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Cellulose protection during ozone treatments of oxygen delignified *Eucalyptus* kraft pulp

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Abstract

Various totally chlorine-free sequences with a Z stage (XOZP, XOAZP, XOZRP, and XOAZRP) were implemented with a view to examining the individual and combined effects of using an additive (A), consisting of oxalic acid and a post-treatment (R) based on sodium borohydride on the properties of the resulting pulp and effluents. The performance of the reagents was analyzed through the study of: chain scission number in the cellulose chain; selectivity and efficiency of the process; crystallinity and carbohydrates composition of the pulps. Finally, the pulp, paper and effluents properties of the sequence including both treatments (XOAZRP) were compared with an ECF sequence of the XODPD type. The results were highly favorable.

Keywords: Kraft pulp; *Eucalyptus*; Bleaching; Totally chlorine-free; Ozone; Oxalic acid; Sodium borohydride; Chain scission number; Selectivity; Efficiency; Cristallinity; X-ray diffraction; Carbohydrates; High-performance liquid chromatograph; Effluents; Paper properties

1. Introduction

The appearance in recent years of new laws regulating processes generating pollution is the result a new social awareness of ecology and the environment. This trend to ecology, with the support of new laws, is bringing pressure to bear on industry and obliging it to make changes, adaptations and/or improvements to its processes in order to attain procedures that are more environmentally friendly, i.e. that have a lower environmental impact.

In connection with innovation in the paper industry, it is at pulp bleaching plants that the greatest changes have taken place, since this is the portion of the pulp and paper manufacturing process that generates the greatest degree of pollution.

The advent of totally chlorine-free (TCF) sequences has confronted scientists with new problems that have raised the need to examine and optimize the new, resulting bleaching stages. Avoiding the use of chlorine and its derivatives in order to obtain TCF pulp entails using alternative bleaching agents such as oxygen or hydrogen peroxide. However, a combination of these two agents has proved inadequate to match the efficiency of chlorination. The incorporation of an ozone-based stage (Z) appears to be a good choice for circumventing this shortcoming, as ozone possesses a high oxidation potential.

Bleaching sequences including an ozonation stage usually lead to a phenomenon that negatively influences the selectivity of the process. This work examines the individual and combined effects of the use of an oxalic acid additive (Roncero, Colom, & Vidal, 2000) and a post-treatment based on sodium borohydride (Roncero, Colom, & Vidal, 2002) on the properties of the resulting pulp and effluents. The performance of the reagents was analyzed through the study of: chain scission (CS) number in the cellulose chain; selectivity and efficiency of the process; crystallinity and carbohydrates composition of the pulps.

Once the TCF sequence was optimized in terms of pulp properties, it was refined in order to ensure the best possible physical and mechanical properties in the paper sheets obtained from them. Thus, the final sequence, XOAZRP, was completed by using a PFI mill at 3000 and 4500 rpm to examine the physical properties of paper. The results were compared with those provided by a conventional ECF sequence of the XODPD type.

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Table 1
Bleaching stage conditions (X, O, A, Z, R, and P) of the sequences: XOZP, XOAZP, XOZRP, and XOAZRP

Stage	X	O	A	Z	R	P
Temperature (°C)	60	110	Amb.	Amb.	Amb.	85
Time (min)	120	60	10	–	60	180
Consistency (% o.d.p.)	10	10	10	40	10	10
Xylanase doses (EXU/kg)	500	–	–	–	–	–
Pressure O_2 (MPa)	–	0.6	–	–	–	–
O_3 inlet concentration (mg/l)	–	–	–	35	–	–
Flow O_3/O_2 (LN/h)	–	–	–	150	–	–
O_3 consumed (% o.d.p.)	–	–	–	0.4	–	–
$NaBH_4$ charge (% o.d.p.)	–	–	–	–	0.5	–
Na_2CO_3 charge (% o.d.p.)	–	–	–	–	1	–
H_2O_2 charge (% o.d.p.)	–	–	–	–	–	2
NaOH charge (% o.d.p.)	–	1.5	–	–	–	1.8
$MgSO_4{\cdot}7H_2O$ charge (% o.d.p.)	–	0.5	–	–	–	0.2
Initial pH	7–8	–	–	2.3	–	–

o.d.p.: oven dry pulp.

2. Material and methods

2.1. Raw material

The unbleached material used in this section is an *Eucalyptus globulus* kraft pulp from an industrial source. The characteristics of this pulp, as measured in the laboratory, are the following: kappa number, 12.5; brightness, 35.3% ISO; viscosity, 1062 ml/g.

2.2. Bleaching sequences

The TCF bleaching sequences studied are XOZP, XOAZP, XOZRP, and XOAZRP, where: X, enzymatic pre-treatment with xylanases; O, oxygen delignification; A, additive with oxalic acid; Z, ozone bleaching; R, reductive treatment with sodium borohydride; P, hydrogen peroxide bleaching. The conditions of the different bleaching stages are shown in Table 1. The equipment and methods used for the different bleaching stages were published earlier (Roncero et al., 2000, 2002).

2.3. Characterization of pulps and effluents

The pulp was characterized in terms of its kappa number, brightness and viscosity ISO standards 302, 5351/1, and 3688, respectively. These properties were determined following each bleaching stage in order to follow the course of the process and elucidate the effects of the additive and post-treatment.

The selectivity of the sequence as regards the decrease in kappa number (IK) and the increase in brightness (Bl) relative to XO pulp was calculated from the following equations:

$$\text{Selectivity}_{\text{IK}}(\text{Slc}_{\text{IK}}) = \frac{\text{IK}_{\text{O}} - \text{IK}_{\text{P}}}{\text{Vis}_{\text{O}} - \text{Vis}_{\text{P}}} 100 \quad (1)$$

$$\text{Selectivity}_{\text{Bl}}(\text{Slc}_{\text{Bl}}) = \frac{\text{Bl}_{\text{P}} - \text{Bl}_{\text{O}}}{\text{Vis}_{\text{O}} - \text{Vis}_{\text{P}}} 100. \quad (2)$$

Also, the efficiency of the last P stage relative to the brightness gain was calculated from:

$$\text{Efficiency}_{\text{Bl}}(\text{Efc}_{\text{Bl}}) = \frac{\text{Bl}_{\text{P}} - \text{Bl}_{\text{O}}}{\text{peroxide consumption}}. \quad (3)$$

In Eqs. (1)–(3), 'Vis' denotes viscosity and subscripts 'O' and 'P' the values obtained following oxygen delignification and bleaching with hydrogen peroxide, respectively.

After each bleaching stage, effluents were characterized in terms of chemical oxygen demand (COD) and color, which were determined according to ASTM D1252-95 and D1209-79, respectively.

2.4. Refining and physical properties of the paper

The XOAZRP pulp obtained was refined by using a PFI mill at 3000 and 4500 rpm as per ISO 5264-2. The drainage resistance of the pulp was measured by using the Schopper Riegler method (ISO 5267-1), its water retention value (WRV) according to TAPPI UM 256 and Merkblatt IV/33/57 and its fiber length by using a Kajaani apparatus (TAPPI T 271pm-91). Refined and unrefined pulp was used to obtain 10 paper sheets that were subjected to the following determinations: basis weight (ISO 536); thickness and bulk (ISO 534); and physical properties including Bendtsen permeability (ISO 5636/3), tensile strength (ISO 1924-1), folding endurance (ISO 5626), tear index (ISO 1974) and burst index (ISO 2758). The results were subjected to the Grubbs test (Grubbs & Beck, 1972) in order to discard outliers.

2.5. Determination of carbohydrates

For determination of carbohydrates, the pulp was hydrolyzed after being subjected to extraction in an

Table 2
Pulp properties after bleaching stages of the TCF sequences (XOZP, XOAZP, XOZRP, and XOAZRP)

	Kappa number	Brightness (% ISO)	Viscosity (ml/g)	CS	Residual peroxide (% o.d.p.)	Slc_{IK}	Slc_{BI}	Efc_{BI}
Initial	12.5	35.3	1062					
X	11.2	36	1066					
XO	7.1	53.9	956					
XOZ	3.8	66.3	688					
XOZP	2.2	83.5	568	0.78	0	1.3	7.6	14.8
XOAZ	4.3	72.4	768					
XOAZP	0.8	87.4	636	0.57	0.61	2.0	10.5	24.1
XOZR	3.3	70.3	778					
XOZRP	2.1	84.7	674	0.47	0	1.8	10.9	15.4
XOAZR	1.3	77.4	865					
XOAZRP	0.7	90	807	0.21	0.99	4.3	24.2	35.7

alcohol–benzene mixture (1:2) to eliminate the extractives present in the pulp (UNE standard 57035-74). Measurement of the sugars present in the hydrolyzed samples (Vidal & Colom, 1984) was carried out with a high-performance liquid chromatograph (HPLC) fitted with a refractive index detector. Nomenclature used: XYL, xylose; GLC, glucose.

2.6. Determination of crystallinity by X-ray diffraction method

The samples to be analyzed were used to prepare laboratory sheets in accordance with ISO standard 5269-2, aiming to make the sheets as homogeneous as possible (Browning, 1967).

A SIEMENS D-500 BRAG-BRENTANO $\theta/2\theta$ geometry X-ray diffractometer was used. Cu Kα radiation ($\lambda = 1.5418$ Å) at 40 kV and 30 mA. Graphite secondary monochromator. Divergence aperture of 0.3° and reception aperture of 0.05°. Sweeps of 5° to 5° 2θ were made with a step size of 0.05° and step time measurement of 10 s.

Various methods and approaches for determining the percentage of crystallinity of the sample on the basis of the diffractograms obtained have been proposed in the literature consulted. A simple approach used by many authors (Bailey, Honold, & Skau, 1958; Browning, 1967; Buschle-Diller, & Zeronian, 1992, 1994; Roberts, 1991; Segal, Creely, Martin, & Conrad, 1959) consists of taking from the diffractogram a suitable maximum and a minimum intensity to give a 'crystallinity value' (CrI), defined as

$$\mathrm{CrI} = \left[\frac{I_{002} - I_{\mathrm{am}}}{I_{002}}\right]100 = \left[1 - \frac{I_{\mathrm{am}}}{I_{002}}\right]100 \quad (4)$$

where I_{002} is the intensity of the crystalline peak at the maximum at 2θ between 22 and 23° for cellulose I (between 18 and 22° for cellulose II) and I_{am} is the intensity at the minimum at 2θ between 18 and 19° for cellulose I (between 13 and 15° for cellulose II).

3. Results and discussion

3.1. Comparison of the results provided by the four TCF sequences. Effects of the additive and post-treatment

Unbleached pulp was initially subjected to the enzyme treatment (X), which was followed by oxygen delignification.

Table 3
Effluents properties (DQO and color) of the four TCF sequences studied (XOZP, XOAZP, XOZRP, and XOAZRP) and the ECF sequence XODPD

		TCF					ECF (XODPD)
		XOAZRP	XOZRP	XOAZP	XOZP		
COD (kg O_2/t pulp)	X	41.5	41.5	41.5	41.5	X	50.9
	O	33.2	33.2	33.2	33.2	O	48.6
	A	3.6		3.6		D	4.6
	R	13.3	12.1			P	9.8
	P	1.1	1.4	1.6	5.6	D	3.8
	Total	92.7	88.2	79.9	80.3	Total	117.8
Color (kg Pt/t pulp)	X	21.8	21.8	21.8	21.8	X	58.5
	O	19.8	19.8	19.8	19.8	O	38.3
	A	0.3		0.3		D	2.3
	R	1.4	0.4			P	0.3
	P	0	0.2	0.15	0.2	D	0.7
	Total	43.3	42.2	42.1	41.9	Total	100.2

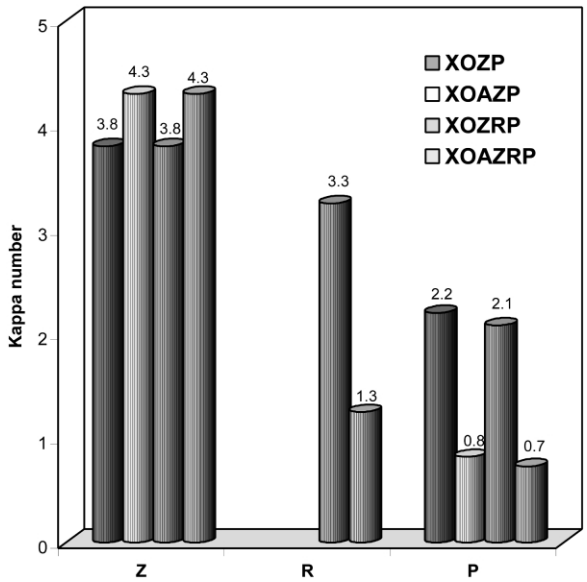

Fig. 1. Kappa number, after Z, R, and P stages, of the XOZP, XOAZP, XOZRP, and XOAZRP sequences.

The resulting XO pulp possessed a kappa number of 7.1; 53.9% ISO brightness and a viscosity of 956 ml/g. XO pulp was subjected to the different bleaching stages in order to implement the four TCF sequences studied, namely: XOZP, XOAZP, XOZRP, and XOAZRP. Following each bleaching stage, the kappa number, brightness and viscosity of the pulp, were measured, as was the amount of residual peroxide after P stage. The results are shown in Table 2. A waste liquor sample was collected at the end of each bleaching stage to determine COD and color in the effluent (Table 3). As can be seen from Table 3, the XOAZRP sequence provided pulp of 90% ISO brightness and 800 ml/g viscosity.

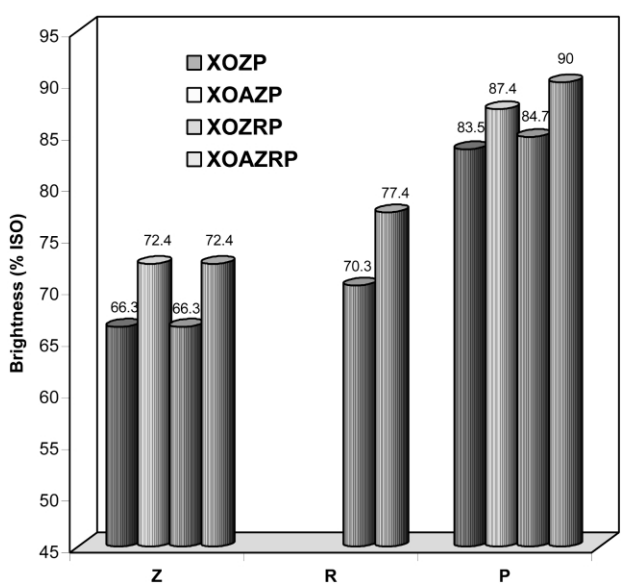

Fig. 2. Brightness, after Z, R, and P stages, of the XOZP, XOAZP, XOZRP, and XOAZRP sequences.

3.1.1. Kappa number

The kappa number exhibited a special behavior typical of sequences using an additive (XOAZ: 4.3) (Fig. 1). In fact, it exceeded that of the control sequence (XOZ: 3.8) after Z stage but was nearly 1.5 units lower than it at the end of P stage (XOZP: 2.2; XOAZP: 0.8; XOAZRP: 0.7). The oxalic acid improves delignification; the effect, however, was only observed after a subsequent alkaline stage (R or P). This might be the result of lignin being selectively oxidized and fragmented and, also, decolorized during Z stage; however, because such a stage was conducted under acid conditions, only part of degraded lignin was dissolved.

The borohydride post-treatment, which allowed the XOZP–XOZRP and XOAZP–XOAZRP sequence pairs to be compared, did not increase delignification, which is logical as it was intended to reduce carbonyl groups in order to maintain pulp viscosity during bleaching with hydrogen peroxide.

3.1.2. Brightness

As can be seen by comparing the results of the XOZP (83.5% ISO) and XOAZP (87.4% ISO) sequences, the use of the additive increased pulp brightness by almost 4 units (see Fig. 2). Therefore, oxalic acid is more effective in decolorizing lignin and removing chromophores from the pulp.

A comparison of the results for the XOZP (83.5% ISO) and XOZRP (84.7% ISO) sequences reveals the borohydride post-treatment to increase brightness by 1.2 units, as the likely result of the reduction of carbonyl groups to hydroxyl groups. Kraft pulp possesses a dark brown color by virtue of the chromophores formed in carbohydrates and, especially, lignin, during cooking. The structure of these chromophores is not accurately known; in any case, pulp color is assumed to arise primarily from the presence of conjugate bonds with aromatic rings and quinones. The chromophores present in lignin are largely carbonyl, ethylene and aromatic groups (Dence & Reeve, 1996; McGrouther, Pasco, & Suckling, 1995). Consequently, in reducing carbonyl groups to alcohol groups, R stage removes part of the chromophores that give pulp its color.

A comparison of the results obtained with the control sequence (XOZP: 83.5% ISO) and that involving both the additive and the post-treatment (XOAZRP: 90% ISO) reveals an increase in brightness by 6.5 units, more than their combined individual effects (i.e. 5.2 units). This suggests the presence of a synergistic effect or that the additive results in the formation of an increased number of carbonyl groups that are subsequently reduced during R stage (thereby increasing brightness).

3.1.3. Viscosity

As can be seen from Table 2, both the additive (A) and the post-treatment (R) resulted in increased viscosity, which rose from 568 ml/g with the control sequence (XOZP) to 807 ml/g with the combined used of both treatments (the

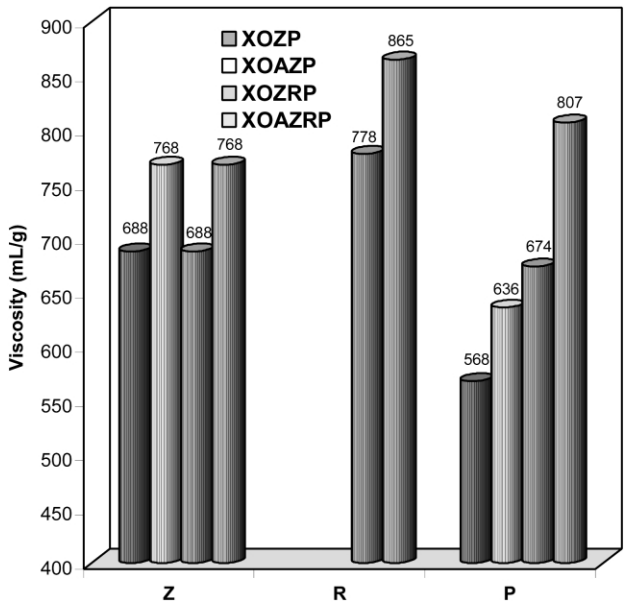

Fig. 3. Viscosity, after Z, R, and P stages, of the XOZP, XOAZP, XOZRP, and XOAZRP sequences.

XOAZRP sequence). The use of oxalic acid (XOAZP) maintained the viscosity above the level achieved with the control sequence (636 versus 568 ml/g), which confirms the protective effect of the additive. However, it is also important to perform the reducing treatment in order to reduce carbonyl groups, which make cellulose sensitive to a subsequent alkaline treatment.

As can be seen from Fig. 3, the viscosity increase obtained from R stage in the sequence excluding the additive (XOZP–XOZRP, 106 ml/g), was smaller than that provided by the sequence including it (XOAZP–XOAZRP, 171 ml/g). Again, this may be the result of a synergistic effect between both treatments or of an increasing amount of carbonyl groups being reduced. This can possibly be

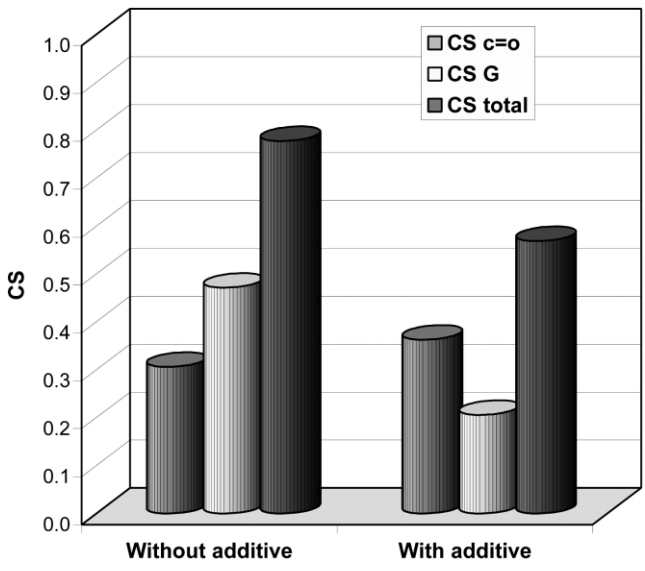

Fig. 4. $CS_{C=O}$, CS_G and CS_{total} of the sequences with and without additive.

explained in terms of the average CS number in the cellulose chain, defined mathematically as (Bouchard, Morelli, & Berry, 2000; Lindholm, 1990)

$$CS = \frac{DP_O - DP}{DP} \quad (5)$$

where DP_O is the degree of polymerization of the sample following oxygen delignification (XO pulp) and DP that at the end of the last stage using hydrogen peroxide. The CS values obtained are shown in Table 2.

The following equations are proposed

$$CS_{without\ R} = CS_G + CS_{C=O} \quad (6)$$

$$CS_{with\ R} = CS_G \quad (7)$$

where $CS_{wihout\ R}$ and $CS_{with\ R}$ are the numbers of cellulose chain scissions in the sequences excluding (XOZP and XOAZP) and including R stage (XOZRP and XOAZRP), respectively; CS_G is the combined CS number in the cellulose chain by direct attack of ozone, by-products and radicals during Z and P stages; and $CS_{C=O}$ is the CS number in the cellulose chain in the β-elimination reaction taking place around carbonyl groups (Fuhrmann, Li, & Rautonen, 1997; Godsay & Pearce, 1984; Hartler, Grandlund, Sundin, & Tubek-Lindblom, 1991) (Fig. 4).

Eq. (7) yields CS_G; also, the difference between Eqs. (6) and (7) gives CS number by effect of the presence of carbonyl groups ($CS_{C=O}$) in the sequences with and without additives:

$$CS_{C=O} = CS_{without\ R} - CS_{with\ R}. \quad (8)$$

The overall cellulose CS number is the combination of CS_G and $CS_{C=O}$. As can be seen from Fig. 4, the use of oxalic acid as additive substantially decreases the number of CS resulting from the direct attack of ozone, by-products and radicals formed during stages Z and P (CS_G); this is consistent with previous results of Bouchard et al. (2000). The decreased degradation of cellulose can be ascribed to its accessibility being reduced through decreased swelling in the presence of oxalic acid. In fact, some authors (Kamishima, Fujii, & Akamatsu, 1984; Mbachu & Manley, 1981; Ruiz, Freer, Rodríguez, & Baeza, 1997) claim that cellulose swelling is diminished by the presence of organic acids. Less strongly swollen cellulose may hinder access of ozone and radicals, and hence be degraded to a lesser extent. However, $CS_{C=O}$ (the number of cellulose CS due to the presence of carbonyl groups) was found to increase during Z stage (i.e. the number of carbonyl groups formed during such a stage was greater), which is consistent with the more marked increase in brightness obtained by combining the additive and the post-treatment). Chirat and Lachenal (1995) found the formation of carbonyl groups in the cellulose chain to be the sole result of a direct reaction with ozone. According to Dence and Reeve (1996), carbonyl groups are formed mainly by direct reaction with ozone some, however, can form from hydroxyl radicals. This suggests that, in the presence of oxalic acid, ozone might be

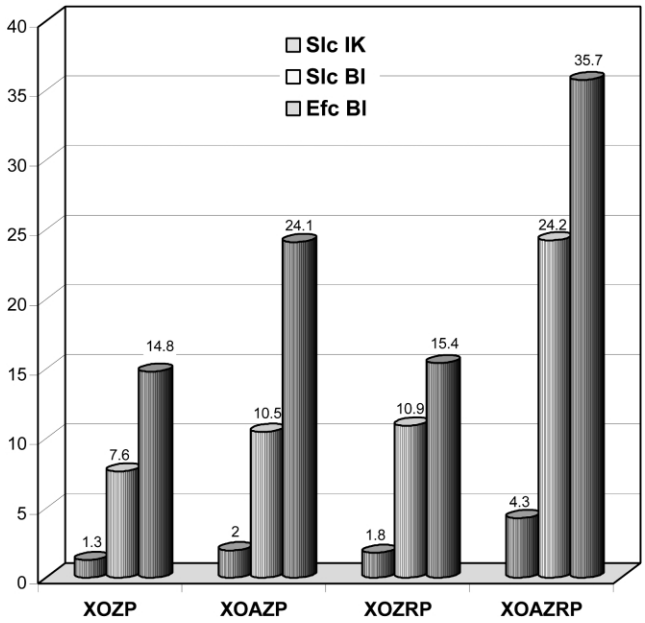

Fig. 5. Efficiency of the P stage and selectivity of the sequences: XOZP, XOAZP, XOZRP, and XOAZRP.

more readily dissolved and hence decomposes to a lesser extent, thereby producing fewer radicals and leading to decreased cellulose degradation. However, an increased amount of molecular ozone would result in more carbonyl groups being formed in cellulose. Even so, the increase in the amount of carbonyl groups was very small, so the possibility of decreased swelling (and of decreased accessibility as a result) is as plausible as a decreased decomposition of ozone into highly oxidizing radicals.

3.1.4. Residual peroxide

The amount of peroxide remaining after P stage was found to be zero (Table 2) in the absence of additive and nearly 1% in the XOAZRP sequence (i.e. only 50% of the initial amount was consumed). The use of oxalic acid saved reagent (either in P stage or Z), thereby decreasing the cost of the bleaching sequence.

3.1.5. Selectivity and efficiency

Fig. 5 shows the selectivity of the studied sequences towards the kappa number and brightness (Eqs. (1) and (2)) and the efficiency of P stage in terms of brightness (Eq. (3)). The selectivity towards both parameters relative to the control sequence (XOZP) was increased by the use of the additive (XOAZP) and post-treatment (XOZRP); their effect was very similar. The increase was more pronounced when both treatments are used (with the XOAZRP sequence); in fact, the process becomes more selective with the addition of oxalic acid in Z stage and of sodium borohydride following it.

The efficiency also increased markedly (63%) upon addition of the additive and, especially, in combination with the post-treatment (141%); however, the post-treatment appears to exert no appreciable effect by itself (the difference with the control sequence was only 4%). The increased efficiency resulted in increased brightness with the same amount of hydrogen peroxide. Again, both treatments have favorable effects.

In conclusion, the use of oxalic acid as additive and sodium borohydride as post-treatment significantly improves all pulp properties. Consequently, the XOAZRP sequence is the most selective and also that yielding the best pulp.

3.1.6. Properties of the effluents: COD and color

Table 3 shows the COD and color values for the effluents as measured after each bleaching stage of the TCF sequences studied and compared with an ECF sequence. The highest COD was obtained with the sequence using both the additive and the post-treatment (XOAZRP) and exceeded that for the control sequence (XOZP) by 15%. The contribution of the additive to this COD increase in the XOAZRP and XOAZP sequence was in the region of 3.9 and 4.5%, respectively; that of the post-treatment was 14.4 and 13.7% in the XOAZRP and XOZRP sequence, respectively. The increased COD obtained in the XOAZRP sequence was thus largely the result of the sodium borohydride treatment.

Regarding color, cumulative final values were all very similar; however, the highest ones were again observed in the XOAZRP sequence as the likely result of the increased lignin removal efficiency and brightness. The contribution of the additive to the overall effect was very small and similar for the XOAZRP and XOAZP sequences (ca. 0.6%): on the other hand, the post-treatment contributed 3.2% in the XOAZRP sequence and only 0.9% in the XOZRP sequence.

The post-treatment thus increases COD, whether or not the additive is present; this suggests more efficient removal of organic matter. In the sequence using the additive (XOAZRP), organic matter contributes to the effluent color much more substantially than in that not using it (XOZRP). This suggests that, in the former sequence, the post-treatment removes lignin (as confirmed by the decrease in kappa number observed in R stage of the XOAZRP sequence). This is not the case in the absence of additive as no significant decrease in kappa number is observed; it is carbohydrates that are potentially removed under these conditions.

The increased COD of the XOAZRP sequence can be diminished by recycling the effluent from the enzyme pre-treatment and the oxygen delignification (the two stages most strongly contributing to COD discharge) to the brownstock washing and recovery boiler; this, however, may require substantial investments (Grace & Malcolm, 1969; Siles, Torres, Colom, & Vidal, 1996).

Table 4
Physical properties, of the TCF (XOAZRP) and ECF (XODPD) sequences

	Rev.	°SR	Energy (W h)	WRV (%)	Basis weight (g/m^2)	Thickness (μm)
XOAZRP	0	14	–	118	66.5	133
	3000	25	38	148	67.3	106.3
	4500	32	57	160	66.7	103.7
XODPD	0	15	–	117	63.1	126.9
	3000	23	40	148	63.5	98.7
	4500	30	61	154	63.4	95.1

	Bulk (cm^3/g)	Permeability (μm/Pa s)	Tensile index (N m/g)	Folding endurance
XOAZRP	2.00	57.5 ± 0.58	22.5 ± 2.0	0.94 ± 0.049
	1.58	20.8 ± 0.39	56.0 ± 3.3	3.01 ± 0.084
	1.55	10.8 ± 0.36	67.5 ± 3.7	3.39 ± 0.092
XODPD	2.01	60.2 ± 0.40	19.0 ± 0.3	0.81 ± 0.027
	1.56	31.4 ± 0.52	61.5 ± 3.3	2.95 ± 0.161
	1.50	19.0 ± 0.34	68.5 ± 2.7	3.21 ± 0.044

	Tear index (mN m^2/g)	Burst index (kN/g)
XOAZRP	7.15 ± 0.37	1.20 ± 0.076
	12.5 ± 0.46	4.05 ± 0.177
	12.2 ± 0.76	4.45 ± 0.193
XODPD	4.50 ± 0.51	0.90 ± 0.049
	13.1 ± 0.27	3.80 ± 0.137
	12.6 ± 0.52	4.35 ± 0.222

Confidence intervals with a confidence of 95%.

3.2. Refining and measurement of the physical properties of pulp produced by the XOAZRP sequence. Comparison with an ECF sequence of the XODPD type

It is interesting to examine not only the properties of pulp but also of paper made from it. One shortcoming of TCF pulp is that it seemingly cannot match the resistance properties of pulp obtained with conventional, ECF sequences (Sacon & Yang, 1993; Seisto, Poppius-Levin, & Fuhrmann, 1998; Sun, Nguyen, & Wallis, 1995; Van Lierop, Berry, & Roy, 1997; Yang, Sacon, Law, & Eriksson, 1993). We thus compared the physical properties of pulp obtained with a TCF sequence (XOAZRP) with those of pulp provided by an ECF sequence of the XODPD type. Both sequences were found to provide high values for the physical properties examined. Viscosity was 100 units higher with the XODPD sequence but brightness was 2 units higher with the XOAZRP sequence. Viscosity and the physical properties of pulp are closely related. In fact, ensuring good physical properties entails using a viscosity of at least 700 ml/g; also, the higher the viscosity is, the better usually are the physical properties of the resulting pulp (Chirat & Lachenal, 1993; Fuhrmann, Malinen, Rautonen, Áhusalo, & Sågfros, 1995; Lindholm, 1990; Patt, Hammann, & Kordsachia, 1991). We found a viscosity above 800 ml/g in all experiments.

Table 3 shows the values for the properties (COD and color) of the effluents from the TCF XOAZRP and ECF XODPD sequences. The ECF sequence exhibits higher COD and color values in the effluents. This, together with the fact that it discharges AOX, since it uses chlorine dioxide for bleaching, makes the ECF sequence more polluting than the TCF sequence studied.

Table 4 compares the values of the physical properties determined in the TCF and ECF sequences. As can be seen, the ECF sequence requires more energy to obtain the same revolutions or match the Schopper Riegler value (°SR) of the TCF sequence; consequently, TCF pulp is easier to refine and uses less energy than ECF pulp. This is consistent with previous results of some authors (Secrist & Singh, 1971; Soini, Jäkärä, Koljonen, & Gullichsen, 1998), who ascribed them to fiber surfaces being altered, and fiber swelling and fibrillation being favored, during ozone bleaching.

Unrefined TCF pulp exhibits greater values, of tear index and tensile strength, which according to Lindholm (1990) means that ozone modified the bleached fiber surfaces possess an increased binding capacity. As both types of pulp are refined, their indices tend to coincide those for ECF pulp is slightly higher, consistent with the results of Sun et al. (1995).

The burst index increases with increasing refining; it is slightly higher for TCF pulp but the difference decreases as the pulp is refined. The folding endurance, which also increases with increasing refining, is very similar for both types of pulp but slightly higher for that provided by the TCF sequence.

At a given bulk ECF pulp is more permeable to air than is TCF pulp (i.e. the structure of the former is more close). According to Lindholm (1990), the decreased permeability of the TCF pulp may be a result of fiber surfaces being altered by ozone during bleaching. However, the closer

Table 5
Glucose (%GLC) and xylose (%XYL) contents after each bleaching stage of the TCF (XOZP, XOAZP, XOZRP, XOAZRP) sequences

Pulp		%GLC	%XYL	IC
TCF	Initial	81.2	18.9	0.47
	X	83.7	16.3	0.52
	XO	84.1	15.9	0.66
	XOZ	85.6	14.4	0.53
	XOZP	85.8	14.2	0.12
	XOA	86.7	13.3	0.33
	XOAZ	84.3	15.7	0.06
	XOAZP	85.2	14.8	0.50
	XOZR	85.6	14.4	0.37
	XOZRP	85.7	14.3	0.46
	XOAZR	84.4	15.6	0.27
	XOAZRP	85.3	14.7	0.43

IC: confidence interval for 95% of confidence.

structure of TCF pulp results in no higher values of its physical properties.

In summary, the studied TCF sequence provides pulp the physical properties of which are comparable to those of conventional pulp. It should be noted that the ECF pulp used for comparison possessed a higher viscosity, which normally results in better physical properties.

3.3. Effect of bleaching stages on carbohydrates composition. Determination by HPLC

Analysis of the sugars present in wood pulp using HPLC has been proposed as a method for ascertaining the changes occurring in polysaccharides (cellulose and xylans) during the bleaching process.

In order to determine the effect of the oxalic acid used as an additive and of the sodium borohydride use as a post-treatment in the TCF sequence, we compared the results obtained after each stage of the XOZP, XOAZP, XOZRP, and XOAZRP sequences.

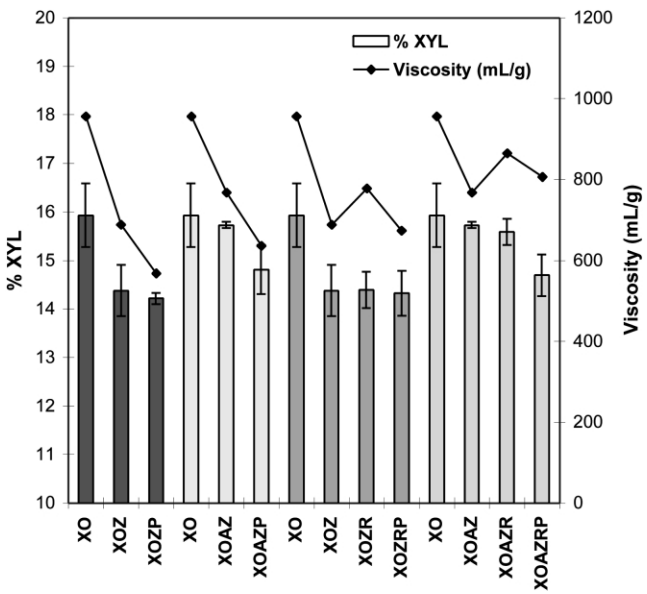

Fig. 6. Xylose content and viscosity of the TCF sequences: XOZP, XOAZP, XOZRP, and XOAZRP.

3.3.1. Additive (A)

Table 5 shows that the use of oxalic acid (XOA) results in a decrease of 16.4% in the xylose content in comparison with the XO pulp. This may be due the elimination of hemicelluloses that dissolve readily in an acid medium and are eliminated in the course of filtration of the pulp to obtain a consistency of 40% to carry to out ozone bleaching. In fact, the study of effluent shows that the additive contributes to the COD by 3.4 and 4.5% in the XOAZRP and XOAZP sequences, respectively. This contribution to the COD could be due to this dissolution of hemicelluloses.

3.3.2. Ozone stage (Z)

Fig. 6 shows the values for xylose content and viscosity of the different TCF sequences. Non-use of an additive in the Z stage (XOZ versus XOAZ) results in a lower xylose content, giving 14.4 and 15.7% of XYL for ozone bleaching treatments without an additive (XOZ) and with an additive (XOAZ), respectively. If we compare XOZ (14.4% XYL) and XOAZ (15.9% XYL), there is a 9.7% drop in xylose content during the Z stage, which would indicate the elimination of hemicelluloses. Fuhrman et al. (1995) mentioned in their study that hemicelluloses, mainly of the xylose type, are dissolved during the ozone stage. If we compare XO (15.9% XYL) and XOAZ (15.7% XYL), the glucose–xylose (GLC–XYL) ratio remains practically unchanged, which may be due to a previous elimination of xylose during the application of the additive (XOA), going from 15.9% in XO to 13.3% in XOA.

Although there is a dissolution of hemicelluloses in both XOZ and XOAZ pulps, either during Z or during A, viscosity decreases in both cases, also indicating degradation of the cellulose. However, the viscosity of the XOAZ pulp (768 ml/g) is higher than that of the XOZ pulp (688 ml/g), from which we can deduce that when the additive is applied, the ozone appears to react in a more homogeneous and selective manner. The percentage of GLC decreases from XOA to XOAZ, indicating that glucose is being eliminated, although it must be cellulose with a low molecular weight, since viscosity is higher in XOAZ than in XOZ. Thus, the additive might prevent ‘uncontrolled’ degradation by the ozone, i.e. it might direct the action of the ozone towards more heterogeneous regions with lower molecular weight, while preserving the more crystalline regions with higher molecular weight.

3.3.3. Hydrogen peroxide stage (P)

Results obtained after the P stage (Fig. 6), in comparison with the preceding stage, show no significant variation in the percentage of xylose in the sequences not including an additive (XOZP and XOZRP), while in the sequences including an additive (XOAZP and XOAZRP) there is a

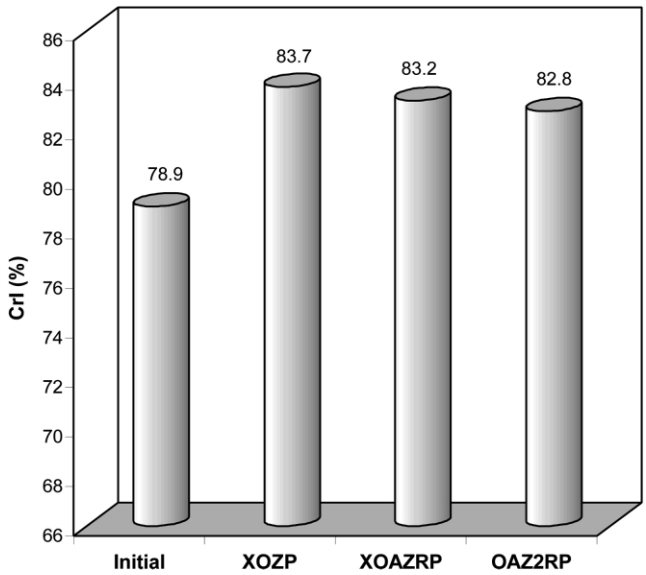

Fig. 7. CrI (%) of the bleached pulps: XOZP and XOAZRP.

reduction, indicating the dissolution of hemicelluloses. However, the final value for XYL in the latter sequences is higher than in the former, indicating that the pulp obtained via the sequences using an additive has a higher final content of xylans. Even with the higher XYL content, viscosity is also higher, confirming once again that the application of oxalic acid prevents the massive degradation of cellulose with a higher molecular weight, and possibly greater crystallinity, in the course of ozone bleaching.

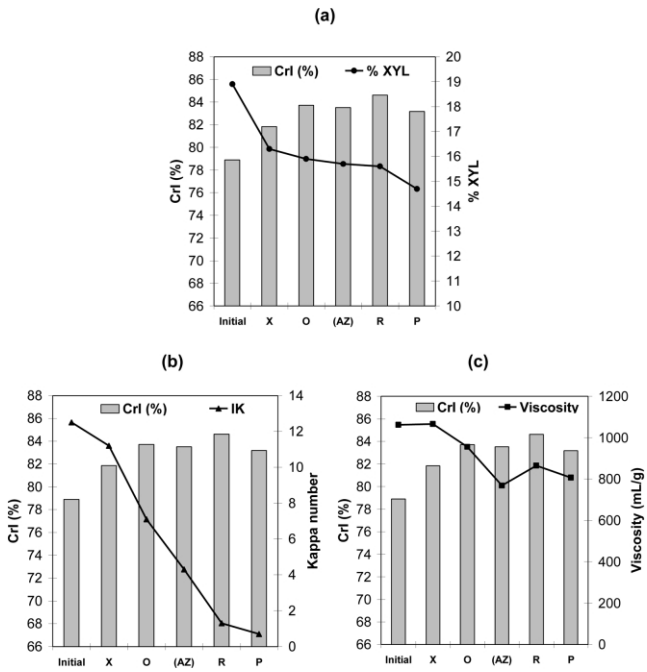

Fig. 8. (a)–(c) CrI evolution of the sequence XOAZRP versus %XYL, kappa number and viscosity, respectively.

3.3.4. Post-treatment (R)

Post-treatment with sodium borohydride (Fig. 6) shows no clear-cut effect, since xylose content is similar in comparison with the preceding stage (Z), with a slight decrease in the XOZR pulp (14.4% XYL) in comparison with the XOAZR pulp (15.6% XYL), allowing us to state that the effect appears to depend on whether or not the additive has been applied during ozone bleaching. The study of the properties of the effluent shows that post-treatment contributes to the COD value in both the XOAZRP (13.3 kg O_2/t of pulp) and the XOZRP (12.1 kg O_2/t of pulp). In the sequence including an additive (XOAZRP), this organic material contributes to the color of the effluent (1.4 kg Pt/t of pulp), while for the sequence not including an additive (XOZRP), contribution to the color (0.4 kg Pt/t of pulp) is less significant. This leads us to believe that application of the additive during post-treatment causes elimination of lignin, which is corroborated by the decrease in the kappa value during the R stage of the XOAZRP sequence. However, hexenuronic acid groups (Vuorinen, Teleman, Fagerström, Buchert, & Tenkanen, 1996) those contribute to the kappa value and are hemicelluloses could also be eliminated, which would reduce the %XYL. This is not the case when the additive is not applied, which might result in the elimination of carbohydrates; since there is no significant decrease in the kappa value either. These carbohydrates could be mainly cellulose with low molecular weight, giving rise to a decrease in the %GLC.

3.4. Effect of bleaching stages on crystallinity. Determination by XRD

Cellulose fiber is a polycrystalline aggregate formed of crystalline and amorphous regions, which may be related to the behavior of the fiber in the presence of different reagents and to the final properties of the pulp. The XRD technique (Evans, Newman, Roick, Suckling, & Wallis, 1995; Focher, Capretti, Marzetti, Kotka, Hua, & Kaliaguine, 1994; Goswami, Saikia, Baruah, & Sarma, 1996; Stewart & Foster, 1976), it is a sufficiently reliable technique to determine crystallinity in paper pulp.

Fig. 7 gives crystallinity values for the XOZP and XOAZRP sequences. All of these sequences show higher final crystallinity in comparison with raw pulp, since bleaching of the pulp removes amorphous regions of the fibers and the remaining cellulose is more crystalline. The CrI for the bleached pulps are not very different.

Fig. 8 give crystallinity values after each stage of the XOAZRP sequence. Crystallinity remains the same after ozone bleaching (AZ). In respect of sodium borohydride (R), it is observed that crystallinity increases by 1.3%. The bleaching stage with hydrogen peroxide (P) results in a decrease of 1.7%.

The bleaching process increases the crystallinity of the pulp. But what is the cause of the changes in crystallinity that occur during the different bleaching stages? In order to

determine this cause, we have taken into account values for the percentage of xylose (%XYL), the kappa number (IK) and the viscosity, which are shown in comparison with results for the CrI in Fig. 8(a)–(c), respectively.

3.4.1. Ozone stage with oxalic acid (AZ)

During ozone (AZ) bleaching, the CrI does not change in comparison with the previous stage of oxygen delignification. The %XYL does not change either, meaning that xylose is not being eliminated; otherwise the CrI would increase. But lignin content (IK) decreases, which should result in an increase in the CrI. This means that although the ozone reacts with the cellulose, oxalic acid appears to protect mainly the ordered portion of the cellulose or to make it less accessible.

3.4.2. Post-treatment (R)

Crystallinity increases slightly during this stage, from 83.5 to 84.6%, in comparison with the Z stage. However, the %XYL remains unchanged, while the kappa number decreases, which could explain the increase in crystallinity (Fig. 8). An increase in viscosity is also observed. In the studies of bleaching in this R stage, rather high DQO values were obtained (13.3 and 12.1 kg/t of pulp), which were attributed to the possible elimination of lignin and even carbohydrates with low molecular weight. Taking into account the values for crystallinity and viscosity, we could even say that this involves a less ordered or amorphous portion of the cellulose, since both crystallinity and viscosity increase during this stage.

3.4.3. Hydrogen peroxide stage (P)

In this case, crystallinity decreases slightly in comparison with the R stage, going from CrI 84.6 to 83.2%. However, the xylose content drops from XYL 15.6 to 14.7% and the kappa number also drops, meaning that the CrI should increase (Fig. 8) Thus, since viscosity also decreases, from 865 to 807 ml/g, this means that degradation of cellulose during bleaching with hydrogen peroxide appears to affect primarily the more ordered portion, leading us to deduce that hydrogen peroxide can react with the more crystalline parts of cellulose.

We observe that different bleaching agents act in different ways on cellulose, thereby affecting crystallinity, i.e. the proportion of crystalline regions to amorphous regions in pulp.

4. Conclusions

Oxalic acid used as additive facilitates the removal of lignin; the effect, however, is not observed until the subsequent alkaline stage (P), possibly because the prevailing acid conditions prevent efficient dissolution of lignin. Oxalic acid also results in increased brightness and viscosity, which reflects its protective effect on cellulose.

The use of a post-treatment based on sodium borohydride has no appreciable effect on the kappa number. On the other hand, it increases brightness by about 1 unit, possibly through reduction of carbonyl groups, which contribute to pulp color. The most interesting effect, however, is the increased viscosity resulting from the reduction of carbonyl groups, which makes cellulose sensitive to a subsequent alkaline stage.

The additive and the post-treatment appear to have a synergistic effect; alternatively, the additive may produce more carbonyl groups for reduction in R stage. The study of the CS (chain scissions number in the cellulose chain) confirms an increased formation of carbonyl groups and decreased degradation by direct attack of ozone, by-products and radicals formed during Z and P stages. The additive thus reduces cellulose degradation, albeit at the apparent expense of a slight increase in the formation of carbonyl groups.

The additive and the post-treatment increase both the selectivity of the process and its efficiency, particularly when used in combination. The XOAZRP sequence provides 90% ISO brightness and a viscosity of 800 ml/g. As regards effluents, the sequence using the additive and the post-treatment (XOAZRP) exhibits the highest COD and also the highest color, the latter, however, is very similar among TCF sequences. The sodium borohydride used in the post-treatment accounts for the greater part of COD increase observed; this reagent dissolves lignin and/or carbohydrates.

The physical properties of XOAZRP pulp were compared with those of pulp produced by an ECF sequence of the XODPD type. TCF pulp was found to be easier to refine than ECF pulp. The two differ in their strength properties, some of which are better in TCF pulp and others in ECF pulp. Overall, the TCF sequence provides pulp with physical properties comparable to those of conventional pulp. Consequently, the resistance of paper made from TCF pulp need not be a hindrance to its commercialization. In addition, the ECF sequence exhibits higher COD and color values in the effluents; this, together with the fact that it discharges AOX, makes it more pollutant than the TCF XOAZRP sequence.

Application of the additive results in a decrease in the percentage of xylose (XYL), due probably to dissolution of hemicelluloses that are readily solubilized in an acid medium, which in turn contributes to the COD of the effluent. However, ozone bleaching results in a decrease in the amount of glucose (GLC), leading us to deduce that the additive might prevent uncontrolled degradation by ozone, preserving the more crystalline regions with higher molecular weight. Lastly, the pulps bleached using an additive have a higher XYL content. The effect of application of sodium borohydride appears to depend on whether or not the additive is applied during ozone bleaching.

In ozone bleaching, with oxalic acid, the degree of crystallinity is maintained, indicating that oxalic acid acts to

diminish the accessibility of crystalline cellulose and therefore prevents the ozone from degrading the more ordered portion of the cellulose excessively. With R (sodium borohydride) treatment, crystallinity and viscosity increase slightly and a high DQO is obtained, which would appear to indicate that the amorphous and less ordered portion of cellulose with a low molecular weight is eliminated during this stage. In P bleaching, crystallinity decreases slightly, as do the percentage of xylose, the kappa number and viscosity, from which we may deduce that the degradation of cellulose that occurs during bleaching with hydrogen peroxide appears to take place primarily in the more crystalline portions of the cellulose.

Different bleaching agents act in different ways on cellulose, thereby affecting crystallinity, i.e. the ratio of amorphous and crystalline regions in the pulp.

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