Available online at www.sciencedirect.com

ScienceDirect

Carbohydrate Polymers 67 (2007) 275–281

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Polysaccharide degradation during ozone-based TCF bleaching of non-wood organosolv pulps

Anatoly A. Shatalov *, Helena Pereira

Centro de Estudos Florestais, Universidade Técnica de Lisboa, Instituto Superior de Agronomia, Tapada da Ajuda, 1349-017 Lisboa, Portugal

Received 27 July 2005; received in revised form 8 May 2006; accepted 25 May 2006

Abstract

Carbohydrate behaviour of ASAM (alkali-sulfite-anthraquinone-methanol), Organocell (alkali-anthraquinone-methanol) and ethanol-alkali giant reed organosolv pulps during TCF (totally chlorine free) ZEP bleaching (Z-ozone stage; E-alkaline extraction; P-hydrogen peroxide stage) has been examined and compared with conventional kraft pulp. The moderate carbohydrate losses of 4.1–5.5% were noted, as a result of transition metals removal before ozonation and reduction of ozonated pulp before alkaline treatment. Xylan and cellulose (as the principal polysaccharides) were degraded respectively by 12% and 2.5%, without significant variation between different pulps. The drop in intrinsic viscosity of kraft pulp was more intensive in comparison with organosolv (21% versus 12–18%, respectively). The substantial loss of hexenuronic acids (by 58–76% for organosolv and 67% for kraft pulp) was observed during bleaching.

Keywords: *Arundo donax* L.; Giant reed; Organosolv pulping; Ozone bleaching; Polysaccharide degradation; Hexenuronic acids

1. Introduction

The present environmental pressure to reduce toxic effluents from pulp and paper mills, particularly chlorinated organics from bleach mill effluents, caused substantial interest in technological approaches with minimized ecological impact. Organic solvent-based delignification (so-called “organosolv pulping”) and totally chlorine free (TCF) pulp bleaching using oxygen-containing oxidative chemicals (such as molecular oxygen, ozone and hydrogen peroxide) proved to be among the best potential alternatives to conventional sulfur- and chlorine-based industrial pulping and bleaching technologies (Reeve, 1996; Stockburger, 1993).

Oxidants are very important for chemical pulp bleaching since they oxidatively degrade lignin thereby decreasing its molecular size and increasing its water and alkali solubility (Dence & Reeve, 1996). However, the carbohydrate complex is also subjected to attack by the active bleaching species. The pulp yield and strength (as the fundamental properties of bleached pulps) are determined by the degree of polysaccharides (particularly cellulose) preservation during bleaching. The carbohydrate degradation and loss with bleaching are therefore the controlling factors for the potential usability of the bleached pulp and suitability of the bleaching process as a whole.

Of all the oxidants used in chemical pulp bleaching, ozone is the most powerful and effective bleaching chemical, but less selective toward lignin (Byrd, Gratzl, & Singh, 1992; Liebergott, Van Lierop, & Skothos, 1992). As a strong electrophile, ozone preferably attracts electron-rich sites of carbohydrates such as acetal (glycosidic) linkages, hydroxyl groups and reducing end groups (Gierer, 1990a, 1990b). The direct attack on the acetal linkages causes the acetal cleavage and leads to a corresponding loss in viscosity (i.e. degree of polymerisation, or DP) and strength of bleached pulps (Pan, Chen, Chang, & Gratzl, 1981). The oxidation of hydroxyl groups is initiated by radical species (e.g. hydroxyl and perhydroxyl radicals) formed through ozone decomposition

---

* Corresponding author. Tel.: +351 21 363 4662; fax: +351 21 364 5000.
E-mail address: anatoly@isa.utl.pt (A.A. Shatalov).

0144-8617/$ - see front matter
doi:10.1016/j.carbpol.2006.05.028

and leads to formation of carbonyl (keto and aldehyde) groups (Reitberger & Gierer, 1988), which then readily undergo alkali-induced β-alkoxy elimination reactions with polysaccharide chain scission during subsequent alkaline extraction of ozonated pulps and peroxide bleaching stage, also resulting in a decrease in pulp viscosity and loss of pulp strength (Theander, 1980). Finally, the oxidation of reducing (aldehyde) end groups to carboxyl ones during ozonation increases the polysaccharide solubility in the following bleaching stages.

Besides the ozone-induced carbohydrate degradation reactions, a stepwise depolymerization (so-called "peeling"-reaction) and alkaline hydrolysis of glycosidic bonds of polysaccharides also take place under the alkaline conditions of the subsequent bleaching stages (e.g. alkaline extraction and hydrogen peroxide stage) of the ozone-based sequence (Fengel & Wegener, 1984; Sjöström, 1993). In the hydrogen peroxide bleaching stage the substantial carbohydrate degradation can also be caused by active oxygen species (i.e. hydroperoxide onion, hydroxyl radical and superoxide anion radical) formed through the alkaline-induced peroxide decomposition catalysed by transition metals present in the bleaching solution and in the pulp (Colodette, Rothenberg, & Dence, 1988). The effective control of metals by addition of chelating agents as well as the application of peroxide stabilizers can therefore minimize carbohydrate losses (Colodette & Dence, 1989; Lapierre, Bouchard, Berry, & van Lierop, 1995).

High quality papermaking fibres were recently produced from the agro-fibre crop giant reed (*Arundo donax* L.) using ecologically friendly organosolv pulping technologies (Shatalov & Pereira, 2001, 2004a). The high bleachability of these pulps by simple TCF peroxide bleaching was reported (Shatalov & Pereira, 2005). The bleaching results were further improved with introduction of ozone into the bleaching sequence (Shatalov & Pereira, 2006). In the present paper, the carbohydrate behaviour of reed organosolv pulps during ozone-based TCF bleaching is reported.

2. Experimental

2.1. Materials

Three organosolv pulps (ethanol-alkali, alkali-sulfite-anthraquinone-methanol or ASAM, alkali-anthraquinone-methanol or Organocell) and one conventional kraft (reference) pulp from the agro-fibre crop giant reed (*Arundo donax* L.) were prepared for subsequent bleaching experiments. The detailed description of pulping conditions and treatment has been reported elsewhere (Shatalov & Pereira, 2005, 2006). The principal pulp properties are listed in Table 1.

The chemicals used were of analytical grade purity and purchased by Sigma, Aldrich, Riedel-de Haen and Fluka companies.

Table 1
Principal properties of unbleached organosolv and kraft (ref.) pulps from giant reed

	Pulping process			
	Ethanol–alkali	ASAM	Organocell	Kraft (ref.)
Yield (% on oven-dry reed)	46.8	46.5	45.7	43.2
Lignin (% on oven-dry pulp)	4.04	4.30	3.28	3.58
Intrinsic viscosity (ml g^{-1})	1146	1142	967	1078
Brightness (% ISO)	40.5	38.9	31.8	30.2

2.2. Methods

2.2.1. Pulp bleaching

All pulps were bleached by a simple ozone-based ZEP sequence (where Z is an ozone stage, E is an alkaline extraction stage and P is a hydrogen peroxide stage), without oxygen pre-bleaching. To increase the selectivity of the ozone stage towards lignin, an acidic pulp treatment with a solution of sulfuric acid with subsequent pressing step (A-stage) was performed before ozonation. The reducing agent (sodium borohydride) was added to the alkaline extraction stage (E_R-stage) to convert the alkali-sensitive carbonyl groups of the carbohydrates to hydroxyl groups, thus preventing the alkali-induced carbohydrate degradation (Lindholm, 1993). Before peroxide bleaching, the pulps were pre-treated with the chelating agent (Q-stage) EDTA (ethylenediaminetetraacetic acid) to limit the effect of transition metals on alkaline decomposition of peroxide. The Epsom salt (magnesium sulfate) and DTPA (diethylenetriaminepentaacetic acid) were used as the additional chemicals during peroxide bleaching stage to minimize the radical degradation reactions of carbohydrates. The experimental design and bleaching performance as well as the pulp treatment after each bleaching stage have been detailed elsewhere (Shatalov & Pereira, 2006). The specific bleaching conditions and the principal properties of bleached pulps are listed in Tables 2 and 3.

Table 2
Bleaching conditions

	Bleaching stage				
	A	Z	E_R	Q	P
Pulp consistency (%)	3	3	10	3	10
Temperature (°C)	20	20	60	50	90
Time (min)	30	20	60	50	90
O_3 (% on oven-dry pulp)	–	0.8	–	–	–
H_2O_2 (% on oven-dry pulp)	–	–	–	–	2.5
NaOH (% on oven-dry pulp)	–	–	1.0	–	1.5
EDTA (% on oven-dry pulp)	–	–	–	0.3	–
DTPA (% on oven-dry pulp)	–	–	–	–	0.2
$MgSO_4$ (% on oven-dry pulp)[a]	–	–	–	–	0.3
$NaBH_4$ (% on oven-dry pulp)	–	–	0.1	–	–
pH[b]	2.0	2.0	–	4.5	–

[a] Magnesium sulfate was applied as $MgSO_4 \cdot 7H_2O$.

[b] pH was adjusted by diluted sulfuric acid.

Table 3
Principal properties of bleached organosolv and kraft (ref.) pulps from giant reed

	Pulping process			
	Ethanol–alkali	ASAM	Organocell	Kraft (ref.)
Bleached yield (% on oven-dry unbleached pulp)	93.4	91.0	90.9	92.1
Lignin (% on oven-dry bleached pulp)	1.65	1.89	1.26	1.66
Intrinsic viscosity (ml g^{-1})	988	1009	789	852
Brightness (% ISO)	83.7	79.4	83.4	79.6

Table 4
Experimental data on carbohydrate composition of organosolv and kraft (ref.) pulps from giant reed after each bleaching stage (% on initial carbohydrate content in unbleached pulp)

	Unbleached	AZ	AZE$_R$	AZE$_R$QP	Unbleached	AZ	AZE$_R$	AZE$_R$QP
	Ethanol-alkali				ASAM			
Rha[a]	0.02 ± 0.001	0.02 ± 0.002	0.01 ± 0.001	0.02 ± 0.001	0.02 ± 0.003	0.01 ± 0.001	0.01 ± 0.001	0.02 ± 0.002
Fuc	0.11 ± 0.014	0.09 ± 0.005	0.10 ± 0.011	0.10 ± 0.009	0.12 ± 0.008	0.09 ± 0.010	0.09 ± 0.009	0.10 ± 0.011
Ara	1.45 ± 0.072	1.24 ± 0.051	1.21 ± 0.034	1.17 ± 0.060	1.28 ± 0.041	1.18 ± 0.032	1.07 ± 0.056	1.02 ± 0.038
Xyl	20.72 ± 0.128	19.49 ± 0.099	19.23 ± 0.105	18.94 ± 0.117	18.37 ± 0.231	16.87 ± 0.157	16.60 ± 0.106	16.01 ± 0.148
Man	0.05 ± 0.003	0.04 ± 0.002	0.05 ± 0.002	0.04 ± 0.003	0.09 ± 0.004	0.08 ± 0.003	0.07 ± 0.003	0.07 ± 0.002
Gal	0.19 ± 0.010	0.13 ± 0.014	0.08 ± 0.009	0.05 ± 0.008	0.18 ± 0.009	0.14 ± 0.008	0.13 ± 0.011	0.09 ± 0.007
Glc	72.65 ± 0.241	72.06 ± 0.183	71.32 ± 0.350	70.97 ± 0.276	73.61 ± 0.185	73.16 ± 0.251	72.91 ± 0.303	72.04 ± 0.249
Total	95.19 ± 0.505	93.07 ± 0.356	92.00 ± 0.512	91.29 ± 0.474	93.67 ± 0.481	91.53 ± 0.462	90.89 ± 0.498	89.35 ± 0.457
	Organocell				Kraft (ref.)			
Rha[a]	0.02 ± 0.001	0.02 ± 0.002	0.02 ± 0.002	0.01 ± 0.001	0.02 ± 0.001	0.01 ± 0.003	0.02 ± 0.001	0.02 ± 0.002
Fuc	0.10 ± 0.009	0.08 ± 0.010	0.09 ± 0.010	0.05 ± 0.012	0.12 ± 0.011	0.11 ± 0.014	0.10 ± 0.009	0.10 ± 0.010
Ara	1.21 ± 0.071	0.98 ± 0.064	0.89 ± 0.038	0.87 ± 0.047	1.17 ± 0.063	0.88 ± 0.048	0.69 ± 0.051	0.56 ± 0.033
Xyl	20.50 ± 0.221	19.00 ± 0.174	18.49 ± 0.185	17.94 ± 0.152	18.34 ± 0.193	17.36 ± 0.235	16.90 ± 0.170	15.98 ± 0.196
Man	0.06 ± 0.001	0.05 ± 0.003	0.04 ± 0.002	0.04 ± 0.001	0.06 ± 0.002	0.05 ± 0.004	0.05 ± 0.002	0.04 ± 0.003
Gal	0.14 ± 0.011	0.10 ± 0.010	0.07 ± 0.014	0.07 ± 0.007	0.12 ± 0.013	0.04 ± 0.006	0.03 ± 0.007	0.03 ± 0.005
Glc	71.59 ± 0.403	70.99 ± 0.327	70.59 ± 0.399	69.50 ± 0.285	72.80 ± 0.364	71.80 ± 0.471	71.66 ± 0.191	70.93 ± 0.208
Total	93.62 ± 0.717	91.22 ± 0.590	90.19 ± 0.650	88.48 ± 0.505	92.63 ± 0.647	90.25 ± 0.781	89.45 ± 0.431	87.66 ± 0.457

[a] Expressed as the homopolymers by multiplying the content of the corresponding monosaccharides by correlation factor 0.89 (for rhamnose and fucose), 0.88 (for arabinose and xylose) and 0.90 (for mannose, galactose and glucose) (Browning, 1967).

2.2.2. Carbohydrate analysis

Carbohydrate composition was determined by GC (Hewlett Packard 5890) as alditol-acetate derivatives of monosaccharides after pulp Saeman hydrolysis (Saeman, Moore, & Millet, 1963) using the following conditions: SP-2330 column (30 m × 0.32 mm ID, 0.20 μm film); injector temperature 240 °C; detector temperature 250 °C; initial column temperature 230 °C; final column temperature 240 °C; 2 °C/min rate; 2-deoxy-D-glucose as an internal standard.

2.2.3. Uronic and hexenuronic acids

Uronic acids were determined colorimetrically with *m*-phenylphenol (Blumenkrantz & Asboe-Hansen, 1973) using glucuronic acid as a standard.

Hexenuronic acid groups were quantified by selective hydrolysis in formic acid–sodium formate buffer followed by UV-spectroscopy (Shimadzu, UV-160A) of the formed 2-furoic acid at 245 nm (Vuorinen, Fagerström, Buchert, Tenkanen, & Teleman, 1999).

2.2.4. Aldehyde groups

The content of aldehyde groups in bleached pulps was measured spectroscopically at 546 nm (Shimadzu, UV-160A) after reaction with 2,3,5-triphenyltetrazolium chloride (TTC), as described elsewhere (Obolenskaya, Elnitskaya, & Leonovitch, 1991).

2.2.5. Pulp viscosity

The pulp intrinsic viscosity was measured in cupriethylenediamine (CED) solution (Carlo Erba reagent) according to SCAN-CM 15:88 standard.

3. Results and discussion

The fate of carbohydrates during ozone-based totally chlorine free bleaching of ecologically friendly ASAM, Organocell and ethanol-alkali organosolv pulps from the agro-fibre crop giant reed was examined and compared with conventional kraft pulp. The polysaccharide degradation was assessed in each stage of the applied bleaching sequence through the changes in pulp carbohydrate composition and intrinsic viscosity.

The experimental data on pulp monosaccharide analysis are summarised in Table 4. As evident, only limited carbohydrate degradation takes place during bleaching, what leads to moderate carbohydrate losses of only 4.1–4.6% (in respect to total carbohydrates in unbleached pulp) of ethanol-alkali and ASAM, and 5.4–5.5% of Organocell and

Table 5
Total carbohydrate losses during bleaching of organosolv and kraft (ref.) pulps from giant reed

Bleaching stage	Ethanol-alkali		ASAM		Organocell		Kraft (ref.)	
	% on init.	%	% on init.	%	% on init.	%	% on init.	%
AZ	2.23[a]	54.4[b]	2.28	49.5	2.56	46.6	2.57	47.9
AZE$_R$	3.35	27.3	2.97	15.0	3.66	20.0	3.43	16.0
AZE$_R$QP	4.10	18.3	4.61	35.6	5.49	33.3	5.37	36.1

[a] % on initial carbohydrate content in unbleached pulp.

[b] % on total carbohydrate losses during complete bleaching.

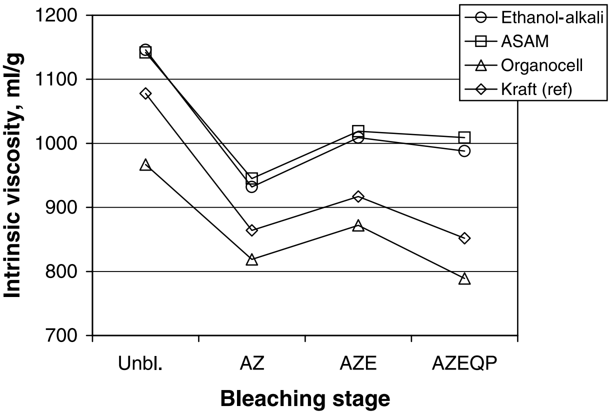

Fig. 1. Change in intrinsic viscosity of organosolv and kraft (ref.) pulps from giant reed during each bleaching stage.

kraft (ref.) pulps (Table 5). This provided thereby the fairly high values of the bleached pulp yield (Table 3). The intensity of the intra-molecular degradation reactions, leading to polysaccharide shortening without substantial yield loss, can be estimated from the values of pulp intrinsic viscosity. A moderate drop in viscosity was observed (Fig. 1), corresponding to a decrease by 11.6–13.8% for ASAM and ethanol-alkali pulps versus 18.4–21.0% for Organocell and kraft. The overall rate of the chain scission reactions was therefore slow, with $5.0–6.0 \times 10^{-5}\,\mathrm{min}^{-1}$ versus $10.7–11.0 \times 10^{-5}\,\mathrm{min}^{-1}$, respectively (Table 6).

It can be seen from Tables 5 and 6, that the different bleaching stages have different effects on the carbohydrate complex of bleached pulps, what obviously depends from the oxidation power of the applied active bleaching chemical and from the degree of polysaccharide protection against its oxidative degradation. Despite the acidic pulp pre-treatment (A-stage) to remove the transition metal ions before ozonation and to minimize thereby the ozone decomposition with release of unselective radical species, about 50% of total carbohydrate losses occurred during the ozone-bleaching stage, leading to removal of 2.2–2.6% of the total polysaccharides (relative to the unbleached pulp) irrespective of the kind of bleached pulp. As illustrated in Fig. 1, the drop in pulp intrinsic viscosity takes place during pulp ozonation, by 15.3–18.7% for organosolv and by 20.0% for kraft pulps, as a result of direct cleavage by ozone of glycosidic bonds in polysaccharide macromolecules.

The very high oxidizing potential of ozone (2.07 eV) causes the formation of a large number of carbonyl groups, which content was roughly assessed through the quantification of aldehyde (CHO) groups (Table 6). The reduction of ozonated pulps with sodium borohydride in the alkaline extraction (E$_R$)-stage allowed to convert the alkali-sensitive carbonyl groups to alkali-stable hydroxyl groups, thereby preventing the alkali-induced polysaccharide degradation by β-alkoxy elimination. As can be seen from Table 6, the intensity of the chain scission reactions during E$_R$-stage was substantially slowed down with the decrease of CHO-groups. It is remarkable that the intrinsic viscosity of all tested pulps was improved after the alkaline extraction stage (Fig. 1). The inhibition of the degradation reactions in the presence of a strong reducing agent as well as the dissolution of the oxidized low molecular polysaccharide fragments (along with degraded lignin) by the alkaline solution are the obvious reasons of the observed phenomena of increased viscosity. After the alkaline extraction stage, the overall carbohydrate losses were only of 0.7–1.1% for organosolv and 0.9% for kraft pulps.

Table 6
Effective rate constant of polysaccharide chain scission (k) and the content of aldehyde (CHO) groups during bleaching of organosolv and kraft (ref.) pulps from giant reed

Bleaching stage	Ethanol-alkali		ASAM		Organocell		Kraft (ref.)	
	$k \times 10^{-5}$ (min^{-1})	CHO (mmol/100 g)	$k \times 10^{-5}$ (min^{-1})	CHO (mmol/100 g)	$k \times 10^{-5}$ (min^{-1})	CHO (mmol/100 g)	$k \times 10^{-5}$ (min^{-1})	CHO (mmol/100 g)
Unbleached	–	0.3[b]	–	0.8	–	0.7	–	1.0
AZ	8.7[a]	11.5	7.9	5.4	8.5	6.2	10.2	8.0
AZE$_R$	5.1	1.7	4.5	2.1	5.1	0.9	7.2	2.1
AZE$_R$QP	6.0	1.0	5.0	1.2	10.7	0.7	11.0	1.0

[a] Rate constant of polysaccharide chain scission was calculated as $k = 1/\mathrm{DP}\text{-}1/\mathrm{DP}_o$, where DP_o and DP is a degree of polymerization of respectively unbleached and bleached pulp, calculated by equation $\mathrm{DP}^{0.76} = [\eta]/2.28$ (SCAN-CM 15:88 standard).

[b] Content was expressed in mmol of CHO-groups per 100 g of oven-dry bleached pulp.

The harmful effect on carbohydrates of the final hydrogen peroxide bleaching stage was minimized by pulp chelating (Q-stage) with ethylenediaminetetraacetic acid (EDTA) to remove the transition metals ions responsible for peroxide decomposition with formation of active radical species. The stability of peroxide was further improved by application of Epsom salt (peroxide stabilizer) and diethylenetriaminepentaacetic acid (DTPA, chelating agent) during the bleaching process. These precautions allowed to reduce the carbohydrate losses in the peroxide bleaching stage to a minimum (0.9–1.8% loss for organosolv pulps and 1.9% loss for kraft, Table 5), with only a moderate drop in pulp viscosity (by 0.8–1.9% for ASAM and ethanol-alkali pulps and 6.1–8.6% for Organocell and kraft, Fig. 1).

The cellulose and xylan are the main two polysaccharides of giant reed, together accounting for about 56% (on oven-dry basis) of the reed stem material (Shatalov, Quilhó, & Pereira, 2001) and about 98% of each bleached pulp (Table 4). The xylan is not homogeneous and represents the arabino-4-*O*-methylglucuronoxylan, covering over 90% of the total non-cellulosic carbohydrates (Joseleau & Barnoud, 1976). It is therefore the degradation of cellulose and xylan during bleaching that makes the critical impact on the yield and properties of bleached pulps. The dynamics in the loss of glucosyl, xylosyl and arabinosyl units (as the neutral monomers of the cellulose and heteroxylan) with each bleaching stage is shown in Fig. 2. As evident, only 2.1–2.9% of cellulose (expressed as a glucan) is lost after complete bleaching irrespectively of the type of bleached pulp. Most of the cellulose losses of organosolv pulps (about 55% of total) occur during the peroxide bleaching stage, while the kraft cellulose degrades more intensively during the ozonation.

As illustrated in Fig. 2, a xylan loss of 8.6–12.9% and an arabinan loss of 19.3–28.1% (expressed as the homopolymers) were observed after bleaching of organosolv pulps (versus respective loss of 12.9% and 52.1% for kraft). This shows a moderate degradation of the xylan backbone with a more intensive removal of the short arabinosyl side-chains of the heteroxylan, presuming however that all the detected arabinose is incorporated into the heteroxylan structure and that the other reactive arabinose-containing species (e.g. the pectin arabinan) were previously removed during pulping and bleaching (Rydholm, 1965). The bulk of the xylan as well as the arabinan losses occurred during the ozone bleaching stage (respectively, 58.6–69.3% and 68.0–75.0% for organosolv versus 41.5% and 47.6% for kraft pulp) indicating the predominance of the radical-induced degradation of heteroxylan during bleaching.

The uronic acid profile of ozone-based bleaching of giant reed pulps is shown in Fig. 3. The source of uronic acids (UA) in the stem-wall material of giant reed is a 4-*O*-methylglucuronic acid (MeGlcA) of heteroxylan (Joseleau & Barnoud, 1976) and a galacturonic acid of pectins (i.e. acidic polysaccharide (rhamno)galacturonan, Fengel & Wegener, 1984). Considering the absolute abundance of heteroxylan and the almost complete pectin removal under

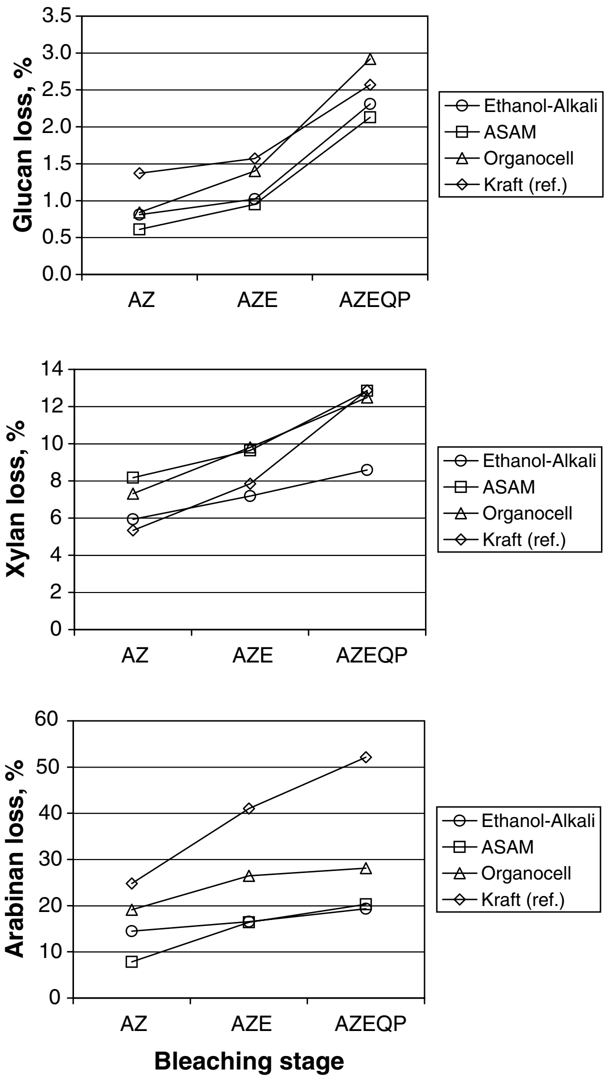

Fig. 2. Loss in principal neutral carbohydrate components (expressed as individual homopolysaccharides) of organosolv and kraft (ref.) giant reed pulps during each bleaching stage.

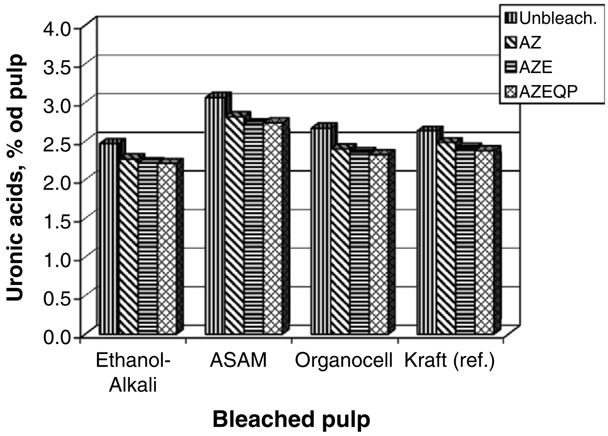

Fig. 3. Uronic acid (UA) profile of ozone-based TCF bleaching of organosolv and kraft (ref.) pulps from giant reed (% on oven-dry bleached pulp).

alkaline pulping conditions, the total UA quantified in bleached pulps can be assigned to MeGlcA directly linked to heteroxylan (Laine, Buchert, Viikari, & Stenius, 1996). The term "UA" is used here because of applied procedure for integrated quantification of all uronic acid moieties in pulp. As evident from Fig. 3, the UA loss by only 10.5–13.0% (i.e. 0.26–0.35% of oven-dry pulp material) takes place during bleaching of organosolv pulps (versus 9.7% - for kraft). Similar to Ara and Xyl, most of the UA (or MeGlcA groups) degradation (approx. 73.2–77.5% and 58.9% of total losses for organosolv and kraft pulps, respectively) occurs during the ozone bleaching stage, underlining the critical importance of this stage to carbohydrates.

At least a portion of the residual MeGlcA of any alkaline pulp is converted to hexenuronic acid (HexA) by β-elimination of methanol through the intermediate product 4-*O*-methyliduronic acid (Buchert et al., 1995; Chai, Yoon, Zhu, & Li, 2001; Shatalov & Pereira, 2004b). Due to its unsaturated nature, the HexA was shown to have a detrimental effect in pulp bleaching, connected with an increased consumption of bleaching chemicals (such as ozone and chlorine dioxide) and decreased pulp optical properties (Jiang, van Lierop, & Berry, 2000; Chakar, Allison, Ragauskas, McDonough, & Sezgi, 2000). The HexA content in the tested giant reed pulps was estimated as 27.5, 18.2, 16.1 and 15.4 μmol/g, respectively, of ethanol-alkali, ASAM, Organocell and kraft pulp. It is substantially lower than those HexA values reported for industrial wood pulps (e.g. 45–65 μmol/g for birch kraft pulps, Li & Gellerstedt, 1997), suggesting thereby the reduced negative impact on pulp bleaching. It can be seen from Fig. 4 that the significant degradation of HexA moieties occurs during bleaching i.e. by 84.4% for ASAM, by 76.3% for ethanol-alkali and by 58.1% for Organocell pulp (versus 67.4% for kraft). As would be expected, the main HexA losses take place during the ozone bleaching stage (51.0–58.2% and 49.7% of total HexA losses for organosolv and kraft pulp, respectively), as an obvious result of ozone reactions with the enone structures in HexA groups. The referred alkali sensitivity of HexA was demonstrated during the subsequent alkaline extraction and alkaline peroxide bleaching stage which led to further HexA degradation (by 17.6–33.0% and 6.6–14.2%, respectively) with final HexA content of only 2.8 μmol/g in ASAM and 6.5–6.8 μmol/g in ethanol-alkali and Organocell bleached pulps (5.0 μmol/g in kraft pulp).

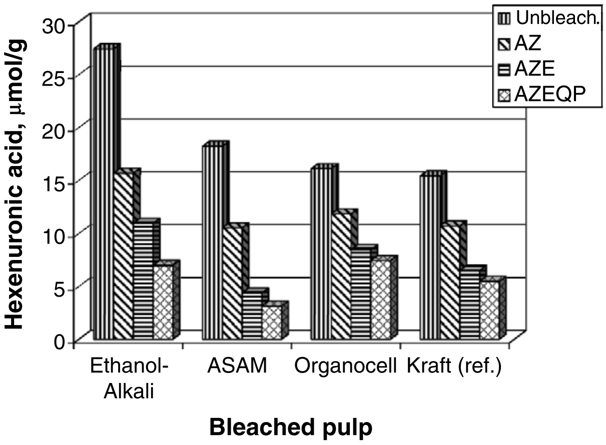

Fig. 4. Hexenuronic acid (HexA) profile of ozone-based TCF bleaching of organosolv and kraft (ref.) pulps from giant reed (μmol of HexA per gram of oven-dry bleached pulp).

The accuracy of carbohydrate analysis allowed to follow the bleaching tendency of the minor non-cellulosic polysaccharides presented in very small proportion in pulps and composed of mannosyl, galactosyl, rhamnosyl and fucosyl residues. The first one forms (together with glucose) the hemicellulosic polysaccharide glucomannan, while the other could be the constituents of the residual pectin substances (such as galactan and rhamnogalacturonan with side chains of fucose units, Fengel & Wegener, 1984), which are normally almost completely removed during pulping process, i.e. before bleaching (Rydholm, 1965). As can be seen from Table 4, the residual Rha, Fuc and Man are fairly resistant to the chosen bleaching conditions, while the Gal is lost by about 50% from ASAM and Organocell and by about 75% from ethanol-alkali and kraft pulps, apparently as a result of a fast degradation of the residual galactan. In general, a negligibly small quantity of reed polysaccharides other than cellulose and xylan in the pulps used for bleaching can have only a slight effect on yield and properties of bleached pulps.

4. Conclusions

Moderate carbohydrate degradation (by 4.1–5.5%) takes place during totally chlorine free AZE$_R$QP-bleaching of organosolv and kraft (reference) giant reed pulps. After complete bleaching, the ASAM and ethanol-alkali pulps lose about 12–14% of the starting viscosity and Organocell and kraft – about 18–21%. Approximately 12% of xylan and 2.5% of cellulose (as the principal reed polysaccharides) are degraded, without significant variation between different pulps. Uronic acid moieties (assigned mainly to MeGclA of heteroxylan) are removed by only 10–12%. The substantial loss of hexenuronic acids (by about 60–80%) takes place during bleaching. The bulk of carbohydrate losses (about 50% of total) occur during pulp ozonation.

Acknowledgement

The financial support of the Fundação para a Ciência e a Tecnologia (Portugal) within research contract SFRH/BPD/9376/2002 is gratefully acknowledged.

References

Blumenkrantz, N., & Asboe-Hansen, G. (1973). New method for quantitative determination of uronic acids. *Analytical Biochemistry, 54*, 484–489.

Browning, B. L. (1967). *Methods of wood chemistry*. New York: Wiley and Sons.

Buchert, J., Teleman, A., Harjunpää, V., Tenkanen, M., Viikari, L., & Vuorinen, T. (1995). Effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp. *TAPPI Journal, 78*(11), 125–130.

Byrd, M. V., Jr., Gratzl, J. S., & Singh, R. P. (1992). Delignification and bleaching of chemical pulps with ozone: a literature review. *TAPPI Journal, 75*(3), 207–213.

Chakar, F. S., Allison, L., Ragauskas, A. J., McDonough, T. J., & Sezgi, U. (2000). Influence of hexenuronic acids on U.S. bleaching operations. *TAPPI Journal, 83*, 62–72.

Chai, X.-S., Yoon, S.-H., Zhu, J. Y., & Li, J. (2001). The fate of hexenuronic acid groups during alkaline pulping of loblolly pine. *Journal of Pulp and Paper Science, 27*(12), 407–411.

Colodette, J. L., Rothenberg, S., & Dence, C. W. (1988). Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps. Part I. Hydrogen peroxide stability in the absence of stabilizing systems. *Journal of Pulp and Paper Science, 14*(6), J126–J132.

Colodette, J. L., & Dence, C. W. (1989). Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps. Part II. Hydrogen peroxide stability in the presence of magnesium and combination of stabilizers. *Journal of Pulp and Paper Science, 15*(2), J45.

Dence, C. W., & Reeve, D. W. (1996). Chemistry of chemical pulp bleaching. In C. W. Dence & D. W. Reeve (Eds.), *Pulp bleaching. Principles and practice* (pp. 125–159). Atlanta: TAPPI Press.

Fengel, D., & Wegener, G. (1984). *Wood (chemistry, ultrastructure, reactions)*. Berlin, New York: Walter de Gruyter.

Gierer, J. (1990a). Basic principles of bleaching, Part 1: cationic and radical processes. *Holzforschung, 44*(5), 387–394.

Gierer, J. (1990b). Basic principles of bleaching, Part 2: anionic processes. *Holzforschung, 44*(6), 395–400.

Jiang, Z.-H., van Lierop, B., & Berry, R. (2000). Hexenuronic acid groups in pulping and bleaching chemistry. *TAPPI Journal., 83*, 167–175.

Joseleau, J. P., & Barnoud, F. (1976). Cell wall carbohydrates and structural studies of xylan in relation to growth in the Arundo donax. *Applied Polymer Symposia, 28*, 983–992.

Laine, J., Buchert, J., Viikari, L., & Stenius, P. (1996). Characterization of unbleached kraft pulps by enzymatic treatment, potentiometric titration and polyelectrolyte adsorption. *Holzforschung, 50*(3), 208–213.

Lapierre, L., Bouchard, J., Berry, R. M., & van Lierop, B. (1995). Chelation Prior to Hydrogen Peroxide bleaching of Kraft Pulps: an overview. In *81st CPPA annual meeting preprints* (p. B233). Montreal: Tech. Sect. CPPA.

Li, J., & Gellerstedt, G. (1997). The contribution to kappa number from hexenuronic acid groups in pulp xylan. *Carbohydrate Research, 302*, 213–218.

Liebergott, N., Van Lierop, B., & Skothos, A. (1992). A survey of the use of ozone in bleaching pulps, Part 1. *TAPPI Journal, 75*(1), 145–152.

Lindholm, C.-A. (1993). Alkaline extraction of ozone-bleached pulp, Part 4. Comparison of E, (EB), (EO), (EP) and (EOP) treatment. *Journal of Pulp and Paper Science, 19*(3), 108–113.

Obolenskaya, A. V., Elnitskaya, Z. P., & Leonovitch, A. A. (1991). In *Laboratory practicum on wood and cellulose chemistry* (pp. 211–212). Moscow: Ecology.

Pan, G., Chen, C.-L., Chang, H.-M., & Gratzl, J. S. (1981). Model experiments on the splitting of glycosidic bonds by ozone. In *Proceedings of the international symposium on wood and pulping chemistry* (Vol. II, p. 132). SPCI: Stockholm.

Reeve, D. W. (1996). Introduction to the principles and practice of pulp bleaching. In C. W. Dence & D. W. Reeve (Eds.), *Pulp bleaching. Principles and Practice* (pp. 1–24). Atlanta: TAPPI Press.

Reitberger, T., & Gierer, J. (1988). Chemiluminescence as a means to study the role of hydroxyl radicals in oxidative processes. *Holzforschung, 42*(6), 351–356.

Rydholm, S. A. (1965). *Pulping processes*. New York, London, Sidney: Interscience Publishers.

Saeman, J. F., Moore, W. E., & Millet, M. A. (1963). In R. L. Whistler (Ed.), *Methods in carbohydrate chemistry* (pp. 54–69). New York: Academic Press.

Shatalov, A. A., & Pereira, H. (2001). Arundo donax L. reed: New perspectives for pulping and bleaching–2. Organosolv delignification. *TAPPI Journal, 84*(11), 1–14.

Shatalov, A. A., Quilhó, T., & Pereira, H. (2001). Arundo donax L. reed: New perspectives for pulping and bleaching–1. Raw material characterization. *TAPPI Journal, 84*(1), 1–12.

Shatalov, A. A., & Pereira, H. (2004a). Arundo donax L. reed: New perspectives for pulping and bleaching–3. Ethanol reinforced alkaline pulping. *TAPPI Journal, 3*(2), 27–31.

Shatalov, A. A., & Pereira, H. (2004b). Uronic (hexenuronic) acid profile of ethanol-alkali delignification of giant reed Arundo donax L. *Cellulose, 11*(1), 109–117.

Shatalov, A. A., & Pereira, H. (2005). Arundo donax L. reed: New perspectives for pulping and bleaching–4. Peroxide bleaching of organosolv pulps. *Bioresource Technology, 96*(8), 865–872.

Shatalov, A.A., & Pereira, H. (2006). Arundo donax L. reed: New perspectives for pulping and bleaching–5. Ozone-based TCF bleaching of organosolv pulps, Bioresource Technology, submitted paper.

Sjöström, E. (1993). *Wood chemistry, fundamentals and applications*. New York: Academic Press.

Stockburger, P. (1993). An overview of near-commercial and commercial solvent-based pulping processes. *TAPPI Journal, 76*(6), 71–74.

Theander, O. (1980). In J. S. Gratzl, J. Nakano, & R. P. Singh (Eds.), *Chemistry of delignification with oxygen, ozone and peroxide* (pp. 43–59). Tokyo: Uni Pub. Co..

Vuorinen, T., Fagerström, P., Buchert, J., Tenkanen, M., & Teleman, A. (1999). Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. *Journal of Pulp and Paper Science, 25*(5), 155–162.