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Carbohydrate Polymers 59 (2005) 435–442

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Kinetics of polysaccharide degradation during ethanol–alkali delignification of giant reed—Part 1. Cellulose and xylan

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Received 12 July 2004; revised 21 September 2004; accepted 25 October 2004
Available online 2 December 2004

Abstract

The degradation kinetics of the principal polysaccharides (cellulose and xylan) of the agro-fibre crop *Arundo donax* L. (giant reed) during ethanol–alkali delignification is reported. Based on the properties of a multi-component reaction system, the degradation kinetics of both polysaccharides was accurately described in terms of two simultaneous irreversible first-order reactions corresponding to removal of two kinetically homogeneous fractions. The moderate cellulose losses during pulping (about 4.5%) result mainly from the removal of the more reactive cellulose fraction, that accounted for 4% of initial cellulose. The bulk of the cellulose (96%) degrades slowly with three orders lower rate with pulping progress. The apparent activation energy of cellulose fractions degradation was estimated as 105.2 and 106.5 kJ mol^{-1}, respectively. Substantial loss of xylan during pulping (about 55%, as a homoxylan) is caused by fast removal of the first very reactive fraction, covering about 48% of total xylan. The degradation rate of the second xylan fraction is only one order higher of the bulk cellulose degradation. The activation energy of xylan fractions degradation was found as 74.4 and 140.9 kJ mol^{-1}, respectively.

Keywords: *Arundo donax* L.; Giant reed; Organosolv pulping; Ethanol–alkali delignification; Polysaccharide degradation; Kinetics; Cellulose; Xylan

1. Introduction

Carbohydrate dissolution and degradation are undesirable side-reactions of the pulping process, taking place simultaneously with the delignification reaction and decreasing substantially pulp yield and papermaking properties. The alkaline degradation of carbohydrates is an important factor of the conventional kraft and soda industrial pulping technologies, affecting strongly the process efficiency and economics.

A number of different degradative reactions have effect on carbohydrates in alkaline medium under elevated process temperatures. In the first pulping period, at a high alkalinity and low temperature (about 100 °C), a direct dissolution of the low-molecular non-cellulosic polysaccharides occurs. At the same time, a stepwise progressive removal of reducing end-groups of the remaining polysaccharides (so-called ‘peeling’) starts and proceeds with pulping extension. At higher temperatures, an alkaline hydrolysis of glycosidic bonds with random scission of polysaccharide macromolecules takes place, thereby allowing secondary peeling reactions. The peeling reaction is responsible for yield losses during pulping, while the alkaline hydrolysis leads to a drop in the degree of polymerisation, affecting the strength properties of the pulp (Fengel & Wegener, 1984; Rydholm, 1965; Sjöström, 1993).

The chemical and morphological heterogeneity of plant carbohydrates, caused by a substantial compositional and structural variability of hemicellulosic polysaccharides and, in part, by the complex supramolecular organisation of cellulose consisting of regions with different molecular order (or degree of cristallinity), lead to kinetic heterogeneity during chemical processing. In alkaline pulping, the kinetic description of polysaccharide degradation is normally based on the division of the entire process on a few phases (stages) with different reactivity, followed by direct application of the first-order kinetic model to each individual stage, similar to kinetics of delignification

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doi:10.1016/j.carbpol.2004.10.010

(De Groot, Van Dam, & Van't Riet, 1995; Miranda & Pereira, 2002; Young & Liss, 1978). In this way, only the last reaction stage (involving the less reactive residual structures, as a kinetically homogeneous system) can be accurately described, since the direct application of the first-order kinetics to the earlier reaction stages, when simultaneous degradation of the structural elements with different reactivity takes place, is not so correct and is a source of errors during kinetic calculations.

Recently, the application of ecologically friendly organic solvent-based (organosolv) pulping technologies to potential agro-fibre crop *Arundo donax* L. (or giant reed) has been studied (Shatalov & Pereira, 2000, 2001). The ethanol–alkali pulping was selected as a more promising process (Shatalov & Pereira, 2004a). The influence of process variables on carbohydrates and uronic acids of giant reed in ethanol–alkali reaction medium has been detailed elsewhere (Shatalov & Pereira, 2002, 2004b). The present paper, consisting of two separate parts, reports the results on the kinetic study of carbohydrate degradation under ethanol–alkali pulping conditions using a novel approach for kinetic description based on properties of multi-component reaction system. The degradation kinetics of cellulose and xylan (as the principal polysaccharides of *A. donax*) is being considered in the first part, while the second part considers the degradation kinetics of the minor non-cellulosic polysaccharides and uronic acid moieties.

2. Experimental

2.1. Materials

The stems of *Arundo donax* L. with origin from Greece (Athens) were used in this study. The stems were free from leaves and were harvested in September 2002.

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). For the kinetic study the stems were disintegrated manually to an approximate size of 0.5–1 cm length and 2–3 mm width and the moisture content was determined according to TAPPI standards.

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

2.2. Methods

2.2.1. Ethanol–alkali pulping

Kinetic pulping experiments were 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 were as follows: alkali charge (as NaOH) 25% on oven-dry material, ethanol content 40% (by vol.) and liquor-to-material ratio 6/1 (ml g^{-1}). The delignification reaction was terminated by immediate placing the autoclaves into an ice-bath. After cooking the pulps were defibrated, thoroughly washed and weighed for yield determination.

The pulping heating-up period was approximately 1 min and was determined by direct measurement of the reaction mixture temperature inside the autoclaves by contact thermometer built into the top of autoclave.

Two or three experiments were done for each condition set to obtain reproducible data on pulp yield and to fit the weight loss curve. Two independent reaction series were carried out under the same conditions to be used for kinetic modelling and validation tests.

2.2.2. Carbohydrate 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).

2.2.3. Kinetic model

For the kinetic description of polysaccharide degradation during ethanol–alkali pulping, an improved approach for graphical differentiation of kinetic curves ln $P=f(t)$ of polysaccharide (P) removal with pulping time (t) has been applied (Shatalov & Pereira, 2004c). Considering the macromolecular structure of a polysaccharide as a complex of n (where $n=1,2,\ldots,n-1,n$) individual structural elements (i.e. $P_1,P_2,\ldots,P_{n-1},P_n$) with different reactivity (fractions), the polysaccharide degradation can be assumed as a complex of n irreversible first-order reactions with similar final product, (where $K_1>K_2>\ldots>K_{n\text{-}1}>K_n$ are the specific reaction rate constants) and analysed as a multi-component reaction system. Obviously, the curve ln $P=f(t)$ will take the form of a straight line, as a criteria of practical usability of the first-order kinetics, only after disappearance of the more reactive structures. By step-wise elimination from the curve ln $P=f(t)$ of the contributions from the individual structures in order of increasing reactivity, the general kinetic heterogeneity of polysaccharide can be described and the structural elements with different reactivity can be accurately quantified.

In Figs. 2 and 5, the plot of residual polysaccharide content (glucan and xylan, respectively) in ethanol–alkali pulp (logarithmic scale) is shown as a function of pulping time. By slope and intercept of the straight line of the experimental curve ln $P = \mathrm{f}(t)$ (denoted by *1*), the initial content ($P_{n,0}$) of the less reactive P_n-fraction of polysaccharide can be found, and the specific degradation rate constant (K_n) can be calculated by the following equation:

$$K_n = \ln(P_{n,0}/P_t)/t \tag{1}$$

The running content of the P_n-fraction at any instant of reaction time ($P_{n,t}$) can be found as:

$$P_{n,t} = P_{n,0}\exp(-K_n t) \tag{2}$$

The subtraction ($P - P_{n,t}$) at each experimental point gives values for the next kinetic curve ln $(P - P_{n,t}) = \mathrm{f}(t)$ (denoted by *2*), which describes the polysaccharide degradation without contribution of the P_n-fraction.

A similar analysis can be continued with curve ln $(P - P_n) = \mathrm{f}(t)$ to give the next kinetic curve ln $(P - P_n - P_{n-1}) = \mathrm{f}(t)$ and so on. The number of subsequent analytical steps depends on the number of kinetically homogeneous polysaccharide fractions (n) in the reaction system. Kinetic analysis is terminated when the last subsequent subtraction will give a straight line in the semi-logarithmic plot ln $(P - P_\mathrm{n} - \cdots - P_2) = \mathrm{f}(t)$, confirming the presence of only one (P_1) kinetically homogeneous fraction.

The activation energy (E_a) of polysaccharide degradation was found from the logarithmic form of the Arrhenius equation by plotting ln K against $1/T$:

$$\ln K = \ln A - E_\mathrm{a}/RT \tag{3}$$

where A is the Arrhenius constant; R is the universal gas constant (8.314 J mol^{-1} K^{-1}); T is the absolute temperature.

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 the pulp (via monosaccharide composition determined by gas-chromatography after Saeman hydrolysis), using a novel approach for graphical differentiation of kinetic curves. For the sake of simplicity, because of difficulties in establishing exactly the origin of monosaccharide residues during quantification, all residual carbohydrates were expressed as the homopolysaccharides. All glucan has been assigned to cellulose, considering a negligibly small quantity of other glucose-containing polysaccharides in *A. donax* (e.g. the predicted amount of glucomannan-derived glucose is less than 0.2% (on oven-dry reed) taking into account the content of mannose and assuming the ratio of ca. one-to-three between glucose and mannose in the original polysaccharide).

3.1. Kinetics of cellulose degradation

Cellulose is the only fibrous constituent of plant carbohydrate complex. The degree of cellulose degradation and dissolution during plant delignification is a critical factor for potential use of resulting pulps in papermaking.

As can be seen from Fig. 1, only a fairly moderate degradation of cellulose (expressed as glucan) takes place during ethanol–alkali delignification of *A. donax*. Within the tested range of pulping temperature of 130–150 °C, only a cellulose loss of about 4.5% (or 1.2% on oven-dry reed) was observed during pulping for target degree of delignification. The presence of ethanol, which acts as a radical scavenger and suppresses radical-induced alkaline degradation reactions (Nakano, Daima, Hosoya, & Ishizu, 1981), can explain the cellulose preservation during ethanol–alkali pulping.

Results on kinetics of cellulose degradation are shown in Fig. 2 and summarised in Table 1. The analysis, performed for three different process temperatures, showed the same pattern for the cellulose degradation reaction, and two analytical steps were sufficient to make a complete kinetic description. From the two distinguishable cellulose fractions with different reactivity (designated by Glc_1 and Glc_2), the first fraction comprised only about 4% of total cellulose and was rapidly lost during the first-third of pulping. The bulk of cellulose (96%) continuously degraded with very low rate during the pulping (the rate was three orders less than that of the first more reactive cellulose fraction). The specific kinetics of cellulose degradation during ethanol–alkali pulping is defined by morphological structure of cellulose as a semi-crystalline polymer (Emsley & Stevens, 1994). The first cellulose fraction is obviously related to less ordered regions, which are highly accessible to reaction chemicals and primarily removed during pulping. The more ordered cellulose regions and, particularly, the crystalline cellulose portion are very resistant to chemical degradation

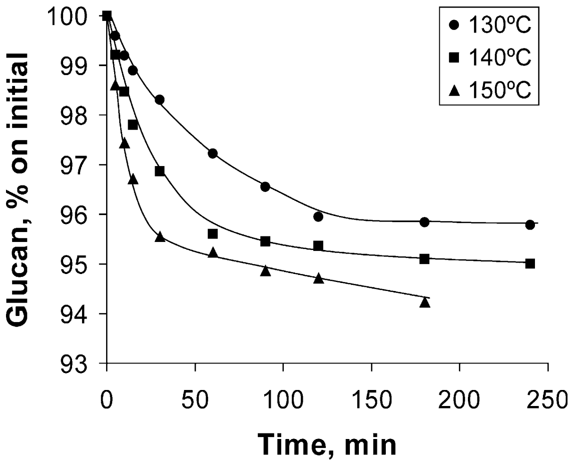

Fig. 1. Cellulose content (expressed as glucan) in ethanol–alkali pulps from giant reed as a function of pulping time and temperature (EtOH/H_2O = 40/60; 25% NaOH).

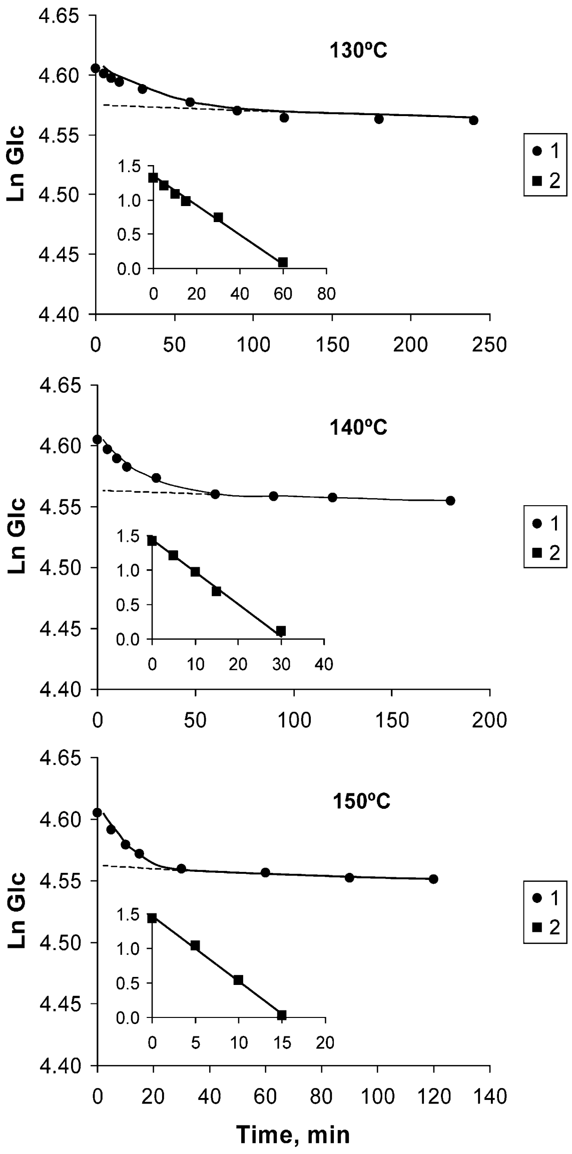

Fig. 2. Kinetics of cellulose degradation during ethanol–alkali delignification of giant reed (EtOH/H_2O=40/60; 25% NaOH), where (1) experimental kinetic curve of cellulose removal ln Glc=ln (Glc_1+Glc_2)=f(t); (2)calculated kinetic curve ln $(Glc\text{-}Glc_2)$=ln Glc_1=f(t) after Glc_2-cellulose fraction subtraction (this curve is given on an enlarged scale); Glc, Glc_1, Glc_2—the total cellulose, the first cellulose fraction and the second cellulose fraction content in pulp, respectively.

and obviously form the basis of the second revealed cellulose fraction.

Comparing the rate of cellulose degradation with the rate of the principal pulping reaction—the delignification (Shatalov & Pereira, 2004c), it is notable, that the first cellulose fraction reacts at almost the same rate as the bulk lignin fraction of *A. donax* (rate constant 0.0204 vs. 0.0271 min^{-1}; 0.0449 vs. 0.0453 min^{-1} and 0.0933 vs. 0.0981 min^{-1} for the first cellulose fraction degradation and bulk delignification at 130, 140 and 150 °C, respectively). The degradation of the major cellulose portion (the second fraction) is about two orders of magnitude slower than the residual (and less reactive) delignification phase (Shatalov & Pereira, 2004c).

Based on kinetic data (Table 1), the cellulose degradation can be accurately described in terms of two irreversible first-order reactions, occurring simultaneously during pulping and corresponding to the reactions of two cellulose fractions. The total amount of cellulose removed at any instant of reaction time (Glc_t) can be calculated from the following equations, respectively for the process temperatures of 130, 140 and 150 °C:

$$Glc_t = 3.75(1-\exp(-0.0204\,t)) + 96.25(1-\exp(-0.0000208\,t)) \tag{4}$$

$$Glc_t = 4.13(1-\exp(-0.0449\,t)) + 95.87(1-\exp(-0.0000450\,t)) \tag{5}$$

$$Glc_t = 4.18(1-\exp(-0.0933\,t)) + 95.82(1-\exp(-0.0000967\,t)) \tag{6}$$

In Fig. 3, the simulated data on cellulose conversion (calculated by Eqs. (4)–(6)) are compared with experimental data for the second set of experiments, which was not used for kinetic analysis. The reproducibility of experimental data by the kinetic model is fairly high and both plotted curves are in very good agreement, confirming generally adequate kinetic description of cellulose degradation during pulping.

The apparent activation energy of cellulose fractions degradation was found from the Arrhenius plot of ln K vs. $1/T$ (Fig. 4). The plot gave two straight lines, justifying application of the first-order kinetics for each reaction (fraction) at the tested temperature range, described by equations:

$$ln\,K_1 = 27.51 - 12.66(1/T) \tag{7}$$

$$ln\,K_2 = 20.98 - 12.81(1/T) \tag{8}$$

The calculated values of activation energy (105.2 and 106.5 kJ mol^{-1}, respectively for the first and the second cellulose fractions) are generally close to those reported for peeling reaction (102.8 kJ mol^{-1}, Haas, Hrutfiord, and Sarkanen (1967) and 84.4–102.4 kJ mol^{-1}, Young and Liss (1978), and also close to those reported for ASAM (alkali-sulfite-anthraquinone-methanol) and kraft processes of eucalypt wood (96.3 and 103.1 kJ mol^{-1}, respectively, Miranda and Pereira (2002), but lower than that for alkaline hemp pulping (124.7 kJ mol^{-1}, De Groot, Van Dam and Van't Riet, (1995)).

3.2. Kinetics of xylan degradation

The content of non-cellulosic, basically of hemicellulosic polysaccharides (normally expressed as pentosans content) in non-wood plant fibres used in papermaking is comparable or only slightly lower of cellulose content

Table 1
Kinetic data on cellulose degradation during ethanol–alkali delignification of giant reed: content of kinetically homogeneous fractions (*Glc*) and their specific reaction rate constant (*K*) and apparent activation energy (E_a) ($EtOH/H_2O=40/60$; 25% NaOH on o.d. reed; L/S = 6/1)

T (°C)	Fraction 1		Fraction 2	
	Glc_1 (%)	K_1 (min^{-1})	Glc_2 (%)	K_2 (min^{-1})
130	3.75	0.0204	96.25	0.0208×10^{-3}
140	4.13	0.0449	95.87	0.0450×10^{-3}
150	4.18	0.0933	95.82	0.0967×10^{-3}
Mean content	4.02	–	95.98	–
E_a (kJ mol^{-1})	105.2		106.5	

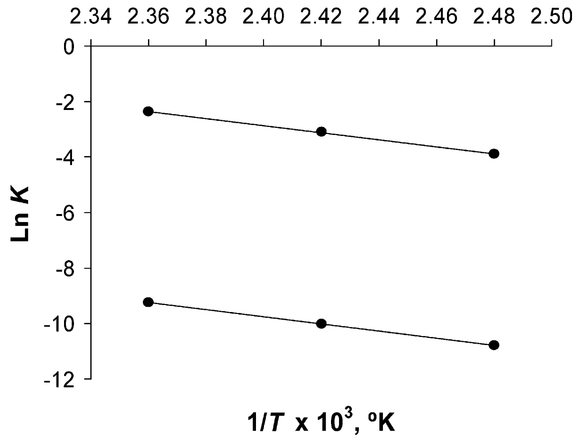

Fig. 4. Logarithm of the effective rate constant of cellulose degradation vs. reciprocal reaction temperature for the first (the upper line) and the second (the lower line) cellulose fractions.

(Atchison, 1993). The retention of hemicelluloses during pulping is, therefore, very important and allows to improve the mechanical properties of pulps by suppression of cross-fibre fragmentation and by promotion of fibrillation and interfibrillar bonds formation during pulp refining and paper sheet formation (Fiserova, Opalena, & Farkas, 1987; Genco, Busayasakul, Medhora, & Robbins, 1990).

Heteroxylan (arabino-4-*O*-methylglucuronoxylan) is a main hemicellulosic polysaccharide of *A. donax* (Joseleau & Barnoud, 1975), accounting for approximately 25% of the wall-stem material (on oven-dry basis) and 90% of the overall non-cellulosic carbohydrates (Shatalov et al., 2001b). Degradation of xylan makes, therefore, a large impact on the pulp yield and properties. As illustrated in Fig. 5, about 55% of giant reed xylan (expressed as a homopolysaccharide) is lost during ethanol–alkali pulping performed for target degree of delignification at temperature range of 130–140 °C.

Kinetic analysis of semi-logarithmic plot ln $Xyl=f(t)$ showed (Fig. 6), that xylan removal proceeds in two phases corresponding to the simultaneous degradation of two polysaccharide fractions with different reactivity (currently as Xyl_1 and Xyl_2). The kinetic data are given in Table 2. The first fraction amounts to about 48% of total polysaccharide. This portion of xylan is extremely reactive and completely degrades during the first minutes of pulping with a very high rate, comparable with the rate of the initial delignification stage (Shatalov & Pereira, 2004c) and one order higher than the degradation rate of the first (more reactive) cellulose fraction (Table 1). The second xylan fraction (approx. 52% of total polysaccharide) slowly degrades during ethanol–alkali pulping with a fairly low rate, which is one order lower than the residual delignification rate and only one order higher than the bulk cellulose degradation rate. The direct dissolution of the low-molecular xylan fractions followed by alkaline hydrolysis and peeling reaction of the dissolved macromolecules under elevated alkali concentrations of the first pulping period (Buchert, Teleman, Harjunpää, Tenkanen,

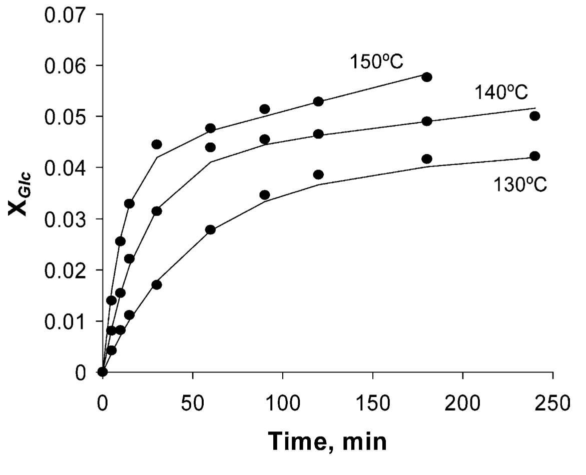

Fig. 3. Comparison of experimental and simulated data (denoted respectively by symbols and lines) on cellulose conversion (X_{Glc}) during ethanol–alkali pulping of giant reed at different reaction temperatures. Where $X_{Glc}=Glc_t/Glc_0$ and Glc_t; Glc_0—current and initial cellulose content.

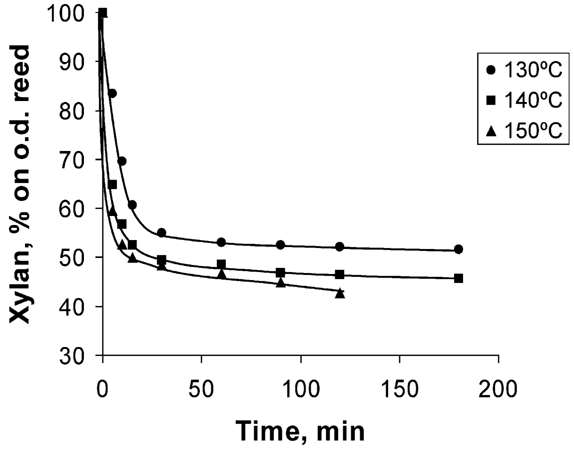

Fig. 5. Xylan content (expressed as homoxylan) in ethanol–alkali pulps from giant reed as a function of pulping time and temperature ($EtOH/H_2O=40/60$; 25% NaOH).

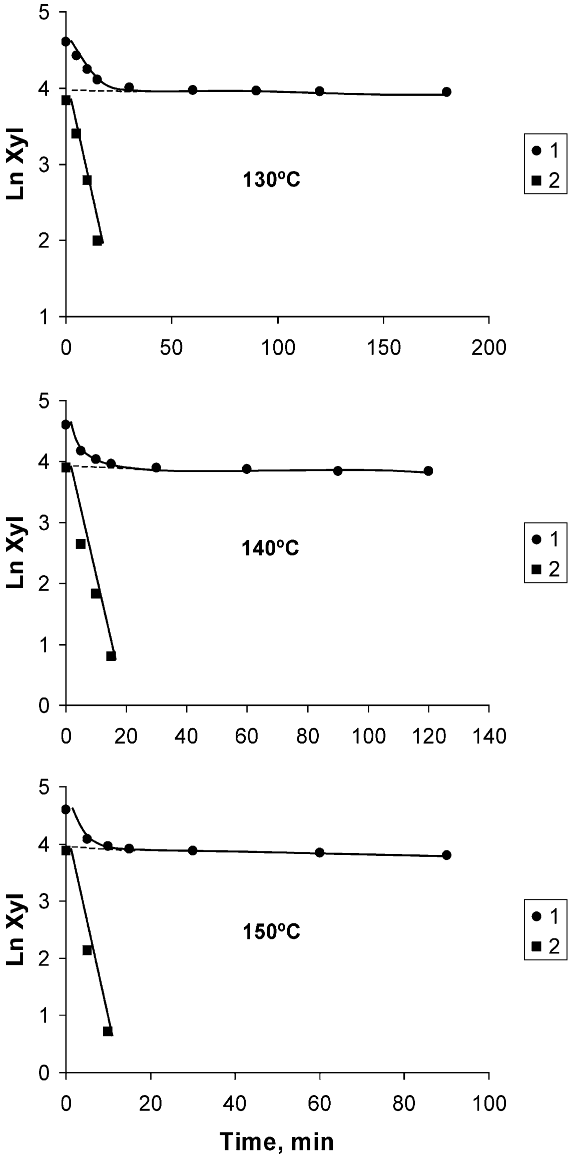

Fig. 6. Kinetics of xylan degradation during ethanol–alkali delignification of giant reed (EtOH/H_2O = 40/60; 25% NaOH), where (1) experimental kinetic curve of xylan removal ln $Xyl = \ln(Xyl_1 + Xyl_2) = f(t)$; (2) calculated kinetic curve ln $(Xyl - Xyl_2) = \ln Xyl_1 = f(t)$ after Xyl_2-xylan fraction subtraction; Xyl, Xyl_1, Xyl_2—content of total xylan, the first xylan fraction and the second xylan fraction in pulp, respectively.

Viikari, & Vuorinen, 1995; Genco et al., 1990) can explain the fast removal of the large portion of reed xylan during ethanol–alkali pulping, assigned to the first fraction. At the same time, the above mentioned protective effect of ethanol on carbohydrate polymers in alkaline reaction medium leads to a slowing down of the of degradative reactions of the remaining xylan in pulp (the second xylan fraction) and, consequently, leads to higher xylan retention in comparison with conventional alkaline processes.

Table 2
Kinetic data on xylan degradation during ethanol–alkali delignification of giant reed: content of kinetically homogeneous fractions (Xyl) and their specific reaction rate constant (K) and apparent activation energy (E_a) (EtOH/H_2O = 40/60; 25% NaOH on o.d. reed; L/S = 6/1)

T (°C)	Fraction 1		Fraction 2	
	Xyl_1 (%)	K_1 (min^{-1})	Xyl_2 (%)	K_2 (min^{-1})
130	46.48	0.1100	53.52	0.0211×10^{-2}
140	49.09	0.1996	50.91	0.0763×10^{-2}
150	48.58	0.3220	51.42	0.1613×10^{-2}
Mean content	48.05	–	51.95	–
E_a (kJ mol^{-1})	74.4		140.9	

Following to kinetic data of Table 2, the xylan degradation during ethanol–alkali pulping of giant reed can be described in terms of two irreversible first-order reactions, corresponding to degradation of the two revealed xylan fractions, respectively for 130, 140 and 150 °C:

$$Xyl_t = 46.48(1 - \exp(-0.1100\,t)) + 53.52(1 - \exp(-0.000211\,t)) \tag{9}$$

$$Xyl_t = 49.09(1 - \exp(-0.1996\,t)) + 50.91(1 - \exp(-0.000763\,t)) \tag{10}$$

$$Xyl_t = 48.58(1 - \exp(-0.3220\,t)) + 51.42(1 - \exp(-0.001613\,t)) \tag{11}$$

The comparison of simulated data on xylan conversion, calculated by Eqs. (9)–(11), with experimental data for the second pulping set in shown in Fig. 7. Similar to cellulose conversion, very good data agreement was observed, confirming the validity of the applied kinetic model.

The apparent activation energy of xylan fractions degradation was estimated, respectively, as 74.4 and 140.9 kJ mol^{-1} (Fig. 8). For the first fraction, the found

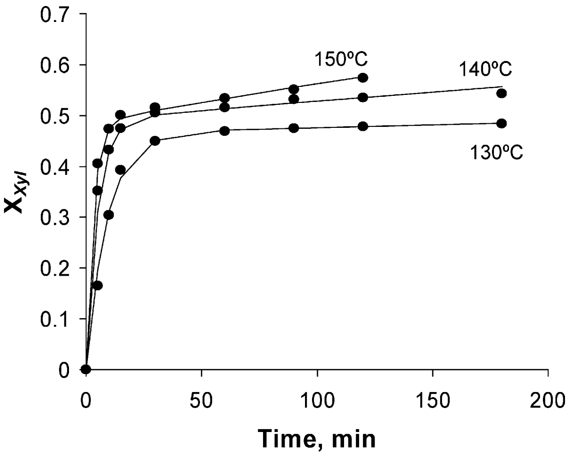

Fig. 7. Comparison of experimental and simulated data (denoted respectively by symbols and lines) on xylan conversion (X_{Xyl}) during ethanol–alkali pulping of giant reed at different reaction temperatures. Where $X_{Xyl} = Xyl_t/Xyl_o$ and Xyl_t; Xyl_o—current and initial xylan content.

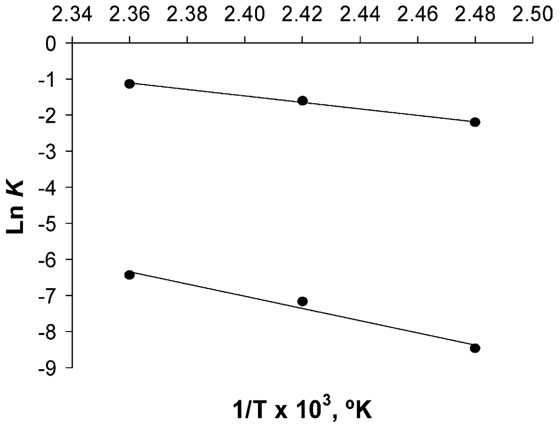

Fig. 8. Logarithm of the effective rate constant of xylan degradation vs. reciprocal reaction temperature for the first (the upper line) and the second (the lower line) xylan fractions.

value of activation energy is close to values of 84.4–102.4 kJ mol^{-1} reported by Young and Liss (1978) for alkaline peeling reaction, and closely matches the 74.8 kJ mol^{-1} reported for the first phase of xylan removal in organosolv (ASAM) eucalypt pulping (Miranda et al., 2002). The activation energy for the second xylan fraction is close to that reported by Lai and Sarkanen (1967) for alkaline hydrolysis of glycosidic bonds in polysaccharides (150.1 kJ mol^{-1}), setting off a dominant role of this reaction in fraction degradation. The value found is also close to that of 152.9 kJ mol^{-1} reported for the second phase of xylan removal in alkaline delignification of hemp woody core (De Groot et al., 1995).

4. Conclusions

Degradation kinetics of the principal polysaccharides (cellulose and xylan) of the agrofibre crop giant reed during ethanol–alkali delignification can be accurately described in terms of two simultaneous irreversible first-order reactions corresponding to degradation of two kinetically homogeneous polysaccharide fractions. Total polysaccharide losses during delignification result mainly from the fast removal of the first more reactive fractions (4 and 48% of cellulose and xylan, respectively). The degradation of the second fractions (96 and 52% of cellulose and xylan, respectively) slowly proceeds with pulping progress with two to three orders lower rate. The apparent activation energy of cellulose (both fractions) as well as of the first xylan fraction degradation is close to that reported for peeling reaction, while the activation energy of the second xylan fraction degradation is close to that for alkaline hydrolysis.

Acknowledgements

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

References

Atchison, J. E. (1993). Data on non.wood plant fibers. In M. J. Kocurec, & C. F. B. Stevens, *Pulp and paper manufacture* (vol. 1) (pp. 157–169). Montreal: CPPA, 157–169.

Browning, B. L. (1967). *Methods of Wood Chemistry*. New York: Wiley.

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.

De Groot, B., Van Dam, J. E. G., & Van't Riet, K. (1995). Alkaline pulping of hemp woody core: kinetic modelling of lignin, xylan and cellulose extraction and degradation. *Holzforschung*, *49*(4), 332–342.

Emsley, A. M., & Stevens, G. C. (1994). Kinetics and mechanisms of the low-temperature degradation of cellulose. *Cellulose*, *1*(1), 26–56.

Fengel, D., & Wegener, G. (1984). *Wood (Chemistry, Ultrastructure, Reactions)*. Berlin, New York: Walter de Gruyter.

Fiserova, M., Opalena, E., & Farkas, J. (1987). Effect of hemicelluloses on the papermaking properties of pulps prepared from poplar wood. *Cellulose Chemistry and Technology*, *21*, 419–430.

Genco, J. M., Busayasakul, N., Medhora, H. K., & Robbins, W. (1990). Hemicellulose retention during kraft pulping. *TAPPI Journal*, *73*(4), 223–233.

Haas, D. W., Hrutfiord, B. F., & Sarcanen, K. V. (1967). Kinetic study on the alkaline degradation of cotton hydrocellulose. *Journal of Applied Polymer Science*, *11*, 587–600.

Joseleau, J. P., & Barnoud, F. (1975). Hemicelluloses of Arundo donax at different stages of maturity. *Phytochemistry*, *14*(1), 71–75.

Lai, Y. Z., & Sarkanen, K. V. (1967). Kinetic study on the alkaline degradation of amylose. *Journal of Polymer Science, Part C*, *28*, 15–26.

Miranda, I., & Pereira, H. (2002). Kinetics of ASAM and kraft pulping of eucalypt wood (*Eucalyptus globulus*). *Holzforschung*, *56*(1), 85–90.

Nakano, J., Daima, H., Hosoya, S., Ishizu, A., (1981). Studies on alkali-methanol cooking. *Proceedings of the Ekman Days international symposium on wood and pulping chemistry* (pp.72–77). Sweden: Stockholm.

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

Saeman, J. F., Moore, W. E., & Millet, M. A. (1963). Methods in Carbohydrate Chemistry. In R. L. Whistler (Ed.),. New York: Academic Press.

Shatalov, A.A., & Pereira, H., (2000). Organosolv pulping of Arundo donax L. as an alternative to the kraft process for production of high quality non-wood fibres. *Proceedings of the 6th European workshop on lignocellulosics and pulp*, EWLP (pp. 571–574). France: Bordeaux.

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., & Pereira, H. (2002). Carbohydrate behaviour of *Arundo donax* L. in ethanol–alkali medium of variable composition during organosolv delignification. *Carbohydrate Polymers*, *49*(3), 331–336.

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. (2004c). Kinetics of organosolv delignification of fibre crop Arundo donax L. Industrial Crops and Products, in press (available on line since 28 May 2004 through the www sciencedirect).

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.

Sjöström, E. (1993). *Wood Cemistry, Fundamentals and Applications*. New York: Academic Press.

Young, R. A., & Liss, L. (1978). A kinetic study of the alkaline endwise degradation of gluco- and galactomannans. *Cellulose Chemistry and Technology*, *12*, 399–411.