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Kinetics of polysaccharide degradation during ethanol-alkali delignification of giant reed—Part 2. Minor carbohydrates and uronic acids

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Abstract

The degradation kinetics of the minor neutral carbohydrates (composed of arabinosyl, galactosyl and mannosyl residuals) and uronic acid moieties of the agrofibre crop *Arundo donax* L. (giant reed) under conditions of ethanol-alkali delignification has been studied. Based on properties of multi-component reaction system, the degradation of arabinan, galactan and mannan (expressed as homopolymers) was accurately described in terms of two simultaneous irreversible first-order reactions, corresponding to two kinetically homogeneous polysaccharide fractions. The first and more reactive fraction accounted for about 30, 73 and 4% of total arabinan, galactan and mannan, respectively, and is rapidly lost during the first pulping period. The respective values of apparent activation energy were estimated as 65, 45 and 82 kJ mol^{-1}. The second fraction slowly degraded during pulping with two-order lower rate (activation energy of 88–98 kJ mol^{-1}). The degradation of uronic acids as well as the formation of hexenuronic acids was accurately described in terms of three simultaneous first-order reactions, corresponding to three kinetically homogeneous fractions. The overall rate of hexenuronic acid formation during ethanol-alkali pulping was found to be one-order lower of the overall rate of uronic acids degradation.
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Keywords: *Arundo donax* L.; Giant reed; Organosolv pulping; Ethanol-alkali delignification; Polysaccharide degradation; Kinetics; Non-cellulosic carbohydrates; Uronic acids

1. Introduction

Alkaline pulping (kraft and soda) is a dominating process in chemical pulp production from wood as well as non-wood (agrofibre) crops on the commercial scale. The drastic conditions of the principal pulping reaction of delignification also have an adverse effect on carbohydrates, causing a direct dissolution of the low-molecular polysaccharide fractions by the alkaline reaction solution under elevated temperatures and a substantial degradation and modification of the residual polysaccharides (Clayton et al., 1993), thereby affecting the yield and properties of the resulting pulps. The peeling reaction (or stepwise progressive removal of reducing end-groups) and the alkaline hydrolysis of glycosidic bonds (with random scission of the polysaccharide macromolecules) were identified as the main degradative reactions, which are responsible, respectively, for the carbohydrate losses and the drop in pulp viscosity during delignification (Fengel &Wegener, 1989; Sjöström, 1993).

Uronic acid moieties are also subjected to intensive destructive attack from the alkaline pulping solution, and about 75–90% (depending on pulped species and pulping method) of glucuronic acid (GlcA) and 4-*O*-methylglucuronic acid (MeGlcA) linked to heteroxylan are lost during pulping (Buchert, Teleman, Harjunpää, TenKanen, Viikari, & Vuorinen, 1995; Buchert, Laine, Tenkanen, Vuorinen, & Viikari, 1997; Chai, Luo, Yoon, & Zhu, 2001; Chai, Yoon, Zhu, Li, 2001; Shatalov & Pereira, 2004a), while the uronic acids (UA) of xylan were estimated to account for 80–90% of total carboxylic groups of conventional alkaline pulps (Laine, Buchert, Viikari, & Stenius, 1996). The residual MeGlcA in pulp are almost completely (by 83–88%) converted to 4-deoxy-β-L-*threo*-hex-4-enopyranosyluronic acid (hexenuronic acid or HexA) by β-elimination of

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methanol via the intermediate product 4-*O*-methyliduronic acid (Buchert et al., 1995; BucKert et al., 1997b; Shatalov & Pereira, 2004a; Teleman et al., 1995). Due to its unsaturated nature, HexA has a substantial detrimental effect on the following pulp bleaching, connected with increased consumption of bleaching chemicals, decreased pulp optical properties and deposit accumulation in the equipment (Buckert, Bergnor, Lindblad, Viikari, & Ek, 1997; Elsander, Ek, & Gellerstedt, 2000; Vuorinen, Fagerström, Buchert, Tenkanen, & Teleman, 1999).

Addition of aliphatic alcohols (such as methanol and ethanol) to alkaline pulping solution was shown to have a positive effect on carbohydrate preservation during pulping, thus improving pulp yield and papermaking properties (Nakano, Daima, Hosoya, & Ishizu, 1981; Shatalov & Pereira, 2002). Ethanol-reinforced alkaline pulping was successfully applied to potential agro-fibre crop *Arundo donax* L., or giant reed (Shatalov & Pereira, 2001, 2004b). The degradation kinetics of the principal polysaccharides (cellulose and xylan) of giant reed under conditions of ethanol-alkali delignification has been detailed in the first part of the present paper (Shatalov & Pereira, 2005b). In this second part, the results on degradation kinetics of the minor non-cellulosic carbohydrates and uronic acid moieties of giant reed during ethanol-alkali pulping are reported. As in the previous paper, the kinetics of polysaccharides degradation was described using a novel analytical approach based on properties of multi-component reaction system.

2. Experimental

2.1. Materials

Stems of *A. donax* L. (free from leaves) with origin from Greece (Athens) harvested in September 2002 were used in this study. For the kinetic study the stems were disintegrated manually to an approximate size of 0.5–1 cm length and 2–3 mm width.

Chemical analysis of the whole stem material (including nodes and internodes) revealed 21.12% of lignin (as Klason and acid-soluble), 31.06% of cellulose (as α-cellulose), 30.26% of hemicelluloses, 2.75% of uronic acids, 12.10% of extractives and 5.5% of ash with 1.2% of silicates as SiO_2 (Shatalov, Quilhó, & Pereira, 2001).

The chemicals used were of analytical grade purity and were supplied by Fluka, Sigma and Aldrich companies.

2.2. Methods

Ethanol-alkali pulping was carried out in 100 ml stainless steel autoclaves rotated in an oil bath, using 10 g (on oven-dry base) material on each pulping. The process variables were: time (0.5–360 min) and temperature (130, 140 and 150 °C). The cooking conditions as well as the pulp treatment after cooking were described in details elsewhere (Shatalov & Pereira, 2004b).

Carbohydrate composition was determined as the TMS-derivatives of monosaccharides after Saeman hydrolysis (Saeman, Moore, & Millet, 1963) by GC, using conditions described by Shatalov and Pereira (2005b). Content of individual homopolysaccharides was calculated by multiplying the content of the 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 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 et al., 1999).

The kinetic description of polysaccharide degradation was performed using an improved approach for the graphical differentiation of kinetic curves $\mathrm{Ln}\, P = f(t)$ of polysaccharide (P) removal with pulping time (t), first developed by Shatalov and Pereira (2005a) for delignification reaction and then adapted for carbohydrate degradation in the previous part of the present paper (Shatalov & Pereira, 2005b). The method is based on successive elimination from the curve $\mathrm{Ln}\, P = f(t)$ of the contributions from the individual polysaccharide structures (or groups of different structures with close reactivity, i.e. polysaccharide fractions P_1, $P_2 \ldots P_n$, corresponding to the kinetically homogeneous systems) in order of increasing reactivity (see Shatalov & Pereira, 2005b). Thus, the kinetics of polysaccharide degradation as a whole can be described through the precise quantification of the various kinetically homogeneous polysaccharide fractions and of the specific degradation rate constants (k_1, $k_2 \ldots k_n$) for each individual fraction.

The activation energy (E_a) of polysaccharide degradation was calculated for each kinetically homogeneous polysaccharide fraction from the logarithmic form of the Arrhenius equation ($\ln k = \ln A - E_a/RT$, where k is the specific degradation rate constant; A is the Arrhenius constant; R is the universal gas constant (8.314 J mol^{-1} K^{-1}); T is the absolute temperature) by plotting $\ln k$ against $1/T$.

3. Results and discussion

The kinetics of polysaccharide degradation during ethanol-alkali delignification of giant reed was assessed through the change in residual carbohydrate content in pulp, using a novel approach for graphical differentiation of kinetic curves, as it was mentioned in the first part of the present paper (Shatalov & Pereira, 2005b). For the sake of simplicity, because of difficulties to establish exactly the origin of monosaccharide residues during quantification, all

residual carbohydrates were expressed as the corresponding homopolysaccharides.

3.1. Minor carbohydrates

Minor non-cellulosic carbohydrates of giant reed are composed of arabinosyl, galactosyl, and mannosyl monosaccharide residues and account for only about 5% of total carbohydrates, or 2.7% of oven-dry cell-wall material.

3.1.1. Arabinan

Arabinose is the most abundant of these three monosaccharides (about 2.8% of total carbohydrates, or 1.5% of oven-dry reed). The source of arabinose in *A. donax* is the complex polysaccharide arabino-4-*O*-methylglucuronoxylan, or the homopolymer arabinan of the pectin substances (Joseleau & Barnoud, 1975, 1976). Considering the xylose content in giant reed (approx. 20.3%, Shatalov & Pereira, 2005b) and the reported ratio between xylosyl and arabinosyl residues in heteroxylan (9.20/0.66, Joseleau & Barnoud, 1976), the heteroxylan-derived arabinose was estimated to cover about 95% of total detected arabinose.

The (1→3)-attachment of arabinosyl substituent to the xylan backbone is very sensitive to degradation in hot alkaline solution (Rydholm, 1965), and arabinose is therefore easily removed from the xylan during alkaline pulping. As can be seen from Fig. 1, about 45% of the initial arabinose (expressed as an arabinan) is lost during ethanol-alkali pulping of giant reed to target degree of delignification (0.9 in respect of initial reed lignin) under 130–150 °C. This value of arabinan losses is substantially lower than that reported for traditional alkaline processes (e.g. 71% for wood kraft pulping, Clayton et al., 1993) and should be the result of the above mentioned general protective effect of alcohol on carbohydrate polymers against degradation in alkaline pulping medium (Shatalov & Pereira, 2002).

Kinetic analysis of arabinan removal showed the general heterogeneity of the degradation reaction and the presence of two kinetically distinguishable polysaccharide fractions with different reactivity (Fig. 2 and Table 1). The first and more reactive arabinan fraction (Ara_1) accounts for about 30% of the original polysaccharide and completely degrades during the first-sixth of pulping time independently of the process temperature (i.e. during approx. 60, 30 and 15 min under 130, 140 and 150 °C, respectively). The reaction rate is close to that obtained for the first xylan fraction (Shatalov & Pereira, 2005b) and two times lower than the delignification rate during the initial stage (Shatalov & Pereira, 2005a). The second arabinan fraction (Ara_2), amounting to about 70% of the total polysaccharide, continuously degrades during pulping with a two-order lower rate that is three times higher than that for the second xylan fraction and comparable with the residual delignification rate.

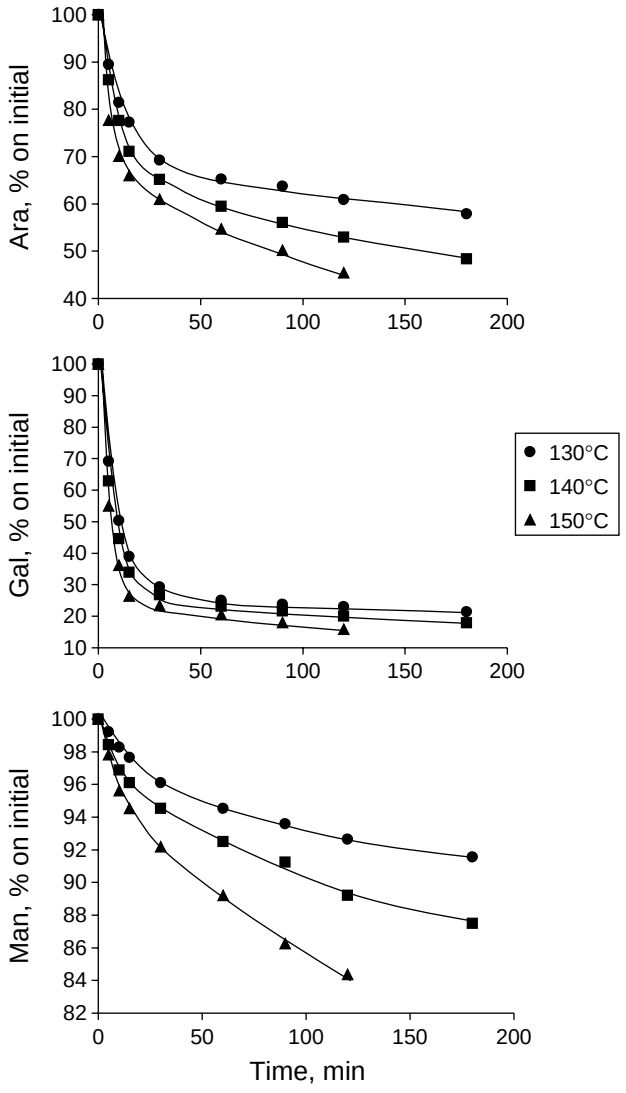

Fig. 1. Content (% on initial content in raw material) of arabinan, galactan and mannan (expressed as homopolysaccharides and denoted by *Ara*, *Gal* and *Man*, respectively) in ethanol-alkali pulps from giant reed as a function of pulping time and temperature ($EtOH/H_2O = 40/60$; 25% NaOH).

The apparent activation energy of arabinan removal (Fig. 3) was estimated for both fractions respectively as 65.2 and 87.7 kJ mol^{-1} and was generally close to the reported values for the peeling reaction (88.6 kJ mol^{-1}, Lai & Sarkanen, 1969). It is likely that some physical dissolution of heteroxylan in the first pulping period (Genco, Busayasakul, Medhora, & Robbins, 1990), along with the fast removal of pectins, decrease the activation energy of the degradation of the first arabinan fraction.

Based on the kinetic data (Table 1), the arabinan degradation during ethanol-alkali delignification of giant reed can be described in terms of two simultaneous irreversible first-order reactions, corresponding to the removal of two kinetically homogeneous fractions, and expressed by the following Eqs. (1)–(3), respectively for

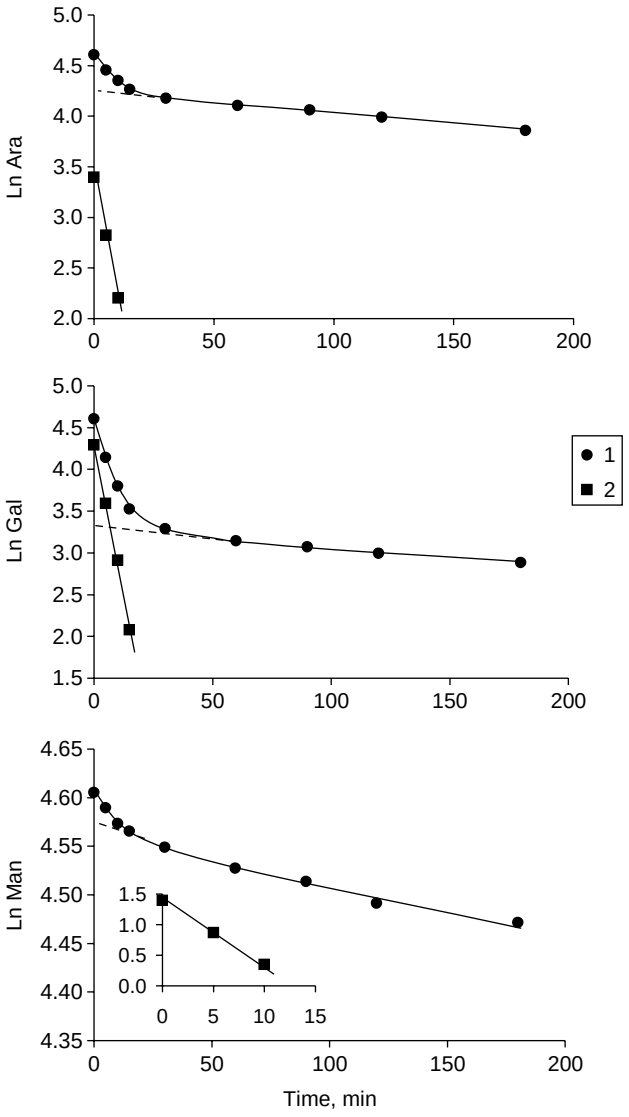

Fig. 2. Kinetics of arabinan, galactan and mannan degradation during ethanol-alkali delignification of giant reed at 140 °C (EtOH/H_2O=40/60; 25% NaOH), where (1)—experimental kinetic curve of polysaccharide removal Ln P=Ln(P_1+P_2)=$f(t)$; (2)—calculated kinetic curve Ln(P−P_2)=Ln P_1=$f(t)$ after P_2-fraction subtraction (this curve is given on an enlarged scale in the bottom plot of mannan removal); P, P_1, P_2—the total polysaccharide, the first polysaccharide fraction and the second polysaccharide fraction content in pulp, respectively.

process temperature of 130, 140 and 150 °C:

$$Ara_t = 30.59(1 - \exp(-0.0933t)) + 69.41(1 - \exp(-0.001011t)) \quad (1)$$

$$Ara_t = 29.89(1 - \exp(-0.1197t)) + 70.11(1 - \exp(-0.002183t)) \quad (2)$$

$$Ara_t = 30.24(1 - \exp(-0.2392t)) + 69.76(1 - \exp(-0.003583t)) \quad (3)$$

Table 1
Kinetic data on arabinan degradation during ethanol-alkali delignification of giant reed: content of kinetically homogeneous fractions (*Ara*) and their specific reaction rate constant (k) and apparent activation energy (E_a) (EtOH/H_2O=40/60; 25% NaOH on o.d. reed; liquid-to-solid ratio=6/1)

T (°C)	Fraction 1		Fraction 2	
	Ara_1 (%)	k_1 (min^{-1})	Ara_2 (%)	k_2 (min^{-1})
130	30.59	0.0933	69.41	0.1011×10^{-2}
140	29.89	0.1197	70.11	0.2183×10^{-2}
150	30.24	0.2392	69.76	0.3583×10^{-2}
Mean content	30.24	–	69.76	–
E_a (kJ mol^{-1})	65.20		87.65	

where Ara_t is a total amount of arabinan removed at pulping time t.

The experimental data on arabinan conversion during pulping were plotted versus simulated ones, calculated by

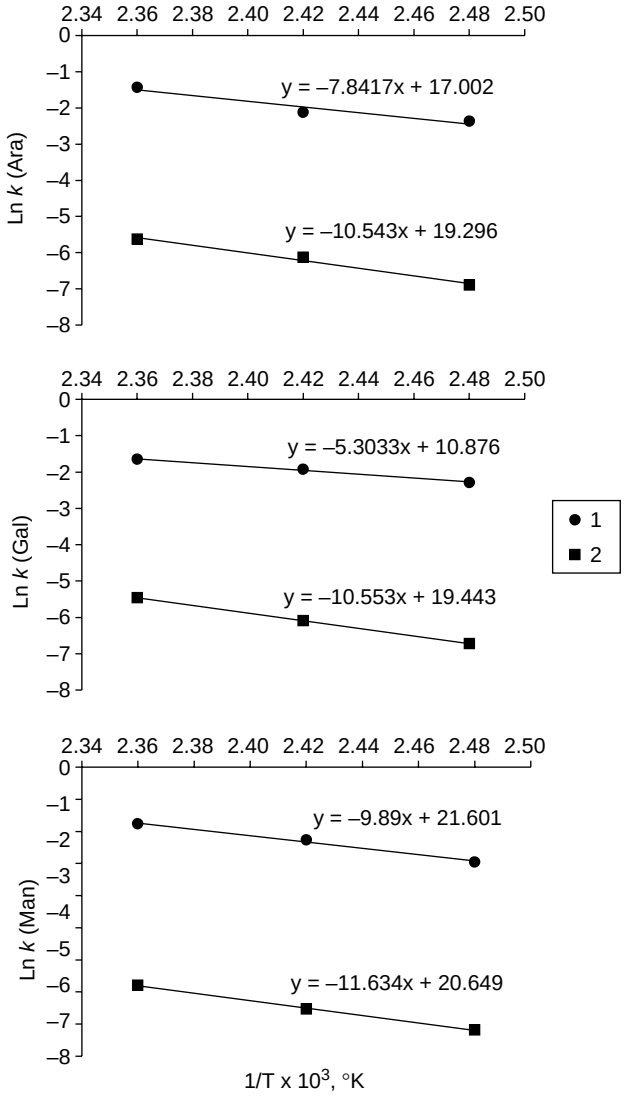

Fig. 3. Logarithm of the effective rate constants of arabinan, galactan and mannan degradation vs. reciprocal reaction temperature for the first (1) and the second (2) polysaccharide fractions.

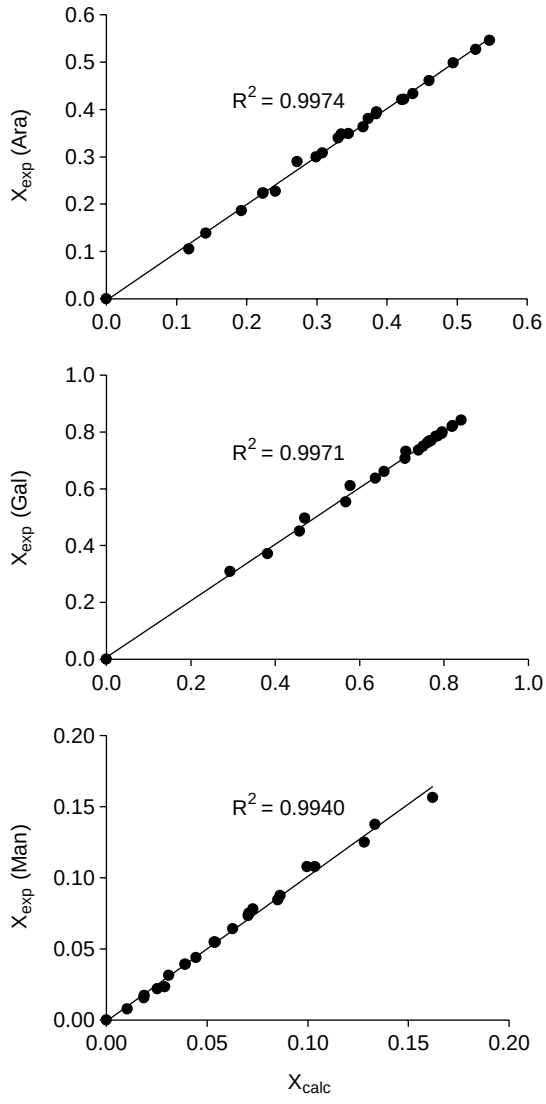

Fig. 4. Comparison of experimental and simulated data on arabinan, galactan and mannan conversion (X) during ethanol-alkali pulping of giant reed at temperature range of 130–150 °C. Where $X = P_t/P_o$ and P_t; P_o—current and initial polysaccharide content.

Eqs. (1)–(3). As can be seen from Fig. 4, the data from all cooking runs fall on a straight line with R^2-value of 0.9974, pointing thereby to the good data reproducibility and the validity of the applied kinetic model.

3.1.2. Galactan

Galactose accounts for about 1% of total monosaccharides of giant reed, covering thereby only 0.6% of oven-dry cell-wall material. The galactosyl residues in giant reed form mainly the structure of the water-soluble polysaccharide galactan in pectin substances, which are normally rapidly and completely lost during conventional alkaline pulping (Clayton et al., 1993). In part, galactosyl residues can also be the structural constituents of the mixed mannans, which were detected in small quantities in some grasses (Rydholm, 1965).

Table 2
Kinetic data on galactan degradation during ethanol-alkali delignification of giant reed: content of kinetically homogeneous fractions (*Gal*) and their specific reaction rate constant (k) and apparent activation energy (E_a) (EtOH/H_2O = 40/60; 25% NaOH on o.d. reed; liquid-to-solid ratio = 6/1)

T (°C)	Fraction 1		Fraction 2	
	Gal_1 (%)	k_1 (min^{-1})	Gal_2 (%)	k_2 (min^{-1})
130	73.42	0.1010	26.58	0.1196×10^{-2}
140	73.16	0.1460	26.84	0.2264×10^{-2}
150	73.56	0.1909	26.44	0.4243×10^{-2}
Mean content	73.38	–	26.62	–
E_a (kJ mol^{-1})	44.09		87.74	

As illustrated in Fig. 1, the addition of ethanol to the alkaline reaction solution does not change the general tendency of fast galactose degradation during pulping, but this degradation is less intensive in comparison with simple alkaline system and about 20% of galactose (expressed as a galactan) is retained in pulp. Kinetic analysis revealed two galactan fractions (Gal_1 and Gal_2) degrading with different rate during pulping (Fig. 2 and Table 2). About 73% of initial galactan (first fraction) is completely lost during the first-third of pulping time. The degradation rate of this galactan fraction is similar to that of the first xylan fraction and two times lower of the initial delignification rate, while the degradation rate of the second galactan fraction (approx. 27% of initial polysaccharide) is close to the residual delignification rate.

The activation energy of degradation of both galactan fractions (Fig. 3) was found respectively as 44.1 and 87.7 kJ mol^{-1}. The low first value obviously resulted from the high solubility of the pectin galactan. The activation energy of the second fraction is close to that reported for the peeling reaction (88.6 kJ mol^{-1}, Lai & Sarkanen, 1969) and, probably, related to mannan-linked galactose.

Similar to arabinan, the galactan degradation during pulping can be described by two simultaneous first-order reactions corresponding to removal of two revealed polysaccharide fractions and expressed by the following Eqs. (4)–(6) in the tested range of pulping temperature of 130–150 °C, respectively:

$$Gal_t = 73.42(1 - \exp(-0.1010t)) + 26.58(1 - \exp(-0.001196t)) \quad (4)$$

$$Gal_t = 73.16(1 - \exp(-0.1460t)) + 26.84(1 - \exp(-0.002264t)) \quad (5)$$

$$Gal_t = 73.56(1 - \exp(-0.1909t)) + 26.44(1 - \exp(-0.004243t)) \quad (6)$$

In Fig. 4, the simulated data on galactan conversion during pulping (calculated by Eqs. (4)–(6)) are compared with the experimental ones ($R^2 = 0.9971$), suggesting high

reproducibility of experimental data by kinetic model, that is an adequate description of the real process.

3.1.3. Mannan

Mannose is a basic structural element of such plant heteropolysaccharides as glucomannan and galactoglucomannan, which are common for wood hemicelluloses (Fengel & Wegener, 1989), but present in very small (trace-) quantity, or even absent in many herbaceous species used in papermaking (Atchison, 1993). In giant reed, the mannosyl residuals (expressed as a homopolymer mannan) account for only about 1% of total polysaccharides, or about 0.5% of the cell-wall material.

As evident from Fig. 1, this fairly small proportion of mannan in *A. donax* is very resistant to degradation under conditions of ethanol-alkali delignification, and about 86–87% of original polysaccharide is retained after complete pulping to target degree of delignification at 130–150 °C. The remarkable stability of mannan to alkaline degradation was previously examined using a model compound of mannobiose. The lower (in comparison with other glycosides) rate of peeling reaction was attributed to a slower isomerization of mannoside to fructose moiety (Lai, 1973). The presence of 2-hydroxyl in *cis*-position makes mannosidic bonds much more stable to alkaline hydrolysis (Hon & Shiraishi, 1991).

The kinetic data on mannan degradation are shown in Fig. 2 and Table 3. Two-step analysis was performed to complete the kinetic description and two kinetically homogeneous polysaccharide fractions were revealed. Generally, mannan degradation during ethanol-alkali pulping is rather uniform. Only about 4% of total polysaccharide (attributed to the first and more reactive fraction, Man_1) is rapidly and completely degraded during the first-twelfth of pulping time (i.e. during 30, 15 and 7 min at 130, 140 and 150 °C, respectively), with two times higher rate than that of the first cellulose fraction, but two-three times lower of the degradation rate of the first xylan fraction and of the initial delignification rate (Shatalov & Pereira, 2005a,b). This mannan fraction could be associated with the presence in the cell-wall tissue of the highly soluble galactoglucomannan polymers. The major portion of mannan (Man_2), accounting for about 96% of original polysaccharide and, obviously, involving the less reactive glucomannan polymers, is being removed slowly with pulping progress. The effective degradation rate of this mannan fraction is comparable with that of the second (less reactive) xylan fraction and is one-order lower of the residual delignification rate.

Table 3
Kinetic data on mannan degradation during ethanol-alkali delignification of giant reed: content of kinetically homogeneous fractions (*Man*) and their specific reaction rate constant (k) and apparent activation energy (E_a) ($EtOH/H_2O = 40/60$; 25% NaOH on o.d. reed; liquid-to-solid ratio = 6/1)

T (°C)	Fraction 1		Fraction 2	
	Man_1 (%)	k_1 (min^{-1})	Man_2 (%)	k_2 (min^{-1})
130	3.94	0.0520	96.06	0.0278×10^{-2}
140	4.03	0.1030	95.97	0.0533×10^{-2}
150	4.13	0.1704	95.87	0.1122×10^{-2}
Mean content	4.03	–	95.97	–
E_a (kJ mol^{-1})	82.23		96.73	

The values of apparent activation energy of fractions degradation were estimated respectively as 82.2 and 96.7 kJ mol^{-1} (Fig. 3), and were generally close to the reported values of polysaccharide peeling reaction (84.4–102.4 kJ mol^{-1}, Lai & Sarkanen, 1967).

Considering the data of kinetic analysis (Table 3), the mannan degradation during ethanol-alkali pulping can be described by the following Eqs. (7)–(9) (respectively for 130, 140 and 150 °C):

$$Man_t = 3.94(1 - \exp(-0.0520t)) + 96.06(1 - \exp(-0.000278t)) \quad (7)$$

$$Man_t = 4.03(1 - \exp(-0.1030t)) + 95.97(1 - \exp(-0.000533t)) \quad (8)$$

$$Man_t = 4.13(1 - \exp(-0.1704t)) + 95.87(1 - \exp(-0.001122t)) \quad (9)$$

The accuracy of the kinetic description of mannan degradation is evident from Fig. 4, where the experimental and calculated (by Eqs. (7)–(9)) data on mannan conversion during pulping correlate with $R^2 = 0.9940$.

3.2. Uronic acids

The principal acidic polysaccharide of giant reed is an arabino-4-*O*-methylglucuronoxylan, with 4.5% of MeGlcA (Joseleau & Barnoud, 1975, 1976). The content of heteroxylan in the reed used in this study accounts for about 25% (on oven-dry basis), what covers about 90% of the total non-cellulosic carbohydrates (Shatalov & Pereira, 2002). Thus, when considering the UA of giant reed, we actually refer to MeGlcA and to its modification products generated during the pulping, such as HexA. The term 'UA' is used here because of the applied procedure of integrated quantification of the all uronic acid moieties in the pulp.

The detailed chemical behaviour of total UA and of HexA of *A. donax* during ethanol-alkali delignification has been reported elsewhere (Shatalov & Pereira, 2004a). However, the kinetics of UA degradation and of HexA formation were studied using the traditional consecutive kinetic model with rough division of the kinetic curve on a few periods (stages) considered to a first approximation as linear, followed by application of the first-order kinetics to each reaction stage (Shatalov & Pereira, 2004a). To avoid the obvious limitations of the consecutive model and the associated erroneous estimation of the kinetic parameters, we consider here the application of the novel substantially

improved kinetic approach based on properties of multi-component reaction system.

As illustrated in Fig. 5, a substantial degradation of UA moieties (up to 90%) takes place during ethanol-alkali pulping of giant reed at 130–150 °C for target degree of delignification. At the same time, the progressive formation of HexA starts from the beginning of pulping, converting almost completely (by 84%) the residual UA (or residual MeGlcA side groups of heteroxylan) to HexA in the final pulps.

These two parallel UA reactions (i.e. UA degradation and UA modification to HexA), that take place concurrently during pulping, can be analysed using two kinetic curves, respectively $\mathrm{Ln}\ UA_t = f(t)$ and $\mathrm{Ln}(UA_o - HexA_t) = f(t)$, where UA_o is the initial content of UA in reed, UA_t and $HexA_t$ are the running content of UA and HexA in pulp at time t. The validity of the second equation follows from the reaction scheme of UA conversion to HexA (Shatalov & Pereira, 2004a), where one mole of MeGlcA forms one mole of HexA.

The results of kinetic analysis are shown in Fig. 6 and Tables 4 and 5. A three-step analysis was sufficient to complete the kinetic description of both reactions and three kinetically homogeneous UA as well as HexA fractions

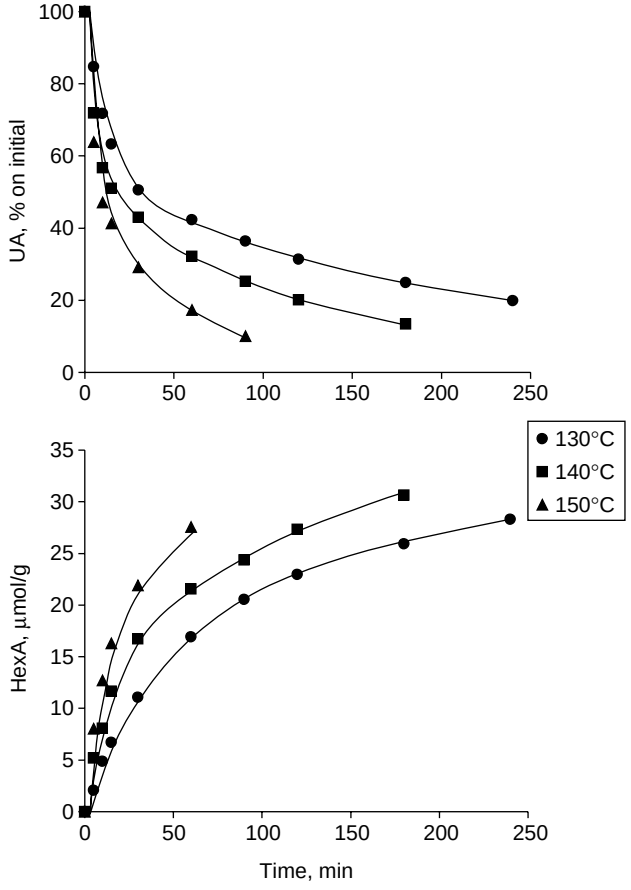

Fig. 5. Content of total uronic (% on initial content in raw material) and hexenuronic (µmol per gram of pulp) acids (denoted by *UA* and *HexA*, respectively) in ethanol-alkali pulps from giant reed as a function of pulping time and temperature ($EtOH/H_2O = 40/60$; 25% NaOH).

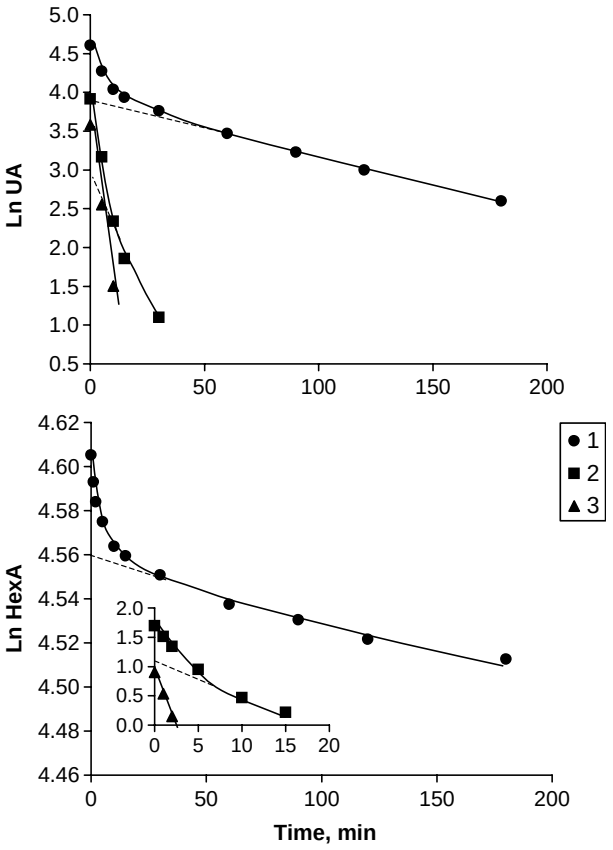

Fig. 6. Kinetics of uronic acids degradation (the upper plot) and uronic acids conversion to hexenuronic acid (the lower plot) during ethanol-alkali delignification of giant reed ($EtOH/H_2O = 40/60$; 25% NaOH), where (1)—experimental kinetic curves, respectively, of *UA* removal $\mathrm{Ln}\ UA = \mathrm{Ln}(UA_1 + UA_2 + UA_3) = f(t)$ and *HexA* formation $\mathrm{Ln}\ HexA = \mathrm{Ln}(HexA_1 + HexA_2 + HexA_3) = f(t)$; (2)—calculated kinetic curves, respectively, $\mathrm{Ln}(UA - UA_3) = \mathrm{Ln}(UA_1 + UA_2) = f(t)$ after UA_3-fraction subtraction and $\mathrm{Ln}(HexA - HexA_3) = \mathrm{Ln}(HexA_1 + HexA_2) = f(t)$ after $HexA_3$-fraction subtraction; (3)—calculated kinetic curves, respectively, $\mathrm{Ln}(UA - UA_3 - UA_2) = \mathrm{Ln}\ UA_1 = f(t)$ after UA_3- and UA_2-fractions subtraction and $\mathrm{Ln}(HexA - HexA_3 - HexA_2) = \mathrm{Ln}\ HexA_1 = f(t)$ after $HexA_3$- and $HexA_2$-fractions subtraction; UA, UA_1, UA_2, UA_3 and $HexA$, $HexA_1$, $HexA_2$, $HexA_3$—the total, the first fraction, the second fraction and the third fraction content respectively of *UA* and *HexA* in pulp. The curves (2) and (3) are given on an enlarged scale in the bottom plot of *HexA* formation.

were detected and accurately quantified. The first UA fraction (UA_1) accounts for about 36% of total UA and is rapidly removed from reed during the first-twelfth of pulping time, independently of process temperature. The degradation of this UA fraction proceeds with almost the same rate as the degradation of the first (more reactive) xylan fraction (Shatalov & Pereira, 2005b) and close to the initial delignification rate (Shatalov & Pereira, 2005a). During the same pulping period, about 23% of residual UA in pulp are converted to HexA with two times higher rate, forming the first HexA fraction ($HexA_1$) that accounts for about 30% of total HexA generated during pulping.

The degradation of the second UA fraction (UA_2, approx. 14%) as well as the formation of the second HexA fraction ($HexA_2$, approx. 35% of total HexA, or 29% of residual UA)

Table 4
Kinetic data on uronic acids degradation during ethanol-alkali delignification of giant reed: content of kinetically homogeneous fractions (*UA*) and their specific reaction rate constant (k) and apparent activation energy (E_a) (EtOH/H_2O = 40/60; 25% NaOH on o.d. reed; liquid-to-solid ratio = 6/1)

T (°C)	Fraction 1		Fraction 2		Fraction 3	
	UA_1 (%)	k_1 (min^{-1})	UA_2 (%)	k_2 (min^{-1})	UA_3 (%)	k_3 (min^{-1})
130 °C	36.65	0.1083	14.44	0.0250	48.91	0.3748×10^{-2}
140 °C	35.95	0.2060	14.15	0.0517	49.90	0.7389×10^{-2}
150 °C	35.37	0.2653	14.73	0.1027	49.90	1.7851×10^{-2}
Mean content	35.99	–	14.44	–	49.57	–
E_a (kJ mol^{-1})	62.06		97.99		108.14	

Table 5
Kinetic data on hexenuronic acids formation during ethanol-alkali delignification of giant reed: content of kinetically homogeneous fractions (*HexA*) and their specific reaction rate constant (k) and apparent activation energy (E_a) (EtOH/H_2O = 40/60; 25% NaOH on o.d. reed; liquid-to-solid ratio = 6/1)

T (°C)	Fraction 1		Fraction 2		Fraction 3	
	$HexA_1$ (%)	k_1 (min^{-1})	$HexA_2$ (%)	k_2 (min^{-1})	$HexA_3$ (%)	k_3 (min^{-1})
130 °C	26.41	0.1704	34.39	0.0254	39.20	0.0133×10^{-2}
140 °C	27.80	0.3760	33.90	0.0600	38.31	0.0208×10^{-2}
150 °C	29.35	0.7680	37.03	0.1030	33.63	0.0467×10^{-2}
Mean content	27.85	–	35.11	–	37.05	–
E_a (kJ mol^{-1})	104.32		97.00		87.01	

is completed during the first-third of pulping time, with 3–6 times lower rate in comparison with the first fraction.

The major portion of UA residuals (about 50%) degrades with constant one-order lower rate through the whole pulping, forming the last and less reactive UA fraction (UA_3). The degradation rate of this UA fraction is however one-order higher than that of the second (and less reactive) xylan fraction and three-times higher of the residual delignification rate (Shatalov & Pereira, 2005a,b). About 37% of total HexA (the third $HexA_3$ fraction) are continuously formed during pulping with very slow rate, which is more than two-orders lower than that of the second HexA fraction. Thus, some portion of the residual MeGlcA in pulp xylan (about 31%) is fairly resistant to β-elimination reaction and is slowly converted to HexA with one-order lower rate than the rate of MeGlcA degradation reaction. The variation in reactivity of MeGlcA substituent in heteroxylan (which is responsible for existence of UA and HexA fractions) is obviously related with the irregular chemical structure of this complex polysaccharide and with the general morphological heterogeneity of the cell-wall tissue, causing the different accessibility of MeGlcA moieties to chemicals during pulping.

The proportion of UA and HexA fractions was somewhat different from that found in the previous study using traditional consecutive kinetic model (Shatalov & Pereira, 2004a). The excluded possibility of fractions overlapping during quantification by the new analytical approach allows determining the fractions content more precisely, improving thereby the accuracy of the kinetic description as a whole.

The activation energy was found from Fig. 7 and the values were estimated as 62.1, 98.0, and 108.1 kJ mol^{-1} and 104.3, 97.0, and 87.0 kJ mol^{-1} for the first, the second and the third UA and HexA fractions, respectively. The somewhat low value of the first UA fraction (62.1 kJ mol^{-1}), which is however close to that of the first Ara and Xyl fractions (62.5 and 74.4 kJ mol^{-1}, respectively), is probably caused by a partial dissolution of low-molecular

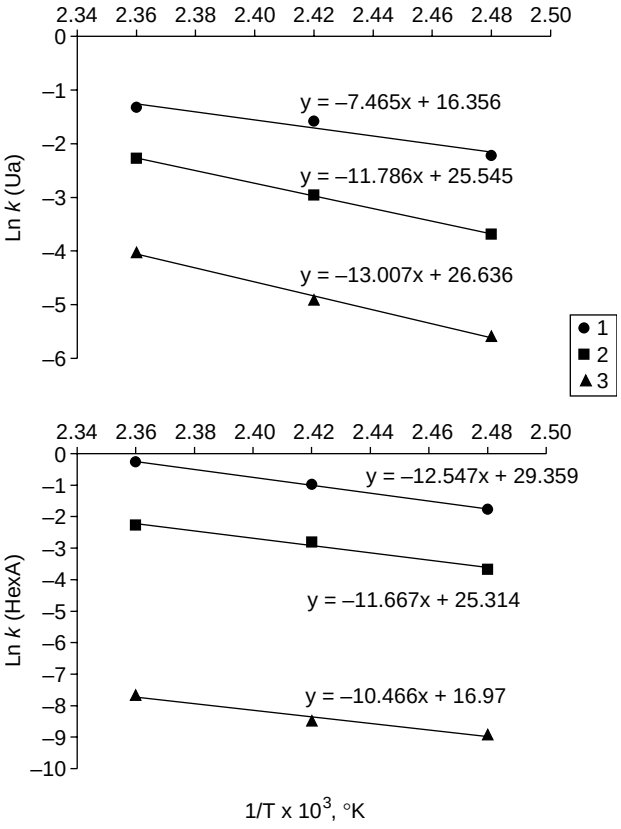

Fig. 7. Logarithm of the effective rate constants of uronic acids degradation and hexenuronic acid formation vs. reciprocal reaction temperature for the first (1), the second (2) and the third (3) fractions.

heteroxylan fractions during the first period of alkaline pulping, as first noted by Buchert et al. (1995).

To summarise the data of kinetic analysis, the UA degradation and HexA formation during ethanol-alkali pulping of giant reed can be modelled in terms of three simultaneous irreversible first-order reactions and described by the following equations for pulping temperature of 130, 140 and 150 °C, respectively:

$$UA_t = 36.35(1 - \exp(-0.1083t)) + 14.44(1 - \exp(-0.0250t)) + 48.91(1 - \exp(-0.003748t)) \quad (10)$$

$$UA_t = 35.95(1 - \exp(-0.2060t)) + 14.15(1 - \exp(-0.0517t)) + 49.90(1 - \exp(-0.007389t)) \quad (11)$$

$$UA_t = 35.37(1 - \exp(-0.2653t)) + 14.73(1 - \exp(-0.1027t)) + 49.90(1 - \exp(-0.017851t)) \quad (12)$$

$$HexA_t = 26.41(1 - \exp(-0.1704t)) + 34.39(1 - \exp(-0.0254t)) + 39.20(1 - \exp(-0.000133t)) \quad (13)$$

$$HexA_t = 27.80(1 - \exp(-0.3760t)) + 33.90(1 - \exp(-0.0600t)) + 38.31(1 - \exp(-0.000208t)) \quad (14)$$

$$HexA_t = 29.35(1 - \exp(-0.7680t)) + 37.03(1 - \exp(-0.1030t)) + 33.63(1 - \exp(-0.000467t)) \quad (15)$$

The comparison of experimental and simulated (by Eqs. (10–15)) data on UA conversion during pulping (Fig. 8) showed the high data reproducibility by applied kinetic model and the accuracy of the kinetic description of UA reactions as a whole.

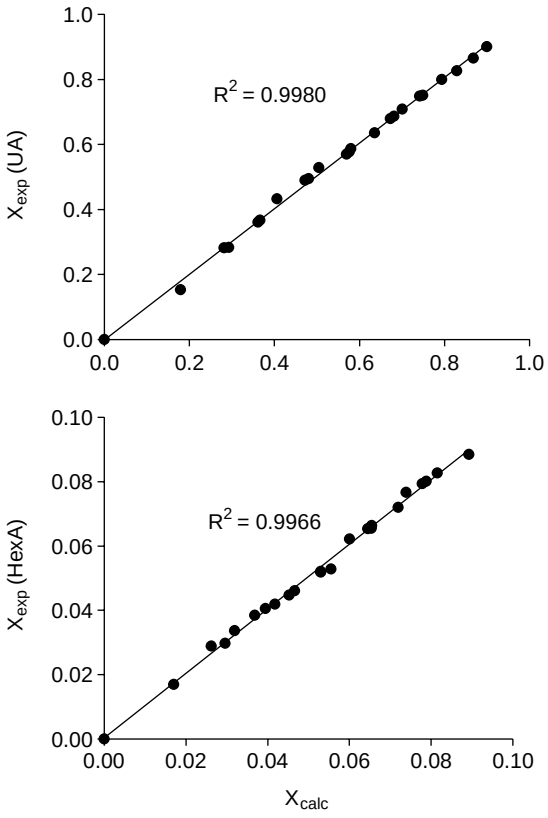

Fig. 8. Comparison of experimental and simulated data on uronic acids conversion (X) to degradation product (upper plot) and to hexenuronic acid (lower plot) during ethanol-alkali pulping of giant reed at temperature range of 130–150 °C. Where $X = UA_t/UA_o$ and UA_t; UA_o—current and initial content of uronic acids.

4. Conclusions

The degradation kinetics of the minor neutral carbohydrates (composed of arabinosyl, galactosyl and mannosyl residuals) of giant reed during ethanol-alkali delignification can be accurately described in terms of two simultaneous first-order reactions, corresponding to two kinetically homogeneous carbohydrate fractions. The first and more reactive fraction (accounting for about 30, 73 and 4%, respectively of arabinan, galactan and mannan, expressed as the homopolysaccharides) is rapidly removed during the first pulping period, while the degradation of the second and less reactive fractions slowly proceeds with pulping with two-order lower rate.

The degradation kinetics of uronic acid moieties (composed mainly of methyl-glucuronic acid linked to heteroxylan and its modification product, hexenuronic acid) can be accurately described in terms of three simultaneous first-order reactions, corresponding to three kinetically homogeneous fractions. The degradation of the first two uronic acids fractions (about 50% of total UA) as well as the formation of the first two hexenuronic acid fractions (about 63% of total formed HexA) proceeds with similar rates and is completed within the first-third of pulping time. The last (less reactive) HexA fraction is formed with one-order lower rate than the degradation rate of the last UA fraction.

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