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Carbohydrate behaviour of *Arundo donax* L. in ethanol–alkali medium of variable composition during organosolv delignification

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Abstract

The effect of medium alkalinity, organic solvent concentration and liquor-to-material ratio on the main carbohydrate constituents of *Arundo donax* L. stem (cellulose, hemicelluloses and uronic acids) under conditions of ethanol–alkali delignification has been examined. A protective action of alcohol addition against carbohydrate degradation was observed. The amount of non-cellulosic polysaccharides as well as the intrinsic viscosity of pulps increased with a rise in ethanol content in the reaction mixture. The increase in medium alkalinity was found to have a detrimental effect on carbohydrates and caused substantial loss of hemicelluloses. Elevated alkali and solvent concentrations were found to favour uronic acid groups degradation and hexenuronic acid formation during ethanol–alkali pulping. The liquor-to-material ratio had only some effect on uronic acid behaviour without any appreciable influence on cellulose and hemicelluloses.

Keywords: *Arundo donax* L; Ethanol–alkali pulping; Carbohydrate degradation; Uronic acid groups; Hexenuronic acids

1. Introduction

The use of alternative non-wood sources of fibre in papermaking has received substantial attention. There are two important reasons for the continuous interest in this area. Firstly, there is a decrease in wood availability with the increasing demand for market pulp in some rapidly developing countries in Asia, Africa and Latin America. Secondly, the current overproduction of food in the Western European countries has stimulated a search for new non-food crops for industrial utilisation (Moore, 1996; Leminen, Johansson, Lindholm, Gullichsen, & Yilmaz, 1996).

Arundo donax L. (or giant reed) is a widely distributed perennial rhizomatous grass. The high degree of adaptability to different ecological conditions (Perdue, 1958), annual harvesting period and high biomass productivity (Dalianis, Sooter, & Christou, 1994) make *Arundo donax* of interest as a fibre crop for pulp and paper production.

The first comparative experiments on organic solvent based delignification (so-called 'organosolv' pulping) of *Arundo donax* showed the potential of this approach for the production of high quality non-wood fibres (Shatalov & Pereira, 2000, 2001a). The more promising results were obtained by ethanol reinforced alkaline pulping (ethanol–soda or ethanol–alkali pulping). First tested on softwoods (Nakano, Daima, Hosoya, & Ishizu, 1981), the ethanol–alkali pulping was successfully applied to such crops as bagasse and wheat straw (Liang, Zhou, Xiao, & Wang, 1988).

In the present paper, we present the results on the influence of reaction medium composition on the carbohydrate complex of *A. donax* L. reed under conditions of ethanol–alkali delignification.

2. Experimental

2.1. Material

The stems of *A. donax* L. reed were supplied by the Agricultural University of Athens, Greece (Plant Production Department) in short culms, free from leaves. For pulping experiments the stems were disintegrated manually to a size of approximately 1–1.5 cm length, 2–3 mm width. The humidity of the material was determined.

2.2. Methods

2.2.1. Organosolv delignification

Ethanol–alkali pulping of *Arundo donax* was carried out in 100-ml stainless steel autoclaves rotated in an oil bath

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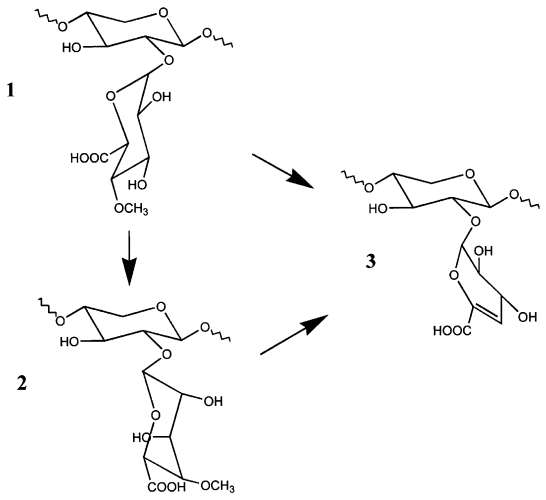

Scheme 1.

with full temperature control. The process variables were the ethanol content in the pulping liquor (20–60% by vol.), alkali charge on pulping (5–25% NaOH on o.d. material) and liquor-to-material ratio (5/1–8/1 ml/g). Pulping temperature and duration were kept constant in all experiments (140 °C and 180 min, respectively).

2.2.2. Pulp analysis

Carbohydrate composition of pulps was determined by GC (Hewlett Packard 5890) as TMS-derivatives of monosaccharides after Saeman hydrolysis (Saeman, Moore, & Millet, 1963). The conditions of GC-analysis were as follows: DB-5MS column (60 m × 0.25 mm i.d., film thickness 0.25 μm); helium as carrier gas; injector temperature 240 °C; detector temperature 240 °C; initial column temperature 140 °C; final column temperature 220 °C; rate 2 °C/min, *myo*-inositol as internal standard. Content of individual homopolysaccharides was calculated by multiplying the content of corresponding monosaccharides with the correlation factor 0.88 (for xylose and arabinose) and 0.90 (for glucose, mannose and galactose) (Browning, 1967).

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

Hexenuronic acid groups in pulps 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 (Vuorunen, Fagerström, Buchert, Tenkanen, & Teleman, 1999).

Intrinsic viscosity of pulps after dissolution in cadoxen solution was determined as described elsewhere (Obolenskaya, Elnitskaya, & Leonovitch, 1991). Cadoxen solution was prepared according to Sjöström and Enström (1966).

Table 1
Effect of organic solvent concentration in alkaline solution on the carbohydrate complex of *A. donax* L. reed under conditions of ethanol–soda delignification (140 °C, 3 h, 25% NaOH on o.d. reed)

Homopolysaccharides	Ethanol content (% by volume)					
	0%	20%	30%	40%	50%	60%
Glucan	30.50[a]	30.18	30.46	31.19	30.70	29.83
Xylan	8.10	8.57	10.23	11.40	12.03	12.13
Arabinan	0.62	0.62	0.72	0.81	0.88	0.89
Mannan	0.12	0.18	0.20	0.19	0.19	0.21
Galactan	0.10	0.10	0.11	0.12	0.14	0.14

[a] Content of individual homopolysaccharides in pulps is expressed as % on oven dry reed.

3. Results and discussion

3.1. Background

During alkaline delignification the polysaccharide complex of plants is subjected mainly to two degradation reactions caused by the action of hydroxide ions under elevated temperatures: so-called 'peeling' reaction (or stepwise progressive removal of reducing end-groups) and alkaline hydrolysis. The 'peeling' reaction is the main contributor to a low polysaccharide yield, while the alkaline hydrolysis leads to substantial drop in the degree of polymerization (Rydholm, 1965). The intensity of these reactions during pulping defines substantially the quality parameters of the resulting pulps.

The carboxyl groups in pulps may have a pronounced effect on pulp properties such as swelling, ion exchange with metal cations, brightness reversion and consumption of some bleaching chemicals (Sjöström, 1993; Vuorunen et al., 1999). The total amount of carboxyl groups in conventional alkaline (kraft) pulps was reported to be 85–125 mmol/kg depending on the wood species, where 80–90% were estimated as carboxyl groups of uronic acids linked to xylan (Laine, Buchert, Viikari, & Stenius, 1996).

The main source of uronic acids (UA) in *Arundo donax* pulps is arabino-4-*O*-methyl-glucuronoxylan, with 4.5% of 4-*O*-methyl-α-D-glucopyranosyluronic acid (MeGlcA) by weight in the native polysaccharide (Joseleau & Barnoud, 1975). Under alkaline conditions of ethanol–soda delignification the structure of xylan can be extensively modified by loss of glucuronic acid side groups and in part by conversion of MeGlcA to 4-deoxy-β-L-*threo*-hex-4-enopyranosyluronic acid (hexenuronic acid or HexA) by β-elimination of methanol via the intermediate product 4-*O*-methyl-β-L-idopyranosyluronic acid (4-*O*-methyl-iduronic acid or MeIdoA) according to Scheme 1 (Epimerization and degradation of 4-*O*-methylglucuronic acid groups of heteroxylan in alkaline medium: (1) α-D-MeGlc*p*A-(1 → 2)-β-D-xyl*p*-, (2) β-L-MeIdo*p*A-(1 → 2)-β-D-Xyl*p*-, (3) β-L-Hex*p*A-(1 → 2)-β-D-Xyl*p*-) (Johansson & Samuelson, 1977). Thus, the UA in pulps can be considered to consist of three components: native MeGlcA, its epimerization product MeIdoA and decomposition product HexA. Of

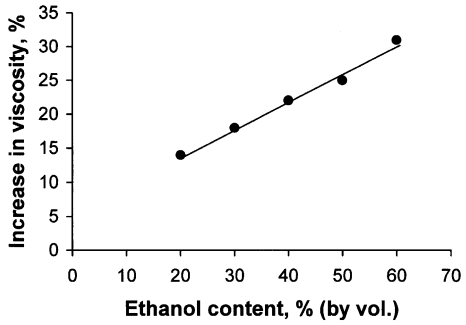

Fig. 1. Relative increase in intrinsic viscosity of ethanol–alkali pulps from *A. donax* L. with increase in ethanol concentration in the reaction solution (in relation to viscosity of pulp produced without ethanol addition).

these three uronic acid moieties, HexA has the most harmful influence on the following chemical processing of pulps due to its unsaturated nature (Jiang, van Lierop, & Berry, 2000). The formation and stability of HexA during pulping is known to be strongly affected by the cooking conditions. In this connection, the influence of organic solvent addition on chemical behaviour of UA during alkaline pulping of *Arundo donax* was a subject of much our interest.

3.2. Polysaccharide reactions

As can be seen from Table 1, the addition of organic solvent to alkaline pulping solution has a positive effect on protection of carbohydrates of *Arundo donax* against degradation during ethanol–alkali pulping. With an increase in ethanol concentration in the reaction mixture from 20 to 60% (by vol.) at a fixed alkali charge of 25% (on o.d. reed) the amount of xylan, the principal hemicellulosic polysaccharide of *Arundo donax* (Shatalov & Pereira, 2001b), increases from 8.6 to 12.1%. The preservation of minor non-cellulosic polysaccharides under elevated solvent concentrations was also observed.

The suppression of degradative processes is illustrated in Fig. 1. The intrinsic viscosity of ethanol–alkali pulps in cadoxen solution builds up in direct proportion to organic solvent content in the reaction mixture indicating the inhibition of intermolecular cellulose chain scission reactions caused by alkaline hydrolysis. It is remarkable, that no cellulose losses occur within the examined range of ethanol concentrations (as given by the constant values of glucan content in Table 1), which suggests the cellulose peeling reaction is suppressed even for low proportions of organic solvent in the alkaline solution. Improved polysaccharide stability during alkaline pulping of wood in the presence of low molecular weight aliphatic alcohols (such as methanol) was also observed by Nakano et al. (1981). It was suggested that the action of alcohols as radical scavengers suppress the radical-induced degradation processes of carbohydrates during pulping. The suppression of peeling reaction of polysaccharides was explained by acceleration of 'stopping'—reaction or by inhibition of aldehyde end group transformation into keto.

Table 2
Effect of medium alkalinity on the carbohydrate complex of *A. donax* L. reed under conditions of ethanol–soda delignification (140 °C, 3 h, EtOH/H_2O:40/60)

Homopolysaccharides	Alkali charge (% on o.d. reed)			
	5%	15%	25%	35%
Glucan	31.54[a]	31.29	32.35	32.17
Xylan	16.91	12.41	12.30	11.48
Arabinan	1.52	1.08	0.96	0.83
Mannan	0.22	0.21	0.20	0.21
Galactan	0.35	0.14	0.13	0.11

[a] Content of individual homopolysaccharides in pulps is expressed as % on oven reed.

The increase in alkali charge from 5 to 35% (on o.d. material) at a fixed ethanol content of 40% (by vol.) leads to substantial hemicelluloses degradation during ethanol–alkali pulping (Table 2). Under these conditions the amount of xylan in pulps decreases from 16.9 to 11.5% (on o.d. material), and loss of arabinan and galactan also takes place. Mannan was found to be more stable to change in medium alkalinity and its level remained constant at about 0.2%. Thus, similar to conventional alkaline processes (kraft and soda) the alkalinity of the reaction solution is one of the controlling factors for hemicelluloses degradation and consequently for pulp yield in ethanol–alkali pulping.

As evident from Table 2, cellulose is protected against degradation under increased medium alkalinity. The intrinsic viscosity of pulps in cadoxen solution rises steeply (by 55%) with change in alkali charge from 5 to 35% on o.d. material (Fig. 2). It was noted elsewhere (Genco, Busayasakul, Medhora, & Robbins, 1990), that increased concentration of hydroxyl ions in alkaline pulping causes substantial loss of hemicelluloses through direct dissolution of low molecular polysaccharide fractions. Considering the contribution of both the cellulose and hemicelluloses to pulp viscosity, the increase in ethanol–soda pulp viscosity (Fig. 2) can be explained by a higher molecular weight of residual hemicelluloses with increased alkali concentration. Thus, the effect of alkali during ethanol–soda pulping is more likely to assist the physical dissolution of polysaccharides rather than to reinforce chemical degradation.

The change in liquor-to-material ratio from 5 to 8 ml/g does not have any appreciable effect on carbohydrates of *Arundo donax* (Table 3), and no changes in pulp viscosity were observed. Thus, it is possible to vary the volume of the pulping liquor within the examined range of liquor-to-material ratios without any detrimental influence on the carbohydrate complex. Low liquor-to-material ratios are economically attractive, however, as was found experimentally, the use of a liquor-to-material ratio less than 5 ml/g for the ethanol–alkali pulping of *Arundo donax* reduces pulping efficiency because of reduced diffusion.

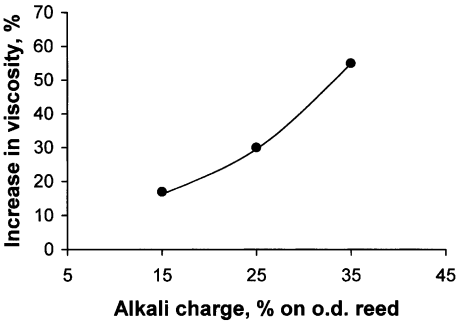

Fig. 2. Relative increase in intrinsic viscosity of ethanol–alkali pulps from *A. donax* L. with increase in alkali charge on pulping (in relation to viscosity of pulp produced with alkali charge 5%).

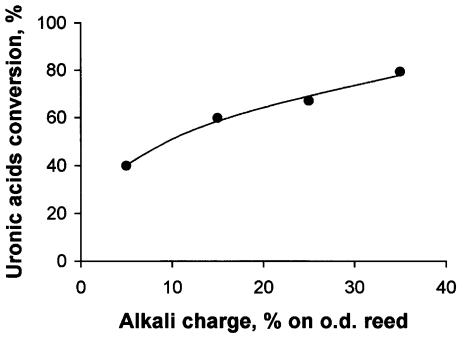

Fig. 3. Uronic acid groups conversion (% from initial content in material) during ethanol–alkali pulping of *A. donax* L. as a function of alkali charge on pulping.

3.3. Uronic acid groups transformation

An increase in alkali charge from 5 to 35% (on o.d. reed) at a fixed ethanol concentration of 40% (by vol.) leads to decrease in UA content in pulps from 1.65 to 0.57% (on o.d reed), that equals a 40% loss from the initial content in *Arundo donax* (Fig. 3). Thus, similar to conventional soda or kraft processes, the increased alkalinity of organic solvent–water reaction mixture causes substantial degradation of uronic acid side groups of heteroxylan during pulping.

Alkali concentration has an important effect on the formation of HexA during ethanol–soda pulping. Increase in solution alkalinity up to some critical concentration accelerates the transformation of MeGlcA to HexA. It can be seen from Fig. 4 that the maximal rate of this reaction may be reached with alkali charge 25%, when the amount of HexA rises sharply from 11.8 to 20.1 μmol/g. The subsequent increase in alkalinity causes the degradation of HexA (8.5 μmol/g with alkali charge 35%). The same effect of low HexA stability under high alkali concentrations was also noted for conventional kraft process (Tenkanen et al., 1999).

With increase in ethanol content from 20 to 60% (by vol.), at a fixed alkali charge of 25%, the amount of UA in pulps decreases from 1.5 to 1.2% (on o.d. reed). Hence, the addition of organic solvent also assists the degradation of UA during ethanol–soda pulping. However, the adverse effect of solvent on UA is not so high and leads to only about 10% loss of UA of *Arundo donax* within the examined range of ethanol concentrations (Fig. 5).

The addition of ethanol promotes the generation of HexA, which builds-up from 6.9 to 10.9 μmol/g with change in ethanol content from 20 to 60% (Fig. 6). The range of solvent concentration 30–50% is more favourable for conversion of MeGlcA to HexA with maximal rate, and the subsequent increase of ethanol proportion does not have any essential influence.

It is obvious from Figs. 7 and 8 that liquor-to-reed ratio has some effect on UA during ethanol–soda pulping. The decrease of liquor-to-reed ratio from 8 to 5 ml/g at fixed alkali charge (25% on o.d. reed) and ethanol concentration (40% by vol.) leads to a drop in UA content in pulps from 1.1 to 0.5% (on o.d. reed), and simultaneously accelerates HexA formation from 11.4 to 26.4 μmol/g. The lower liquor-to-reed ratios correspond to higher effective alkali concentration in the liquor caused by the change in volume of the reaction solution. Thus, the effect of liquor-to-reed ratio on UA is the result of change in medium alkalinity, to which the UA of *Arundo donax* are more sensitive than cellulose and hemicelluloses, as considered above. The more substantial degradation of UA takes place with low

Table 3
Effect of liquor-to-raw material ratio on the carbohydrate complex of *A. donax* L. reed under conditions of ethanol–soda delignification (140 °C, 3 h, EtOH/H_2O:40/60, 25% NaOH on o.d. reed)

Homopolysaccharides	Liquor-to-reed ratio (ml/g)			
	5/1	6/1	7/1	8/1
Glucan	30.47[a]	29.64	30.21	28.88
Xylan	13.19	12.90	11.89	12.92
Arabinan	0.88	0.83	0.78	0.86
Mannan	0.21	0.19	0.20	0.21
Galactan	0.11	0.11	0.12	0.11

[a] Content of individual homopolysaccharides in pulps is expressed as % on oven reed.

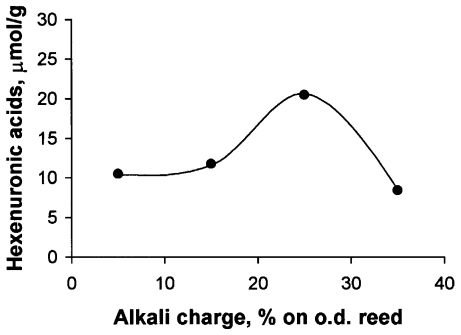

Fig. 4. Hexenuronic acid formation during ethanol–alkali pulping of *A. donax* L. as a function of alkali charge on pulping.

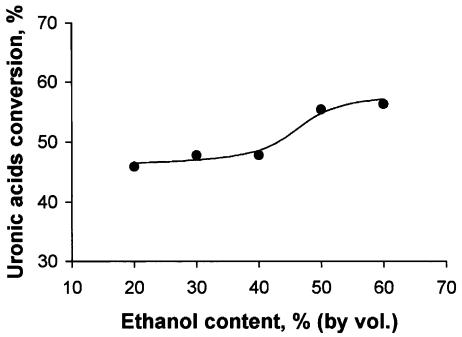

Fig. 5. Uronic acid groups conversion (% from initial content in material) during ethanol–alkali pulping of *A. donax* L. as a function of ethanol concentration in reaction solution.

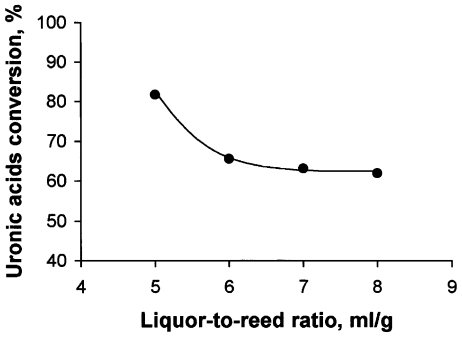

Fig. 7. Effect of liquor-to-material ratio on uronic acid groups conversion (% from initial content in material) during ethanol–alkali pulping of *A. donax* L.

liquor-to-reed ratios (less than 6 ml/g), when effective alkali concentration in the reaction mixture is higher (Fig. 7). The maximal rate of HexA formation occurs at high liquor-to-reed ratios, when the medium alkalinity is lower (Fig. 8).

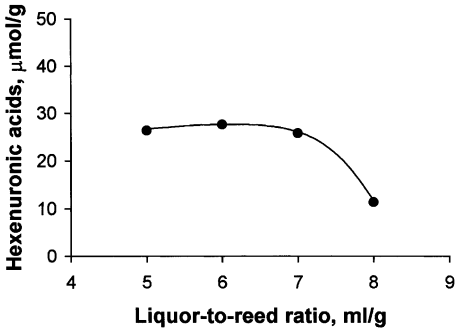

Fig. 8. Effect of liquor-to-material ratio on hexenuronic acid formation during ethanol–alkali pulping of *A. donax* L.

4. Conclusions

The addition of organic solvent to the alkaline solution has a positive effect on prevention of carbohydrate degradation during ethanol–alkali delignification of *A. donax* L. reed. The controlling factor for polysaccharide preservation is the medium alkalinity. The progressive loss of hemicelluloses occurs with increase in alkali concentration in the reaction mixture. Uronic acid moieties in *Arundo donax* are strongly affected by composition of the reaction solution. Increase in alkalinity as well as in ethanol content assists the uronic acid groups degradation and promotes the formation of hexenuronic acid.

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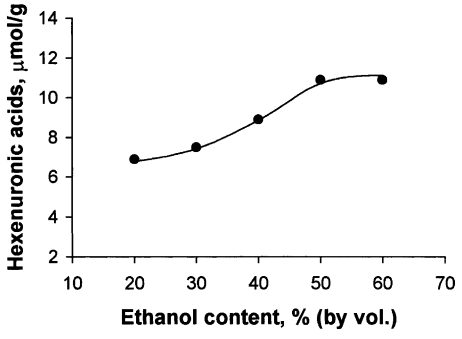

Fig. 6. Hexenuronic acid formation during ethanol–alkali pulping of *A. donax* L. as a function of ethanol concentration in reaction solution.

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