process, even in the residual delignification phase. This behavior, when compared to softwoods, is probably attributable to the milder conditions used in the pulping and/or to topochemical effects, rather than to differences in the chemical structures of glucuronoxylans. Active alkali, sulfidity, temperature, and liquor-to-wood ratio strongly affect the content of HexA in pulp. The interpretation of the dependency of HexA content on pulping parameters is complex and should take into account formation and degradation of HexA and dissolution of xylan. The pulps obtained by changing pulping conditions (constant kappa number) showed different bleaching responses in a DEDED bleaching sequence. A general increase in bleachability occurred as the HexA content of the unbleached pulp decreased. **TJ**

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