Prebleaching kraft pulp by xylanases; the effect of water prehydrolysis

Alexandra Pekarovičová, Daniela Rybáriková, Martin Košík, and Mária Fišerová

ABSTRACT: The effect of water prehydrolysis of beechwood on biobleaching of prehydrolyzed kraft pulp was investigated. Beechwood chips were prehydrolyzed (yield loss: 3.3 to 22.1%) and used for laboratory kraft cooking (18% Na_2O, 25% sulfidity, 1:3 wood-to-liquor, 168° C, 90 min). Sulfate pulps were then treated with xylanases isolated from Aspergillus fumigatus, wild strain (activity: 833.5 nkat·ml^{-1}), for 120 min at pH 5.5, using 500 nkat/g pulp. Prebleached samples showed kappa numbers of 8.25–2.76 and brightness of 30.94–45.95% ISO. Effectiveness of bleaching increased with the severity of water prehydrolysis, which is probably caused by increased accessibility and diminished xylan resorption onto the fiber surface of prehydrolyzed pulps.

KEYWORDS: Bleaching, Fagus, kraft pulping, porosity, prehydrolysis, xylanase.

Prebleaching by xylanases

In enzymatic pulp bleaching, the first attempts to increase brightness were reported with the use of lignin-degrading fungi *(1)*, then with combinations of ligninases and xylanases *(2)*, and with xylanases alone *(3)*. Later, it was shown that prebleaching performed with xylanases alone permitted a 30–35% savings in chlorine *(4)* or chlorine dioxide *(5)* while achieving the same brightness.

Xylanases have a favorable effect on the pulp fiber. They degrade xylans bound to the residual lignin that is difficult to remove during chemical bleaching. This favorable effect is caused by the xylanases decreasing the size of the lignin–carbohydrate fragments, which results in an increased freedom for the lignin to diffuse from the hemicellulose–lignin matrix *(6)*.

The main positive effect of the xylanases is that they promote the degradation of deacetylated xylans reprecipitated onto the fibers at the end of sulfate cooking *(7)*, when the alkalinity of the medium is low. The reprecipitated xylan creates a mechanical barrier to the penetration of bleaching chemicals and to the extraction of lignin out of the fiber during the bleaching.

The xylanase prebleaching stage can be combined with various sequences, as for example: XC(D)EDED, XEC(D)EDHD *(8)*, X(EO)C(D)EOD, X(EO)D(EOP)D, and DX(EO)D(EOP)D *(9)*. The pre-bleaching stage is typically placed before all the chemical bleaching sequences and used not only in combination with classical but also newer bleaching processes.

The application of xylanases has been tested on common sulfate hardwood and softwood pulps *(4, 10, 11)* as well as on hardwood and softwood thermomechanical pulps *(12)*. Here the increased accessibility to xylanases after alkali treatment of thermomechanical pulp was found *(13)*.

Until now, attention has been centered on testing bacterial or fungal xylanase producers and on thermotolerant or alkaline xylanase utilization *(14)*. Despite the study of various enzymes on pulps, no attention has been paid to the study of the pulp–fiber accessibility for xylanases as, for example, the influence of porosity, lignin content, or the influence of hemicelluloses on the efficiency of pulp prebleaching by xylanases. This work explores the effect of water prehydrolysis on the efficiency of xylanase prebleaching of sulfate pulps.

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Experimental

Water prehydrolysis

Beechwood, *Fagus silvatica* L., was disintegrated to chips. Then 300 g of o.d. beechwood chips was weighed into bombs and distilled water was added so that the resulting liquor:wood ratio corresponded to 1:2.5. The bombs were put in an oil bath heated to 178°C. The temperature was regulated so that it would rise to 168°C within 15 min. The temperature was held at 168°C for 1–60 min (**Table I**). The experimental flowsheet is outlined in **Fig. 1.**

Sulfate cooking

After removing the prehydrolyzate, the chips hydrolyzed at different regimes were subjected to sulfate cooking under the following conditions: active alkali charge 18% on o.d. wood, liquor:wood 1:3, sulfidity 25%. The bombs were submerged in an oil bath heated to 100°C. During 90 min, they were heated to 168°C and held at this temperature for an additional 90 min. The weight loss after cooking and the kappa numbers are given in Table I.

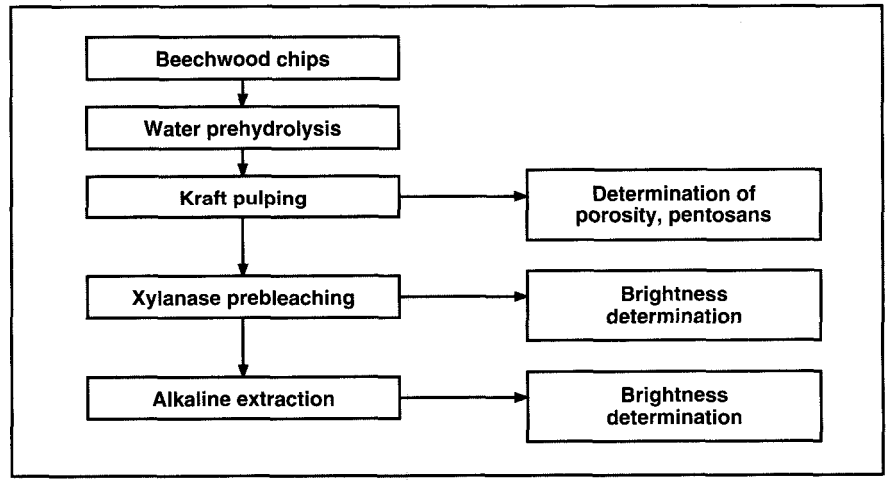
Prebleaching conditions

For experiments with prebleaching, xylanases isolated from a wild strain of *Aspergillus fumigatus* were used. The microorganism was isolated from decayed wood and it had an endo-ß-xylanase activity of 833.5 nkat/mL (nanokatals per millimeter) and a filter paper activity, estimated by the Somogy-Nelson method *(15, 16)*, of 0.16 nkat/mL after 4 days' cultivation on Mandels medium *(17)* with 10 g/L beechwood xylan as the carbon source. The endo-ß-xylanase activity was measured by the DNS-stopping assay *(18)*. Prebleaching of variously prehydrolyzed sulfate pulps, which were suspended for 30 min in a citrate buffer and stirred with a magnetic stirrer prior to mixing with the enzyme, was carried out in a water bath (Elpan 357) at 150 rpm, 50°C, for 120 min. Consistency of the pulp was 3% (w/v) and the pH of 5.5 was adjusted with 0.1 *M* citrate buffer. The xylanase dose was 500 nkat/g pulp, the total volume of pulp suspension 500 mL in 1000 mL Erlenmeyer flasks. After prebleaching and filtering, the pulp was thoroughly washed, first with 500 mL of distilled water (80°C), and then with 1000 mL of cold water. Alkaline extraction was performed using 1% NaOH on pulp, at 70°C, for 90 min, at a consistency of 10% w/v.

I. Effect of water prehydrolysis on the bleaching ability of kraft pulps

Prehydrolysis		Kappa number			Brightness	
Time, min	Weight-loss, %	Before enzym. treat.	After enzym. treat.	After enzym. and alkal. extract.	After enzym. treat., %	After enzym. and alkal. extract., %
0	---	15.26	9.63	8.25	30.94	35.65
1	3.3	14.85	9.64	7.85	29.71	35.55
30	11.8	11.79	7.09	5.15	30.87	40.54
60	18.1	8.20	4.90	2.98	34.17	45.91
70	20.0	9.78	5.01	2.89	32.75	45.95
80	20.7	9.75	5.01	2.86	33.32	43.85
90	22.1	9.10	4.74	2.76	33.45	45.94

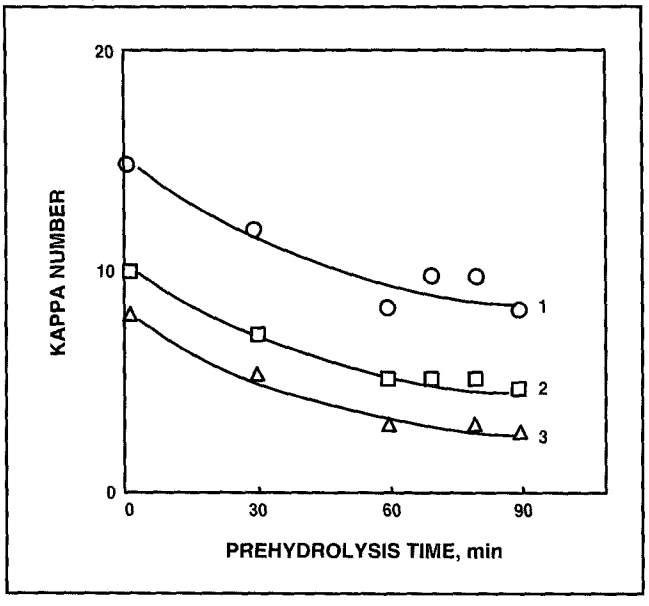
1. Experimental flowsheet



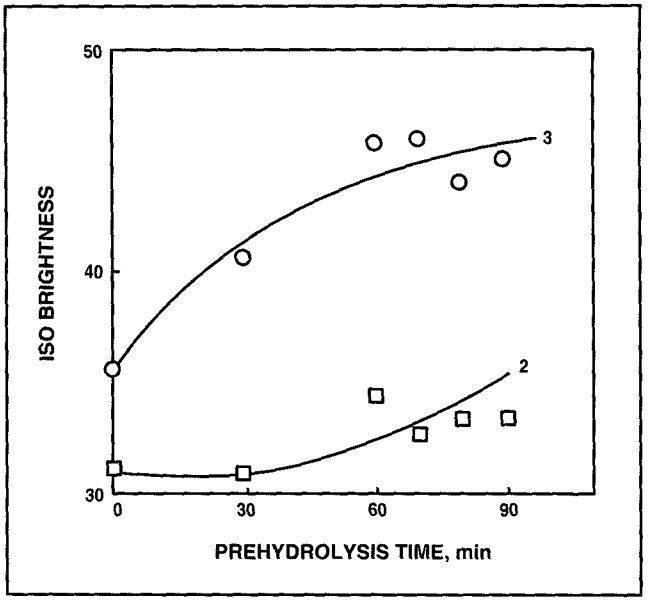
Analyses

The kappa numbers were determined according to the Czechoslovak standard Č SN 50 0258. The brightness was measured according to the ISO standard. The porosity of pulps was estimated by means of sorptometric equipment (Carlo Erba Instruments SO 1900) with volumetric registration of adsorbed nitrogen. The specific surfaces were calculated using the BET equation *(19)*. Before sorption measurements, all samples were equally treated by solution exchange tech-

2. Decrease of kappa numbers: 1—after water prehydrolysis and kraft cooking; 2—after xylanase treatment of water-prehydrolyzed pulps; 3—after xylanase treatment and alkaline extraction of water-prehydrolyzed pulps



3. ISO brightness of water prehydrolyzed kraft pulps: 2—after xylanase prebleaching, 3—after xylanase prebleaching and alkaline extraction



nique. The samples were subsequently suspended in water, filtered, then suspended in ethanol, acetone and, finally, in *n*-hexane. The remaining solvent was removed under vacuum (10^{-3} torr, 60°C, 30 min).

Results and discussion

Hardwood xylans are highly acetylated, but the acetyl groups are readily saponified when wood is processed under alkaline conditions. Thus, acetyl and methylglucuronic acid side groups are mostly removed during pulping, and the hemicelluloses which are most accessible to the xylanases consist mainly of pure xylan. Endoxylanases alone are the most effective enzymes in enzymatic prebleaching *(7, 20)*.

The results in Table I and **Figs. 2 and 3** show a positive prehydrolysis effect on the kappa number and on brightness values determined after xylanase treatment. The kappa number of unbleached, non-prehydrolyzed pulps is the highest (15.26). The prehydrolyzed kraft pulps have a lower kappa number (9.10; 8.20). The decrease in kappa number diminishes after 60 min of prehydrolysis (at a weight loss of 18–20%). Treatment of kraft pulp samples prepared in the same manner using xylanases results in a further reduction in the kappa number (5.01–4.74). After alkaline extraction of prehydrolyzed and enzymatically treated pulps, the kappa number decreases to 2.98–2.76 (Fig. 2).

Similarly, the brightness of prebleached pulps increased from 30.94% to 33.45% and, after alkaline extraction, from 35.65% to 45.94%, when water prehydrolysis was used (Fig. 3).

Xylanase prebleaching results in higher degradation and extraction of xylan, and in a decreasing size of lignin–carbohydrate fragments that are more alkali soluble and freer to move than the corresponding fragments without xylan hydrolysis. The content of pentosans (**Table II**) also diminished from 22% in the original wood to 4.8% in the 80-min prehydrolyzed kraft pulp and to 9.2% in the non-prehydrolyzed kraft pulp.

It is possible that the prehydrolyzed pulp does not reprecipitate xylan to the extent of non-prehydrolyzed pulps because they contain less xylan. The xylanases act first on the xylan located on the surface of the fibers *(7)*. In water-prehydrolyzed pulp, where less of this xylan is present, xylanases can effectively degrade the residual xylan located inside the fibers. This results from different morphological properties of the fibers, which are evident from porosity measurements. The prehydrolyzed kraft pulp samples have higher accessibility and porosity than non-prehydrolyzed ones. Sorption measurements have shown that the content of pores, which could be decisive for the penetration of xylanases into fibers (mesopores with a diameter up to 50 Å), is higher in prehydrolyzed sulfate pulps than in non-prehydrolyzed (**Fig. 4**). In the case of cellulases, where the accessibility of the cellulose substrate was thoroughly investigated, the rate limiting pore volume was found to be 43-45 Å. This pore size fits well with the size of cellobiohydrolase enzyme, the diameter of which is 44 Å *(21)*. The molecular weight of cellulases was found to be 58000+ 500Da [Dalton] *(22)*. The molecular weight of fungal xylanases corresponds to 22900–24000 Da *(23, 24)*, up to a maximum of 34300 Da *(25)*. Xylanase is a substantially smaller protein than cellulase. Therefore pores smaller than 45 Å can be important for the accessibility to xylanases. Perhaps also mesopores of 20-Å diameter, the content of which was consid-

erably increased after water prehydrolysis, will play an important role in xylanase penetration inside the cell wall. Sorption measurements (Fig. 4), confirm the increase of adsorption of nitrogen at a lower pressure and, simultaneously, to an increase in the specific surface to 42.5 m^2/g in the case of the most deeply prehydrolyzed pulp (80 min) compared to the non-prehydrolyzed one, 36.5 m^2/g (Table II). The increased porosity and accessibility of prehydrolyzed pulps probably allow xylanase enzymes better penetration into the kraft pulp fibers, so that xylanase can more effectively attack the lignin-carbohydrate complex and decrease the chain length of xylan. The decreased size of xylan-lignin fragments can result in their increased diffusion out of the pulp fibers.

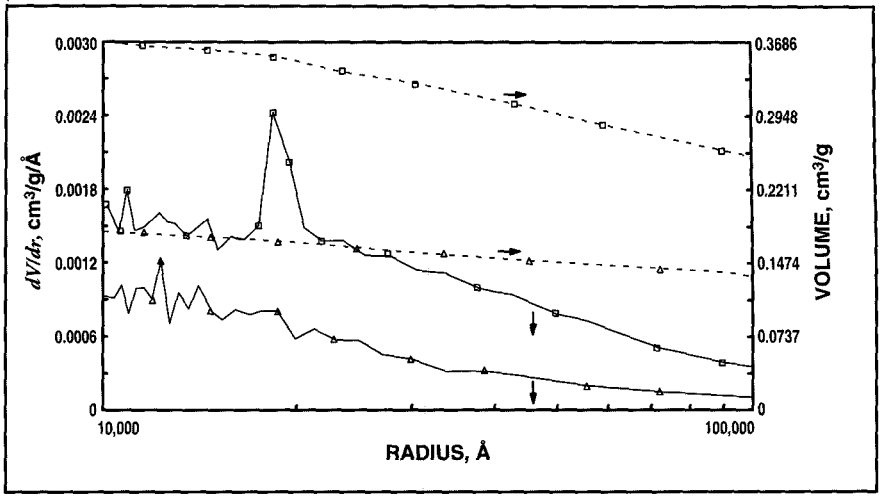
Conclusion

Water prehydrolysis of kraft pulp prepared from hardwood *(Fagus silvatica)* affects the biobleaching process. Prehydrolyzed pulps after similar xylanase treatment achieved a higher brightness and lower kappa number. The favorable effect of prehydrolysis can be explained by an increase in porosity and accessibility of severely prehydrolyzed kraft pulp. In the prehydrolyzed pulp resorption of xylan during the kraft cook is also diminished, and this allowed xylanase to penetrate into the fiber and split the residual xylan, which finally results in better bleaching parameters. ■

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II. Effect of water prehydrolysis and kraft pulping on pentosan content and specific surface of unbleached pulps

Prehydrolysis time, min	*Pentosans, %*	*Specific surface, m^2/g*
0	9.2	36.5
30	6.5	37.6
80	4.8	42.5

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