Preparation of acetate-grade dissolving pulp from eucalyptus by processes including alkaline pretreatment and combined post-treatments with xylanase and alkali

WEN LIU, SHUKE ZHOU, XIAOHUA QI, AND JUNWEN PU

ABSTRACT: In this investigation, alkaline pretreatment before kraft pulping and combined post-treatments with xylanase and alkali after bleaching were applied to obtain an acetate-grade dissolving pulp. Bleaching sequences using oxygen or hydrogen peroxide were also studied. The brightness, α-cellulose content, and degree of polymerization (DP) of the bleached pulps from different bleaching sequences were evaluated. Alkaline pretreatment resulted in a higher α-cellulose content in the pulp. When a D_1ED_2P bleaching sequence was applied, the pulp obtained had an ISO brightness of 87.5%, a DP of 1050, and an α-cellulose content of 92.7%. The requirements for an acetate-grade dissolving pulp can then be met when followed by combined post-treatments with xylanase and alkali under the optimal conditions of 120 IU•g^{-1} xylanase dosage and 4% sodium hydroxide concentration.

Application: Mills potentially could use the new process, which is different from the traditional prehydrolysis kraft process, to obtain acetate-grade dissolving pulp.

Dissolving pulp is a high purity pulp that is commonly used in the production of viscose and acetate fibers. In 2008, the total world production capacity for acetate fibers reached 863000 tons/year, and this number is expected to reach 912000 tons/year in 2013 [1]. Acetate fibers are mainly used in the cigarette and textile industries. As a high grade pulp, acetate-grade dissolving pulp must contain no less than 95% α-cellulose. The hemicellulose, ash, and extractive contents in the pulp have many negative effects in the manufacturing process or the quality of acetate fibers and hence must be kept very low [2,3].

Cotton linter and wood are the main raw materials used for dissolving pulp production, although bamboo has also been used in recent years [4]. The soda process is usually applied for cotton linters, and a sulfite or prehydrolysis kraft process is more often used for wood. The prehydrolysis kraft process typically includes four stages: pretreatment, cooking, bleaching, and purification. The main purpose for the cooking and bleaching stages is to remove lignin and hemicelluloses. Cold caustic extraction is included in the bleaching stage and its main purpose is to remove residual and redeposited hemicelluloses. The pretreatment and purification stages also enhance the removal of hemicelluloses. The prehydrolysis kraft process uses steam for the prehydrolysis treatment. It is currently a well-established technology that has been put into commercial application. However, because prehydrolysis is carried out under high temperature and acidic conditions, the associated drawbacks are also well known. On one hand, the high prehydrolysis temperature causes lignin (its glass transition temperature is at a lower temperature of 120°C to 135°C) to soften, some of which may adsorb onto fiber surfaces and form a glassy covering layer when the temperature is lowered. These portions of lignin tend to become even more difficult to remove during the following cooking stage [4]. On the other hand, under the acidic condition, the equipment is easily corroded, which puts higher requirements on the equipment metallurgy used and results in higher capital investment.

The objective of this investigation was to develop a new process for the preparation of dissolving pulp so that the previously mentioned drawbacks can be overcome. Alkaline pretreatment before chemical pulping has been widely studied in recent years. Even though the goals were mainly to isolate hemicellulose for the production of biofuels [5-7], the results nevertheless indicated that alkaline pretreatment could also be applied just like the prehydrolysis process to remove hemicelluloses from raw materials. Some studies also showed that alkaline pretreatment could effectively reduce the alkali demand and cooking time in the kraft pulping process [5]. Because alkaline pretreatment is not nearly as

effective as prehydrolysis in removing hemicelluloses, additional purification after cooking and bleaching is needed in order to make dissolving pulp. For this purpose, research on the use of xylanase to selectively isolate xylan could provide valuable insight to our work [8-11]. Other researchers had further showed that xylanase treatment by itself had limited effect in removing hemicelluloses, while the combined treatment with xylanase followed by alkali could achieve a much greater result [12,13].

In this work, a fast-growing eucalyptus was used to prepare a dissolving pulp through a new process that consists of alkaline pretreatment, kraft pulping, elemental chlorine free bleaching and combined post-treatments with xylanase and alkali. The pulp obtained demonstrated a high α-cellulose content (≥96%), high brightness (≥90% ISO), high degree of polymerization (≥900), and low S-10 (<5%) that meets the requirements for an acetate-grade dissolving pulp.

MATERIAL AND METHODS

Raw material

Eucalyptus urophylla was supplied by Jin Hai pulp mill of Hai Nan Province, China. **Table I** shows the characteristics of this wood.

Preparation of acetate-grade dissolving pulp

Unbleached pulp was obtained from traditional kraft pulping (KP) and from alkali-preimpregnated kraft pulping (NaOH-KP) processes. The sodium hydroxide (NaOH) process was carried out with NaOH at 10% dosage under the following conditions: solid to liquid ratio at 1:4, temperature at 120°C, retention time at 30 min, and sodium lauryl benzenesulfate (ABS) dosage at 1.75%. The KP cooking process was carried out under the following conditions: NaOH (as Na_2O) dosage at 17% of ovendry chip weight, sulfidity at 16%, and anthraquinone (AQ) dosage at 0.05%. AQ was added to replicate the current conventional pulping process for unbleached market pulp, which will be used to produce acetate grade dissolving pulp. However, the addition of AQ is not necessary; it stabilizes hemicellulose and increases the pulp yield as a result. It is likely that AQ will not be used in future studies. The time it took to reach the max temperature of 170°C was 180 min, and the duration kept at 170°C was 60 min. The weight ratio of liquid to eucalyptus chips was 4:1.

Ingredient	Composition (%)
Holocellulose	77.93
Lignin	22.24
1% NaOH extractive	13.75
Benzene-alcohol extractive	0.94
Ash	0.53

***I. Chemical composition of* Eucalyptus urophylla.**

The alkali-preimpregnated kraft pulp (NaOH-KP) was used in the bleaching process. All bleaching experiments were carried out in heat-proof polyethylene bags, except for the oxygen delignification, which was carried out in a reactor. The pulp was kneaded every 15 min. After each stage, the pulp was removed from the bag, filtered, and washed with distilled water.

The bleaching process was completed in five stages, using oxygen delignification (O), chlorine dioxide treatment (D), alkali extraction (E), and hydrogen peroxide bleaching (P). Five different sequences (O, OD_1ED_2, D_1ED_2, OD_1ED_2P, and D_1ED_2P) were studied to identify the optimal bleaching sequence. **Table II** shows the experimental conditions for each stage. Dilute sulfuric acid was used to adjust the initial pH of the pulp.

Following the bleaching process, the pulp underwent xylanase AU-PE89 treatment (X) and alkaline extraction (E). Xylanase AU-PE89 was supplied by Sukahan (Weifang) Bio-Technology Co. (Weifang, Shandong, China). The optimal pH of xylanase AU-PE89 was 6.0, and its optimal temperature was 60°C. Xylanase AU-PE89 demonstrates high bio-catalysis performance when the temperature is controlled in the range of 50°C to 60°C. In the X stage, the dosages of xylanase used were 20, 40, 80, 120, and 160 IU•g^{-1}, respectively. Other conditions were as follows: pulp consistency at 3%, treatment temperature at 60°C, retention time at 120 min, and pH at 6.0.

	O	D_1	E	D_2	P
Consistency of pulp, %	10	10	10	10	10
Temperature, °C	100	70	75	70	70
Duration, min	60	90	60	90	90
Pressure, Mpa	0.5	/	/	/	/
Consistency of ClO_2, %	/	3.6	/	0.9	/
Consistency of NaOH, %	2.0	/	6.0	/	2.5
Consistency of H_2O_2, %	/	/	/	/	2.5
Consistency of $MgSO_4$, %	1.0	/	/	/	/
pH	/	3.5	/	3.5	/

II. Bleaching conditions and chemical dosages for each stage.

Acetic acid-sodium acetate buffer solution was used to adjust the pH of the pulp. The E step was carried out at 10% pulp consistency, 20°C, 60 min retention time, and NaOH concentrations of 2%, 4%, 6%, and 8%, respectively.

Analysis and characterization of acetate-grade dissolving pulp

The analyses of final pulp were conducted according to the respective TAPPI Test Methods: T 9 m-54 (now Useful Method 249) "Holocellulose in wood," T 204 "Solvent extractives of wood and pulp," T 211 om-02 "Ash in wood, pulp, paper, and paperboard: combustion at 525°C," T 212 om-02 "One percent sodium hydroxide solubility of wood and pulp," T 222 "Acid-insoluble lignin in wood and pulp," and T 242 cm-83 "Iron in pulp." Brightness levels were determined with a brightness tester that can measure ISO brightness (i.e., R457 brightness). The α-cellulose content, namely the pulp fraction resistant to the treatment of an aqueous solution containing 17.5% sodium hydroxide, was determined according to Chinese Standard GB/T 744-1989. The degree of polymerization (DP) of pulp was determined through intrinsic viscosities [η], which were measured using a capillary viscometer in cupri-ethylene-diamine solution at 25°C according to GB/T1548-1989, using the formula of $DP^{0.905} = 0.75[\eta]$ for the calculation.

To characterize the final pulp produced per standard of acetate-grade dissolving pulp, two pulp samples were used for the following application tests. One is the experimental wood pulp made from *E. urophylla* chips in our lab with the new process reported in this paper, the other is a control wood pulp that is a commercial acetate-grade dissolving pulp imported from the United States. Acetylation reactions of cellulose fibers can be described in Eq. (1) and Eq. (2). Both acetylation reactions are strongly exothermic, and therefore, the temperature of the system will increase steadily with the progress of acetylation reaction. The relationship between temperature and reaction time during acetylation of two pulp samples were investigated. After acetylation, the time for completing dissolution of the two pulp samples in a 3% acetone solution was recorded. The number of insoluble particles in the acetone solution, which is a direct indication of the amount of solid and gel impurities in the acetate pulps, was measured by particle counter. The haze data of acetone solutions of the acetylated wood pulp samples was also determined to evaluate the amount of unreacted long fibers in the acetone solution. Gel permeation chromatography (GPC) was used to determine the molecular weight and molecular weight distribution, as molecular weight and molecular weight distribution would greatly affect yarn quality and the spinning production process. The GPC instrument used was one that is coupled with multiple detectors, including refractive index, low angle laser light scattering, and four-capillary differential viscosity.

$$Cell-(OH)_x(OAc)_{3-x} + mAc_2O \xrightarrow{H_2SO_4} Cell-(OH)_{x-m}(OAc)_{3-x+m} + mAcOH \quad (1)$$

$$Ac_2O + H_2O \longrightarrow 2AcOH \quad (2)$$

RESULTS AND DISCUSSION

Table III shows pulp properties from two cooking processes (KP and NaOH-KP). Through the comparison of pulp properties, it can be seen that pretreatment with NaOH could increase the α-cellulose content and reduce the lignin content (or kappa number) of the pulp, which are both positive, but would also decrease the DP and yield of the pulp, which is negative. Apparently some hemicellulose was extracted during the alkaline pretreatment process, resulting in a pulp of higher α-cellulose content. But at the same cooking time, more severe alkaline degradation of cellulose also occurred when compared with the traditional kraft cooking, causing a drop in DP and pulp yield. If the cooking time is reduced with the NaOH-KP process, it is likely that this degradation might be lessened.

Only the alkali-pretreated kraft pulp (NaOH-KP) was used for the bleaching experiments. The goal was to identify a bleaching sequence that could produce a pulp with high brightness, high α-cellulose content and high DP. **Table IV** shows the properties of bleached pulp from different bleaching sequences.

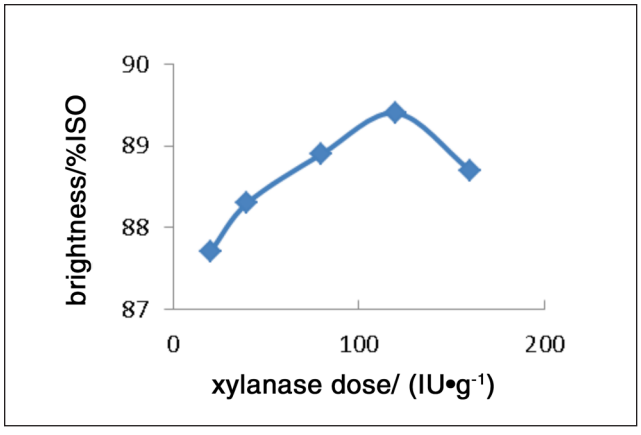
Oxygen and hydrogen peroxide are both environmentally friendly chemical agents commonly used for bleaching processes. In this study, both were used to improve pulp brightness. Table IV also shows that different bleaching sequences appeared to have no effect on α-cellulose content of the bleached pulp. It seemed that hydrogen peroxide was more effective than oxygen in promoting the brightness in the long

	KP	NaOH-KP
Kappa number	15.0	14.0
DP	1526	1236
α–cellulose, %	89.6	91.6
Yield, %	49.8	44.2

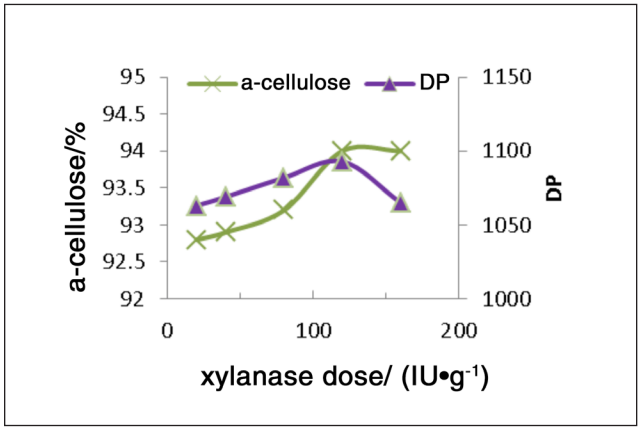
III. Comparison of pulp properties between traditional kraft pulping (KP) and alkali-preimpregnated kraft pulping (NaOH-KP) cooking processes.

Bleaching Sequence	Brightness (%ISO)	α-cellulose (%)	DP
O	51.8	91.3	1197
OD_1ED_2	85.1	92.7	1015
D_1ED_2	83.6	92.7	1208
OD_1ED_2P	88.9	92.8	969
D_1ED_2P	87.5	92.7	1050

IV. Properties of bleached pulp from different bleaching sequences.



1. Brightness versus xylanase dosage in xylanase post-treatment stage.



2. Degree of polymerization and α-cellulose content versus xylanase dosage in xylanase post-treatment stage.

sequence, and both of them had negative impact on the degree of polymerization. Although the OD_1ED_2P sequence appeared to produce the highest brightness, it also resulted in the lowest DP (969) and failed to satisfy the DP requirement for acetate-grade pulp after subsequent treatments. Therefore, according to the results (Table IV), D_1ED_2P should be considered to be the optimal bleaching sequence among all those that were tested.

Data in Table IV demonstrate that after a D_1ED_2P bleaching process, the α-cellulose content in the bleached pulp was still too low for a high-grade dissolving pulp (≥96%). More hemicellulose must be removed to generate a high-purity cellulose pulp. To do that, a combined further treatment with xylanase and alkali was conducted.

Xylanase treatment, although widely applied in practical production, is usually carried out before all bleaching steps to promote brightness. In this study, however, it was not used as a pretreatment bleaching agent, but rather as a post-treatment purifying agent to remove xylan from the pulp. **Figures 1** and **2** show the experimental results.

It can be seen from Fig. 1 that the maximum brightness of more than 89% could be achieved when the xylanase dosage was at 120 IU•g^{-1}. The ISO brightness of the pulp was improved by a maximum of 2% with the xylanase treatment.

NaOH Concentration (%)	Brightness (%ISO)	α-cellulose (%)	DP
2	88.9	94.1	1 102
4	90.5	96.8	1 163
6	90.1	97.2	1 168
8	89.4	98.3	1 166

V. Effects of NaOH concentration in alkaline extraction on pulp properties.

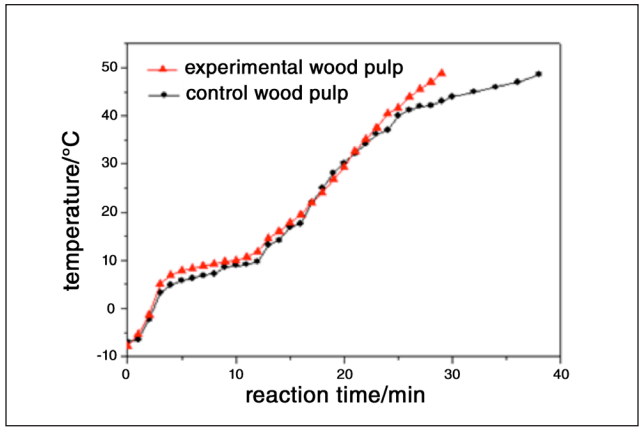
Brightness, %ISO	90.5
α-cellulose, %	96.8
DP	1163
iron ion, mg·kg^{-1}	2.6
Ash, %	0.11
S-10, %	4.33

VI. Final properties of the acetate-grade dissolving pulp obtained with the new process.

Figure 2 shows that the α-cellulose content in the pulp increased with the increase in xylanase dosage and reached a plateau when the xylanase dosage was increased to 120 IU•g^{-1}. Beyond that, no further increase in α-cellulose content could be achieved. This result indicated that a portion of xylan could be removed by xylanase post-treatment, and a xylanase dosage of 120 IU•g^{-1} was sufficient to remove this portion of the hemicellulose. Higher xylanase dosage would provide no further benefit.

Figure 2 also shows that, with the increase of xylanase dosage, the degree of polymerization increased until it reached the peak value at 120 IU•g^{-1} xylanase dosage. The initial increase of DP was likely because of the dissolution and removal of hemicelluloses, which are known to contain low molecular weight components. When the dosage of xylanase was further increased beyond 120 IU•g^{-1}, the dissolution of xylan reached a maximum. At the same time, the tendency of the enzyme to degrade cellulose became significant, causing the degree of polymerization to decline. Even so, at high xylanase dosage, the DP was never lower than when there was no enzyme treatment.

After xylanase treatment, NaOH was applied to further extract the residual hemicelluloses. **Table V** shows the effects of NaOH concentration on properties of treated pulp. When the concentration of NaOH exceeded 4%, the α-cellulose content in the pulp increased steadily. When NaOH concentration was at 4%, the α-cellulose content in the obtained pulp can meet the requirement for an acetate-grade dissolving pulp (≥96%). At this NaOH concentration, it



3. Temperature curve during acetylation of wood pulps (experimental sample vs. control sample).

appeared that the brightness and degree of polymerization of the treated pulp were slightly improved.

Table VI shows the final properties of the acetate-grade dissolving pulp obtained with the new process. The process conditions used to prepare the pulp are as follows: NaOH-KP cooking, D_1ED_2P bleaching sequence, xylanase post-treatment at dosage of 120 IU•g^{-1}, and alkaline post-treatment at NaOH concentration of 4%. Table VI also shows that the main properties of the final pulp obtained all meet the requirements for an acetate-grade dissolving pulp, which are α-cellulose content ≥96%, ISO brightness ≥90%, DP ≥900, and S-10 <5.0%.

Figure 3 shows the temperature curves during the acetylation reactions for the experimental and the control wood pulp samples. The rate of temperature increase is a direct indication of acetylation reactivity of pulps. The higher the rate, the greater the reactivity of cellulose in the pulps, which illustrates a more complete acetylation reaction within the same period. For the experimental pulp sample, the average rate of temperature increase was 1.93°C/min, the peak temperature was 48.9°C, and the time it took to reach the peak temperature was 29 min (Fig. 3); for the control pulp sample, these numbers were 1.46°C/min, 48.6°C, and 38 min, respectively. These data clearly suggested that the experimental pulp had greater acetylation reactivity than the control pulp. Acetylation reaction of dissolving pulp is the most important reaction in the process of the reaction performance test. Generally speaking, fast reaction rate is beneficial to this reaction. Unfortunately, a likely reason for this phenomenon is that the experimental pulp might contain a higher amount of amorphous hemicellulose, which is more prone to the acetylation reaction.

After acetylation, the experimental wood pulp and the commercial wood pulp (control) were dissolved in a 3% acetone solution. Both acetylated pulp samples could complete dissolution in the acetone solution within 8 min.

A particle counter was used to measure the size and number of insoluble particles in the acetone solution. The number of insoluble particles existing in the acetone solution is a direct indication of the amount of solid and gel impurities in the acetate pulps. The higher the particle numbers, the higher the impurity content. When a wood pulp contains relatively high hemicellulose content, more insoluble particles will be in its acetone solution. Such pulp tends to cause more operation and stability problems in the spinning production process. **Table VII** shows that there are slightly more insoluble particles in the acetone solution of experimental pulp that are no larger than 50 μm.

Table VIII shows haze data of acetone solutions of the acetylated wood pulp samples. The haze of the experimental pulp sample is slightly higher than the imported commercial wood pulp. The acetone solution of the acetylated experimental sample also has a lower L value and higher b value, indicating that it contains a higher amount of unreacted long fibers and it is slightly more yellowish.

Table IX shows the molecular weight and molecular weight distribution of the acetylated experimental and control wood pulps. Table IX shows that the number average molecular weight (Mn) and the weight average molecular weight (Mw) of the experimental wood pulp are both lower than those of the control wood pulp. The Mw/Mn ratio of the experimental wood pulp is 1.606, while that of the control wood pulp is 1.489, indicating that the former has a wider Mw distribution.

	2μm	5μm	10μm	25μm	50μm	75μm
Experimental pulp	33876	8377	3391	308	158	3
Control pulp	22916	7168	2389	201	130	2

VII. Number of insoluble particles in 3% acetone solution of acetylated wood pulps.

	L	a	b	Haze
Experimental pulp	89.47	-0.01	5.74	10.4
Control pulp	95.39	0.12	4.58	8.6

VIII. Haze data of acetone solutions of acetylated wood pulps.

Sample	Mn	Mw	Mw/Mn Ratio
Experimental pulp	51117	82085	1.606
Control pulp	74008	110209	1.489

IX. Molecular weight and molecular weight distribution of acetylated wood pulps.

CONCLUSIONS

Alkaline pretreatment can be applied to replace prehydrolysis in the kraft pulping process to prepare a high-grade dissolving pulp. Although the pulp obtained has a high ISO brightness value (≥90%) after a D_1ED_2P bleaching sequence, the α-cellulose content was still below the requirement. Therefore, a xylanase post-treatment was used in combination with cold alkali extraction to remove more hemicelluloses from the pulp. The optimal xylanase dosage and concentration of NaOH during the post-treatments were 120 IU•g^{-1} and 4%, respectively. With the new process of NaOH-KP pulping, D_1ED_2P bleaching, and the combined post-treatments for further purification with xylanase and alkali under the optimal conditions, the final wood pulp obtained could meet the property requirements for an acetate-grade dissolving pulp. Application tests performed with the experimental wood pulp obtained from this new process indicated that its processing performance was similar to that of an imported commercial acetate-grade dissolving pulp. With some further refinement of the treatment conditions, a satisfactory acetate-grade dissolving pulp can most likely be produced with the new process. **TJ**

ACKNOWLEDGMENTS

The authors are thankful for the funding support of the National Science and Technology Pillar Program during the Eleventh Five-Year Plan Period (Grant No.2006BAD18B0502).

LITERATURE CITED

1. Thomas, L.V., "The capacity of acetate-grade dissolving pulp is growing steadily worldwide [in Chinese]," July 25, 2010. Available [Online] http://www.zgxws.com/news/show-294.html.
2. Funaki, Y., Ueda, K., Saka, S., et al., *J. Appl. Polym. Sci.* 48(1): 419(1993).
3. Neal, J.L., *J. Appl. Polym. Sci.* 9(6): 947(1965).
4. He, Jianxin, Cui, Shizhong, and Wang, Shan-yuan, *J. Appl. Polym. Sci.* 107(2): 1029(2008).
5. Waleed, W.A. and Ulrike, W.T., *TAPPI J.* 7(6): 3(2008).
6. Waleed, W.A. and Ulrike, W.T., *Holzforschung* 64(6): 411(2010).
7. Helmerius, J., von Walter, J.V., Rova, U., et al., *Bioresour. Technol.* 101(15): 5996(2010).
8. Lu, W.J., Pu, J.W., and Qi, X.H., *Pap. Sci. Technol.* 2(26): 16(2007).
9. Bajpai, P. and Bajpait, P.K., *Appita J.* 54(4): 381(2001).
10. Christov, L.P., Akhtar, M., and Prior, B.A., *Holzforschung* 50(6): 579(1996).
11. Gübitz, G.M., Lischnig, T., Stebbing, D., et al., *Biotechnol. Lett.* 19(5): 491(1997).
12. Jackson, L.S., Heitmann, J.A., and Joyce, T.W., *TAPPI J.* 18(3): 171(1998).
13. Lu, W.J., Pu, J.W., Yan, Z.P., et al., *Chem. Ind. For. Prod.* 28(1): 59(2008).

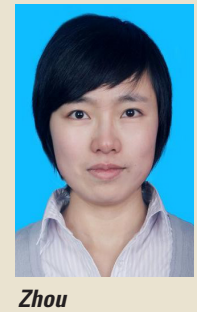
ABOUT THE AUTHORS

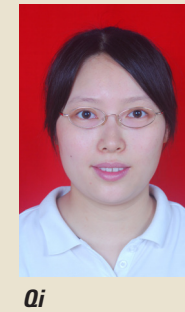
This work aims to overcome some of the drawbacks of the prehydrolysis kraft process, which is currently widely adopted in China. The combined post-treatment with xylanase and alkali can remove hemicellulose very well, such that it may replace the prehydrolysis kraft process.

Alkaline pretreatment is not nearly as effective as prehydrolysis in removing hemicelluloses. Therefore, the combined post-treatment with xylanase and alkali is used to achieve the desired result in this work.

It is shown that the combination of alkaline pretreatment and xylanase post-treatment can be used to replace the prehydrolysis process. The next step is to optimize the treatment conditions and then work with mills for the commercialization of this new process.


Liu


Zhou


Qi


Pu

Liu is a Ph.D. student at the College of Materials Science and Technology, Beijing Forestry University; Zhou and Qi are graduate students at the College of Materials Science and Technology, Beijing Forestry University; and Pu is a professor at the College of Materials Science and Technology, Beijing Forestry University, Beijing, China. Email Liu at specialpaper2012@aliyun.com or xiaoleicoolcool@126.com.