Effect of Phosphoric Acid in the Pre-hydrolysis Process of Dissolving Pulp Production from Bamboo-willow

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Bamboo-willow is a type of fast-growing wood with a high hemicellulose content. In the present study, the effects of phosphoric acid addition on the main components of bamboo-willow and pre-hydrolysis liquor (PHL) were explored, and subsequently the pre-hydrolyzed bamboo-willow chips were cooked, O–H–P bleached, and acid post-treated to produce dissolving pulp. The results showed that adding phosphoric acid to the pre-hydrolysis stage effectively removed hemicellulose and increased the cellulose content of the pre-hydrolyzed bamboo-willow. The major component of the hemicelluloses was xylan/xylose, which represented approximately 62% to 78% of the total sugars in the PHL. Glucose was the most abundant sugar that was produced, apart from xylose, and represented approximately 12% to 25% of the total sugars in the PHL. Additionally, 73% to 83% of the total sugars in the PHL were in an oligomeric form. The obtained bamboo-willow dissolving pulp could be used to produce viscose rayon with a 92.1% α-cellulose content, 4.77% hemicellulose content, and 675 degree of polymerization.

Keywords: Bamboo-willow; Dissolving pulp; Phosphoric acid; Pre-hydrolysis liquor

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INTRODUCTION

Bamboo-willow (zhuliu in Chinese) is a genus of Salicaceae (*Salix*) and has a variety of excellent features, such as a high planting density, fast growth, good resistance (cold, salt, drought, waterlogging, disease, *etc*.), high strength, high natural whiteness, high survival rate, and a wide range of uses (Li *et al*. 2012; Meng and Zhang 2013). Furthermore, bamboo-willow contains three major components of lignocellulosic materials: cellulose, hemicellulose, and lignin. Therefore, it is a potential resource for dissolving pulp production and biorefinery.

Forest biorefinery has been regarded as a new concept to revisit in the pulping industry. Using the concept of forest biorefinery, the lignocellulose waste from pulping and papermaking can be converted into high value-added products (Reardon 2014). The pre-hydrolysis kraft-based dissolving pulp production process may be a representative example of an integrated forest biorefinery. Wood chips that are left over after the pre-hydrolysis process can be subsequently used for pulping and papermaking, while hemicellulosic sugars (oligosaccharides and monosaccharides) that are dissolved in pre-hydrolysis liquor (PHL) in the pre-hydrolysis step can be further processed to produce biofuels, biochemicals, bioplastics, or functional oligosaccharides (Fig. 1). Pre-hydrolysis liquor contains a diverse palette of degradation products, including lignin derivatives, acetic acid, formic acid, levulinic acid (LA), hydroxymethyl furfural (HMF), and furfural

(Wang *et al*. 2014b). Furfural and HMF are key degradation products of monomeric sugars under acidic hydrolysis conditions (Chen *et al*. 2013). Levulinic and formic acids are formed during further degradation of HMF and furfural during the hydrothermal conversion process (Wei *et al*. 2011). Furfural is mainly used as a chemical feedstock for the production of resins and as an intermediate for synthetic stabilizers, biofuels, plastics, pharmaceuticals, and agrochemicals. Esters of LA can be used in either the flavoring and fragrance industry or as blending components in biodiesel (Girisuta *et al*. 2008). The lignin in the PHL can be sulfur-free and can be used to produce carbon fibers or polyurethanes (van Heiningen 2006). The xylose in PHL can be used to produce xylitol by hydrogenation in the presence of catalysts (Peréz-Bibbins *et al*. 2016). However, the presence of lignin in PHL is detrimental for value-added utilization of hemicelluloses.

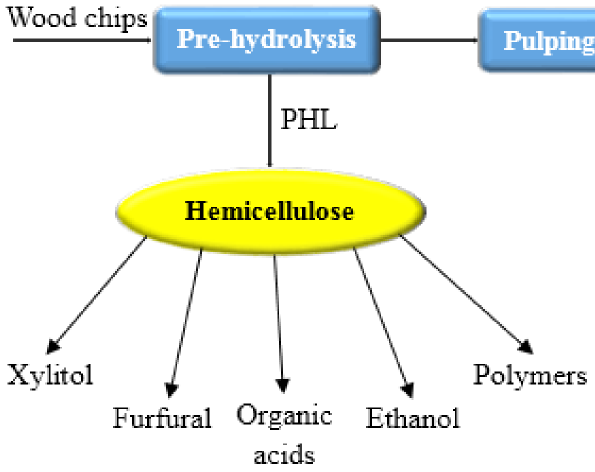

Fig. 1. Conversion of PHL-derived hemicellulose to valuable products in a kraft-based dissolving pulp production process

Dissolving pulps have a high purity of α-cellulose (> 90%), but low hemicellulose (1% to 10%) and lignin contents (< 0.05%) (Sugesty *et al*. 2015). They can be used as raw materials to produce a range of cellulose derivatives, such as cellulose nitrate, cellulose xanthate (rayon fibers), cellophane, cellulose acetate, cellulose ethers, and grafted or crosslinked cellulose derivatives (Wu *et al*. 2018). Worldwide, over 70% of dissolving pulp is utilized in the production of viscose staple alone (Kumar and Christopher 2017). In recent years, the demand for dissolving pulp has been increasing, especially for one of the largest consumers of viscose fibers (China), which will stimulate the growth of dissolving pulp output. However, China lacks forest resources, and its lignocellulosic materials for the pulping and papermaking industry are mainly wood materials (23%), non-wood materials (15%, mainly wheat straw), and imported waste paper (62%, mainly from the United States, Japan, Britain, *etc*.) (Guo 2010). This limits the development of the dissolving pulp industry in China. Because of the many good features of bamboo-willow, it is a resource that has the potential to solve this problem.

Because of the low hemicellulose content required for dissolving pulp, pre-treatment is essential for dissolving pulp production. The purpose of pre-treatment is to remove as much hemicellulose as possible from lignocellulosic materials before delignification operations (cooking). The common pre-treatment methods are auto-hydrolysis, acid hydrolysis (dilute and organic acid), alkali treatment (Jun *et al*. 2012), mechanical and swelling treatments, enzymatic (xylanase) hydrolysis alone or combined with alkaline extraction (Ibarra *et al*. 2010), *etc*. Auto-hydrolysis includes steam and hot water treatment, and generally requires a treatment temperature of 180 °C to 200 °C. During the auto-hydrolysis stage, acetic acid is formed from the cleavage of acetyl groups in the hemicellulose (Wei *et al*. 2011), which contributes to the completion of pre-hydrolysis. Unfortunately, at high temperatures, the sugar yield is reduced because of side reactions that generate byproducts, such as furfurals (Jun *et al*. 2012). Tong *et al*. (2016) reported that 40% to 43% of the hemicelluloses were removed by the addition of 0.1% to 0.7% boric acid (based on the oven dry weight of material) to the pre-hydrolysis stage of *Whangee* (a genus of bamboo). According to Pitarelo *et al.* (2010), dilute sulfuric and dilute phosphoric acids were used for impregnation and pretreatment of cane bagasse during steam explosion. The results showed that impregnation with dilute phosphoric acid resulted in a better selectivity towards hemicellulose hydrolysis. Furthermore, the dilute phosphoric acid in high temperature pretreatment of corn stover could effectively hydrolysis hemicellulose and further convert pentosans into furfural at the same time preventing the degradation of cellulose (Avci *et al*. 2013).

The objectives of this study were to determine the effects of phosphoric acid addition in the pre-hydrolysis process on the main components of bamboo-willow and PHL, and the impact on the resource utilization of PHL. Subsequently, the feasibility of using bamboo-willow as a raw material to produce dissolving pulp was analyzed using four steps: (1) pre-hydrolysis with phosphoric acid (with various times and temperatures), (2) kraft pulping, (3) O–H–P bleaching, and (4) acid post-treatment.

EXPERIMENTAL

Materials

Raw materials

Bamboo-willow (*Salix* sp or zhuliu in Chinese) was provided by one of the forestry centers in the Xinjiang autonomous region of China. Chipped bamboo-willow was screened to obtain chips with the dimensions 15 mm to 20 mm × 10 mm to 20 mm × 3 mm to 5 mm. A portion of the wood chips was taken for moisture determination for subsequent experiments. Another portion of the wood chips was ground into powder, and the particles that passed through a 40-mesh to 60-mesh screen were kept for chemical analysis. Standard TAPPI methods were used to analyze the α-cellulose (TAPPI T203 cm-99 1999), pentosan (TAPPI T223 cm-01 2001), acid insoluble lignin (TAPPI T222 om-11 2011), acid-soluble lignin (TAPPI UM 250 2000), ash (TAPPI T211 om-02 2002), and alcohol-benzene extractives contents (TAPPI T204 cm-07 2007). The ferric ion content in the raw materials was determined according to ISO 779 (2005). The holocellulose content in the bamboo-willow chips was measured using the acidified sodium chlorite method (Leopold 1961). The α-cellulose was then separated from the holocellulose using a 17.5% sodium hydroxide solution.

Methods

Pre-hydrolysis

Pre-hydrolysis was performed in an electrically heated stainless-steel digester with a 1-L capacity at a reaction temperature of 165 °C for 60 min. Deionized water was added to reach a 6:1 liquid-to-wood ratio. Various dosages of phosphoric acid were added (0%, 0.1%, 0.3%, 0.5%, 0.7%, and 0.9%, based on the oven-dried weight of materials) to explore the optimum acid dosage in the pre-hydrolysis stage. Subsequently, phosphoric acid pre-hydrolysis was done at 150 °C, 160 °C, and 170 °C for 60 min, 90 min, and 120 min, respectively. The dosage of phosphoric acid was 0.5% (based on the oven-dried weight of the materials). Upon completion of pre-hydrolysis, the temperature of the digester was cooled by decompressing the exhaust valve, which subsequently separated the PHL from the solid mass. The hydrolyzed bamboo-willow chips were thoroughly washed with tap water until a neutral pH was achieved. Afterward, the hydrolyzed chips were air-dried for the chemical composition analysis, with the same methods and standards used as mentioned above. The collected PHL was filtered using two-tiers of slowly quantitative filter paper and kept refrigerated until analysis.

Solid content

The total solid content in the PHL was determined gravimetrically by drying a 10-mL sample at 105 °C until a constant weight was achieved.

Analytical methods

The dissolved lignin in the PHL was measured *via* ultraviolet visible (UV-vis) spectroscopy at a wavelength of 205 nm, according to TAPPI UM 250 (2000).

The sugars (dissolved hemicelluloses) content of the PHL was measured using an indirect method based on quantitative acid hydrolysis of the liquid sample. To convert the oligomeric sugars of the PHL to monomeric sugars, the PHL was acid hydrolyzed using 4% (wt.) sulfuric acid at 121 °C for 1 h in an oil bath (Shen *et al*. 2011; Sluiter *et al*. 2006). The acid-hydrolyzed PHL was then diluted, and the content of monomeric sugars was measured. The monomeric sugars were measured using high-performance anion-exchange chromatography coupled with a pulsed amperometric detector (HPAEC-PAD) and an HPAEC-PAD system (ICS-5000, Thermo Fisher, Sunnyvale, USA) equipped with a CarboPac PA20 analytical column (3 mm × 150 mm) (Thermo Fisher) and guard column (3 mm × 30 mm). The samples were filtered through 0.22-μm syringe filters prior to injection (Wang *et al*. 2015). The concentration of the sugars after this additional hydrolysis stage reflected the total sugars (hemicelluloses) content of the PHL. The oligomeric sugar content of the PHL was determined by considering the monomeric sugar and total sugar contents of the samples before and after this additional acid hydrolysis stage (Shen *et al*. 2011).

The degradation byproducts from carbohydrates in the PHL, such as formic acid, acetic acid, and furfural, were analyzed by a high performance liquid chromatography system (Shimadzu, Japan) equipped with a Symmetry® C18 column (4.6 × 150 mm, 5 μm) (Waters, Milford, MA, USA) and a UV-vis detector at 210 nm and 30 °C, with 0.1% H_3PO_4 (v/v) used as the eluent at a flow rate of 0.5 mL/min (Wang *et al*. 2014b). The samples were filtered through 0.22-μm syringe filters prior to injection.

Kraft cooking

The kraft cooking of pre-hydrolyzed bamboo-willow (at 160 °C for 90 min with a 0.5% phosphoric acid dosage) was done in the same digester that was used for pre-hydrolysis, but at a constant cooking temperature of 165 °C for 120 min. The liquid-to-wood ratio was 1:5 (g/mL). The active alkali (as Na_2O) charge was 18 wt% with a sulfidity of 1.0% (Wu *et al*. 2018). After kraft cooking, the pulp was washed thoroughly with tap water until a neutral pH was achieved before being screened by a laboratorial screener equipped with a 0.2-mm slotted plate to remove the rejects.

O–H–P bleaching

The pre-hydrolyzed kraft pulps were bleached with O–H–P bleaching sequences. Oxygen delignification (O) was performed in an oxygen bleaching tank (1 L). The oxygen pressure was 0.6 MPa, the NaOH charge was 2.0%, the $MgSO_4$ charge was 0.5%, and the temperature was 100 °C for 60 min. Sodium hypochlorite bleaching (H) was performed in a plastic bag with an active chlorine charge of 2.0%, and the temperature was 40 °C for 60 min. Peroxide bleaching (P) was done in a plastic bag with 0.5% NaOH, 0.5% $MgSO_4$, and 0.2% iminodisuccinic acid with an H_2O_2 charge of 3.0%, and the temperature was 90 °C for 120 min. The pulp consistency was 10% in all of the bleaching stages. After each respective bleaching stage, the pulp was washed thoroughly with tap water until a neutral pH was achieved and the pulp properties were determined.

Acid post-treatment

The acid post-treatment was performed in a plastic bag with a hydrochloric acid (HCl) charge of 1.2% and 0.2% iminodisuccinic acid. The temperature was 30 °C for 60 min, and the pulp consistency was 5%. After acid post-treatment, the pulp was washed thoroughly with deionized water and kept refrigerated until pulp analysis.

Evaluation of the pulps

The following pulp properties were tested in accordance with standard TAPPI methods: ash content (TAPPI T211 om-02 2002), pentosan content (TAPPI T223 cm-01 2001), α-cellulose content (TAPPI T203 cm-99 1999), kappa number (TAPPI T236 om-99 1999), and brightness (TAPPI T525 om-02 2002). The ferric ion content in the pulp was measured according to ISO 779 (2005). The average degree of polymerization (DP) of the pulp was determined and calculated ($DP^{0.905} = 0.75\eta$) using the intrinsic viscosity (η), which was measured according to the Chinese national standard FZ/T 50010.3 (2011). The reaction property of the dissolving pulp made from bamboo-willow was determined *via* a two-step method, according to FZ/T 50010.13 (2011) and Wu *et al*. (2014). The only difference from the standard was that the addition volume of CS_2 was 8 mL for the wood dissolving pulp, instead of 11 mL for non-wood dissolving pulp during the viscose preparation process. The reactivity is considered to be the most important property of dissolving pulp and is related to the accessibility of chemicals to the cellulose, which means the relative ease in which the hydroxyl groups can be obtained by chemical reagents (Martino *et al*. 2017). A shorter reaction time corresponds to a greater reactivity of the dissolving pulp.

Equations

The pre-hydrolysis yield was calculated using Eq. 1,

$$Y = \frac{a_1 \times (1\text{-}w_1)}{a \times (1\text{-}w)} \times 100\% \tag{1}$$

where Y is the pre-hydrolysis yield (%), a_1 is the weight of wood chips after pre-hydrolysis (g), w_1 is the moisture content of wood chips after pre-hydrolysis (%), a is the weight of wood chips before pre-hydrolysis (g), and w is the moisture content of wood chips before pre-hydrolysis (%).

The pentosan removal was calculated using Eq. 2:

$$\textit{Pentosan Removal}\ (\%) =$$

$$\frac{\textit{Pentosan content in raw material}\ (\%) - \textit{Pentosan content in prehydrolysis solid}\ (\%) \times \textit{Prehydrolysis yield}\ (\%)}{\textit{Pentosan content in raw material}(\%)} \times 100\% \tag{2}$$

The pre-hydrolysis factor (P-factor) was calculated using Eq. 3 (Brasch and Free 1965),

$$P = \sum_{\mathrm{i}=0} P_{\mathrm{i}} = \sum_{\mathrm{i}=0} \frac{\left[3^{\frac{T_{\mathrm{i}}-100}{10}} + 3^{\frac{T_{\mathrm{i}+1}-100}{10}}\right] \times \Delta t_{\mathrm{i}}}{2} \tag{3}$$

where P is the P-factor at a certain reaction temperature and time, P_i is the pre-hydrolysis factor corresponding to the i^{th} time interval, T_i is the reaction temperature at a certain time (°C), and Δt_i is the time interval (h).

RESULTS AND DISCUSSION

Raw Materials

The chemical composition of the bamboo-willow is listed in Table 1. The *α*-cellulose content of the bamboo-willow was lower than that of bamboo and willow, and the pentosan and holocellulose contents were higher than those of bamboo. These are challenges for using bamboo-willow as a raw material to produce dissolving pulp because dissolving pulp is required to have a low hemicellulose content and high *α*-cellulose content (Sugesty *et al*. 2015). However, a large amount of hemicellulose will be removed in the subsequent pre-hydrolysis stage. Fortunately, the acid insoluble lignin, ethanol-benzene extractives, and ash contents were lower than those of bamboo. These are beneficial qualities for the production of dissolving pulp.

Table 1. Chemical Composition of the Bamboo-willow

Parameter (%)	Bamboo-willow (experiment)	Bamboo* (Sugesty *et al*. 2015)	Willow (Barimani *et al*. 2014)
Holocellulose	77.2	56.81 - 68.25	68.19
α-Cellulose	40.4	44.36 - 48.60	45.61
Pentosan	24.1	18.37 - 21.61	-
Acid-insoluble Lignin	20.3	22.41 - 25.27	25.5
Acid-soluble Lignin	3.46	-	-
Extractive (Ethanol-Benzene)	2.34	3.41 - 8.38	-
Ash	0.661	1.66 - 6.09 (SNI)	-
Ferric Ion (mg/kg)	31.8	-	-

* Contains four species of bamboo (*apus*, *sembilang*, *petung*, and *mayan*); SNI - Indonesian National Standard

Pre-hydrolysis

Phosphoric acid addition in the pre-hydrolysis stage

To investigate the effect of phosphoric acid addition in the pre-hydrolysis stage on the main components of bamboo-willow and to determine the optimum phosphoric acid dosage, various phosphoric acid dosages were added in the bamboo-willow pre-hydrolysis stage. Table 2 lists the effects of the addition of various phosphoric acid dosages on the chemical composition of the pre-hydrolyzed bamboo-willow. As the phosphoric acid dosage increased (from 0% to 0.9%), the α-cellulose content of the pre-hydrolyzed bamboo-willow gradually increased (from 45.6% to 52.7%), while the α-cellulose content in the raw material was 40.4%. The pentosan content gradually decreased (from 22.4% to 13.8%), and the content in the raw material was 24.1%. This illustrated that the addition of phosphoric acid to the pre-hydrolysis stage effectively removed hemicellulose and increased the cellulose content of the pre-hydrolyzed bamboo-willow. However, it had little effect on the lignin and holocellulose contents, and most of the lignin will be removed mainly in the subsequent cooking and bleaching stages of the dissolving pulp production process.

Table 2. Effect of the Phosphoric Acid Dosage on the Chemical Composition of the Pre-hydrolyzed Bamboo-willow

Phosphoric Acid Dosage (%)	Pre-hydrolysis Yield (%)	α-Cellulose Yield (%)	Holocellulose Yield (%)	Pentosan Yield (%)	Total Lignin Yield (%)
0	86.1	39.3 (45.6)	53.0 (61.5)	19.3 (22.4)	18.1 (21.0)
0.1	84.8	39.5 (46.6)	53.4 (63.0)	18.5 (21.8)	16.9 (19.9)
0.3	83.8	39.9 (47.6)	53.0 (63.2)	16.8 (20.0)	18.0 (21.5)
0.5	82.9	40.0 (48.2)	52.1 (62.8)	15.5 (18.7)	16.2 (19.6)
0.7	78.4	39.1 (49.9)	48.5 (61.8)	12.2 (15.5)	16.2 (20.7)
0.9	75.7	39.9 (52.7)	49.2 (65.0)	10.4 (13.8)	15.8 (20.9)

Parenthesis indicates α-cellulose, holocellulose, pentosan, or total lignin content in the pre-hydrolyzed bamboo-willow; yield = (component content in the pre-hydrolyzed bamboo-willow × pre-hydrolysis yield) / 100%

Pre-hydrolysis not only removes hemicellulose as much as possible, but it also ensures that cellulose is not damaged. When the dosage of phosphoric acid was 0.5%, the highest yield of α-cellulose yield was 40.0%, and the yield of pre-hydrolysis was 82.9%. Although pentosan yield decreased from 15.5% to 12.2% when the dosage of phosphoric acid increased from 0.5% to 0.7%. However, when the phosphoric acid dosage was 0.7%, the pre-hydrolysis yield was only 78.4%. Therefore, considering the quality requirements, the 0.5% phosphoric acid dosage was considered to be the optimum concentration in the bamboo-willow pre-hydrolysis stage. Furthermore, the total lignin content was the lowest at 19.6% in the pre-hydrolyzed bamboo-willow with a phosphoric acid dosage of 0.5%, which was beneficial to the subsequent cooking and bleaching process.

Various temperatures and times during pre-hydrolysis

Temperature and time are key factors that affect pre-hydrolysis. To maximize the dissolution of hemicellulose, bamboo-willow was pre-hydrolyzed at various temperatures and times. The compositions of the bamboo-willow after the various pre-hydrolysis conditions are listed in Table 3. Partial dissolution of the hemicellulose resulted in an increase in the cellulose content. With an increase in the P-factor, the α-cellulose content of the pre-hydrolyzed bamboo-willow gradually increased (from 44.0% to 54.6%), and the content in the raw material was 40.4%. The pentosan content gradually decreased (from 25.6% to 9.70%), and the content in the raw material was 24.1%. The pentosan yield decreased to 6.71% at 170 °C for 120 min from 23.6% at 150 °C for 60 min, which indicated that the removal of hemicellulose increased from 2% to 72%. The total lignin content of the material was 23.8%, while that of the pre-hydrolyzed bamboo-willow was in the range of 19.4% to 22.5%. This result demonstrated that some of the lignin was removed in the pre-hydrolysis stage. Additionally, the degradation of lignin was more pronounced under strong pre-hydrolysis conditions.

Table 3. Composition of the Bamboo-willow after Pre-hydrolysis at Various Conditions

Temperature (°C)	Time (min)	P-factor	Yield (%)	*α*-Cellulose Yield (%)	Pentosan Yield (%)	Total Lignin Yield (%)
150	60	346	92.1	40.5 (44.0)	23.6 (25.6)	19.3 (21.0)
150	90	449	89.2	40.1 (44.9)	21.8 (24.4)	18.9 (21.2)
150	120	571	86.9	40.4 (46.5)	19.6 (22.5)	19.6 (22.5)
160	60	922	86.1	40.7 (47.3)	19.2 (22.3)	18.8 (21.8)
160	90	1286	83.2	39.9 (48.0)	16.6 (19.9)	16.3 (19.6)
160	120	1651	80.4	39.7 (49.4)	15.3 (19.0)	15.6 (19.4)
170	60	2759	80.2	40.5 (50.5)	14.0 (17.4)	17.7 (22.1)
170	90	3852	72.9	39.1 (53.6)	9.26 (12.7)	15.7 (21.5)
170	120	4946	69.2	37.8 (54.6)	6.71 (9.70)	13.4 (19.4)

Figure 2 shows that the dissolution of biomass increased linearly with the temperature for a lower soaking time range (60 min), and its rate became slightly higher with a higher temperature (160 °C) and longer time. This illustrated that temperature and time were the key factors that affected pre-hydrolysis.

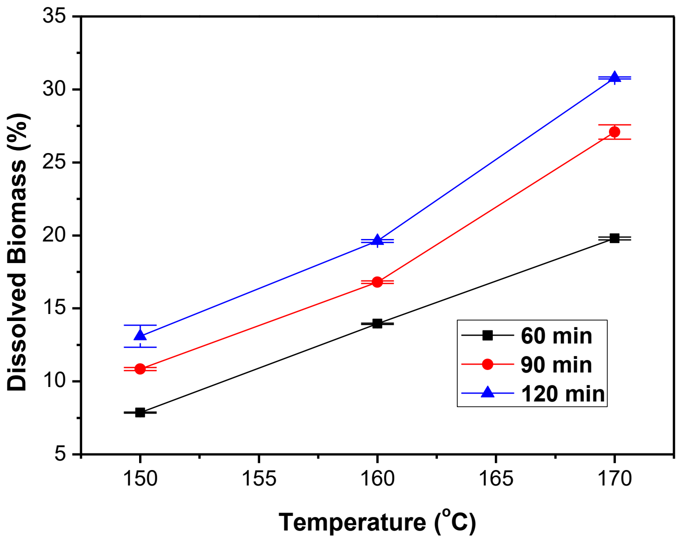

Fig. 2. Effect of the temperature and time on the dissolution of biomass from the bamboo-willow; Dissolving biomass = 100% - pre-hydrolysis yield

The effects of various pre-hydrolysis conditions on the compositions of the PHL from bamboo-willow are shown in Table 4. Lignin, sugars (monomeric and oligomeric sugars), formic acid, acetic acid, and furfural were found in the PHL. As the pre-hydrolysis severity (temperature and time) increased, more hemicellulose was dissolved in the PHL, which resulted in a higher acetic acid production (0.34 g/L to 2.17 g/L). Kaur and Ni (2015) demonstrated that the concentration of acetic acid in the PHL increased from 1% (in nano-filtration permeate) to 5% by using reverse osmosis at a volume reduction factor of 4.24.

Furfural was formed by the acid-catalyzed dehydration of five-carbon sugars (xylose and arabinose) in the hemicellulose under acidic conditions (Chen *et al.* 2013). Table 4 shows that as the pre-hydrolysis severity increased, the acetic acid content increased, which led to an increase in the furfural (0.03 g/L to 2.58 g/L). Formic acid was further converted from furfural, and its content in the PHL ranged from 0.52 g/L to 2.95 g/L. Additionally, the increase in the pre-hydrolysis severity also led to an increase in the dissolution of lignin from the raw material. The lignin degradation products in the PHL mainly existed in the form of oligomers, dimers, and monomers that were rich in phenolic hydroxyls (Wang *et al.* 2014b). Based on the concept of biorefinery, it is necessary to remove lignin to successfully exploit hemicellulose and acetic acid in PHL. If these substances in the PHL can be fully recycled, it will bring huge benefits to the dissolving pulp industry.

Table 4. Effect of the Various Pre-hydrolysis Conditions on the Compositions of the PHL

Temperature (°C)	Time (min)	pH	Solid Content (g/L)	Total Sugar (g/L)	Lignin (g/L)	Formic Acid (g/L)	Acetic Acid (g/L)	Furfural (g/L)
150	60	3.3	12.7	8.90	1.23	0.52	0.34	0.03
150	90	3.2	16.4	11.4	1.65	0.70	0.38	0.04
150	120	3.2	18.6	13.2	1.84	0.72	0.38	0.07
160	60	3.1	21.3	14.8	1.71	0.88	1.80	0.42
160	90	3.0	25.9	18.6	2.00	0.87	2.07	0.29
160	120	3.0	27.9	19.5	2.23	1.09	2.16	0.15
170	60	3.0	28.9	20.7	2.33	1.40	2.17	1.09
170	90	3.0	31.2	20.9	2.92	2.08	2.17	2.05
170	120	2.9	28.6	16.5	3.24	2.95	2.05	2.58

The solid content of the PHL increased to 31.2 g/L at 170 °C and 90 min, then decreased to 28.6 g/L at 170 °C and 120 min. The total sugar content also correspondingly decreased from 20.9 g/L to 16.5 g/L. This may have been because the acidic pre-hydrolysis conditions were relatively stronger at 170 °C and 120 min, which resulted in the further dehydration of the monosaccharides and led to their transformation into furfural, formic acid, and other products.

The effects of various pre-hydrolysis conditions on the hemicellulose concentrations in the PHL are listed in Table 5. Xylan/xylose was the major component, which represented approximately 62% to 78% of the total sugars in the PHL under the applied conditions. This was mainly because the major components of hemicellulose in the raw material are five-carbon sugars (pentoses). Wang *et al.* (2014a) reported that the major component in hemicellulose was xylose/xylan, which represented approximately 74% of the total sugars in the original PHL. The sugars in the PHL were mainly in the oligosaccharide form, which accounted for 73% to 83% of the total sugars. Tong *et al.* (2016) stated that oligomeric sugars accounted for 81% to 84% of the total sugars in the PHL. Therefore, the PHL could be a potential resource for the production of functional oligosaccharides. Glucose was the most abundant sugar that was produced, apart from xylose, and represented approximately 12% to 25% of the total sugars in the PHL. This may have been because of a certain degree of degradation of cellulose, in addition to hemicellulose, during the pre-hydrolysis process.

Table 5. Effect of the Various Pre-hydrolysis Conditions on the Hemicellulose Concentrations in the PHL

Temperature (°C)	Time (min)	Arabinose (g/L)		Galactose (g/L)		Glucose (g/L)		Xylose (g/L)		Mannose (g/L)	
		Mono-	Oligo-	Mono-	Oligo-	Mono-	Oligo-	Mono-	Oligo-	Mono-	Oligo-
150	60	0.28	0.10	0.07	0.06	0.34	0.71	0.77	6.25	0.05	0.27
150	90	0.36	0.15	0.11	0.10	0.59	1.18	1.16	7.11	0.11	0.53
150	120	0.43	0.18	0.13	0.12	0.77	1.59	1.28	7.82	0.17	0.71
160	60	0.53	0.21	0.20	0.19	1.05	2.05	1.53	8.24	0.14	0.66
160	90	0.54	0.22	0.29	0.25	1.69	3.05	2.01	9.59	0.18	0.78
160	120	0.59	0.23	0.38	0.37	1.75	3.13	2.21	9.84	0.19	0.81
170	60	0.59	0.24	0.48	0.47	1.81	3.32	2.58	10.1	0.20	0.91
170	90	0.53	0.27	0.62	0.61	1.54	3.41	2.60	10.3	0.18	0.79
170	120	0.34	0.15	0.52	0.51	0.89	1.72	1.81	10.2	0.12	0.25

The glucose in the PHL can be used to produce ethanol by fermentation (Yu *et al*. 2017). Galactose and mannose were the sugars with the lowest concentrations in the PHL. Therefore, it is challenging to separate and purify PHL to produce high value-added products.

Cooking, Bleaching, and Acid Post-treatment

The properties of the pulp after cooking, O–H–P bleaching, and acid post-treatment are listed in Table 6. The main task of cooking was to dissociate the lignocellulosic materials into pulp (delignification). The kraft cooking of the pre-hydrolyzed bamboo-willow (at 160 °C for 90 min, 0.5% phosphoric acid concentration) was at a constant cooking temperature of 165 °C for 120 min. The required amount of sulfidity was lower (1.0%) to obtain a relatively low kappa number (21.8) in the cooked pulp.

Table 6. Properties of the Pulp after Cooking, O–H–P Bleaching, and Acid Post-treatment

Parameter	Cooking	O–H–P Bleaching	Acid Post-treatment
Total Yield (%)	39.2	34.8	-
Kappa Number	21.8	2.08	1.91
Viscosity (mL/g)	923	480	485
DP	1375	668	675
Brightness (%ISO)	38.7	82.7	83.6
Holocellulose Content (%)	92.7	-	-
Pentosan Content (%)	5.15	4.98	4.77
α-Cellulose Content (%)	-	91.8	92.1
Ash Content (%)	-	0.430	0.103
Ferric Ion Content (mg/kg)	-	40.2	18.5
Reactivity (second)	-	25.0	8.10

The purpose of bleaching is to remove residual lignin from the cooked pulp and to improve the brightness of the pulp. The brightness of the bleached pulp increased to 82.7% ISO after O–H–P bleaching from 38.7% ISO for the unbleached pulp, which was expected. The average DP of the pulp reflects the average length of the cellulose molecular chains in the pulp, *i.e.*, *n* in the cellulose formula ($(C_6H_{10}O_5)_n$). The viscosity or DP of the bleached pulp was greatly reduced compared with that of the unbleached pulp. This was because of a certain degree of oxidative degradation of the cellulose during the bleaching process. However, bleaching had a slight effect on the pentosan content of the pulp.

Table 6 shows that the ash and ferric ion contents in the bleached pulp were high, which could have a negative effect on the filtering of dissolving pulp and its color in rayon manufacturing (Wu *et al*. 2018). Acid post-treatment could remarkably reduce the ash and ferric ion contents (to 0.103% and 18.5 mg/kg, respectively) in the bleached pulp (from 0.430% and 40.2 mg/kg, respectively). Additionally, the acid post-treatment can slightly improve the reaction property of bamboo-willow dissolving pulp. Acid post-treatment had a slight effect on the other properties of the bamboo-willow dissolving pulp, such as the viscosity or DP, brightness, *α*-cellulose content, and pentosan content.

The purity of the final bamboo-willow dissolving pulp reached a 92.1% *α*-cellulose content, which was close to the content found when dissolving pulp was produced from jute stick (92.3%) (Matin *et al*. 2015). This purity was higher than the purity of dissolving pulp produced from eucalyptus (89.4%) (Martino *et al*. 2017) and lower than the purity found in bamboo (*Mayan*) (96.57%) (Sugesty *et al*. 2015). The pentosan content of the bamboo-willow dissolving pulp was 4.77%, which was slightly higher than that of hardwood dissolving pulp (4.5%) (Martino *et al.* 2017) and lower than that of non-wood dissolving pulp (6.9%) (Matin *et al*. 2015). The brightness of the bamboo-willow dissolving pulp was 83.6% ISO, which was not high for dissolving pulp. However, based on the requirements of the *α*-cellulose content (> 90%) in viscose-grade dissolving pulp reported by Behin and Zeyghami (2009), it could be used to produce viscose rayon. Therefore, bamboo-willow can be used as a raw material to produce qualified dissolving pulp by a phosphoric acid pre-hydrolysis Kraft process.

CONCLUSIONS

1. Adding phosphoric acid to the pre-hydrolysis stage can effectively remove hemicellulose from bamboo-willow.
2. During the pre-hydrolysis process, a variety of degradation products from bamboo-willow fiber raw materials were dissolved in the PHL, such as lignin, sugars (monomeric and oligomeric sugars), formic acid, acetic acid, and furfural. The content of these substances in the PHL increased with an increase in the pre-hydrolysis conditions (P-factor). The dissolved hemicelluloses in the PHL were mostly xylan/xylose, and most of the sugars in the PHL were in the oligosaccharide form.
3. The α-cellulose content, pentosan content, and DP of the final produced bamboo-willow dissolving pulp were 92.1%, 4.77%, and 675, respectively. Also, the reactivity of the final bamboo-willow dissolving pulp reached 8.10 s. Therefore, bamboo-willow may be used as a lignocellulosic material for the production of viscose-grade dissolving pulp.

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