PREPARATION OF DISSOLVING PULP FROM BAMBOO FOR TEXTILE APPLICATIONS. PART 2. OPTIMIZATION OF PULPING CONDITIONS OF HYDROLYZED BAMBOO AND ITS KINETICS

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Kraft pulping of hydrolyzed green bamboo (*Dendrocalamopsis oldhami*) chips was performed under various conditions to determine the effects of process variables (alkali charge, sulfidity, cooking temperature, and cooking time) on the dissolution of the lignocellulosic components, i.e. lignin, pentosans, and cellulose. Meanwhile, the kinetics of kraft delignification of hydrolyzed bamboo was investigated. The results showed that both an increase of alkali charge and sulfidity could result in a clear reduction in kappa number and yield, but the effect of alkali charge was more significant than that of sulfidity. Even though severe conditions were able to purify fiber, the cellulose degradation occurred intensively. Active alkali charge 23%, sulfidity 26%, cooking temperature 170°C, and cooking time 60 min were selected as the optimum conditions for the consideration of selective delignification. As a consequence, the properties of the pulp produced at optimum cooking conditions were determined to be: kappa number 6.3, pentosans 5.0%, α-cellulose 90.2%, and viscosity 30.3 mPa • s. The data analysis confirmed that the reaction order of delignification was approximate to 1.1, and the activity energy of the hydrolyzed bamboo was 53 kJ/mol.

Keywords: Green bamboo; Kraft pulping; Kinetics; Prehydrolyzed; Dissolving pulp; Optimization

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INTRODUCTION

Bamboo can be classified generally as a long-fibered or semi long-fibered fibrous material, as the length of fibers in many bamboo species is comparable to that of softwood fibers (Mân Vu et al. 2004). Due to its abundant availability in Asia and suitable fiber morphology, together with the similar chemical compositions to that of softwood, bamboo chemical pulps have attracted increasing attention in China. The high strength put the bamboo pulps at further advantage in using for more versatile paper products or other high value added product, such as cellulose esters, cellulose ethers, and textile fibers (Christov et al. 1998). Nowadays, the market for dissolving pulp is very good, and its future will be bright due to demographic growth and a shortage in other fibrous materials. More importantly, the technology for the conversion of bamboo chips into dissolving pulp has attracted increasing attention during the past few years, and has been driven by growing interest for the bamboo textile fiber production (He et al. 2009; Salmela et al. 2008; Yang et al. 2008; Xu and Tang 2007). Dissolving pulp can be manufactured by either a modified kraft or sulfite process, which is different from the traditional paper-grade pulping process; the objective of these processes is to obtain a relatively pure and uniform cellulose product with a controlled degree of polymerization.

Both lignin and hemicelluloses are considered as contaminants and are to be removed. Otherwise, high hemicelluloses and lignin content in dissolving pulps would result in poor cellulose processability (e.g. fiber swelling, filterability, and xanthation) and a negative effect on properties of the cellulose-end product (Christov and Prior 1993). Beside these two traditional methods, organsolv pulping or directly upgrading paper-grade pulp to dissolving pulp by reducing hemicelluloses amount are also alternative methods, including post-alkaline, nitren, or cuen extractions, or by applying xylanases alone or in combination with alkaline extraction (Janzon et al. 2008; David et al. 2010). The pre-hydrolysis kraft process is also an applicable method for better quality of dissolving pulp as well as high delignification rate, yield, and viscosity, while giving low hemicelluloses content. The performance of a kraft process depends on a great number of variables (temperature, alkali charge, sulfidity, heating rate, cooking time, and liquor ratio), which directly affect the yield and properties of the pulp obtained.

In our study, a pre-hydrolysis kraft pulping process was used to produce dissolving pulp. The pre-hydrolysis process was studied in previous projects (Ma et al. 2011). The aim of this work was to study the effects of pulping variables on the dissolutions of the lignocellulosic components and thus to optimize the pulping conditions to minimize the cellulose degradation of the final pulp. A kinetic model was established, and the activation energy of prehydrolyzed bamboo (*Dendrocalamopsis oldhami*) was determined, which will be useful in controlling the degree of cooking and predicting the pulping yield.

EXPERIMENTAL

Materials

Green bamboo (*Dendrocalamopsis oldhami*) was obtained from a local forestry center. Before pulping, the raw material was hydrolyzed in water in a 15 L stainless steel digester, rotating at 1 rpm. The hydrolysis conditions were: liquor to bamboo ratio 3:1, heating rate 7°C/10 min, cooking time 60 min, and cooking temperature 170 °C (Ma et al. 2011). The main chemical composition of raw material and hydrolyzed material is listed in Table1.

Table 1. Chemical Composition of Bamboo Material

Raw material			Hydrolyzed bamboo		
Pentosan /%	Cellulose/%	Lignin/%	Pentosan /%	Cellulose/%	Lignin/%
17.5	49.6	23.1	9.0	60.3	18.1

Pulping Process

All pulping trials were carried out in the same digester. In order to determine optimum kraft pulping conditions of hydrolyzed bamboo, the liquor-to-bamboo ratio was held constant at 3:1, which is the typical pulping condition in the mill. Alkali (active alkali) charge, time at maximum temperature, maximum temperature, and sulfidity are listed in Table 2.

Kinetic Mechanism of Kraft Pulping

A total of 9 series of 36 cooks were carried out in a digester (YYQ-10×1.25) with oil bath. The pulp was cooled with tap water and then transferred to the bags, then thoroughly washed before stored for further analyses.

Table 2. Cooking Conditions of Alkali, Sulfidity, Time, Temperature

Alkali (as Na_2O)(%)	17, 20, 23, 26
Sulfidity(%)	20, 23, 26, 29
Liquor-to-hydrolyzed bamboo ratio (l/kg)	3
Cooking temperature (°C)	150, 160, 170, 180
Heating rate (°C/10min)	7
Time at maximum temperature(min)	30, 60, 90, 120

Pulp Characterization

Pulp tests were performed according to the TAPPI Standard Methods with the exception of viscosity (Ma et al. 2011), which was measured by the Copper Ammonia Solution-Ubbelohde Viscometer method; the measurement procedure was the same as in T230om-08, and the viscosity of the pulp were calculated by the formula as follows,

$$\eta = \rho \times t \times K \tag{1}$$

where η is viscosity (mPa·s), ρ is the density of copper ammonia solution (g/mL), t is the average efflux time (s), and K is a correction factor for the Ubbelohde viscometer.

RESULTS AND DISCUSSION

Optimization of Kraft Pulping Process

The cooking condition targets were optimized for maximum removal of lignin while maintaining cellulose viscosity at a certain level. Kappa number and viscosity of the pulp in each cooking conditions were evaluated and were used as the main criterions for selecting the pulping parameters. The effects of alkali and sulfidity on kappa number, viscosity, pentosans, and yield of the pulps are shown in Tables 3 and 4.

Table 3. Effects of Alkali on Bamboo Kraft Cooking

Alkali/%	Yield/%	Kappa	Pentosans/%	α-Cellulose/%	Viscosity/mPa·s
17	34.3	11.3	5.8	91.0	22.5
20	34.0	9.5	4.9	92.4	19.1
23	33.4	5.8	4.8	92.9	17.3
26	30.6	5.6	4.7	93.3	10.1

Sulfidity 23%, cooking temperature 170 °C; cooking time 120 min

Table 4. Effects of Sulfidity on Bamboo Kraft Cooking

Sulfidity /%	Yield/%	Kappa	Pentosan/%	α-Cellulose/%	Viscosity/mPa·s
20	33.0	6.5	5.8	91.3	16.2
23	32.7	5.8	4.8	92.9	17.3
26	32.4	5.6	4.7	92.9	24.4
29	32.4	5.5	4.6	92.9	24.9

Alkali charge 23%, cooking temperature 170 °C, cooking time 120 min

It was can be shown from Tables 3 and 4 that either an increase in alkali charge (17%-26%) at a fixed sulfidity (23%) level, or an increase in sulfidity (20%-29%) at a fixed alkali (23%) level, resulted in a reduction in yield and kappa number. However, the effect of alkali charge on yield and kappa number was more significant than that of sulfidity. Furthermore, both alkali and sulfidity had a significant influence on viscosity. The figures show that carbohydrate degradation (viscosity loss) occurred with an increase of alkali charge (Table 3). Meanwhile the pulp yield dropped sharply to 30.6% when alkali addition was 26%.

The yield loss was attributed to dissolution of lignin and carbohydrates, and it was clearly demonstrated that the alkali attacked both the lignin and cellulose of bamboo materials, thereby causing nonselective carbohydrate degradation. By contrast, an increase of sulfidity showed a positive effect on viscosity. More specifically, higher sulfidity could protect cellulose from degradation, though the viscosity gain was negligible in the case of sulfidity exceeding 26%.

These results are in accordance with the fact that during kraft cooking, hydrogen sulfide ions were mainly involved in lignin degradation reactions, while carbohydrate degradation reactions were only affected by hydroxide ions (Sixta 2006). It could be expected that an increase of sulfidity at a fixed alkali level would result in an increase in the amount of hydrogen sulfide ions with a simultaneous decrease in the number of hydroxide ions. Hence, the delignification selectivity was enhanced. In these pulping experiments, when a lower kappa number was reached, a clear decrease in viscosity was to be seen (Table 3). Therefore, based on the both the considerations of lower kappa number and higher viscosity, the following chemical addition levels were selected: alkali charge 23%, and sulfidity 26%.

Table 5. Effects of Cooking Temperature on Hydrolyzed Bamboo Kraft Pulping

Temperature/°C	Yield/%	Kappa	Pentosan/%	α-Cellulose/%	Viscosity/mPa·s
150	35.0	10.1	5.8	91.0	25.7
160	32.8	8.9	5.5	91.9	25.0
170	32.4	5.6	4.7	92.9	24.4
180	30.6	5.4	3.9	93.3	20.6

Alkali charge 23%, sulfidity 26%, liquor ratio 1:3, heating rate 7 °C/10min, cooking time 120 min

Table 6. Effects of Cooking Time on Bamboo Kraft Cooking

Time/min	Yield/%	Kappa	Pentosan/%	α-Cellulose/%	Viscosity/mPa·s
30	32.9	8.6	8.9	88.4	30.9
60	32.8	6.3	5.0	90.2	30.3
90	32.6	6.2	4.9	91.6	27.4
120	32.4	5.6	4.7	92.9	24.4

Alkali charge 23%, sulfidity 26%, cooking temperature 170 °C

The effects of cooking temperature and time on yield, kappa number, and viscosity of pulp are shown in Tables 5 and 6. It was found that lower cooking temperature and shorter cooking time resulted in higher kappa number and yield, while higher temperature and longer cooking time was favorable for the dissolution of lignin fragments from the fibers. Also, cooking time and temperature directly affected the delignification (Martínez et al. 1997). Table 5 revealed that at lower temperature range (150 °C to 170 °C), the kappa number decreased sharply, while at higher temperature range (170 °C to 180 °C), the magnitude of decrease in kappa number was not so pronounced. The kappa number variations caused by the increasing of cooking temperature were gradually reduced, which implied that higher severities in the delignification process did not cause further solubilization of lignin. In other words, the delignification in the cooking process was incomplete. A relatively high pulping temperature was required to achieve a sufficient reaction rate and avoid long time exposure of the carbohydrates to the pulping conditions. At higher temperature, the degradation of carbohydrate fractions also increased drastically, thereby resulting in lower pulp viscosity (Malcolm et al 1997). Therefore, there was no need to put either the cooking temperature or time at a high level.

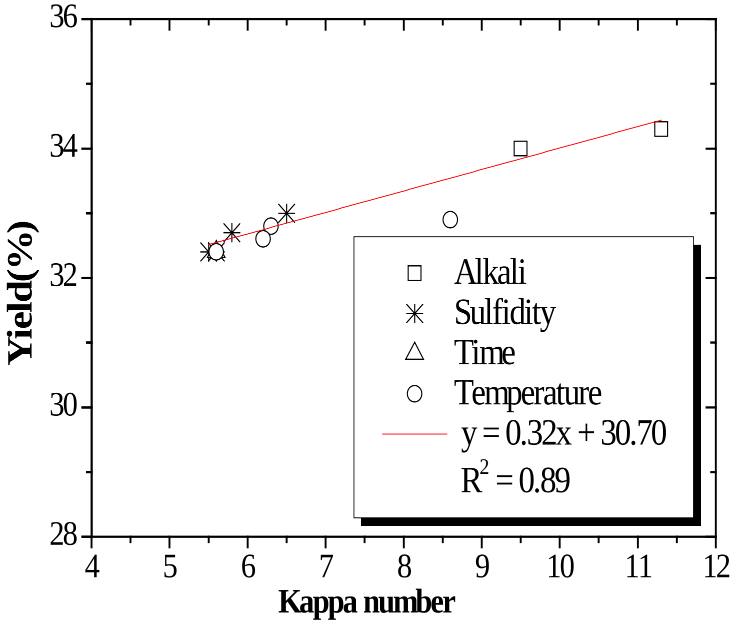

Fig. 1. Kappa number variations with kraft pulp yield

Based on the kappa number and viscosity, a cooking time of 60 min at 170 °C was considered to be the optimum condition for the hydrolyzed bamboo kraft pulping. The properties of the pulp produced by the optimum prehydrolysis kraft pulping method were: kappa 6.3, pentosans 5.0, α-cellulose 90.2%, and viscosity 30.3 $\mathrm{mPa \cdot s}$. Optimization of pulping conditions required not only the selection of a target pulp index, but also the viability of cooking conditions such as temperature and time. Additionally, in Dang' study, it was found that pulp yield decreased linearly with kappa number (Dang and Nguyen 2007a). After removing some experimental error (data not shown), it was found that same result could be obtained in our research.

Kinetic Model of Kraft pulping

Although the cooking temperature used in kraft pulping normally ranges from 110 to 180 °C (Kerr 1970; Nguyen and Dang 2006; Wong et al. 1995), based on the results shown in Table 5 it is apparent that cellulose viscosity in hydrolyzed bamboo kraft pulp decreased significantly once cooking temperature exceeded 170 °C. This is mainly because the physico-chemical structure of bamboo is rigidly disturbed or redistributed during the process of hot-water hydrolysis. To make the process control more reasonable, the temperature used to develop the kinetic model of hydrolyzed bamboo kraft pulping should be lower than 180 °C.

By taking into account of the alkali effect on delignification during kraft pulping, the whole kinetic function can be described as follows,

$$-\frac{\mathrm{d}L}{\mathrm{dt}} = k[OH^-]^a L^b \tag{1}$$

where L is the lignin content of the pulp at time t (% of original o.d.w.), k is the temperature-dependent rate constant, and a and b are reaction orders, which are taken to be constants.

In this experiment, only one initial alkali concentration (1.83mol/L) was used. Therefore, Equation 1 can be derived as,

$$-\frac{\mathrm{d}L}{\mathrm{dt}} = KL^b \tag{2}$$

in which $K = k[OH^-]^a$. Also, delignification rate can be calculated as follows:

$$-\frac{\mathrm{d}L}{\mathrm{dt}} = -\frac{[L(t+\Delta t) - L(t)]}{\Delta t} \tag{3}$$

Combining Equations 2 and 3, and taking the logarithm on both sides of equation, we can find that,

$$Ln\left(-\frac{[L(t+\Delta t) - L(t)]}{\Delta t}\right) = Ln(K) + bLn(L) \tag{4}$$

Therefore, after linear fitting between Ln(*L*) and the delignification rate, the reaction order of lignin removal can be determined from its slope.

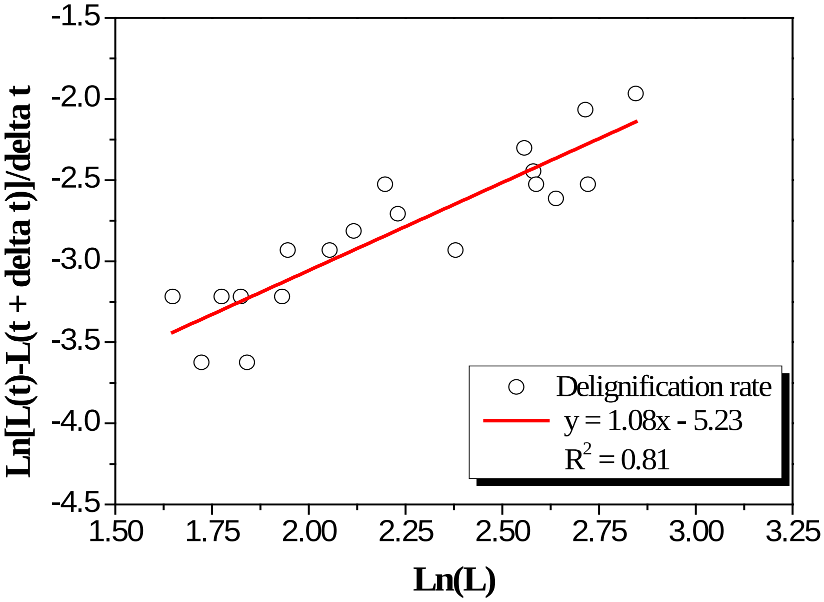

Fig. 2. The dependence of delignification on the logarithm of lignin content in pulps

As shown in Fig. 2, the reaction order of lignin removal can be regarded as 1.1. Furthermore, Dang and Nguyen (2007b) have developed a universal kinetic model for delignification of bamboo kraft pulping and reported that the reaction order of alkali is approximately 0.9. Thus, Equation 1 can be rewritten as

$$-\frac{[L(t+\Delta t)-L(t)]}{\Delta t}=k[OH^{-}]^{0.9}L^{1.1} \tag{5}$$

Obviously, the reaction rate constant at different temperature in function (5) can be simply calculated by linear regression. If one assumes that the effect of temperature on delignification follows Arrhenius rule, the activity energy of this delignification reaction will be determined subsequently by following expression,

$$Ln(k)=Ln(k_0)-\frac{Ea}{RT} \tag{6}$$

where k_0 is the pre-exponential factor and *R* is the molar gas constant, which is equal to 8.314 J/(mol·K).

According to the slope of the line in Fig. 3, the estimated activity energy of delignification for hydrolyzed bamboo kraft pulping was 53kJ/mol, which is lower than 115 kJ/mol reported by Dang and Nguyen (2007b) for traditional kraft pulping of bamboo. Compared to untreated feedstock, this is possibly due to different structure and distribution of lignin in hydrolyzed bamboo. This suggests that pre-hydrolysis by hot water makes the removal of residual lignin in woodchips easier in subsequent kraft pulping. But the pre-exponential factors in our and their research were 79 and 86 min^{-1}, respectively. Therefore, we can propose a hypothesis that pretreatment by hot water extraction before kraft pulping just changes the linkage between lignin and carbohydrate rather than influencing the reaction probability between oxygen hydroxide ion and lignin in the microstructure of bamboo.

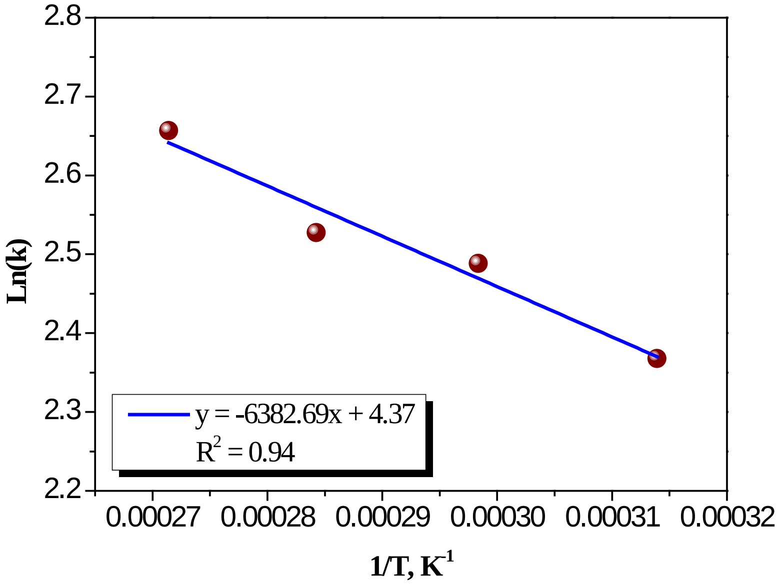

Fig. 3. The relationship between 1/T and Ln(k)

CONCLUSIONS

Prehydrolyzed bamboo chips were subjected to kraft pulping in various conditions to determine a suitable kraft pulping process. It was possible to obtain unbleached pulp with cellulose higher than 92% but pentosan and lignin lower than 5% and 0.6% even without process optimization, respectively, which will be preferential for the production of dissolving pulp. Moreover, it was also found that the cellulose viscosity would be significantly decreased if the temperature and activity alkali charge used in kraft pulping was higher than 170 ^{o}C and 23% (based on od wood). Subsequently, the kinetic model for kraft pulping of hydrolyzed bamboo using cooking temperature ranged from 110 to 170 ^{o}C and activity alkali charge of 23% was conducted. A reaction order of 1.1 and an activation energy of 53kJ/mol were obtained by linear regression. It is reasonable that this activity energy is lower than the reported value of 115 kJ/mol for bamboo without any pretreatment. Results were consistent with the fact that pre-hydrolysis can disturb the three-dimensional structure of bamboo and further break the linkage between lignin and carbohydrate. But a similar pre-exponential factor between hydrolyzed and untreated bamboo suggests that prehydrolysis by hot-water may merely change the lignin structure rather than affecting its distribution.

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