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Pretreatment of moso bamboo with p-toluenesulfonic acid for the recovery and depolymerization of hemicellulose

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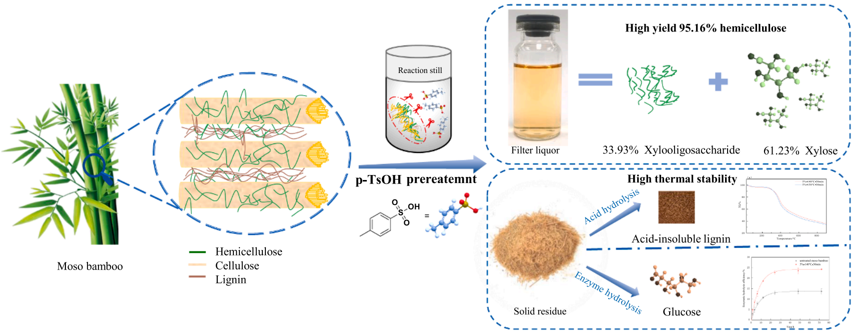
HIGHLIGHTS

- Low concentration p-toluenesulfonic acid pretreatment can effectively extract hemicellulose from moso bamboo.
- The optimal extraction yield of hemicellulose was 95.16%, which included its degradation derivative xylobiose (30.77%) and xylose (61.23%).
- The extracted bamboo residue was rich in thermal stable lignin and cellulase digestible cellulose.

GRAPHICAL ABSTRACT



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ABSTRACT

Bamboo and its mechanical processing residues have broad prospects for high value-added utilization. In this research, p-toluenesulfonic acid was used for the pretreatment of bamboo to investigate the effects of extraction and depolymerization of hemicellulose. The response and behavior of changes of cell-wall chemical components were investigated after different solvent concentration, time, and temperature pretreatment. Results indicated that the maximum extraction yield of hemicellulose was 95.16 % with 5 % p-toluenesulfonic acid at 140 °C for 30 min. The depolymerized components of hemicellulose in the filtrate were mainly xylose and xylooligosaccharide, with xylobiose accounting for 30.77 %. The extraction of xylose from the filtrate reached a maximum of 90.16 % with 5 % p-toluenesulfonic acid at 150 °C for 30 min pretreatment. This research provided a potential strategy for the industrial production of xylose and xylooligosaccharide from bamboo and for the future conversion and utilization.

1. Introduction

In response to the massive depletion of fossil resource and the urgent need to reduce carbon emission, plenty of work has been conducted on the exploration and utilization of renewable biomass (Antar et al., 2021; Saleem, 2022; Scarlat and Dallemand, 2019). As a renewable resource, research on lignocellulosic biomass and its efficient depolymerization is important for transforming the potential of biomass refining into

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industrial reality (Ramos et al., 2022). Cellulose is often used widely as a source for the production of ethanol, paper making or polymer materials (Chen et al., 2022). Lignin has potential applications in medicine, food, health care products, biomass utilization and agricultural production, especially in the preparation of hydrogels. The addition of lignin can effectively improve the mechanical strength and the protein adsorption capacity of hydrogels. (Shu et al., 2021). However, the research on bamboo hemicellulose is relatively rare. Hemicellulose is interwoven with cellulose and lignin to form a complex, hard-to-degrade dense structural system, resulting in its low efficiency of direct extraction of hemicellulose from lignocellulosic biomass, which limits its industrial utilization. Hemicellulose accounts for approximately 15 ∼ 40 % of lignocellulose (Peng et al., 2012), which is a large proportion, so it is also of great significance to carry out research on the extraction of hemicellulose from biomass for the production of high-value chemicals.

Moso bamboo is an attractive substance as a renewable lignocellulosic biomass, owing to its excellent ability in regeneration, high growth rate, and high biomass yield (Zhan et al., 2022). It is widely applied in building materials, paper making, furniture industries and so on. However, due to its large cutting degree and hollow structure, a large amount of residues are often produced during mechanical processing and utilization. Since the lack of proper recycling and treatment technology, the residues usually end up in incineration or landfill, which can lead to a large amount of pollutant such as SO_2, NOx, CO, volatile organic compounds and fine inhalable particles, etc. (Romasanta, et al., 2017; Singh et al., 2020). And moso bamboo as a raw material for lignocellulosic has utilization processes advantages (Jiang et al., 2016). The hemicellulose of moso bamboo is mainly composed of xylan linked by β-1,4 glycosidic bonds from D-xylopyranose units, the hemicellulose amount in bamboo is similar to hardwood and significantly higher than that of softwood (10 % to 15 %), which implies that bamboo can be used as a raw material for hemicellulose exploration (Bai et al., 2022).

Hemicellulose has a lower degree of polymerization (DP) compared with cellulose and lignin, and its highly branched and amorphous nature make it easy to convert, xylan can be degraded to xylooligosaccharide (XOS) or xylose easily during chemical treatments. XOS is a functional oligosaccharide produced through the hydrolysis of xylan, mainly containing xylobiose (X2), xylotriose (X3), xylotetraose (X4), xylopentaose (X5), xylohexaose (X6) and a small amount of xylose, etc. It can be used as a prebiotic to selectively increase the beneficial activity of intestinal flora, and also plays an important role in regulating blood sugar, lowering serum and lipid cholesterol, cancer prevention and food safety (Antov and Đorđević, 2017; Feng et al., 2022a; Marim and Gabardo, 2021; Poletto et al., 2020). In particular, xylooligosaccharides with less degree of polymerization are more effective on the value added of bifidobacterium (Zhao, et al., 2021). Also, xylose obtained from the degradation of hemicellulose has vital applications, it can be dehydrated to make furfural, which can be reduced by hydrogenation to prepare xylitol; oxidation by nitric acid to make 3-hydroxyglutaric acid, or further converted to fuel ethanol, butanediol and lactic acid by some specific microbial fermentation. These can all be widely used for the production or preparation of other downstream chemicals (Kwak and Jin, 2017; Sun et al., 2021; Wettstein et al., 2012). At present, there are much research on xylose preparation for downstream chemicals (Kwak et al., 2019; Sundar and Nampoothiri, 2022), but relatively little research on how to efficiently produce xylose from bamboo. Moreover, compared with other lignocellulosic biomass, cellulose, lignin, and hemicellulose are more difficult to be separated due to the dense rigid structure of bamboo. And the yield of depolymerization products generated by direct treatment with hemicellulose is quite low. It is a challenging topic to find suitable pretreatment methods to obtain low DP XOS and xylose with fewer by-products from bamboo.

Numerous pretreatment techniques have been rapidly developed to improve the conversion rate of lignocellulosic biomass over the decades. Each pretreatment process has unique properties in changing the physical and chemical structure of lignocellulosic biomass. Based on the concept of “hemicellulose first” (Rahmati et al., 2022; Zhao et al., 2022), hemicellulose is priority proposed for the production of small molecular chemicals, to achieve the highly selective dissolution and catalytic conversion of hemicellulose. Then retained cellulose and lignin can be transformed into small molecule chemicals and biomaterials. Thus, the co-production of different products could be achieved as well as the total utilization of biomass. However, first of all, this requires certain pretreatment methods, such as chemical, physicochemical and biological methods. Chemical methods mainly comprise acid pretreatment (Luo et al., 2021), alkali pretreatment (Yang and Pan, 2012; Zhang et al., 2020), hydrothermal treatment (Ge et al., 2020; Lan et al., 2021), organic solvent treatment (Qin et al., 2022) and deep eutectic solvent treatment (Hong et al., 2020). The physicochemical method mainly combines low temperature freezing (Zeng et al., 2022), microwave assisted (Yuan et al., 2019), and ball milling (Ma et al., 2022) on the basis of the chemical method. Combining assistive technology could promote the separation of lignocellulose in a greater extent, but increase process costs which is not conducive to further expanding industrial production. The biological pretreatment reaction conditions are mild, but the reaction time is relatively long (Santibáñez et al., 2021). A novel water-soluble aromatic acid p-toluenesulfonic acid (p-TsOH) pretreatment method has attracted much attention due to its unique advantages recently.

p-TsOH is frequently used in biomass pretreatment studies as a low-cost acidic water-soluble booster with both acid and water properties. Most researchers have applied high concentration of p-TsOH in biomass studies because of its ability to rapidly dissolve lignin at high concentration (Zhu et al., 2021), while retaining large amounts of cellulose in the residues. Ma et al. (2022) carried out ball milling with 55 % p-TsOH treatment of reed and found an obvious reduction in hemicellulose and lignin content in reeds, with 68.64 % cellulose in the residues. Yin et al. (2022) combined a co-solvent pretreatment of moso bamboo with p-TsOH and γ-valerolactone (GVL), the study revealed that over 98 % of the lignin could be degraded into oligomeric phenols while 91.5 % of the cellulose was retained. Yang et al. (2019) used corncobs, wheat straw and *Miscanthus* as raw materials and pretreated with 70 % p-TsOH for 10 min, the results showed a maximum lignin yield of 80.76 %. However, the separation of lignin by p-TsOH generally requires higher concentration of p-TsOH, which as a strong acid solvent can corrode equipment at high concentration and hinder industrial development. The progress of the utilization of low concentration of p-TsOH is environmentally friendly and cost efficient. Due to the excellent acid catalytic properties of p-TsOH, it can dissolve hemicellulose under mild mediums (Bian et al., 2017; Yu et al., 2020), depolymerize hemicellulose and transform into sugar by cracking ether/ester bonds, which is crucial for the research of hemicellulose. Feng et al. (2022b) pretreated bagasse with 3 % p-TsOH, and found that the extraction yield of hemicellulose was 36.02 % at 80 °C for 120 min. A low-temperature freeze-assisted p-TsOH pretreatment was able to increase the hemicellulose separation to 93.26 % (Peng et al., 2022), however, which was lack of attention on the hemicellulose depolymerization products in solution. Most of the p-TsOH pretreatment research focused on lignin and cellulose, only a few studies have been reported on hemicellulose using low concentration of p-TsOH.

In this work, moso bamboo was pretreated with p-TsOH aqueous solution in low concentration, and the effects of reaction time, solvent concentration, and temperature on the depolymerization of hemicellulose were investigated. Analytical characterization of the pretreatment residues was characterized by environmental scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FT-IR), X-ray diffractometry (XRD), etc. It is expected to promote further research of a low concentration of p-TsOH in biomass pretreatment and fulfill the effective separation and depolymerization of hemicellulose into XOS and xylose, so as to explore and provide a novel method for industrial production of xylose and its downstream chemicals using *xylo*-oligosaccharides with low polymerization.

2. Materials and methods

2.1. Materials

Two-year-old moso bamboo (*Phyllostachys pubescens*) was collected in September 2021, from the experimental forest at Taiping Experimental base of the International Centre for Bamboo and Rattan. Crushed the moso bamboo and sifted it to leave a powder less than 0.425 mm in size. Then the extracts of bamboo solubled in either water or ethanol were removed exhaustive by Soxhlet extraction. Finally, the dried bamboo powder was set aside in the oven.

Moso bamboo consisted of 21.55 % xylan, 39.99 % glucan, 1.98 % araban, 1.21 % galactan, 26.46 % acid insoluble lignin (AIL), and 0.35 % acid-soluble lignin (ASL) of as determined according to NREL/TP-510–42618.

p-TsOH (99 % purity) was purchased from Shanghai McLin Biochemical Technology Co., ltd; X2, X3, X4, X5, X6, and other specimens purchased from Shanghai Yuanye Bio-Technology Co., ltd; Glucose, xylose, formic acid, furfural, levulinic acid, 5-hydroxymethyl furfural and acetic acid (all analytical purity) were purchased from Aladdin Biochemical Technology Co., ltd; β-glucosidase (49290-1G, from almonds) and cellulase (C1794-5KU, from *Trichoderma* sp.) were provided by Sigma-Aldrich.

2.2. Pretreatment of moso bamboo

2.0 g moso bamboo powder was loaded into a 100 mL vessel with a certain concentration of 40 mL p-TsOH/H_2O solution, the homogeneous reactor was heated to the target temperature for a certain time and finally cooled to room temperature by the program. Each experiment was conducted in triplicate, with the data recorded as the average ± standard deviation (SD).

Solid-liquid separation of the reaction residue was operated by vacuum filtration and the filtrate was collected. Poured a constant volume of deionized water into the filtrate for precipitation of the separated lignin, following with the analysis of hemicellulose depolymerization in the filtrate; The recovered solid substrates were firstly rinsed with an aqueous solution of p-TsOH with the same concentration of corresponding pretreatment, and then washed with deionized water until the pH of the filtrate was neutral, the contents of xylan, glucan, arabinan, mannan, galactan and lignin in solid residues were measured according to the NREL/TP-510–42618. Finally, heat stability test of the AIL was performed by thermogravimetric analyzer device (TGA, PerkinElmer TGA4000), the 10 mg AIL was loaded into alumina crucibles with the heating speed of 20 °C/min from 30 °C to 900 °C under nitrogen atmosphere (Wang et al., 2021; Zhang et al., 2021).

2.3. Enzymatic hydrolysis of the solid residues

The solid residues after pretreatment were used for enzymatic hydrolysis. Prepared 10 g/L substrate and 10 mL of sodium acetate–acetic acid buffer solution (pH = 4.8) in a 50 mL conical flask supplemented with cellulase (20 FPU/g substrates) and β-glucosidase (20 IU/g substrates), which enzymatic hydrolysis was performed at 50 °C for 72 h with 200 rpm. And 0.1 mL hydrolysate was collected regularly and inactivated for sugar concentration analysis.

2.4. Analytical methods

2.4.1. Determination of sugars and fermentation inhibitors

The concentrations of glucose, xylose, arabinose, and galactose in the acid hydrolysates as well as contents of X2 ~ X6 were measured by ion chromatography (Metrohm 850, Metrohm Corporation, Switzerland) equipped with a Dionex CarboPac™ PA-200 analytical column (3 mm × 250 mm) and guard column (3 mm × 50 mm). The eluent was 1 mM NaOH for monosaccharides; The eluent was a mixture of 100 mM NaOH and 25 mM NaOAc for X2 ~ X6. Oligosaccharides in the pretreatment filtrate subsequently hydrolyzed with 3 % H_2SO_4 at 121 °C for 60 min and then measured using the same method.

The contents of the formic acid, acetic acid, levulinic acid, furfural, and 5-hydroxymethylfurfural (HMF) produced during the p-TsOH pretreatment were analysed and detected by high-performance liquid chromatography (HPLC; UV230II, Elite, Dalian, China).

2.4.2. Characterization of the pretreated bamboo substrates

The surface topography and structure of different pretreated moso bamboo substrates were observed with an environmental scanning electron microscope (SEM, SU8010, Hitachi, Japan). The various residues were enlarged 400 times at an accelerating voltage of 5.0 KV; The functional groups of the substrates prior to and after pretreatment were characterized by fourier transform infrared spectroscopy (FT-IR, Nexus 670, Thermo Electron Corporation, USA); The crystallinity index (CrI) of cellulose in different substrates were measured by X-ray Diffractometer (XRD, Philips, X PERTPRO-30X, The Netherlands), which the spectra were measured within the limits of 5 ~ 45° (2θ) at a rate of 5°/min with Cu Kα radiation at 40 KV and 40 mA. The calculation formula is as follows: (Akbarpour et al., 2018; French and Santiago Cintrón, 2013; Segal, et al., 1959):

$$CrI = (I_{002} - I_{am})/I_{002} \times 100\%$$

In this equation:

I_{002} – Diffraction intensity of the crystalline surface.

I_{am} – Diffraction intensity of non-crystalline regions.

2.5. Calculation

$$\text{The extraction yield of hemicellulose } (\%) = (\text{Xylose content after acid hydrolysis filtrate} \times 0.88)/\text{Initial xylan } (g/L) \times 100\%$$

$$\text{The extraction yield of xylose } (\%) = (\text{The content of xylose in filter liquor} \times 0.88)/\text{Initial xylan } (g/L) \times 100\%$$

$$\text{Total XOS yield } (\%) = ((\text{Xylose content after acid hydrolysis filtrate} - \text{the content of xylose in filter liquor}) \times 0.88)/(\text{Initial xylan}(g/L)) \times 100\%$$

$$\text{X2} \sim \text{X6 yield } (\%) = \text{Total XOS of DP 2} \sim 6\ (g/L)/\text{Initial xylan } (g/L) \times 100\%$$

$$\text{Solid recovery } (\backslash\%)) = \text{Pretreated dry biomass}/\text{Untreated dry biomass} \times 100\%$$

$$\text{The Separation yield of hemicellulose } (\%) = (\text{Initial xylan} - \text{the content of xylan in residual solids})/\text{Initial xylan } (g/L) \times 100\%$$

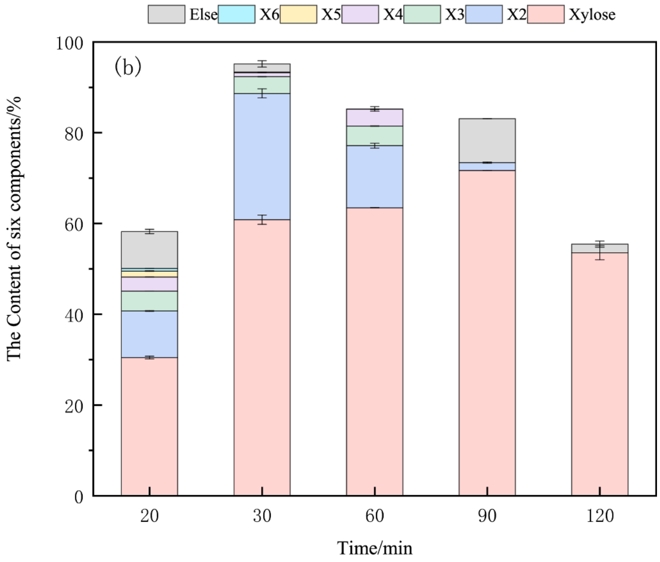

Fig. 1. Components analysis of the filtrate at different reaction time.

$$\text{The retention yield of glucan}\,(\%) = \text{Glucan in pretreated solid}/\text{Glucan in bamboo} \times 100\%$$

$$\text{Enzymatic hydrolysis efficiency}\,(\%) = (\text{Glucose obtained in the liquid after enzymatic hydrolysis} \times 0.9)/\text{Glucan obtained in pretreatmented solid} \times 100\%$$

$$\text{The retention yield of lignin}\,(\%) = \text{Lignin in pretreated solid}/\text{Lignin in bamboo} \times 100\%$$

(Note: 0.9 is a correction coefficient for conversion of glucan to glucose.).

3. Results and discussion

3.1. The influence of pretreatment conditions on extraction and depolymerization of hemicellulose

Research on hemicellulose depolymerization requires good extraction efficiency of hemicellulose from moso bamboo. Important factors include time, temperature, and solvent concentration of the pretreatment affecting hemicellulose extraction. The effect of different time on the depolymerisation of hemicellulose under 140 °C and 5 % p-TsOH is shown in Fig. 1.

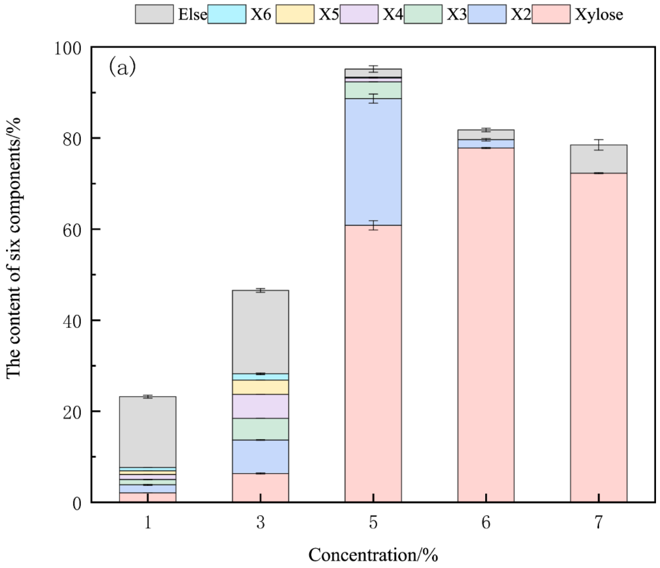

Fig. 2. Components analysis of filtrate after different solvent concentration pretreatments.

The extraction yield of hemicellulose increased initially and then decreased. The same trend was also observed for the total XOS yield. The extraction yield of hemicellulose was 95.16 % at 30 min, with the highest production of xylan at 2.21 g/L. The concentrations of hemicellulose and X2 gradually decreased as time increased due to the separation of a large amount of hemicellulose, but xylose content was enhanced. X2 ~ X6 were basically undetectable in the filtrate except for the majority of xylose after 120 min. Results revealed that fermentation inhibitors were formed in the filtrate (2.79 g/L formic acid, 2.49 g/L acetic acid, 1.52 g/L levulinic acid, and 1.35 g/L furfural). It may be due to the penetration of p-TsOH into the feedstock at this temperature and concentration promoted the breakage of cellulose, hemicellulose, and lignin in the cell wall, which dissolved most of the hemicellulose. Xylose or XOS was acid catalyzed to degraded to increasing fermentation inhibitors gradually.

The concentration of p-TsOH also had effects on hemicellulose depolymerization. The performance of p-TsOH at various concentrations (1 %, 3 %, 5 %, 6 %, 7 %) on hemicellulose depolymerization was investigated at 140 °C for 30 min. Component analysis of filtrate at different concentrations is shown in Fig. 2. The extraction yield of hemicellulose gradually increased and then slowly decreased with concentration of p-TsOH elevated. There was only a modest amount of xylose (0.69 g/L) in the filtrate and the content of X2 increased slightly as well since the concentration of p-TsOH increased to 3 %. As the concentration increased to 5 %, the extraction yield of total XOS reached

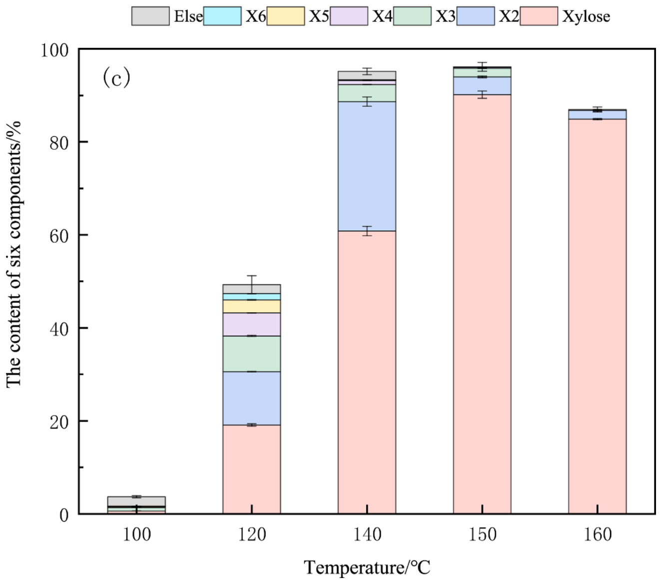

Fig. 3. Components analysis of filtrate at different temperature.

33.93 %, with X2 accounting for the largest proportion. However, the separation of hemicellulose tended to be stable at higher concentration. With 6 % p-TsOH, the xylose content in the filtrate was 8.39 g/L, while the XOS content was only 0.43 g/L. It could be concluded that most of the hemicellulose in the filtrate at low concentration were in the form of polymers and had not been depolymerized massively. The permeability of the solution enhanced with the concentration of p-TsOH increasing. The extracted hemicellulose was essentially converted to monosaccharide at the 5 % p-TsOH. Additionally, Feng et al. (2022b) pointed out that the dissolution and degradation of hemicellulose occurred simultaneously during the p-TsOH pretreatment. Therefore, as the concentration continued to increase, it would inevitably lead to hemicellulose degradation to produce more fermentation inhibitors.

Fig. 3 shows the effect of different temperature on hemicellulose depolymerization at 30 min and 5 % p-TsOH. As can be seen, only a few xylan was dissolved at 100 °C. As the pretreatment temperature increased from 120 °C to 140 °C, the yield of X2 rapidly increased from 11.46 % to 30.77 %, but the yield of X3 to X6 was decreased. The concentration of xylose was 9.72 g/L at 150 °C, at that time the extraction yield of xylose was as high as 90.16 % and a small amount (0.15 g/L) of furfural was detected in the filtrate. It was presumable that the degradation of hemicellulose by p-TsOH maintained poor and the penetration of solvent was also difficult due to the dense structure of moso bamboo at a lower temperature. As the temperature continued to increase, the reason for the rapidly increase of X2 yield may be attributed to the hydrogen ions (H_3O^+) generated by the water, which could further facilitate the degradation of xylan to XOS and xylose (Surek and Buyukkileci, 2017). The hemicellulose of moso bamboo was basically all degraded into xylose and the filtrate contained a small amount of furfural at 150 °C, this phenomenon imaged that the dehydration reaction of xylose in the filtrate was inevitable. In summary, p-TsOH is an effective solvent for the extraction of hemicellulose, and the extraction of hemicellulose and XOS can be enhanced by appropriately temperature raising. It is feasible to produce xylose with fewer by-products and X2 with increased prebiotic activities.

Table 1
Compositions of the spent liquor after p-TsOH pretreatment under different conditions.

Conditions	Sugars (g/L)								ASL (g/L)	Inhibitors (g/L)				
c—T—t %-°C-min	Arabinose	Araban	Galactose	Galactosan	Glucose	Glucan	xylose	Xylan		Formic acid	Acetic acid	Levulinic acid	HMF	Furfural
5-140-20	0.44 ± 0.17	0.74 ± 0.87	ND	ND	ND	0.37 ± 0.01	3.28 ± 0.30	6.28 ± 0.47	0.01 ± 0.00	ND	2.02 ± 0.31	ND	ND	ND
5-140-30	0.39 ± 0.07	0.61 ± 0.16	0.03 ± 0.01	0.04 ± 0.02	0.59 ± 0.08	1.12 ± 0.03	6.60 ± 1.01	10.26 ± 0.71	0.01 ± 0.00	ND	1.49 ± 0.11	ND	ND	ND
5-140-60	0.46 ± 0.08	0.62 ± 0.11	ND	0.03 ± 0.00	0.74 ± 0.14	0.89 ± 0.10	6.84 ± 0.04	9.19 ± 0.51	0.01 ± 0.00	0.88 ± 0.15	1.55 ± 0.09	ND	ND	0.29 ± 0.03
5-140-90	0.61 ± 0.06	0.61 ± 0.07	ND	ND	0.70 ± 0.01	0.65 ± 0.04	7.73 ± 0.01	8.96 ± 0.03	0.01 ± 0.00	1.84 ± 0.04	1.21 ± 0.86	ND	ND	0.65 ± 0.00
5-140-120	0.42 ± 0.09	0.42 ± 0.20	0.10 ± 0.07	0.17 ± 0.14	0.49 ± 0.22	0.34 ± 0.24	5.77 ± 1.55	5.98 ± 0.69	0.01 ± 0.00	2.79 ± 0.23	2.49 ± 0.20	1.52 ± 0.12	ND	1.35 ± 0.09
1-140-30	0.25 ± 0.09	0.26 ± 0.08	ND	ND	ND	0.14 ± 0.11	0.23 ± 0.01	2.50 ± 0.32	0.01 ± 0.00	ND	0.76 ± 0.15	ND	ND	ND
3-140-30	0.23 ± 0.03	0.40 ± 0.11	ND	ND	ND	0.27 ± 0.09	0.69 ± 0.12	5.02 ± 0.41	0.00 ± 0.00	ND	1.85 ± 0.02	ND	ND	ND
5-140-30	0.39 ± 0.07	0.61 ± 0.16	0.03 ± 0.01	0.04 ± 0.02	0.59 ± 0.08	1.12 ± 0.03	6.60 ± 1.01	10.26 ± 0.71	0.01 ± 0.00	ND	1.49 ± 0.11	ND	ND	ND
6-140-30	0.34 ± 0.48	0.34 ± 0.47	0.12 ± 0.01	ND	0.63 ± 0.04	0.49 ± 0.69	8.39 ± 0.11	8.82 ± 0.39	0.00 ± 0.00	ND	1.80 ± 0.04	ND	ND	ND
7-140-30	0.34 ± 0.48	0.43 ± 0.03	0.12 ± 0.01	ND	0.58 ± 0.08	0.21 ± 0.60	7.79 ± 0.12	8.46 ± 1.14	0.01 ± 0.00	ND	1.16 ± 0.91	ND	ND	ND
5-100-30	0.23 ± 0.01	0.24 ± 0.04	ND	ND	ND	ND	0.07 ± 0.01	0.40 ± 0.02	0.01 ± 0.00	ND	0.36 ± 0.26	ND	ND	ND
5-120-30	0.48 ± 0.08	0.74 ± 0.56	ND	0.14 ± 0.00	0.07 ± 0.03	0.43 ± 0.22	2.06 ± 0.25	5.31 ± 1.94	0.00 ± 0.00	ND	1.45 ± 0.10	ND	ND	ND
5-140-30	0.39 ± 0.07	0.61 ± 0.16	0.03 ± 0.01	0.04 ± 0.02	0.59 ± 0.08	1.12 ± 0.03	6.60 ± 1.01	10.26 ± 0.71	0.01 ± 0.00	ND	1.49 ± 0.11	ND	ND	ND
5-150-30	ND	ND	ND	ND	ND	0.85 ± 0.18	9.72 ± 0.79	10.21 ± 0.96	0.01 ± 0.00	4.07 ± 0.37	3.70 ± 1.29	ND	ND	0.15 ± 0.02
5-160-30	0.57 ± 0.05	0.51 ± 0.14	ND	ND	0.36 ± 0.08	ND	9.15 ± 0.12	9.37 ± 0.54	0.00 ± 0.00	1.23 ± 0.72	1.33 ± 0.95	ND	ND	0.25 ± 0.01

ND: Not detectable.

3.2. *Fermentation inhibitors during pretreatment*

In addition to XOS and xylose in the filtrate, there were many sugars and fermentation inhibitors in trace amount after p-TsOH treatment, as shown in Table 1. Fermentation inhibitors produced by the p-TsOH pretreatment increased gradually with the intensity of the pretreatment conditions. The highest content of acetic acid was 3.70 g/L. Since the acetyl group of hemicellulose was shed during acid hydrolysis, the acetic acid produced would reduce the pH of the reaction system, and further promoting the degradation of the polysaccharides to monosaccharides. Owing to the large amount of xylose in the system under these conditions and inevitably which resulted in its dehydration to furfural, the maximum formic acid concentration detected was 4.07 g/L. Moreover, it was evident that the content of glucose was low, indicating at small concentrations of treatment, only a small portion of cellulose in moso bamboo was converted to monosaccharide. This could be a result of the presence of a crystalline structure of cellulose and only a small amount of non-crystalline cellulose regions was degraded (Feng et al., 2022a). The concentration of glucan in the filtrate was 1.12 g/L at optimal condition of 5 % p-TsOH, 140 °C and 30 min. As the temperature increased, the glucan content in residues gradually decreased and the corresponding glucose concentration in the filtrate gradually increased, this phenomenon indicated that a small part of the glucan was hydrolyzed under acidic conditions. Furthermore, glucose can continue to degrade to produce HMF, formic acid and levulinic acid under acidic conditions, while the content of glucan obtained in the system was low, so it could be seen that the content of byproducts was low. And ASL content of the filtrate is also shown in the Table 1. Since ASL could be precipitated by mixing with three times volume of water, the dilution multiple precipitation experiments showed that a large amount of lignin was still pooled in the residues.

3.3. *Analysis of chemical compositions of the solid substrates*

3.3.1. *Chemical compositions of pretreated bamboo substrates*

The different pretreatment conditions will affect the structural characteristics of the resulting residues and their subsequent enzymatic capacity. Thus, the effects of different pretreatment conditions on the chemical composition of the residues were investigated. The proportions of cellulose, lignin, hemicellulose, and the retention yield of each component in the residues under different reaction conditions are showed in Fig. 4.

The yields of solid residues decreased gradually with the increasing of time, temperature, and solvent concentrations. The separation of hemicellulose all showed an increasing trend. When the reaction temperature went up to 160 °C, the separation yield of hemicellulose was 93.67 %, which indicated that the appropriate pretreatment could remove lots of xylan from the bamboo. A portion of the refractory hemicellulose will be successfully degraded under severe conditions, such as high temperature, whereas the easily degradable hemicellulose may be rapidly disintegrated during the pretreatment process. However, the high temperature will inevitably lead to the reduction of cellulose and lignin yield.

As the reaction time increased, the amount of cellulose in the solid substrate first increased and then decreased. The greatest retention of glucan in the substrate was 96.96 % when the samples treated with 5 %

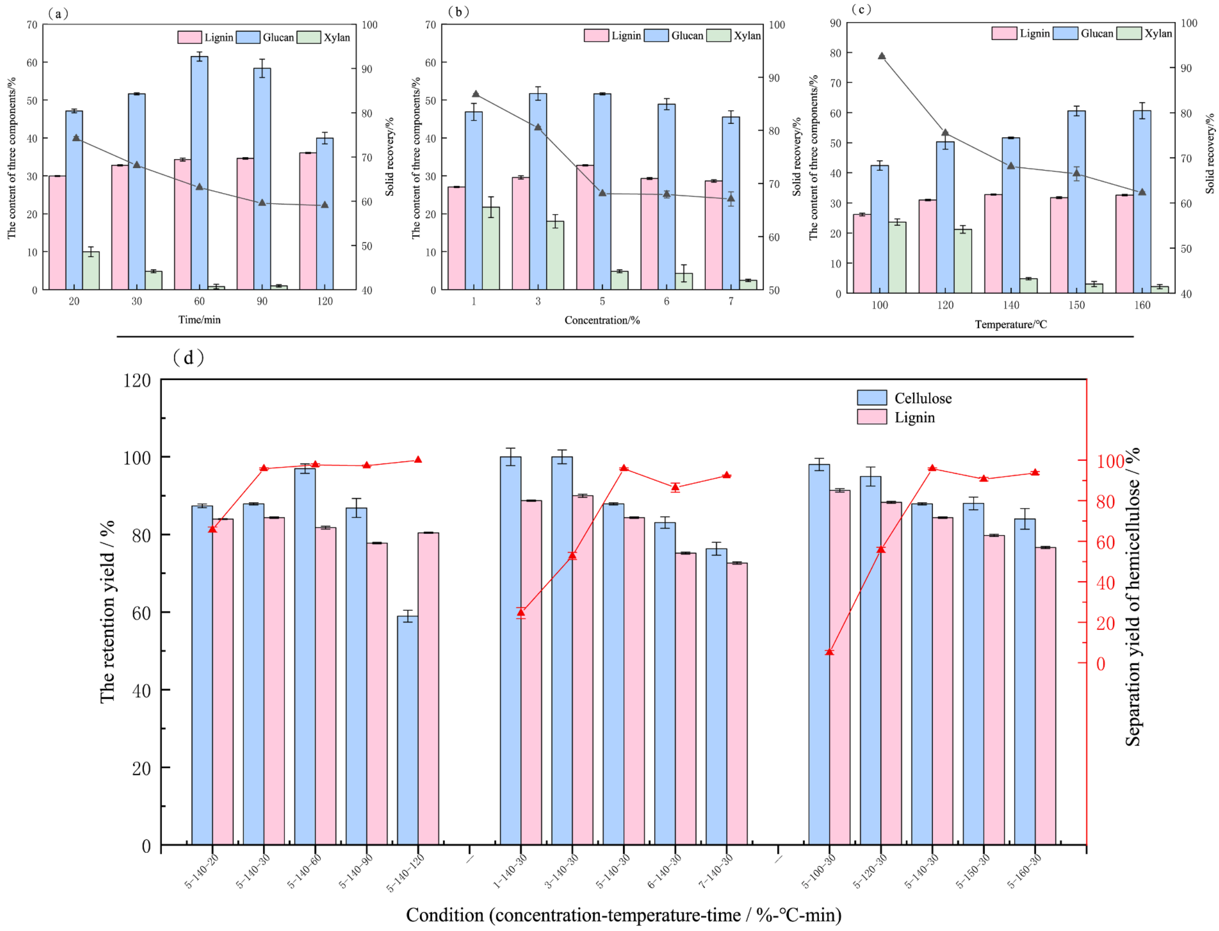

Fig. 4. Fraction analysis of substrates under different reaction conditions. (a) The fractional analysis of the residue at different reaction time. (b) The fractional analysis of the residue at different concentration. (c) The fractional analysis of the residue at different temperature. (d) The retention yield of glucan and lignin and the separation yield of hemicellulose.

p-TsOH at 140 °C for 60 min. The amount of glucan dramatically declined over the course of time, which suggested that the glucan in the substrate was broken down exaggeratedly. A similar trend was observed with glucan, which indicated that prolonging duration time accelerated the degradation of glucan in the substrate. Cellulose in the pretreated material was mostly preserved after treatment at this concentration. Fig. 4 (c) shows that the amount of glucan increases with increasing temperature, indicating that hemicellulose is more easily decomposed than cellulose. The amount of lignin in the residue increased slightly with the acid concentration, and the retention yield of lignin exceeded 72 % for each case. It may suggest that the removal of cell wall polysaccharides at low concentration might have prevented appreciable effects of p-TsOH treatment on lignin degradation.

On the basis of prioritizing the separation of hemicellulose, the p-TsOH pretreatment system showed excellent performance and maintained the majority of cellulose and lignin in the residues, providing a new approach for the comprehensive development and utilization of bamboo. It is also feasible to produce lignin-containing cellulose nanomaterials (LCNMs) and the retention of lignin can improve the hydrophobicity, UV resistance, and antibacterial characteristics of cellulose nanomaterials during the preparation of LCNMs (Ewulonu et al., 2019), all of these can be accomplished by further reaction to separate lignin and cellulose from the residues.

3.3.2. Thermal stability analysis of lignin components

TGA and Differential Thermogravimetric Analysis (DTG) (see supplementary material) were used to compare and understand the thermal stability of the pretreatment residues after acid digestion, AIL-140 (with the highest extraction yield of hemicellulose) and AIL-150 (with the highest extraction yield of xylose). The peak of the DTG curve was found to correlate to the temperature at which the highest degradation rate occurred. The maximum DTG values of AIL-140 and AIL-150 were recorded at 391 °C and 376 °C, which corresponding to the solid residues of 75.16 % and 70.80 %, respectively. The pyrolysis of AIL can essentially be broken down into three phases. At an early stage, the weight decreased attributed to the evaporation of free water and low molecular weight gases at the temperature was below 200 °C; In the next stage, the lignin was severely degraded and the mass loss of the lignin component was significant from 200 °C to 600 °C, where the residual yield of AIL-140 was reduced from 75.26 % to 45.45 %. A large amount of carbon was obtained at 850 °C, the solid residues of AIL-140 and AIL-150 were 35.75 % and 34.10 %, respectively, and mass loss decreased slowly and remains largely unchanged. This may be the result of the stripped of labile carbohydrates from AIL at high temperatures and the cross-linked structure formed by some functional groups in lignin, resulting in higher carbon residues in the samples (Zhang et al., 2021). The content of residues served as a proxy for thermal stability in various aspects. Due to its high residual content and improved thermal stability, AIL has the potential to be used for flame retardant materials.

3.3.3. Micromorphology of the pretreated solid substrates

The micromorphology and surface structures of the samples were observed by SEM under different conditions (see supplementary material). The untreated moso bamboo showed a smooth and tight structure, the enlarged surface was relatively flat and regularly aligned without pores or breaks. However, the surface of the solid residues exhibits “foaming” after being treated with 5 % p-TsOH at 140 °C for 30 min. The surface of the fiber in the residues appeared a large number of cracks and the eversion of internal structures. The amplified fiber showed longitudinal fissures with coarse edges, and the wall layer was peeled off due to the treatment. SEM depicted the fiber bundles in the solid residues arranged loosely and irregularly, and with even some damaged cellulose bundles. This demonstrated that the hemicellulose was mostly separated, cellulose and lignin were slightly dissolved, and the connections between fibers were loosened, all of which created conditions for further separation of cellulose and lignin. In summary, chemical solvents were very difficult to penetrate because of the tight structure of untreated raw materials, and the p-TsOH pretreatment system could effectively destroy the physical barrier on the surface of moso bamboo, making it softer and fluffier, which was conducive to the further utilization of solid residues.

3.3.4. FT-IR spectroscopy analysis of the substrates

The IR peaks were essentially identical before and after pretreatment, indicating that the pretreatment residue still had structural features of cellulose (see supplementary material). The peaks at 3420 cm^{-1} and 2923 cm^{-1} correspond to the tensile vibration of O—H and C—H, respectively. The enhanced intensity of these peaks proved that the β-1,4 glycosidic bond was broken and the degree of polymerization dropped off. 1511 cm^{-1} and 1635 cm^{-1} corresponded to the aromatic skeletal vibrational peaks in the lignin structure, the peak at 1250 cm^{-1} matched with the tensile vibration of the C—O structure and the peak at 833 cm^{-1} was the planar vibration peak of clove-based lignin, all of these peaks indicated that most of lignin remained in the solid residue. The signal peaks at 1463 cm^{-1}, 1426 cm^{-1}, 1371 cm^{-1} and 1245 cm^{-1} represented the bending vibrations of C—H, C—O and –OH in hemicellulose, respectively (Zhan et al., 2022). The 1161 cm^{-1} and 1049 cm^{-1} signals represented the C—O absorption peaks on the glycosidic bond (C—O—C) and glycosidic bond, respectively, which were typical absorption peaks for arabinoxylan. 1730 cm^{-1} represented the acetyl group on the side chain of hemicellulose, and acetyl peaks diminished significantly with the change of reaction conditions, this phenomenon might be due to the hydrolysis of some acetyl groups to produce acetic acid. In summary, the IR spectroscopic analysis indicated that the pretreatment system could effectively promote the degradation of hemicellulose and expose more structure of cellulose and lignin in the substrate.

3.3.5. XRD analysis of the CrI of glucan of the substrates

The changes in the crystallinity of glucan of the solid residues were determined by XRD (see supplementary material). Similar diffraction peaks at 2θ of 15.6°, 22.1° and 34.6° were observed matching with the crystal surfaces (1 0 1), (0 0 2) and (0 3 4), severally. It indicated that the crystalline structure of cellulose I was maintained in the substrate before and after pretreatment. The peak pattern and intensity of the diffraction peak at 22.1° were slightly narrowed and increased, as well as the crystallinity of the residues increased from 36.34 % to 42.42 % with the treatment of 5 % p-TsOH at 140 °C for 30 min, which may be the degradation of lignin and the transformation from hemicellulose to cellulose, greatly increasing the amount of cellulose in the crystalline structure. Additionally, the CrI of the solid residues was 42.46 % with the treatment of 5 % p-TsOH at 150 °C for 30 min. The crystallinity of the cellulose itself increased slightly in the residues with increasing pretreatment temperature, thus exposing more hydroxyl groups and increase the number of hydrogen bonding sites. To sum up, the CrI/glucan of pretreated substrates was much lower (0.91) compared with untreated bamboo, which was beneficial for the utilization of the

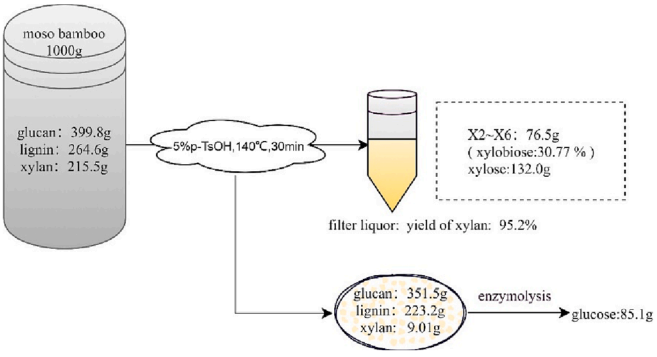

Fig. 5. Mass balances of bamboo substrates by p-TsOH pretreatment.

residues.

3.4. *Enzymatic hydrolysis of solid bamboo substrates*

Compared with the untreated bamboo, the cellulose to glucose conversion efficiency of pretreated moso bamboo by enzymatic hydrolysis was significantly improved (see supplementary material). The cellulose to glucose conversion yield was 24.23 %, which was twice as high as untreated raw materials. This might be attributed to the decrease in the average degree of polymerization of cellulose and the increase in the reaction capacity, which was conducive to enzymatic hydrolysis. Moreover, lignin-rich cellulose residues were obtained after p-TsOH pretreatment. The enzymatic hydrolysis efficiency of cellulose was influenced by lignin, lignin in large amount restrained the efficiency of enzymatic activities via the infiltration, adsorption, and hydrolysis of cellulose.

3.5. *Mass balances of sugars during the pretreatment process*

The mass balance can effectively evaluate the feasibility of the pretreatment route and the economic benefits of industrial production in the future. The mass balance of bamboo sugars during pretreatment is summarized in Fig. 5. 1000 g raw bamboo can recover about 680.7 g of dried substrate after pretreatment, which included 351.5 g glucan, 9.01 g xylan, and 223.2 g lignin, indicating that most of the cellulose and lignin remained in the solid residues. And the extraction of total xylan in the filtrate reached 95.16 %, the XOS with DP of 2 ~ 6 was 76.5 g, of which X2 accounted for 30.77 %. The data above suggested that p-TsOH was an efficient pretreatment process for the production of X2 and xylose. In addition, the p-TsOH solvent system can also be recycled and reused. It showed that the solvent system can be recycled by vacuum distillation, without any reduction in efficiency (Yin et al., 2022). Recycling can effectively relieve the pressure of environmental pollution and facilitate the subsequent amplification of industrial production.

4. Conclusions

The extraction yield of bamboo hemicellulose was 95.16 % with the treatment of 5 % p-TsOH at 140 °C for 30 min. The depolymerized components of hemicellulose in the filtrate were mainly xylose and XOS, of which 61.23 % was xylose. X2 was predominant in XOS, and the extraction yield of X2 was 30.77 %. The extraction yield of xylose was 90.16 % with the treatment of 5 % p-TsOH at 150 °C for 30 min. Compared with untreated bamboo, lignin and cellulose in the extracted residue showed excellent properties. The AIL showed higher thermal stability, and the cellulose-to-glucose conversion yield doubled after enzymatic hydrolysis.

CRediT authorship contribution statement

Meixin Wang: Conceptualization, Investigation, Software, Writing – original draft. **Yawei Zhan:** Investigation, Software, Data curation. **Jiayue Zhao:** Software, Validation. **Zhiqiang Li:** Conceptualization, Methodology, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2023.129006.

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