PRETREATMENT OF MOSO BAMBOO WITH DILUTE PHOSPHORIC ACID

Bo Hong,[a,b] Guoxin Xue,[a,*] Liqing Weng,[a] and Xing Guo [a]

Dilute phosphoric acid pretreatment of moso bamboo materials was studied for producing high quality dissolving pulp for textile applications. The dynamics of dilute acid pretreatment were considered. The Saeman model was found to describe well the acid hydrolysis of moso bamboo hemicelluloses to their monomers under different temperatures and different dilute phosphoric acid concentrations. The initial degradation rate of hemicelluloses was much higher than its subsequent degradation rate, and the xylose generation rate increased with increasing temperature. The change rule of the pentose extraction rate was considered along with the pretreatment factor (P factor). Optimum dilute acid pretreatment conditions were 170 °C and 45 minutes. Based on the optimum conditions and a mass balance of sugars, a weight loss of 26.5% of the solid and liquid fractions combined was observed after the pretreatment. SEM results revealed that the moso bamboo fibers surfaces and cell wall were damaged. With the surface area increasing, the accessible pore areas also increased. At the same time, the crystallinity of the cellulose was reduced, which created a favorable environment for chemical penetration in the subsequent treatment.

Contact information: a: Zhejiang Sci-Tech University, 5 Second Avenue, Xiasha Higher Education Zone, Hangzhou, China; b: Zhejiang Institute of Communications, Moganshan Road, Hangzhou, China;
* Corresponding author:xueguoxin@126.com

INTRODUCTION

With the constant increase of the world's population, the need is increasing for the use of environmentally friendly materials that are biodegradable and able to replace synthetic polymers from fossil feedstock. The viscose fiber is a major component of synthetic polymer fiber, and its market has grown in recent years. At present, China's raw materials for dissolving pulp are primarily from cotton linters and wood. The shortage of wood resources and limited cotton production because of limited cultivated area make it necessary to develop new dissolving pulp raw materials (Zhang and Shen 2003). China has the most abundant moso bamboo resource, a total of 39 genera and 500 species, accounting for 1/3 of the moso bamboo species in the world (Chen 2000). The moso bamboo forest covers an area of 7.2×10^4 km^2, mainly distributed among 17 provinces (municipalities) in southern China (Jiang and Jiang 2002; Qiu and Hong 2001; Xiao 2000). Besides, they are robust, and they can grow into a forest in 3 to 5 years. With 40% to 50% cellulose, about 30% lignin, and about 25% pentosans, moso bamboo can be counted among the high-yield textile fiber raw materials, and it has the potential to become a substitute for hardwood. It is therefore beneficial for the conservation of forest resources (Zeng and Xiang 1987; Li. 2001; Zhu 2003). China has abundant moso bamboo

resources, which can be used to produce dissolving pulp. It is a new way of processing and utilizing moso bamboo fiber in textile purposes, which will greatly enhance the value of the moso bamboo (Shen and Chen 2003; Xie *et al.* 2004).

With the purpose of producing viscose fiber for textile applications, biomass must be pretreated in order to achieve efficient removal of lignin and hemicellulose through pretreatment process. Different pretreatment methods can be employed, including acid or alkaline pretreatment, wet oxidation, steam pretreatment, and ammonia fiber explosion. Of these pretreatment techniques, dilute acid pretreatment has been found to be one of the most promising pretreatment methods for altering the structure of lignocellulosic materials due to simplicity, effectiveness, and lower expense compared to other pretreatment methods (Hendriks and Zeeman 2009).

Dilute acid pretreatment refers to the hydrolysis of hemicellulosic material by acids (typically sulphuric, hydrochloric, or phosphoric acid) at concentrations of 1% to 10%, using a moderate temperature (in the range of 100 ℃ to 180 ℃) (Wingren *et al.* 2003). Dilute acids break down the cellulose and hemicellulose polymers in lignocellulosic biomass to form monomeric sugars (Wyman 2003). Among the three components of raw material, cellulose, hemicellulose, and lignin, cellulose is far more stable than the other two when placed in dilute inorganic acid. In addition, the cellulose is well protected by the matrix of hemicellulose and lignin (Galbe and Zacchi 2005), so it is important to note that hemicellulose is more easily hydrolysed than cellulose (Tjeerdsma and Militz 2005). The advantages of acid hydrolysis are that the acid can penetrate lignin without other pretreatments such as enzymatic, bacterial, high pressure, and temperature methods, and the rate of acid hydrolysis is faster than enzyme hydrolysis. However, cellulose also degrades rapidly under acidic conditions (Cheung and Anderson 1996).

Sulphuric acid and hydrochloric acid are the most commonly used catalysts for hydrolysis of lignocellulosic residues. Phosphoric acid can be more advantageous for hydrolysis. Phosphoric acid is less aggressive than other acids, thus it generates lower concentrations of growth inhibitors of microorganisms such as furfural or acetic acid (Romero *et al.* 2007).

Dilute phosphoric acid has shown the ability to yield higher fermentable sugars and lower inhibitors (acetic acid and furfural) at operating conditions of 6% acid concentration at 100 ℃ for 300 min in sugarcane bagasse hydrolysate (Gámez *et al.* 2004). Similarly on hydrolysate from olive tree pruning, hemicelluloses conversion rates of 77% were achieved with glucose and reducing sugar concentrations being observed as 89% of the hemicellulosic sugars contained in the raw material at conditions of 8% acid concentration at 90 ℃ for 240 min (Romero *et al.* 2007).

Interest in the use of H_3PO_4 is also motivated by the fact that after neutralization of hydrolysates with NaOH, the salt formed is sodium phosphate. The hydrolysates with sodium phosphate are friendly to the environment (Gámez *et al.* 2006).

Many researchers (Ye *et al.* 1998; Nguyen *et al.* 1998, 2000; Saha and Bothast 1999) have studied the dilute acid pretreatment of corn, straw, wood, *etc*. But so far, to the best of our knowledge, dilute acid pretreatment of moso bamboo pulp, especially with phosphoric acid, has little information available in the literature up to the present.

The pretreatment factor was proposed in the 1960s and 1970s. At that time the "pretreatment factor" concept (the P factor), similar to the cooking Factor H, was presented for the water pretreatment process of pine (Brasch and Free 1965; Sears *et*

*al.*1971). Therefore the water pretreatment temperature and time are integrated into one variable, to guide pretreatment process.

The purpose of this study was to investigate the effect of dilute phosphoric acid pretreatment on moso bamboo. In this experiment, with the moso bamboo as raw material, the researchers analyzed the chemical composition of moso bamboo, studied dilute acids pretreatment dynamics, evaluated the change rule of the pentose extraction rate along with P factor, and obtained the best dilute acid pretreatment conditions. Morphological changes of the moso bamboo fiber in dilute acid pretreatment were observed with scanning electron microscopy. The results of this investigation will provide theoretical reference for the moso bamboo dissolving pulp pretreatment, and at the same time shed light on the commercial utilization of moso bamboo for textiles purposes.

MATERIALS AND METHODS

Raw Material

Moso bamboo was obtained from Zhejiang Province, China. The length of bamboo fibers normally ranges from 1 mm to 3 mm with an average less than 2 mm, which makes them suitable for substituting short plant fibers. After the dust and debris were screened out, the qualified raw materials were stored in a sealed plastic bag after air drying to equilibrium moisture for further processing.

Methods

Dilute acid pretreatment of moso bamboo

The pretreatment of the moso bamboo with dilute phosphoric acid was carried out in an YYQ-10x1.25 oil bath cooking pot. The solid-to-liquid ratio was 1:10, the phosphoric acid concentration ranged from 2 % to 6 %, and the pretreated time was 0 to 150 min. The heater was turned on, and when the temperature reached the programmed value, the residence time was counted. At the determined time, the hydrolysis was stopped by immersing the container into an ice bath, which quenched the reaction. Both the heating and cooling times were negligible. After removing the screw cap from the container, the hemicellulosic hydrolysate was quantitatively separated from the pretreated solids, and then it was thoroughly washed with deionizer water and dried in an oven at 105 ℃. The filtrate (hydrolysate plus washing water) was diluted to a net 125 mL, in a volumetric flask, with distilled water.

Kinetics of acid hydrolysis of hemicellulose

A brief overview of the reaction kinetics concerning the acid hydrolysis of cellulose and hemicelluloses is presented here for subsequent discussion on reactor design and operation. The hydrolysis reactions using dilute acid are very complex, mainly because the substrate is in a solid phase and the catalyst in a liquid phase. The reaction rate of hydrolysis depends on a number of variables, such as temperature, acid concentration, liquid ratio, time, substrate concentration, and substrate composition. Kinetic studies on the hydrolysis of various cellulosic materials (*e.g.* paper, sawdust, cane bagasse) are reported in the literature (Rajesh *et al.* 2007; Zhuang 2009; Aguilar *et al.*

2002), and they are characterized by acid and solids concentrations, temperature, and reaction time. It was found that hemicellulose hydrolysis kinetic parameters were strongly dependent on the substrate material.

At high temperatures, the kinetic pattern of hemicellulose hydrolysis can be expressed in a manner similar to that of cellulose hydrolysis (*sequential* first order reactions in series). At lower temperatures (T < 160 ℃), however, hemicellulose hydrolysis is not homogeneous. There is a portion that hydrolyzes rapidly, while the remainder hydrolyzes more slowly. This inhomogeneity affecting the hydrolysis of hardwoods can be characterized in the form of two parallel pseudo first-order reactions, one describing a fast-hydrolyzing fraction, and the other describing a slow-hydrolyzing fraction (McMillan 1992; Grohmann *et al.* 1986).

The hydrolysis of lignocellulose usually conforms to a Seaman Model (Aguilar *et al.* 2002).

$$\text{Xylan} \xrightarrow{\ k_1\ } \text{Xylose} \xrightarrow{\ k_2\ } \text{Decomposition products} \qquad (1)$$

In Eq. (1), k_1 is the rate of the xylose generation reaction, and k_2 is the rate of the xylose decomposition reaction (min^{-1}). Each step is an irreversible first-order reaction, which could be represented as,

$$\rho = \rho_0 e^{-k2t} + \rho'_0 k1/ (k_2 - k_1) (e^{-k1t} - e^{-k2t}) \qquad (2)$$

where ρ and ρ'_0 are the mass concentrations of monosaccharide (xylose) and polysaccharides (xylan, g/L), t is time, and subscript 0 indicates initial conditions. In this work, Eq. 2 has been applied to model the hydrolysis of bamboo.

Analysis and detection

Pulp analysis and other diversity indexes were measured in accordance with the method described by the National Institute of Standards and the analysis and testing for pulp and paper (Shi and He 2003).

Calculation of pentose and hexose dissolution rate

Pentose and hexose dissolution rate during hydrolysis of F and HMF were converted to the molar ratio of the corresponding sugar and pentose and hexose amount measured in the hydrolysate (Hu *et al.* 2009), that is:

$$\text{Pentose dissolution rate} = \{P + F \times 150/96\} \times L/P_{\text{ODB}} \times 100 \% \qquad (3)$$

$$\text{Hexose dissolution rate} = \{H + HMF \times 180/126\} \times L/H_{\text{ODB}} \times 100 \% \qquad (4)$$

In these equations, P is the concentration of pentoses in hydrolysate (g/L); F is the concentration of furfural in hydrolysate (g/L); L is the liquid solid to ratio of bamboo from dilute acid pretreatment, 1:10; P_{ODB} is the pentose content from raw materials in dry bamboo which is pre-extracted, 235 g (counted as monosaccharide); H is the hexose concentrations in the hydrolyzate (g/L); HMF is the hydroxymethylfurfural concentration in the hydrolysate (g/L); and H_{ODB} is the hexose content from raw materials in dry

bamboo that is pre-extracted with hot water, 515 g (counted as monosaccharide).

Scanning Electron Microscopy (SEM)

The morphology of the untreated pulp and samples treated in the dilute acid solution for 2 h at 75 ºC was examined with a DXS-10 scanning electron microscope. Samples were coated with carbon in a Temcarb TB500 sputter coater. An optimum accelerating voltage was 2.00 kV, and magnifications were 500 and 1000X.

RESULTS AND DISCUSSION

Chemical Compositions of Moso Bamboo

The chemical composition of moso bamboo is shown in Table 1. Bamboo cellulose content was found to be similar to the hardwood, with higher content of lignin, but much lower than the cork (27% to 33%); pentosan content was higher than wood; and 1% NaOH extracts content and ash content were higher than wood (Timell 1967). The moso bamboo belongs to grass species, and it contains no glucomannan. The chemical analysis showed that moso bamboo has a high potential for making the high-level dissolving pulp, because of its relatively low lignin content and high cellulose content.

Table 1. Chemical Composition of Moso Bamboo (%)

Extraction (%)		Cellulose	Pentosan	Xylose	Arabinose	Klason Lignin	Ash
1 % NaOH	Hot water	%	%	%	%	%	%
26.69±0.4	6.05±0.3	45.35±0.5	21.94±0.3	5.01±0.2	14.92±0.2	22.92±0.7	1.06±0.2

All data are based on O.D. weight of pulp.

Study on Dilute Acid Pretreatment Dynamics of Moso Bamboo

The purpose of the pretreatment is to maximize the removal of bamboo of hemi-cellulose, accompanied by a small amount of lignin dissolution. To study the effects of temperature on dilute acid pretreatment, the reaction temperatures were set at 100ºC, 120ºC, and 140 ºC, respectively. The heating-up time was 120 min, and the concentra-tions of dilute phosphoric acid added were 2%, 4%, and 6%. The bamboo tablets were put into the digester 120 min later for the dilute phosphoric acid pretreatment. After each pretreatment run, the tubes were removed and placed in cold running water for 1 min and then cooled to 4 °C for 30 min.

Xylose is the main product of the hydrolysis of bamboo. ρ_0 was 0 g/L and ρ'_0 was calculated as follows,

$$\rho'_0 = 150/132 \times x_0 / \text{WSR} \times 10 \tag{5}$$

where x_0 is the initial content for xylan (19.93 g xylan/100 g moso bamboo on dry basis), WSR is the water/solid ratio (10 g water/g moso bamboo), and 150/132 is the ratio of the stoichiometric factors. When substituting in all of these values of parameters given above, the xylose theoretical transformation quantity ρ'_0 is 22.65 g/L.
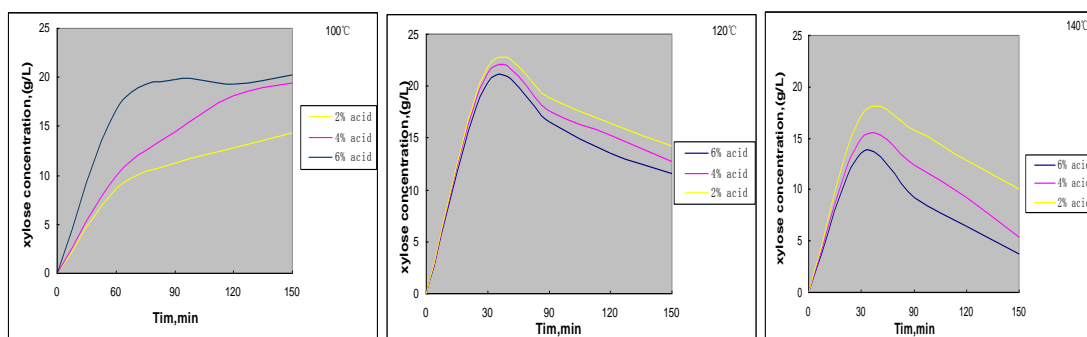
Fig. 1. Experimental and predicted dependence of the xylose concentration on time at several H_3PO_4 concentration and temperature

Figure 1 shows that Eq. (2) described well the entire hydrolytic process. From Table 2 it is apparent that the values of k1/k2 were 89.7, 48, and 56.7 for acid concentrations of 2%, 4%, and 6% at 120 ºC, respectively, and the values were higher when the temperature was 140 ºC. So it can be observed that the kinetic coefficients of xylose generation reactions were 40-fold higher than those of the degradation reactions.

Table 2 shows the fitted kinetic and statistical parameters. The statistical parameters (R^2) corroborate that the two-fraction model fitted well with the process. The values of kinetic coefficients increased with the increase of temperature and the concentration of catalyst. At the same time, the value of k_1 increased with the rise of temperature, indicating that the xylose production rate increased when temperature was elevated.

Table 2. Kinetic and Statistical Parameters of Xylose Released for the H_3PO_4 Hydrolysis of Moso Bamboo

Operational Set	Saeman Model Parameters		
	k_1/min^{-1}	k_2×10^3/min^{-1}	R^2
2 % H_3PO_4 at 100 ºC	0.0244	0	0.987
4 % H_3PO_4 at 100 ºC	0.0186	0	0.987
6 % H_3PO_4 at 100 ºC	0.0767	0	0.976
2 % H_3PO_4 at 120 ºC	0.1866	2.08	0.986
4 % H_3PO_4 at 120 ºC	0.1565	3.26	0.988
6 % H_3PO_4 at 120 ºC	0.2248	3.96	0.976
2 % H_3PO_4 at 140 ºC	0.214	2.97	0.988
4 % H_3PO_4 at 140 ºC	0.4168	3.56	0.988
6 % H_3PO_4 at 140 ºC	0.8144	8.81	0.972

Change Rule of P Factor with Pentose Extraction Rate

The P factor is similar to the H factor that is used in the cooking process. Like the H factor, the P factor is a comprehensive expression of hydrolysis reaction temperature and time. Brasch and Free carried out massive experiments on New Zealand radiata pine and found that the relative reaction rate *R* (Brasch and Free 1965; Chi 2010) met the following equations when the New Zealand radiata pine is pretreated within the range of 140 ºC to 180 ºC.

$$R = 3(T\text{-}100)/10 \tag{6}$$

From Eq. (6) and each reaction stage temperature (T) one can obtain the relative reaction rate (R) for pretreatment, and then the relation curves are made between relative reaction rate (R) and the reaction time (T). The hydrolysis factor (P factor) is given by the area between the $R\text{-}t$ curve and the X axis. In the insulation stage, the relative reaction rate constants can be obtained from the rectangular area under the $R\text{-}T$ curve; when temperature rises, the temperature showed a linear increase with reaction time's extension, and the relative reaction rate exponentially increased. Therefore the pretreatment factor can be derived through an integral method. By the inductive method, Eq. (7), which is used to calculate the pretreatment factors in the whole reaction process, could be derived. In order to make the integral calculation result precise, the selected time interval Δt_i needs to be as small as possible in the computation. Then the pretreatment factor (P factor) can be worked out via the following equation (Brasch and Free 1965).

$$P = \sum_{i=0} P_i = \sum_{i=0} \frac{[3^{(T_i - 100)/10} + 3^{(T_{i+1} - 100)/10}] \times \Delta t_i}{2} \tag{7}$$

In Eq. (7), P stands for the pretreatment factor at a certain temperature and reaction time; P_i is the pretreatment factor corresponding to the i-th time interval (5 min); T_i is a time of reaction temperature (ºC); Δt_i is time interval (h), $\Delta t_i = 0.083$ h; and i is the time interval number from the start of the reaction. To investigate the effect of acid pretreatment under different P factor and its influence to the subsequent pulp, dilute acid pretreatment of moso bamboo was carried out at 165 ºC, 170 ºC, and 175 ºC for three hold times. Three groups of a total of 9 P factor conditions can be obtained from the Eq. (7).

Table 3 shows the acid pretreatment conditions corresponding to each P factor. From Table 4, the total solids content and the pentose content in the extract increased with the increase of P factor, and the pentose extraction rate also increased. A small amount of furfural and hydroxyl methyl furfural were present in the extract, and their contents also increased with the increase of P factor.

Table 3. Acid Pretreatments Condition and Corresponding P Factor

P factor	Maximum Temperature / ºC	Soaking Time /min
410	165	15
730	165	30
1050	165	45
1360	165	60
720	170	15
1270	170	30
1640	170	45
1930	170	60
1030	175	10
1660	175	20
2290	175	30
3020	75	40

Table 4. Pretreatment Results of Different P Factors

P factor	Extracting Solution	
	Pentose content /g·L-1	Extraction rate of pentose /%
410	9.43	17.1
720	10.81	20.45
730	11.21	20.57
1030	11.78	22.32
1050	16.41	31.00
1270	15.74	29.18
1360	17.25	32.17
1640	17.55	33.18
1660	16.65	31.86
1930	18.04	34.12
2290	19.62	37.02
3020	21.16	39.12
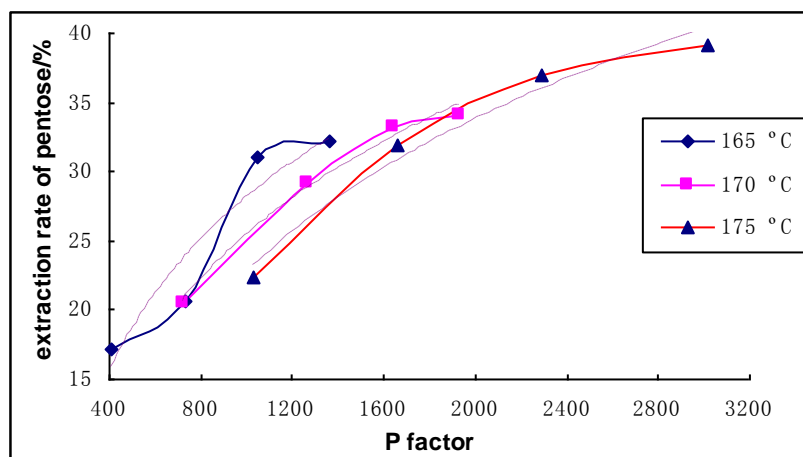
Fig. 2. Relationship of extraction rate of pentose and P factor

Figure 2 shows the relationship between extraction rate of pentose and the *P* factor. From the curves in the figure, the extraction rate of pentose shows an increase trend with the increase of the *P* factor under the different temperatures. When the temperature was 165 ^{o}C, the slope of the curve changed markedly and the extraction rate of pentose increased by 10% as the P factor increased from 730 to 1050, which was significantly higher than the corresponding increase of the extraction rate of pentose (about 2 %) when the *P* factor increased from 1050 to 1360. The increasing trend of the extraction rate of pentose leveled off with further increases in the *P* factor at the same temperature. When the temperature was 170 ^{o}C and 175 ^{o}C, the changes in slope were not so obvious. With the *P* factor increasing from 1050 to 1360, the curve slope leveled off in the range 165 ^{o}C to 175 ^{o}C. This shows that the effect of *P* factor on extraction rate of pentose becomes gradually weaker with the increase of temperature. When the *P* factor reaches a certain value, the increase of the extraction rate of pentose tends to be stable. A general rule can be observed from Fig. 2 that the extraction rate of pentose increases fast initially

(between the two dotted lines as shown in the figure) with the increase of *P* factor. When the *P* factor is more than 1650, the increase in the rate begins to slow down. Therefore, the optimal conditions for dilute acid hydrolysis of moso bamboo are 170 °C and 45 min.

Mass Balances of Sugars from Pretreated Moso Bamboo

Figure 3 presents mass balances for dilute acid pretreatment of moso bamboo at 170 °C for 45 min, which yielded the highest xylose release. After projecting our results to a basis of 100 g of dry moso bamboo, about 50 g of pretreated solids can be recovered after pretreatment. Weight loss of 26.5 % in the overall mass balances of the solid and liquid fractions combined was also observed for dilute acid. This is possibly because the filter paper was not fine enough to capture all the particles in the slurry after pretreatment. On the other hand, some solids became adhered in the filter paper and funnel wall during filtration and could not be collected. Another possible cause of losses could be lack of detection by HPLC of unknown compounds formed by decomposition of hemicellulose and cellulose. In addition, carbon dioxide (CO_2) formation plays a role in the mass loss during the reaction (Leschinsky *et al.* 2009). Finally, lignin solubilization into the liquid may also contribute to the loss of total mass.
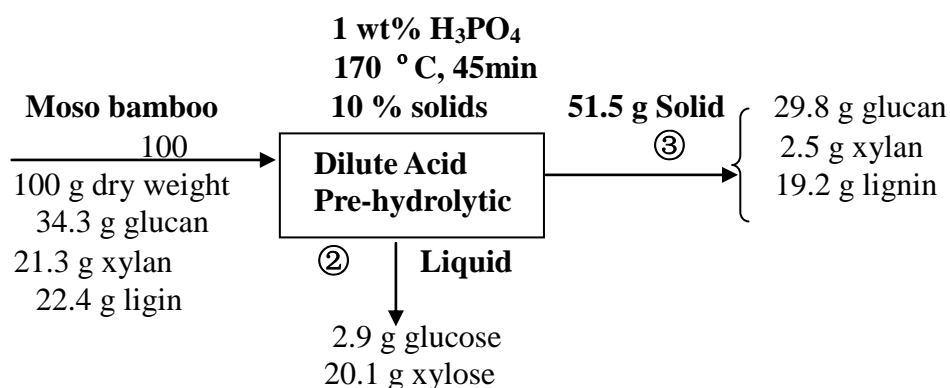

Fig. 3. Xylan and glucan mass balances dilute acid pretreatment of moso bamboo

Structure Changes of Moso Bamboo Fiber Before and After Dilute Acid Pretreatment

Figures 4 and 5 show vascular bundles cross-sections of moso bamboo under SEM. Moso bamboo is a genus of Gramineae, which is known for its porous vascular structure. The vascular bundle structure of the original moso bamboo cross-section is more regular. Compared to pretreated moso bamboo, there was less soluble material visible in the bamboo cross-section. From the SEM micrographs of bamboo fibers, one can see that the pore size of the vascular bundle of moso bamboo fiber increased after pretreatment. The pretreatment damaged the primary cell wall of bamboo, weakening or destroying the connection between the cell wall outer layer of lignin and carbohydrates or connections between each other of carbohydrates. The dissolution of hemicellulose in the cell wall loosens the structure of the bamboo, thus establishing favorable conditions for the penetration of cooking liquor.
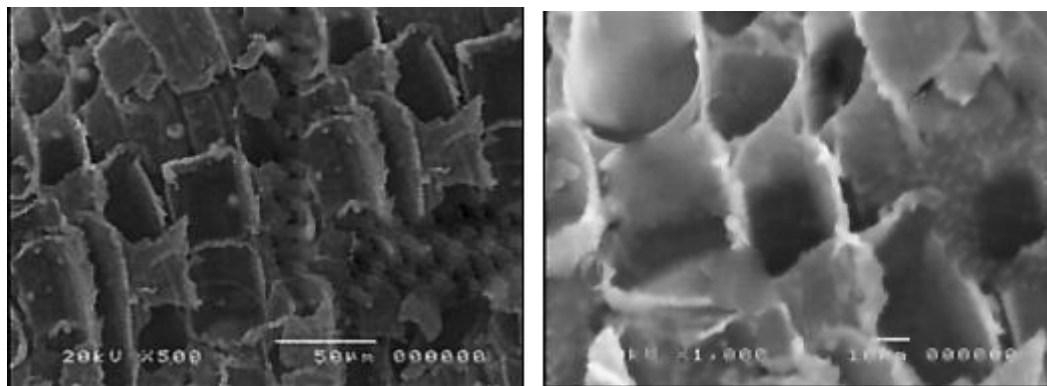
Fig. 4. SEM micrographs of untreated bamboo fibers (Magnification 500x and 1000x)
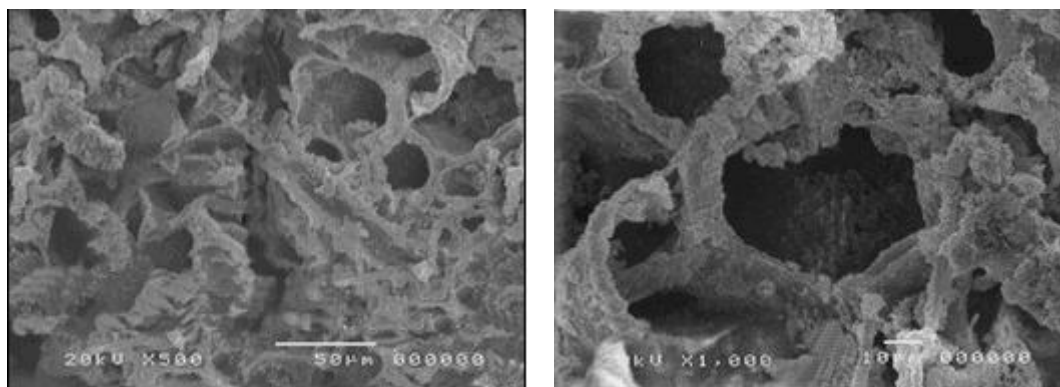
Fig. 5. SEM micrographs of bamboo fibers with dilute acid pretreatment (Magnification 500x and 1000x)

CONCLUSIONS

1. The Saeman model can be used to describe the dynamics of the dilute acid pretreatment of moso bamboo for the production of dissolving pulp. From the Saeman model, the initial formation rate of xylose is high, and then it levels off. The xylose generation rate increases with the rise of temperature.

2. From the investigation of the *P* factor and pentose extraction rate of the pretreatment of moso bamboo with dilute phosphoric acid, the optimal hydrolysis conditions were determined to be: hydrolysis temperature at 170 $^{\circ}$C and 45 min treatment time.

3. 26.5 % loss in the overall mass balances of the solid and liquid was also observed with diluted phosphoric acid pretreatment.

4. The SEM micrographs of cross-section before and after dilute acid pretreatment showed that there are a lot of extractives in bamboo cross-section that are removed during dilute acid pretreatment. The pore size in the vascular bundle of moso bamboo fiber increased after pretreatment, and thus the structure of the bamboo becomes loose.

REFERENCE CITED

Aguilar, R., Ramírez, J. A., and Garrote, G. (2002). "Kinetic study of the acid hydrolysis of sugar cane bagasse," *Journal of Food Engineering*.55 (4), 309-318.

Brasch, D. J., and Free, K. W. (1965). "Prehydrolysis-kraft pulping of *Pinus radiata* grown in New Zealand," *Tappi*. 48(4), 245-248.

Chi, C. C., Zang, Z., Chai, X. S., and Ge, W. W. (2010). "Rapid determination of sugars in hemicellulose extraction liquor by dual-wavelength spectrophotometry," *Spectroscopy and Spectral Analysis* 30(4), 1084-1087.

Chen, S. L. (2000). "The decorative value and utilization of bamboo," *Journal of Bamboo Research*. 19(2), 13-17.

Cheung, S., and Anderson, B. (1996). "Ethanol production from wastewater solids," *Water Environment and Technology*. 8 (5), 55-60.

Galbe, M., and Zacchi,G. (2002). "A review of the production of ethanol from softwood," *Appl. Microbiol.Biotechnol.* 59(6), 68-628.

Grohmann, K., Torget, R., and Himmel, M. (1986). "Dilute acid pretreatment of biomass at high solids concentrations," *Biotechnol. Bioeng. Symp*. (17), 135-151.

Gámez, S., Ramírez, J. A., Garrote, G, and Vázquez, M. (2004). "Manufacture of fermentable sugar solutions from sugar cane bagasse hydrolyzed with phosphoric acid at atmospheric pressure," *Journal* of *Agricultural and Food Chemistry* (74), 4172-4177.

Gámez, S., González-Cabriales, J. J., Ramírez, J. A., Garrote, G., and Vázquez, M. (2006). "Study of the hydrolysis of sugar cane bagasse using phosphoric acid," *Journal of Food Engineering*. 74(1), 78-88.

Hendriks, A. T. W. M., and Zeeman, G. (2009). "Pretreatments to enhance the digestibility of lignocellulosic biomass," *Bioresource Technology*. 100-108.

Hu, H. C., Zhan, H. Y., and Chai, X. S. (2009). "Degradation models of carbohydrates during bamboo hot-water pre-extraction based on modified H factor," *Journal of China Pulp and Paper*. 28(11), 28-32.

Jiang, S. H., and Jiang S. X. (2002). "Research progress of the theory and application for effective utilization of bamboo charcoal," *Journal of Northeast Forestry University* 30(4), 53-56.

Leschinsky, M., Sixta, H., and Patt, R. (2009). "Detailed mass balance of the autohydrolysis of *Eucalyptus globulus* at 170°C," *Bioresources*. 4(2), 687-703.

McMillan, J. D. (1992). "Process for pretreating lignocellulosic biomass: A review," *NREL Report* No. TP-421-4978.

Nguyen, Q. A., Tuckcr, M. P., and Boyntonm, B. L. (1998). "Dilute-acid pretreatment of softwood," *Applied Biochemistry and Biotechnology*. (1), 77-87.

Nguyen, Q. A., Tuckcr, M. P., and Keller, F. A. (2000). "Two-stage dilute-acid pretreatment of softwood," *Applied Biochemistry and Biotechnology*. (1), 561-576.

Qiu, E. F., and Hong, W. (2001). "Chinese bamboo multiplicity and utilization review," *Transactions of the Study on Bamboo*. 20(2), 11-14.

Romero, I., Moya, M., Sánchez, S., Ruiz, E., Castro, E., and Bravo, V. (2007). "Ethanolic fermentation of phosphoric acid hydrolysates from olive tree pruning," *Industrial Crops and Products*. 25(2), 160-168.

Rajesh, K., and Eric Berson, R. (2007). "The effect of particle size on hydrolysis reaction rates and rheological properties in cellulosic slurries," *Applied Biochemistry and Biotecnology* . 7(2), 136-140.

Saha, B. C., and Bothast, R. J. (1999). "Pretreatment and enzymatic saccharification of corn fiber," *Applied Biochemistry and Biotechnology*. (1), 65-77.

Sears, K. D., Beelik, A., and Casebier, R. L. (1971). "Southern pine prehydrolyzates: Characterization of polysaccharides and lignin fragments," *J. Polymer Sci.* (36), 425-433.

Shi, S. L., and He, F. W. (2003). *Pulp and Paper Technical Analysis and Testing*, China Light Industry Press, 2003.

Shen, W. H., and Chen, X. S. (2003). "Viscose bamboo pulp of the bamboo fiber production technology and its textiles," *Synthetic Fiber in China.* (6), 37-39.

Timell, T. E. (1967). "Recent progress in the chemistry of wood hemicelluloses," *Wood Science Technology*. (1), 45-51.

Tjeerdsma, B. F., and Militz, H. (2005). "Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood," *Eur. J .Wood Wood Prod.* 63, 102-111.

Wingren, A., Galbe, M., and Zacchi, G. (2003). "Techno-economic evaluation of producing ethanol from softwood: Comparison of SSF and SHF and identification of bottlenecks," *Biotechnology Progress.* 19(3), 1109-1117.

Wyman, Ch.E., (2003). "Potential synergies and challenges in refining cellulosic biomass to fuels, chemicals, and power," *Biotechnology Progress.* 19, 254-262.

Xiao, J. H. (2000). "Present situation and strategies of bamboo industry development in china," *Journal of Bamboo Research*. 19(1), 1-8.

Xie, Y. F., Xie, G. S., and Yao, Q. Q. (2004). "Present situation and outlook of bamboo resources utilization on china," *Chinese Journal of Tropical Agriculture.* 24(6), 46-52.

Ye, S., and Jay, J. C. (1998). "Dilute acid pretreatment of rye straw and bermudagrass for ethanol production," *Bioresource Technology*. (96), 1599-1606.

Zhang, Y., and Shen, X. P. (2003)."Application and development of bamboo fiber," *Advanced Textile Technology*. (3), 51-52.

Zeng, M.C., and Xiang, Y. M. (1987). "The development of the bamboo cellulose acetate ester," *Journal of Bamboo Research*. 6(2), 39-48.

Zhu, J. F. (2003). "The new darling of the cellulose fibers--bamboo fiber," *Knitting Industry* (6), 23-24.