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Valorizing Waste Lignocellulose-Based Furniture Boards by Phosphoric Acid and Hydrogen Peroxide (Php) Pretreatment for Bioethanol Production and High-Value Lignin Recovery

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Abstract: Three typical waste furniture boards (fiberboard, chipboard, and blockboard) were pretreated with phosphoric acid and hydrogen peroxide (PHP). The fractionation process of these feedstocks was attempted in order to harvest the cellulose-rich fraction for enzymatic hydrolysis and bioethanol conversion; further, lignin recovery was also considered in this process. The results indicated that 78.9–91.2% of the cellulose was recovered in the cellulose-rich fraction. The decreased crystallinity, which promoted the water retention capacity and enzyme accessibility, contributed greatly to the excellent hydrolysis performance of the cellulose-rich fraction. Therefore, rather high cellulose–glucose conversions of 83.3–98.0% were achieved by hydrolyzing the pretreated furniture boards, which allowed for harvesting 208–241 g of glucose from 1.0 kg of feedstocks. Correspondingly, 8.1–10.4 g/L of ethanol were obtained after 120 h of simultaneous saccharification and fermentation. The harvested lignin exhibited abundant carboxyl –OH groups (0.61–0.67 mmol g^{-1}). In addition, approximately 15–26 g of harvested oligosaccharides were integrated during PHP pretreatment. It was shown that PHP pretreatment is feasible for these highly recalcitrant biomass board materials, which can diversify the bioproducts used in the integrated biorefinery concept.

Keywords: furniture boards; ethanol production; lignin; biorefinery

1. Introduction

The energy requirements from the intensive use and consumption in modern society are mainly met by fossil fuels. Sustainability considerations for energy and chemicals have driven industries toward renewable resources [1]. Lignocellulose is the most abundant biomass in nature and is a promising material for producing bioenergy and biochemicals via biorefinery processes [2].

As one typical form of bioenergy, bioethanol production from prevalent lignocellulosic materials, including hardwood/softwood, agricultural residues, and energy crops, has been extensively assessed in recent years [3]. However, some unconventional biomass substrates, such as coconut shells, duckweed, distiller's dried grains, waste cotton fabric biomass, and so forth, are also promising as

sugar platforms through biological processes due to their high cellulose/polysaccharide content [4,5]. Due to rapid urbanization, an increasing amount of used furniture is discarded, approximately 85% of which was produced from lignocellulosic biomass [6]. Fiberboard, chipboard, and blockboard are the most common synthetic boards used in furniture production. Fiberboard is mainly made from reeds, wheat straws, and so forth, while chipboard and blockboard are mainly made from wood chips [7,8]. The common disposal methods of these used/waste furniture boards, such as landfilling and incineration, result in potential soil/air pollution and a great waste of natural lignocellulosic biomass resources [9]. Considering the advantages of their high polysaccharide components, their low cost, and the easy collection of these waste furniture boards, they might be promising substrates for bioethanol production.

However, the rather low digestibility of polysaccharides greatly restricts the bioconversion of lignocellulosic biomass into bioethanol due to the naturally recalcitrant structure of the feedstocks [10]. Lignocellulose-based furniture boards not only have the natural recalcitrance of lignocellulosic feedstocks, but they are also more recalcitrant for bioconversion than natural feedstocks because of the artificially added adhesives, such as phenolic and urea–formaldehyde resins [11]. Moreover, these furniture boards are mainly prepared at a higher temperature and pressure, which further potentially promotes structural recalcitrance to subsequent biological conversion. Obviously, the existence of natural and artificial recalcitrance in these furniture boards is a considerable challenge for the biological conversion process for bioethanol production, suggesting that an efficient pretreatment should be initially considered for these furniture substrates [12].

Our previous work indicated that a phosphoric acid and hydrogen peroxide (PHP) pretreatment could efficiently remove the naturally recalcitrant fractions of lignin and hemicellulose. Moreover, the accessibility of recovered cellulose to hydrolytic enzymes was greatly promoted and achieved more than 90% cellulose–glucose conversion, resulting in a rather high level of bioethanol conversion, even at high solid loadings [13–15]. According to the mechanism of PHP pretreatment on lignin removal, the generated HO^+ could efficiently oxidize lignin via ring-opening and cleaving the ether linkages [16]. The prevalent adhesive of phenolic resins generally displays a quite similar aromatic chemical structure to lignin; thus, it may be possible to degrade these phenolic adhesives to facilitate breaking the recalcitrant fractions. Besides, PHP displayed excellent pretreatment efficiency on various mixed lignocellulosic feedstocks [13], which provides an advantage for working on furniture board feedstocks because they are generally artificially made from mixed lignocellulosic materials through cross-linkage and compression. Therefore, these advantages and possibilities encouraged us to extend this promising PHP pretreatment to unlock the hydrolysis potential of the inner polysaccharide components from these furniture substrates for subsequent enzymatic hydrolysis and bioethanol conversion and, potentially, to recover valuable fractions as well.

In this work, PHP pretreatment was performed on three unconventional biomass substrates, namely, fiberboard, chipboard, and blockboard. The characterizations, enzymatic hydrolysis performances, and the subsequent bioethanol conversion of the pretreated substrates were investigated to assess the pretreatment efficiency. In addition, the valuable fractions, such as lignin and oligosaccharides, were also recovered and integrated into the pretreatment to amplify the feasibility of the whole biorefinery process. Thus, this facile PHP pretreatment might be extended to other unconventional recalcitrant biomass wastes in order to build a multiproduct biorefinery.

2. Materials and Methods

2.1. Feedstocks and Chemicals

Fiberboard, chipboard, and blockboard were obtained from Changan Landfill, Chengdu, China. The thickness and density of the boards were about 15 mm and 0.75 g/m^3, respectively, and the moisture contents of the fiberboard, chipboard, and blockboard were 8.42%, 8.25%, and 9.38%, respectively. Based on our experience, the type of resin used for furniture board production was

phenol–formaldehyde resin (PF). Each kind of board (>3.0 kg) was air-dried and chopped into small pieces. The obtained boards were ground through a 20-mesh screen and stored in a plastic bag for further PHP pretreatment. Chengdu Cologne Chemical Company (China) provided all the chemical reagents, including phosphoric acid (85%, *w*/*w*), hydrogen peroxide (30%, *w*/*w*), acetic acid, sodium acetate, glucose, xylose, and so forth, used in this research. The protein concentration of the employed cellulase of Cellic CTec2 was determined to be 228.72 mg mL^{-1}, which was gifted by the Beijing branch of Novozymes in China.

2.2. The PHP Pretreatment Process

A PHP solution with actual concentrated H_3PO_4 of 79.6% (*w*/*w*) and H_2O_2 of 1.9% (*w*/*w*) was employed in the pretreatment. Eight grams of furniture boards (dry basis) and 80.0 g of PHP solution were mixed in a 250 mL serum bottle. The bottle was shaken at 180 rpm, the optimized pretreatment temperature and duration were 40.2 °C and 2.9 h, respectively [17], and the pretreatment for each waste board was performed in duplicate. According to Figure S1, when pretreatment was complete, 200 mL of ethanol was added to facilitate the subsequent filtration. The liquor from the filtration (called liquid fraction I) was condensed by vacuum evaporation at 60 °C and distilled water (approximately 200 mL) to precipitate the fractionated lignin (called PHP technical lignin). Subsequently, distilled water was used to wash the PHP technical lignin, which was then vacuum-dried (60 °C) for further investigations. The liquor from washing the solid substrates was collected and condensed (called liquid fraction II) at 80 °C, and the dissolved oligosaccharides were precipitated by ethanol (95%, *v*/*v*). The obtained oligosaccharides were centrifuged, washed with ethanol three to five times, and vacuum-dried. Distilled water was employed to wash the resulting cellulose-rich fraction until reaching a pH of nearly 5.0 [18]. In this process, the consumed ethanol and H_3PO_4 can be recycled for subsequent runs, according to a previous report [19]. The washed cellulose-rich fractions were stored at −20 °C and were further investigated for their chemical composition, enzymatic hydrolysis, and bioethanol conversion. All of the lab investigations were conducted at 25 °C with a moisture level of 50–70%.

2.3. Enzymatic Hydrolysis

A sufficiently high enzyme loading of 20 mg protein/g^{-1} cellulose was employed to enzymatically hydrolyze the pretreated substrates. The hydrolysis process was conducted in an orbital shaker at 50 °C and 150 rpm, and hydrolysis for each sample was performed in duplicate in 25 mL serum bottles with a working volume of 12.0 mL. The solid loading for enzymatic hydrolysis was 2% (*w*/*v*, dry basis), and the acetate buffer (0.05 M, pH 5.0) was supplemented to maintain a stable pH throughout the entire hydrolysis process. A tetracycline solution (40 mg L^{-1}) of 60 µL was added to prevent glucose consumption by the growth of microorganisms. The hydrolysate of 500 µL was sampled at 0, 4, 8, 12, 24, 48, and 72 h, which was further inactivated at 100 °C for 5 min and centrifuged at 1.0×10^5 rpm and 4 °C for 5 min. The supernatant was stored at −20 °C for glucose determination.

2.4. Simultaneous Saccharification and Fermentation (SSF) for Ethanol

SSF was performed in 5 mL bottles with a 2 mL working volume at 38 °C in a 170 rpm shaker for 120 h, and two repetitions were conducted on these three pretreated substrates. To facilitate the sample process, in total, seven groups were employed for the fermentation of each substrate, and each group was used for sampling at the time point of 0, 12, 24, 48, 72, 96, and 120 h, respectively. The solid loading for SSF was 2% (*w*/*v*, dry basis) with Cellic CTec2 and a yeast input of 20 mg protein/g^{-1} cellulose and 3.0 g/L, respectively. The obtained samples were inactivated at 100 °C for 5 min and centrifuged at 1.0×10^5 rpm and 4 °C for 5 min, and the supernatant was stored at −20 °C to detect the glucose and ethanol concentration [15].

2.5. Determination of Glucose and Ethanol Concentration

To determine the concentrations of glucose and ethanol, the obtained supernatants from enzymatic hydrolysis and SSF were all analyzed by high-performance liquid chromatography (HPLC) (1260 Infinity II, Aligent, Santa Clara, CA, USA) with a sugar column (SH1011, Shodex, Showa Denko America, Inc., New York, NY, USA) at 60 °C using 0.05 mol/L H_2SO_4 as the mobile phase (flow rate of 0.8 mL/min), with a refractive index detector (50 °C). Glucose (2.0 mg/mL) and ethanol (10.0 mg/mL) as a standard solution was properly diluted by nanopure water to prepare the standard curves, in which 200 µL of lactose (0.5 mg/mL) was added as an internal standard. The sample (10 µL) was autoinjected for HPLC for glucose and ethanol determination, and the standard curves were employed to calculate the concentrations of glucose and ethanol. The determination of glucose and ethanol concentrations by HPLC was performed in two repetitions for all samples.

2.6. Scanning Electron Microscopy (SEM)

To directly observe the structural changes after PHP pretreatment, microscopic views of raw materials and PHP-pretreated substrates were captured by SEM at low vacuum at 20 kV. Vacuum-dried samples were fixed in a stub with carbon tape and coated with 25 nm of Pt/Au. A variable pressure secondary electron (VPSE) detector was used to obtain the microscopic images.

2.7. X-Ray Diffraction (XRD)

An Ultima IV X-ray diffractometer with Cu-K_a radiation (k = 0.1540 nm) at an accelerating voltage of 40 kV and a current of 40 mA was used to collect the XRD patterns. All data were ranged from 10° to 50° with an interval of 0.02°. The degree of crystallinity was expressed by the percentage crystallinity index (% CrI) according to the following equation (Equation (1)); correspondingly, the average crystal size (τ) was determined by the Scherrer equation (Equation (2)):

$$CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

$$\tau = \frac{K\lambda}{\beta \cos \alpha} \quad (2)$$

where I_{002} represents the maximum intensity of 2θ close to 22°; I_{am} corresponds to the minimum intensity of 2θ close to 18°; K is a constant (1.0 in this case), which depends on the crystal shape; β is the full-width at half-maximum in radians; and θ is the position of the peak (half of the plotted 2θ value) [20].

2.8. Water Retention Value (WRV) of Cellulose-Rich Fraction

The pretreated substrates (0.5 g for each sample) were disintegrated and soaked in 8 mL of distilled water overnight. A centrifuge tube with a 200-mesh screen was used to filter the mixture. To prevent the loss of fines, the filtrate was recirculated three times in the centrifuge tube and the remaining pulps were centrifuged at 900× *g* for 5 min at 25 °C. Subsequently, the centrifuged wet samples were weighed (W_1) and dried to a constant weight at 105 °C and weighed again (W_2) (Equation (3)) [21]:

$$WRV = \frac{W_1 - W_2}{W_2} \quad (3)$$

2.9. Simons' Stain (SS)

The SS technique in the pulp and paper industry was adapted here to evaluate the pore structure (internal surface area) of the raw materials and the PHP-pretreated substrates [22]. The wet sample (100 mg based on dry weight) was added to a 25 mL serum bottle with phosphate-buffered saline (PBS), dye, and water, ensuring 10 mL of the total volume. Tightly capped bottles were initially shaken

well to thoroughly disperse the fibers and then placed horizontally in an orbital shaker at 70 °C for 12 h. The absorbance wavelengths of 425 and 625 nm were employed to detect the concentration of direct orange (DO) and direct blue (DB) in the supernatant solution. The adsorbed amount of each dye by the pretreated biomass was determined by the concentration difference before and after adsorption. The maximum amount of either DO or DB adsorbed to the lignocellulosic substrates was calculated by the Langmuir adsorption equation, and the calculated DO/DB was employed to estimate the accessible cellulase of the lignocellulosic sample.

2.10. Lignin Characterization by Nuclear Magnetic Resonance (NMR)

^{31}P NMR spectra were obtained based on the method described in [23]. Briefly, 500 μL of a mixture of anhydrous pyridine and deuterated chloroform (1.6:1, *v*/*v*) was employed to dissolve the vacuum-dried PHP technical lignin (approximately 20 mg). A sample (100 μL) of 10.85 mg mL^{-1} cyclohexanol solution as the internal standard and 100 μL chromium (III) acetylacetonate (5 mg mL^{-1}) as the relaxation reagent (both dissolved in the mixture of anhydrous pyridine and deuterated chloroform, 1.6:1, *v*/*v*) were added to the dissolved lignin sample. Afterwards, 100 μL of 2 chloro-1,3,2-dioxaphospholane was rapidly added and the prepared testing sample was immediately transferred to a 5 mm tube for subsequent NMR spectra acquisition.

3. Results and Discussion

3.1. The Main Fractions of Furniture Boards before and after PHP Pretreatment

The chemical compositions of these three boards before PHP pretreatment are shown in Table 1. Their cellulose contents ranged from 28.2% to 31.6%, which was comparable to that of prevalent lignocellulosic biomass [13]. This indicated that they could possibly be used as feedstocks for ethanol production. The acid-insoluble and acid-soluble lignin contents were relatively high (26.4–31.9%). The content of extractives for fiberboard (9.5%) was higher than that of chipboard (5.4%) and blockboard (5.9%). It appeared that fiberboard was mainly composed of crop straw, while chipboard and blockboard were mainly composed of sawdust or wood chips, since herbaceous biomass likely exhibits more extractives compared with woody biomass [24].

Table 1. Chemical compositions of the three furniture boards.

Feedstocks	Chemical Composition (%)					
	Cellulose [a]	Hemicellulose [b]	Acid-Insoluble Lignin [c]	Acid-Soluble Lignin	Extractives	Ash
Fiberboard	31.6 ± 0.30	10.0 ± 0.35	28.8 ± 0.08	2.6 ± 0.04	9.5 ± 0.01	2.4 ± 0.01
Chipboard	28.2 ± 0.23	8.7 ± 0.42	30.3 ± 0.31	1.6 ± 0.05	5.4 ± 0.01	3.8 ± 0.09
Blockboard	29.5 ± 0.29	10.1 ± 0.42	24.0 ± 0.34	2.4 ± 0.01	5.9 ± 0.47	5.4 ± 0.13

[a] Cellulose content is represented by glucan content. [b] Hemicellulose content is represented by xylan content. [c] Adhesive that could not be dissolved by sulfuric acid was included in acid-insoluble lignin.

To give a fair comparison, the same pretreatment conditions were selected for these three feedstocks (phosphoric acid concentration of 79.6% and H_2O_2 concentration of 1.9% for the PHP solution), which were the optimized conditions determined in a previous work [17]. Table 2 lists the solid yield; the main chemical composition of the pretreated substrates, including the content of cellulose, hemicellulose, and lignin; the cellulose recovery; and the removal of hemicellulose and lignin. The solid yield of these three boards ranged from 39.1% to 50.0%, which was close to that of wheat straw after PHP pretreatment [17]. It was apparent that PHP pretreatment enriched the cellulose fraction by easily removing the recalcitrant fractions of hemicellulose and lignin. The residual hemicellulose content in the pretreated substrates was only 4.0–5.9%, corresponding to its removal efficacy of 70.4–83.5%. Similarly, the lignin content decreased after PHP pretreatment. Lignin contents decreased from 31.4% to 18.3%, 31.9% to 16.6%, and 26.4% to 13.4% for fiberboard, chipboard, and blockboard,

respectively, corresponding to their lignin removal of 74.6–79.7%. The permeation of concentrated H_3PO_4 into the inner portion of the biomass may have been more effective with the efficient lignin removal, which was beneficial for improving the removal of hemicellulose [25]. It has been documented that hemicellulose and lignin are closely associated with cellulose through noncovalent and covalent linkages that limit the process of enzymatic hydrolysis [26]. Properly removing hemicellulose and lignin would increase the pore size and accessible surface of the lignocellulosic substrate by decreasing the physical barrier around the cellulose, thereby facilitating enzyme accessibility and subsequent hydrolysis. The above analysis indicates that PHP pretreatment was flexible for pretreating these three substrates despite their varied biomass species and chemical compositions.

Table 2. Solid yield and main chemical compositions after phosphoric acid and hydrogen peroxide (PHP) pretreatment.

Pretreated Solids	Solid Yield (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Cellulose Recovery (%)	Hemicellulose Removal (%)	Lignin Removal (%)
PHP-Fiberboard	41.7	59.8 ± 0.79	4.0 ± 0.09	18.3 ± 0.01	78.9	83.5	75.7
PHP-Chipboard	39.1	57.1 ± 0.95	5.1 ± 0.17	16.6 ± 0.28	79.3	77.0	79.7
PHP-Blockboard	50.0	53.8 ± 0.12	5.9 ± 0.04	13.4 ± 0.38	91.2	70.4	74.6

In particular, it was shown that the cellulose fraction was significantly enriched (53.8–59.8%) after PHP pretreatment. The corresponding cellulose recovery was 78.9–91.2%, suggesting that a substantial portion of the original cellulose was recovered. This would benefit the subsequent enzymatic hydrolysis, especially for the pretreated blockboard. The high cellulose content in the solid fraction could potentially enhance the sugar/ethanol titer, according to a previous work [27]. The cellulose content of these three boards was higher than previous PHP pretreatments for bamboo residues, oak chips, and spruce chips [13]. Moreover, the cellulose content was higher than that of some pretreatment methods for lignocellulose biomass, such as alkali pretreatment of corn stover, liquid hot water pretreatment of rice straw under catalysis of sulfuric acid/hydrochloric acid, or single phosphoric acid pretreatment of corn stover/wheat straw [13,28,29]. In conclusion, PHP pretreatment could remove hemicellulose and lignin efficiently, which enriched the cellulose fraction for enzymatic hydrolysis.

3.2. Performances of the Cellulose-Rich Fraction for Enzymatic Hydrolysis and Ethanol Conversion

To assess the hydrolysis potential of the pretreated fiberboard, chipboard, and blockboard, enzymatic hydrolysis was conducted with a solid loading of 2% for 72 h to check the glucose yield and cellulose–glucose conversion (see). Obviously, all three furniture boards without pretreatment could almost not be hydrolyzed; thus, their cellulose–glucose conversions were about zero, even after 72 h of hydrolysis. In contrast, it was observed that the hydrolysis rates of fiberboard, chipboard, and blockboard were rather high in the first 24 h, and their corresponding cellulose–glucose conversion rapidly reached 59.9%, 88.5%, and 77.2%, respectively. Their final cellulose–glucose conversion (at 72 h) was further promoted to 83.3%, 98.0%, and 89.6%, respectively (Figure 1). These glucose conversions were very close to those of previously investigated lignocellulosic feedstocks without artificial adhesives being involved [13]. It was suggested that PHP pretreatment could eliminate the structural recalcitrance caused by these adhesives. Furthermore, PHP-pretreated furniture boards gave higher enzymatic hydrolysis rates than the resultant substrates by other prevalent pretreatments, such as alkaline, acid, or peroxide pretreatment [30]. Further calculations indicated that approximately 208, 219, and 241 g of glucose were recovered from 1.0 kg of waste fiberboard, chipboard, and blockboard, respectively, which was higher than lignocellulosic feedstocks, such as poplar pretreated by alkaline–H_2O_2 (approximately 90 g/kg of feedstock) [31]. The high enzymatic hydrolysis efficiency and glucose production suggest that PHP pretreatment is a promising method that can be extended to highly stubborn biomass board feedstocks.

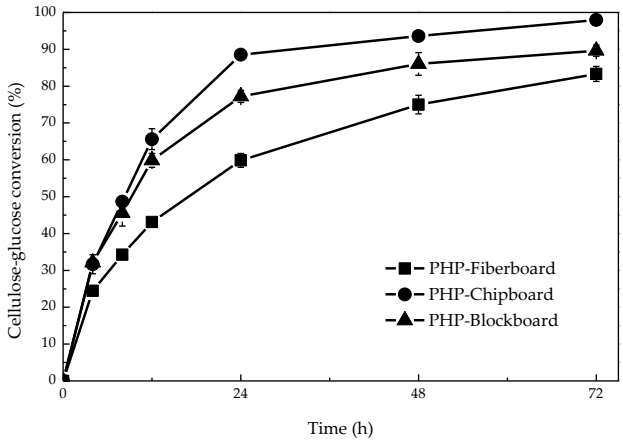

Figure 1. Enzymatic hydrolysis of the three furniture boards after pretreatment.

Apart from lignin and hemicellulose content and distribution, the cellulose crystalline and molecular structure also affects cellulose hydrolysis [32]. To provide a better assessment of how enzymatic hydrolysis was enhanced by PHP pretreatment, XRD was employed to check the crystalline morphology of these pretreated furniture boards (see Figure S2). Overall, the diffraction patterns of these three boards all exhibited typical diffraction cellulose I_β angles (2θ) of around 14.6°, 16.5°, and 22.7°, which were assigned to the diffraction planes of (11( )0), (110), and (200), respectively [20]. However, the CrI of these pretreated furniture boards decreased from 43.56–47.13% to 36.73–42.16% (Table 3). In parallel, the crystal sizes of the pretreated furniture boards were all reduced. Unlike other pretreatments, such as alkali pretreatment, microwave irradiation, or hydrothermal pretreatment, which could significantly increase both crystallinity and crystal size through solubilization/removing amorphous hemicellulose and lignin [33,34], PHP pretreatment actually decreased the extent of the crystalline structure of these substrates via a dissolution/swelling process. Obviously, it could be deduced that the decreased CrI and crystal size offered a more accessible surface for the hydrolytic enzymes, thereby facilitating the hydrolysis performance.

Table 3. The changes of crystallinity, crystal size, water retention value (WRV), and Simons' stain (SS) value before and after PHP pretreatment.

Samples	Crystallinity (%)	Crystal Size (nm)	WRV	Value of SS (DO/DB)
Fiberboard	43.56	4.64	1.04	0.10
PHP-Fiberboard	36.73	3.90	2.67	0.86
Chipboard	46.19	3.74	1.03	0.38
PHP-Chipboard	37.97	3.63	3.43	0.86
Blockboard	47.13	3.88	1.44	0.40
PHP-Blockboard	42.16	3.61	3.47	1.16

When the WRV and SS test were employed to quantitatively check the available surface area for enzymatic hydrolysis, it could be observed that the WRVs of PHP-pretreated substrates were significantly increased to 2.67–3.47 compared with their original values of 1.03–1.44. Apparently, PHP pretreatment could significantly increase the substrate porosity of these three boards, especially for chipboard (Table 3). Further, in the SS test, the dyes of DO and DB were employed as probes to simulate the large and small pores in the fiber, in which the adsorbed DO can reflect the available surface area that can be accessed by cellulase in hydrolysis. Thus, the DO/DB was employed to express the cellulose accessibility. As displayed in Table 3, the DO/DB values of the unpretreated furniture boards of fiberboard, chipboard, and blockboard were 0.10, 0.38, and 0.40, respectively. Such low values from the SS test suggest the very low accessibility of these feedstocks. After PHP pretreatment, DO/DB values greatly increased by 1.3–7.6-fold. Based on these results, it could be found that the

reduced CrIs and crystal sizes of these furniture boards by PHP pretreatment correlated well with the promoted WRVs and DO/DB values. It has also been reported that the promoted WRVs of pretreated substrates benefit enzymatic hydrolysis due to the intensified mass transfer with more free water in the substrate [35]. Further, the increased DO/DB values also significantly correlated well with the enhanced cellulose–glucose conversion during hydrolysis. In addition, the morphology from SEM observations (Figure 2) also demonstrated that the surface of the PHP-pretreated furniture boards became more disordered and separated. Some cracks and fragments could also be observed. In contrast, the substrate surface was smooth and compact for the unpretreated feedstocks. These observations again prove that PHP pretreatment could greatly deconstruct the furniture boards and promote accessibility to enzymes, resulting in efficient enzymatic hydrolysis.

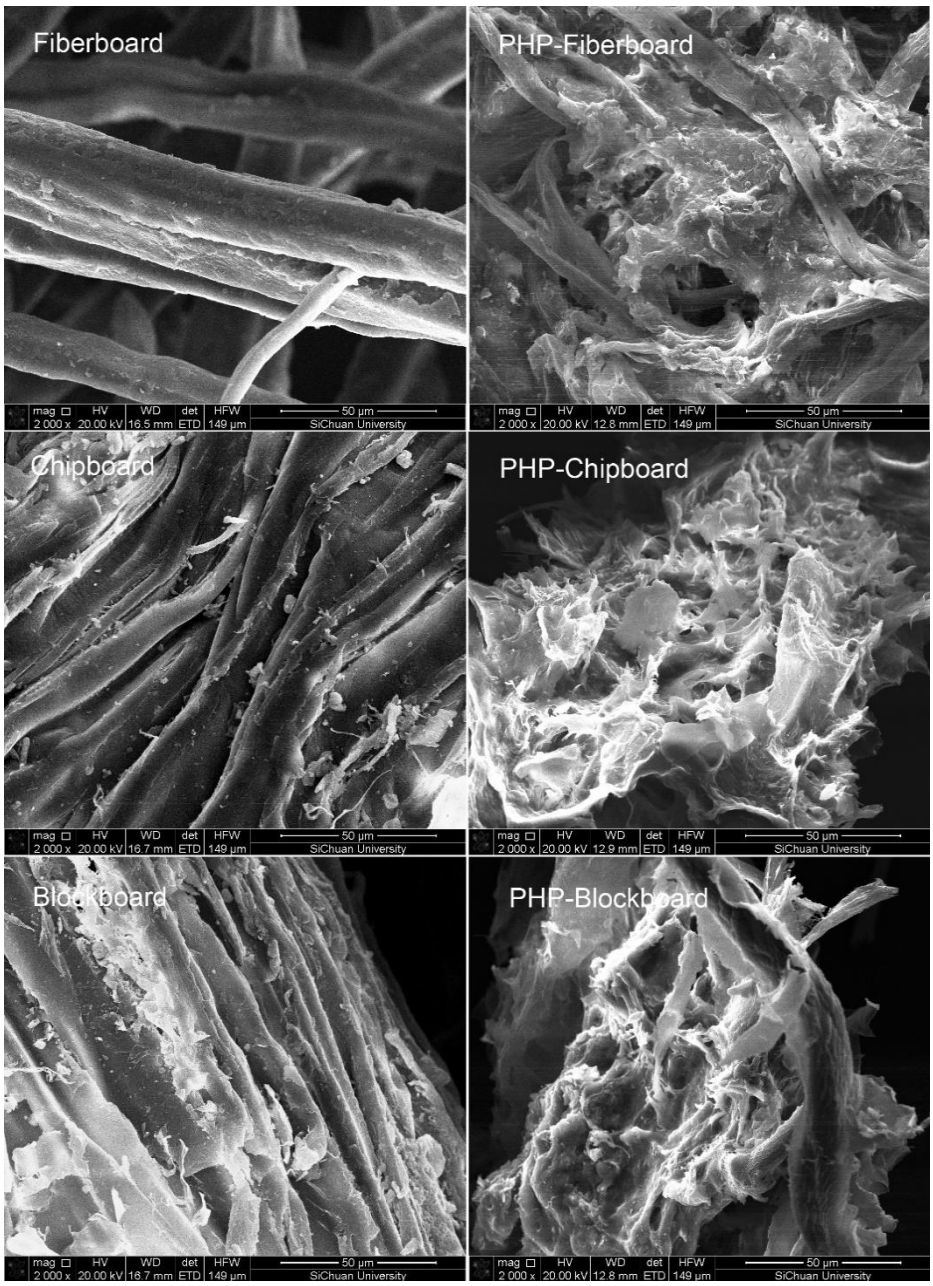

Figure 2. SEM micrographs of the furniture boards and pretreated substrates at 2000× magnification.

Based on the high enzymatic hydrolysis efficiency and glucose yield, SSF was conducted with a solid loading of 2% (*w*/*v*) to further evaluate the potential of ethanol production. Ethanol conversions

of 84.8%, 80.7%, and 95.2% were achieved for fiberboard, chipboard, and blockboard, respectively, after 72 h. When the fermentation time was further extended, the cellulose-rich fraction of these three boards could completely convert into ethanol, with generated ethanol concentrations of 8.2, 8.1, and 10.4 g/L (see Figure 3). This result indicates that no serious inhibitors existed in the PHP-pretreated substrates to subsequent ethanol fermentation. PHP pretreatment and the washing process would remove inhibitors as much as possible. Meanwhile, there was no accumulation of glucose in the SSF system and the residual glucose concentration was almost close to zero, even after 120 h, indicating that the glucose produced during enzymatic hydrolysis was rapidly converted into ethanol.

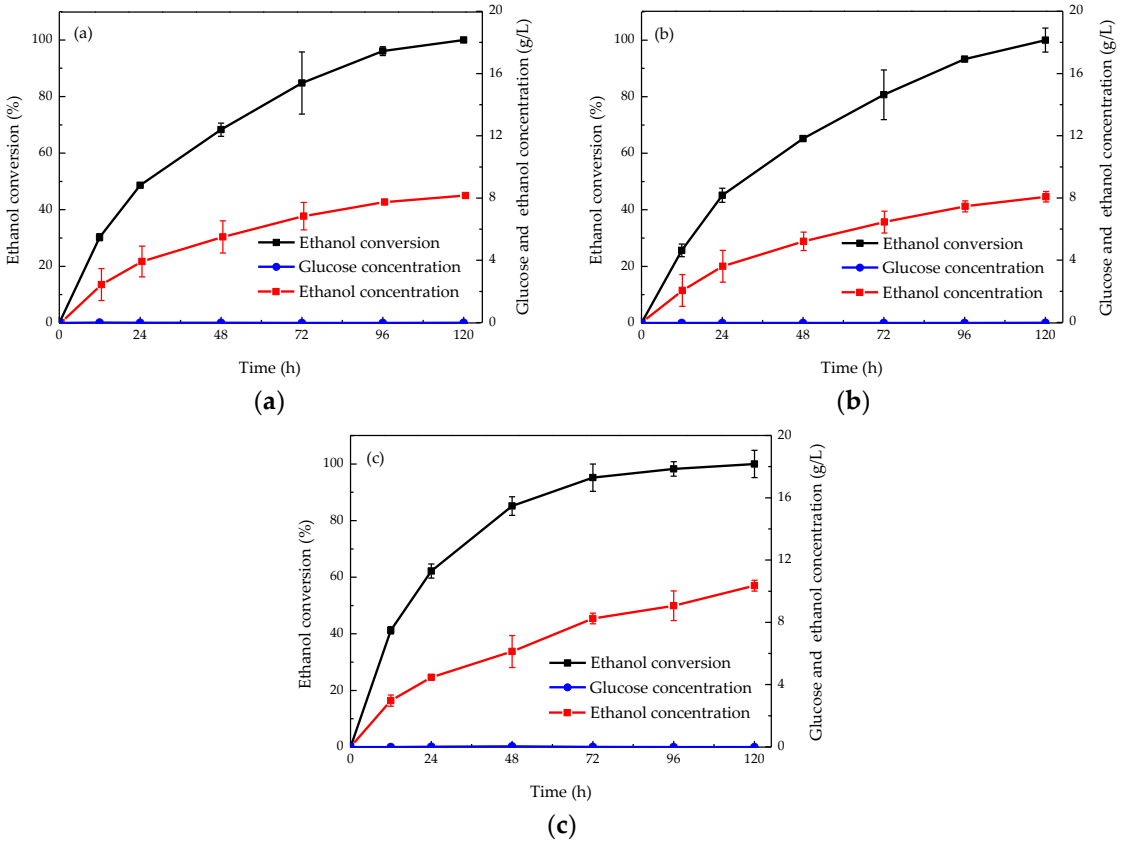

Figure 3. Glucose and ethanol concentrations and ethanol conversion in simultaneous saccharification and fermentation (SSF): (**a**) fiberboard, (**b**) chipboard, and (**c**) blockboard.

3.3. Characteristics of Recovered Lignin from PHP Pretreatment

As shown in Figure S1, the lignin fraction was harvested after PHP pretreatment. As a potential product stream from the designed process, its characteristics relate considerably to its possible applications. To better understand the pretreatment profile of PHP pretreatment on these substrates while providing useful information for the subsequent utilization of the resulting lignin fraction, lignin characterization using ^{31}P NMR was carried out to assess the quantity and location of the main functional groups on lignin.

Quantitative ^{31}P NMR spectra of these three PHP technical lignins are listed in Figure 4, and the results were calculated accordingly (Table 4). The aliphatic –OH content in these PHP technical lignins was relatively low (1.51–1.68 mmol g^{-1}) compared with those of prevalent woody lignin (3.13–5.06 mmol g^{-1}) [36]. The aliphatic –OH was severely dehydrated under the strong acidity of phosphoric acid [37]. It was interesting that all three PHP technical lignins exhibited rather low total phenolic –OH groups (0.47–0.49 mmol g^{-1}), which was greatly different than the typical Kraft lignin or organosolv lignin that has a quite high content of total phenolic –OH groups [38,39]. The possible reason was that the selective oxidation of PHP extensively cleaved phenolic aromatics during PHP

pretreatment and then opened aromatic rings. Thus, the content of carboxyl –OH groups on the lignin increased with the ring-opening reaction. This was further evidenced by the relatively higher content of carboxylic –OH groups, which ranged from 0.61 to 0.67 mmol g^{-1}. Usually, 0.02–0.29 mmol g^{-1} of carboxylic –OH groups are observed in the lignins separated by common technologies, such as organosolv and ionic liquid [40]. These as-obtained PHP technical lignins were abundant in carboxyl –OH groups, and this feature is promising for functional material preparation [41,42].

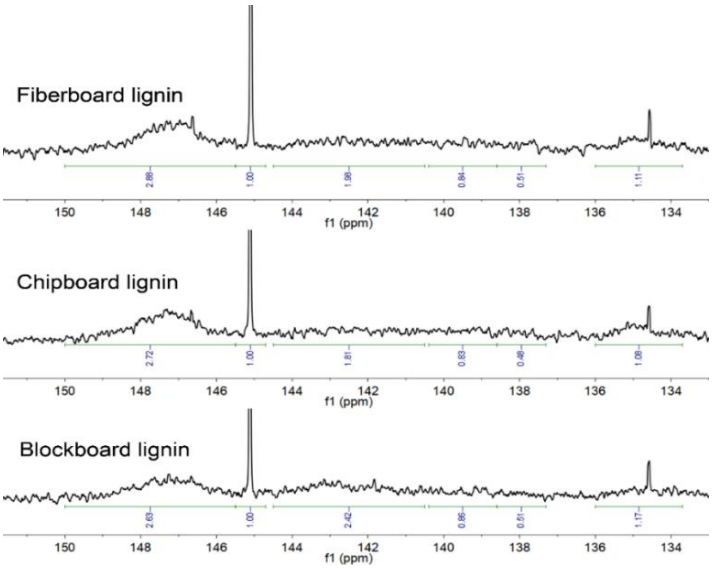

Figure 4. Quantitative ^{31}P NMR spectra of the three PHP technical lignins.

Table 4. PHP technical lignin as determined by quantitative ^{31}P NMR spectroscopy.

Samples	Lignin-Fiberboard	Lignin-Chipboard	Lignin-Blockboard
Aliphatic OH	1.51	1.52	1.68
C-5 substitution	1.38	1.01	1.15
Guaiacyl phenolic OH	0.49	0.47	0.49
p-Hydroxyphenyl OH	0.29	0.27	0.30
Carboxylic OH	0.67	0.61	0.65
Total phenolic OH	2.17	1.75	1.94

According to the above analysis, it appeared that biomass lignin substantially suffered extensive ring-opening by oxidation during PHP pretreatment, which facilitated its fragmentation and solubilization. Regarding the adhesives, most of them contained a phenolic structure, for example, phenolic resin. It can be deduced that the ring-opening that occurred on the lignin may have potentially worked on the adhesives in the furniture boards. Furthermore, the phenolic resin was directly added into the PHP solution to clarify whether the phenolic aromatics can be cleaved by the PHP solution. When it was scanned from 190 to 500 nm using ultraviolet spectrometry (Figure S3), it was obvious that the absorbance spectra before and after phenolic resin addition were different, especially at 232 and 266 nm. This result suggests that the contained adhesives of phenolic resin were also partially degraded in the PHP pretreatment, which could have benefited the reduction of the overall structural recalcitrance of these furniture boards.

3.4. Mass Balance of These Three Furniture Boards by PHP Pretreatment

According to the designed process shown in Figure S1, when these substrates were subjected to the PHP solvent system under mild conditions, the cellulose-rich fraction and PHP technical lignin were obtained through simple filtration via ethanol addition.

The overall mass balance of these three furniture boards after PHP pretreatment is shown in Figure 5. When 1.0 kg of waste furniture boards (dry basis) was employed for the PHP pretreatment, the cellulose-rich fraction of 417, 391, and 500 g (dry basis) could be recovered from fiberboard, chipboard, and blockboard, respectively, and 208, 219, and 241 g of glucose could be yielded by enzymatic hydrolysis. The cellulose-rich fraction was assessed for bioethanol conversion, and it was found that 166.8, 154.8, and 253.8 g of ethanol could be harvested. Further, the precipitated PHP technical lignin could be recovered by 45, 42, and 44 g with abundant carboxyl –OH groups on the basis of the current process. The high-value, water-soluble oligosaccharides were recovered with the yield in the range of 15–26 g from 1.0 kg of dry biomass. Obviously, these results indicate that PHP pretreatment is a feasible way to convert waste furniture boards into multiple products for biofuel and chemicals, which offers a more sustainable way to valorize such organic wastes from urban areas.

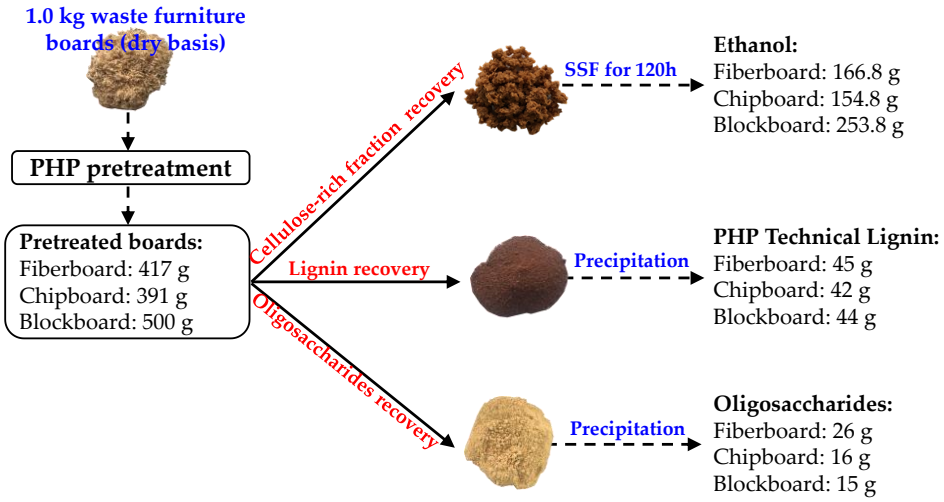

Figure 5. Overall mass balance of PHP pretreatment on the three furniture boards.

4. Conclusions

PHP pretreatment could easily fractionate waste furniture boards into cellulose-rich, lignin, and oligosaccharide fractions. High cellulose–glucose conversion was achieved for all three lignocellulosic biomass furniture boards. The enhanced cellulose accessibility was ascribed to the efficient removal of hemicellulose and lignin fractions and the deconstruction of the cellulose crystalline structure by PHP pretreatment. The strong oxidation capacity of the PHP solution system resulted in abundant carboxyl –OH groups in these recovered PHP technical lignins, which might facilitate its downstream applications. In this designed PHP process, no serious inhibitors were found to exist in the pretreated substrates; thus, a rather high ethanol concentration was observed during the simultaneous saccharification and fermentation process. It was shown that waste furniture boards from urban waste could be used as a promising lignocellulosic biomass for bioethanol production to realize its valorization. Further, this facile PHP pretreatment could also be extended to other unconventional recalcitrant biomass resources in order to build a multiproduct biorefinery.

Supplementary Materials: The following are available online at http://www.mdpi.com/2071-1050/11/21/6175/s1, Figure S1: title.

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