Boosting Oxygen Delignification of Poplar Kraft Pulp by Xylanase Pretreatment

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Enhancement of oxygen delignification is critical to improve subsequent bleaching efficiency while being environmentally compatible. In the present study, xylanase was used to improve the delignification process of poplar kraft pulp. Results showed that the kappa number reduction ratio (KRR) of 14.5% was achieved for the pulp under xylanase-assisted oxygen delignification processes when compared to the control without xylanase treatment. Other pulp properties, such as intrinsic viscosity and brightness, also improved somewhat; *i.e*., viscosity increased by 28 mL/g units and ISO brightness increased 1.4% points. Furthermore, ^{31}P-NMR was employed to characterize the chemical structure of the residual lignin of the pulps before and after oxygen delignification. It showed that the condensed phenolic and syringyl hydroxyl groups decreased significantly for the xylanase-assisted oxygen-delignified pulps.

Keywords: Kraft pulp; Oxygen delignification; Xylanase; Kappa number; Residual lignin

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INTRODUCTION

Kraft pulping is the dominant chemical process employed throughout the world due to its versatility and cost effectiveness (van Heiningen 2006). About 90% of the wood lignin can be removed through its depolymerisation and by the ionization of its fragments into alkaline liquor during the pulping process (Bajpai and Bajpai 1992). To produce fully bleached pulp, the remaining residual pulp lignin needs to be removed by bleaching, such as the commonly used oxidants chlorine and chlorine dioxide (Luo *et al.* 2014). Effluents generated from bleach plants are significant contributors to waste water pollution of the pulping industry. Therefore, element chlorine free (ECF) and total chlorine free (TCF) sequences have been developed and commercialized in order to minimize pollution loads (Souza *et al.* 2014). Typically, oxygen delignification is employed prior to bleaching to remove lignin from kraft pulp (Jafari *et al.* 2014).

Unfortunately, it is not an easy task to remove the small amount of residual brownstock lignin, since it has been heavily modified during the pulping process. It is suspected that the residual lignin is covalently bound to the hemicelluloses in the pulp (Gangwar *et al.* 2014). Therefore, using xylanase to cleave these bonds seems a promising method to enhance oxygen delignification. In fact, xylanase has been investigated in the bleaching process for different purposes. For example, Viikari *et al.* (1986) reported that the chlorine dosage can be reduced 25% for hemicellulase-assisted chlorine bleaching to obtain the similar bleached pulp. Paice *et al.* (1988) observed that the delignification of the pulp increased after the hemicellulase treatment. Valenzuela *et al.* (2014) reported that 23% delignification can be obtained when using xylanase on

soda-AQ sisal pulp. Sharma *et al.* (2014) reported that the sequential treatment of xylanase and laccase improved pulp properties and reduced absorbable organic halogens (AOXs) in bleach plant effluent.

Based on these results reported in the literature, xylanase was used in this work to boost oxygen delignification. The kappa number was measured to evaluate the amount of lignin removal. Other pulp properties, such as intrinsic viscosity and brightness, were also measured. The residual lignin of the brownstocks and bleached pulps were characterized by ^{31}P-NMR to elucidate the changes to the chemical structure of residual lignin.

EXPERIMENTAL

Materials

Fast-grown poplar (dominant in North China) chips were provided by Shandong Sun Paper Industry Joint Stock Co., Ltd. The dimension of chips was 15 to 25 mm in length, 10 to 20 mm in width, and 3 to 5 mm in thickness. Kraft pulping was performed in the laboratory using a 15 L electrically-controlled digester (ZQS, China). Pulping conditions were: active alkali charge (calculated as Na_2O) of 20% based on over dry chips; sulfidity of 24%; liquid-to-wood ratio of 4-to-1; cooking time of 90 min; and a pulping temperature of 165 °C. The screened pulp yield was 49.3%. The brownstock had a kappa number of 18.5, an intrinsic viscosity of 842.7 mL/g, and brightness of 36.5% ISO.

Xylanase, a commercial hemicellulose enzyme without cellulase, was kindly supplied by Novozymes and used as received. The enzyme activity was 4800 IU/mL, which was based on reducing sugar production (Clarke *et al.* 2000). All other chemicals used were of ACS reagent grade and purchased from a chemical supply company.

Methods

Xylanase treatment

Xylanase treatment was performed in plastic bags, which were placed into a thermostatic water bath. Initially, 50 g pulp (based on oven dried mass) was placed into a plastic bag and was well disintegrated; the pulp's consistency was adjusted to 10%. Subsequently, the desired amount of xylanase (2, 4, 6, 8, or 10 IU/L) was added, and mixed thoroughly into the pulp slurry. Other treatment conditions were varied to determine the optimum values: time (30, 60, 90, or 120 min); temperature (45, 50, 55, or 60 °C); and pH (7, 8, 9, or 10). The bags were hand kneaded every 30 min to ensure thorough mixing during the treatment. After xylanase pretreatment, the pulp slurry was thickened and washed with distilled water prior to oxygen delignification. The control sample was performed similarly, where the xylanase was replaced with distilled water.

Oxygen delignification

Oxygen delignification was carried out in a laboratory reactor (JF-DSTE, China), which was equipped with a temperature controller and an agitator. The optimum conditions were: NaOH and $MgSO_4$ dosage of 2.5% and 0.5%, respectively (based on oven dried pulp); oxygen pressure of 0.6 MPa; temperature of 100 °C; and reaction time of 80 min at pulp consistency of 10%. Once the reaction was completed, the pulp was

collected, washed with distilled water, and then stored in the refrigerator awaiting further analysis.

Analysis method for pulp properties

A titration method using 0.1 N potassium permanganate solution was used to measure kappa number of kraft pulp and treated pulps (TAPPI Standard Method T236 cm-85). The viscosity was determined according to TAPPI Method T230 om-94 in cupriethylenediamine (CED) solution at 0.5% cellulose concentration The intrinsic viscosity was then calculated based on Eq. 1 (Mazumder *et al.* 2000):

$$[\eta] = 954 \times \log(\text{viscosity}) - 325 \quad (1)$$

The pulp sheet was made from the bleached pulp, and the brightness of the pulp handsheet was determined according to ISO 2470.

The average of the duplicate determination was reported for all analysis.

Isolation of residual lignin and ^{31}P-NMR analysis

Residual lignins were isolated from the pulps using the enzymatic/mild acid hydrolysis methods of Wang *et al.* (2014), and Wu and Argyropoulos (2003). Initially, 50 g oven-dried pulp was placed into 2 L Erlenmeyer flask, which contained 1 L of an acetic acid-sodium acetate buffer solution (pH 4.5) with 15 mL of cellulase (equivalent to 350 IU/g). The flask was placed into a thermostatic shaker, which was operated at 40 °C for 48 h at 150 rpm. Afterwards, the hydrolysate was acidified to pH 2 with HCl to precipitate the crude lignin. The obtained crude lignin was suspended in acidic dioxane-water mixture (85/15, v/v). This mixture was refluxed under N_2 atmosphere for 2 h. Sodium bicarbonate was used to neutralize the supernatant of the mixture. Then, rotary vacuum evaporator was used to concentrate the solution. The lignin was obtained by acidic precipitation, *i.e.* drop to acidified deionized water (pH = 2). After centrifugation, the mixture was washed and freeze dried; at this point the lignin could be isolated.

^{31}P-NMR analysis was performed on a Bruker 400 MHz spectrometer. The derivatization and ^{31}P-NMR characterization of the isolated lignins followed the procedure described by Zhang *et al*. (2010).

FTIR of pulps

FTIR spectra of the pulps were conducted on a Nexus 670 (Thermo Nicolet) instrument. Spectra wavenumbers ranging from 500 to 4000 cm^{-1} were recorded for each freeze-dried pulp sample. The potassium bromide (KBr) disc method was used for the sample preparation, and the oven-dried KBr was used to reduce the interference of water (Wang *et al.* 2014)

RESULTS AND DISCUSSION

Effect of Xylanase Treatment on Oxygen Delignification

Table 1 presents the results of various xylanase treatments on the oxygen delignification of poplar kraft pulp. As can be seen, the kappa number decreased from 18.5 for all samples; the kappa reduction ratio (KRR) for the xylanase treatments ranged from 3.6 to 14.5%. These results verified the previous hypothesis that lignin removal

could be enhanced by xylanase treatment (Valenzuela *et al.* 2013). Moreover, xylanase dosage and treatment time were interrelated parameters, *i.e.*, increasing the xylanase dosage achieved the same boosting effect in a shorter period of time. On the other hand, the optimal conditions for xylanase treatment were 50 °C and pH 8. Other pulp properties, such as intrinsic viscosity and brightness, were slightly improved by xylanase pretreament. These observations may be explained by the partial removal of the hemicelluloses, which have a low degree of polymerization (DP), and the enhanced delignification, respectively (Kirk and Yang 1979). Similar results have been reported in the literature. In one study, a hardwood brownstock was treated with xylanase followed by alkaline extraction; the pulp's kappa number decreased from 11.7 to 9.5, brightness increased by 6.7 % ISO units, and viscosity increased by 3.5 mPa·s units (Paice *et al.* 1988). In another study with softwoods, the xylanase pretreatment decreased the pulp's kappa number by 1.2 units (Clarke *et al.* 2000). Valenzuela *et al* (2013) also observed that the kappa number was reduced by 1.7 units when using xyan10A treatment of specialty sisal fibres.

Table 1. Effect of Xylanase-Assistant on Oxygen Delignification of Poplar Kraft Pulp

Xylanase dosage (IU/L)	Time (min)	Temperature (°C)	pH	Kappa number	KRR[a] (%)	Viscosity (mL/g)	Brightness (%ISO)
Control	120	55	8	8.3	--	712	58.7
2	120	55	8	7.6	8.4	723	59.1
4	120	55	8	7.5	9.6	729	59.4
6	120	55	8	7.3	12.0	732	59.6
8	120	55	8	7.2	13.3	739	60.0
10	120	55	8	7.1	14.5	736	60.1
8	30	50	8	8.0	3.6	716	59.1
8	60	50	8	7.7	7.2	727	59.5
8	90	50	8	7.3	12.0	734	59.9
8	120	50	8	7.1	14.5	740	60.1
8	120	45	8	7.6	8.4	728	59.4
8	120	50	8	7.2	13.3	739	60.0
8	120	55	8	7.2	13.3	732	60.1
8	120	60	8	7.3	12.0	726	59.8
8	120	50	7	7.7	7.2	736	59.3
8	120	50	8	7.1	14.5	740	60.1
8	120	50	9	7.2	13.3	739	60.0
8	120	50	10	7.4	10.8	729	59.8

Note: [a]KRR = $(K_o-K_{xo})/K_o$, where KRR is the kappa number reduction ratio, K_o is the kappa number of the oxygen delignification control pulp, and K_{xo} is the kappa number of the xylanase-assisted oxygen delignification pulp.

^{31}P-NMR Analysis of Residual Lignin

^{31}P-NMR analyses were conducted to characterize the residual lignins from three pulps, *i.e.*, the unbleached kraft pulp, the oxygen-delignified pulp, and the xylanase-assisted oxygen-delignified pulp. The spectra and integration results are shown in Fig. 1 and Table 2, respectively. These results showed that the hydroxyl groups in the residual lignin decreased after oxygen delignification when compared to kraft brownstock. The xylanase-assisted oxygen delignification further decreased the condensed phenolic and syringyl hydroxyl groups.

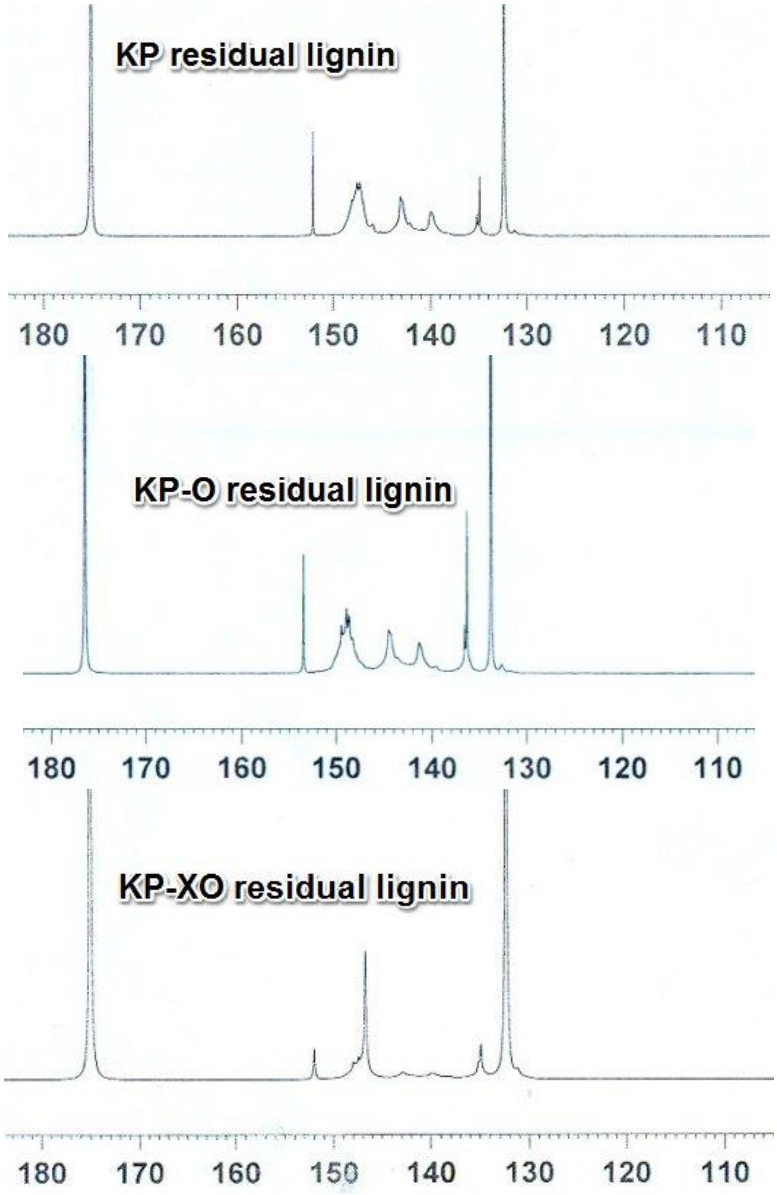

Fig. 1. ^{31}P-NMR spectra of residual lignin (KP is kraft pulp, KP-O is oxygen-delignified kraft pulp and KP-XO is xylanase-assisted oxygen-delignified kraft pulp)

The degradation of condensed phenolic structures formed carboxylic acids, which is the pathway for lignin dissolution according to a previous study (Jafari *et al.* 2014). The carboxyl groups in the lignin increased upon oxygen delignification treatment. These results suggested that the xylanase treatment facilitated the degradation of condensed phenolic and syringyl hydroxyl groups, thus enhancing oxygen delignification. Jafari *et al.* (2014) observed an increase of carboxylic acid content in the range of 50 to 200% when using oxygen delignification to treat unbleached softwood kraft pulps. Sixta *et al.* (2008) reported that the non-condensed –OH groups was decreased due to such groups possessing good reactivity toward oxygen delignification.

Table 2. ^{31}P-NMR Results of Residual Lignin (mmol·g^{-1})

Signal (ppm)	Assignment	KP lignin	KP-O lignin	KP-XO lignin
145.0-150.0	Aliphatic -OH groups	2.49	1.78	1.56
144.6-143.6 142.4-140.2	Condensed phenolic -OH	1.52	1.43	0.83
143.6-142.4	Syringyl -OH	1.27	0.61	0.38
140.2-138.6	Guaiacyl -OH	0.71	0.65	0.63
138.6-137.0	*p*-Hydroxyphenol -OH	3.85	1.78	2.40
136.0-134.0	Carboxyl groups	1.11	2.15	1.91
–	Total free phenolic [a]	7.35	4.47	4.24

Note: [a] Total free phenolic is the sum of condensed, syringyl, guaiacyl and p-hydroxyphenol-OH

FTIR of Original and Oxygen-Delignified Pulps

Figure 2 shows the FTIR spectra of unbleached kraft pulp and oxygen delignification pulps with and without xylanase treatment. It can be seen that all three spectra presented similar IR absorbances over the recorded wavenumber range. A broad peak at 3400 cm^{-1} was attributed to the O-H stretching of hydroxyl groups. The peak at 2900 cm^{-1} belonged to C-H stretching. The peaks at 1125 and 1200 cm^{-1} were attributed to C-O stretching and O-H in-plane bending coupled vibrations (Kondo 1997; Pal *et al.* 2007). As expected, the xylanase-assisted oxygen delignification did not cause significant changes to the chemical structure of the cellulose of the pulps.

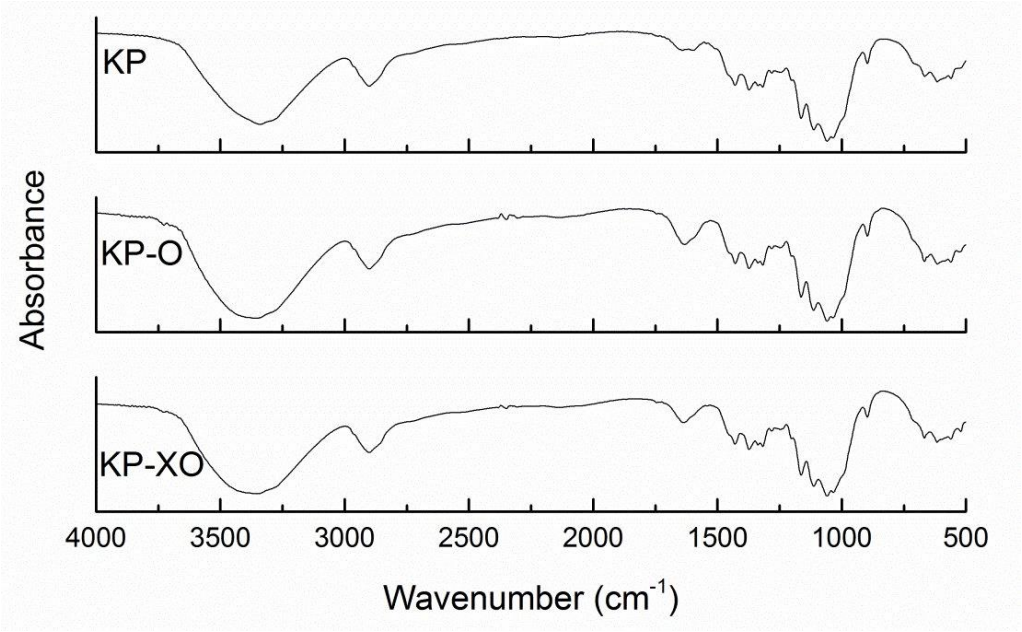

Fig. 2. FTIR spectra of kraft pulp and treated pulps

CONCLUSIONS

1. Xylanase pretreatment was performed on a poplar kraft pulp to boost lignin removal during oxygen delignification. The optimal conditions of the xylanase treatment were: xylanase dosage of 8 IU/L, time of 120 min, temperature of 50 ºC, and pH of 8.

2. A kappa number reduction ratio (KRR) of 14.5% was achieved under the optimal condition of xylanase-assisted oxygen delignification versus the control.
3. ^{31}P-NMR analyses of residual lignins revealed that the condensed phenolic and syringyl hydroxyl groups decreased significantly for pulp treated with xylanase prior to oxygen delignification. FTIR analyses showed that the cellulose chemical structure was not substantially changed upon oxygen delignification, and xylanases assisted oxygen delignification.

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