Torrefaction at 200 °C of Pubescens Pretreated with AlCl₃ Aqueous Solution at Room Temperature

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ABSTRACT: Metal salt soaking–torrefaction conversion technology was investigated. It was found that AlCl₃ pretreatment of pubescens favored observably the yield of liquid and small-molecular products in torrefaction via changing the composition and structure of the raw material. The maximum conversion of pretreated samples, washed (PSW) and Y_liquid were 15.5 and 10.8 wt % (with 0.26 wt % monosaccharides, 0.26 wt % carboxylic acids, 0.38 wt % furan compounds, and 1.28 wt % phenols), where 20.4 wt % hemicellulose, 22.9 wt % cellulose, and 5.7 wt % lignin were converted, respectively. However, for pretreated samples (PS), the maximum conversion and Y_liquid reached 44.2 and 32.1 wt %, respectively, along with 96.0 wt % hemicellulose and 31.8 wt % cellulose converted, yielding 2.39 wt % monosaccharides, 5.14 wt % carboxylic acids, 2.60 wt % furan compounds and 10.52 wt % phenols, indicating obvious catalytic effects of residual AlCl₃ on the decomposition of the three major components in torrefaction. Two-dimensional HSQC and electrospray ionization mass spectrometry (ESI-MS) characterizations further confirmed the dominant formation of oligomers derived from holocellulose, lignin, and cross-linkage involving the lignin–carbohydrate complex, indicating that the catalytic thermal cleavage of β-O-4, C-O-C, β-β, S–S, 4-O-S, Cα–Cβ, and α-O-4 linkages by aluminum species in the samples benefited the yield of liquid as well as monophenols.

1. INTRODUCTION

The increasing depletion of fossil fuel resources and serious environmental problems have led to a large demand for renewable energy.¹−³ Lignocellulosic biomass, mainly consisting of cellulose, hemicellulose, and lignin, is the cheapest and most abundant promising renewable carbon source for the production of energy materials and chemicals.²⁻⁴ However, the majority of biomass feedstock requires preprocessing to achieve deconstruction before upgrading the lignin and carbohydrate intermediates to biofuel or chemicals. The general method is pretreatment, where the recalcitrance of lignocellulosic biomass could be overcome to a certain degree. Moreover, the structural accessibility and reactivity of lignocellulosic components for further processing could be increased, while inhibitory byproducts could be avoided. The numerous pretreatment techniques could be classified into physical/mechanical, chemical, biological, and physical–chemical methods,⁵⁻⁷ where chemical pretreatment has been widely regarded as one of the most promising methods to improve the quality of products in the subsequent conversion of biomass due to its relatively high efficiency and low cost.⁸ One potential way to enhance the value of products obtained via thermal decomposition is through soaking with a metal salt solution, a way of chemical pretreatment, which is a mild pretreatment method for decomposition of lignocellulosic biomass to improve the quality of feedstock for further thermal decomposition.⁹

Besides, torrefaction, one low-temperature thermochemical technology, can lead to the cleavage of weak bonds in biomass to yield liquid, gaseous, and solid products under an inert atmosphere.¹⁰ The combination of torrefaction with metal salt solution soaking could change the pyrolytic behavior and improve product properties significantly.¹¹ Moreover, limited researchers have reported such metal salt soaking–torrefaction coupling technology in biomass conversion. The present work proposes an integrated pretreatment–catalytic torrefaction thermal conversion technology. The focus of this research, therefore, is on comparing torrefaction of the treated sample using different mass ratios of aluminum salts to biomass under the same conditions with and without washing the residual aluminum salts by examining the difference in liquid, solid, and gaseous products, which might further promote the biomass torrefaction technology based on these data.

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2. RESULTS AND DISCUSSION

2.1. Effect of Pretreatment with AlCl₃·6H₂O.

2.1.1. Thermogravimetric Analysis (TGA). TG analysis was introduced to determine the thermal degradation of PSW and PS samples. The detailed TGA and difference thermogravimetry (DTG) for the pubescens heating from ambient temperature to 800 °C are shown in Figures 1 and 2, respectively. As shown in Figure 1, the main weight loss of aluminum chloride hexahydrate was observed within the temperature range below 200 °C. A shift of the TG curve of the sample pretreated with pure water to a lower temperature range was observed, which might be due to the swelling effect and decomposition of easy degradable parts after pure water pretreatment (PSW-0 wt % and PS-0 wt %). A slight shift of TG curves of PSW 5−20 wt % compared to that of Raw was observed, indicating the different thermal chemical properties of PSW 5−20 wt % samples in comparison with that of PSW-0 wt % and raw pubescens.

As shown in Figure 1b, the initial decomposition temperature range of PS samples was affected significantly in the presence of residual aluminum salts, where the initial decomposition temperature was defined as the corresponding temperature for weight loss of 90−70% in the literature.¹² The temperature range involving initial decomposition of the treated sample was lowered from 265−302 to 126−260 °C in the presence of residual aluminum salts.

As shown in Figure 2, the decomposition peak of aluminum chloride hexahydrate was observed at about 170 °C. Limited changes were observed in the sample treated with pure water. Limited promotion effect was observed in the PSW samples via pretreatment as well. However, significant changes in DTG were observed in the PS samples, where all of the peaks were moving to a lower temperature range, indicating promoted decomposition of the samples.

The ash content (shortened as AC) variation of treated sample sets is given in Figure 3. At least 0.2 wt % AC remained for raw
The slight increase in AC after being treated with pure water might be caused by the fact that although limited biomass was converted, the ash content after distilled water pretreatment remained unchanged. The slight increase in AC in PSW samples might also be due to the promoted conversion of biomass, which further increases the proportion of AC. Moreover, an obvious increase in AC was observed in the PS set in Figure 3b, where AC soared to 2.21 from 0.2 wt % in the presence of aluminum salts (PS-5 wt %) and then slightly increased from 2.21 to 4.32 wt % due to the presence of residual aluminum salts as well as the conversion of biomass.

2.1.2. X-ray Diffraction (XRD) Analysis of Pubescens and Pretreated Samples after Torrefaction. The raw pubescens as well as the pretreated samples after torrefaction were characterized by XRD (Figure S2). For the raw pubescens, a limited decrease in CrI from 70.5 to 69.1% was observed after torrefaction, indicating limited thermal degradation of cellulose. For the sample treated with pure water, further decrease in the CrI value from 70.5 to 68.2% was observed. As shown in Figure S2 for PSW samples, CrI values decreased continuously from 68.2 to 41.3%, which further confirmed the effect of pretreatment with AlCl₃·6H₂O aqueous solution on further thermal degradation of pretreated samples. Significant variation of CrI values was observed in PSW samples, where the CrI decreased obviously from 68.2 to 35.1%. It was worth noting that the corresponding CrI value of each PS sample was lower than that of PSW samples after torrefaction. These results indicated that the decomposition of the crystal structure of cellulose in PSW samples was promoted by the presence of residual aluminum salts in comparison with PSW samples in each designed concentration of the AlCl₃·6H₂O aqueous solution pretreated sample during torrefaction, which resulted in a major decrease in the relative crystallinity value, comparatively. The results were in accordance with results obtained from Van Soest titration and Fourier transform infrared (FT-IR) spectra.

2.1.3. FT-IR Analysis of Samples after Torrefaction. The FT-IR spectra of raw pubescens and pretreated samples after torrefaction are displayed in Figure 4. The characteristic absorption bands of cellulose, hemicellulose, and lignin in raw pubescens and pretreated samples after torrefaction were assigned according to the literature. The characteristic absorbance of lignin occurred at 1635, 1605, 1513, 1462, 1426, 1029, and 834 cm⁻¹, where the weak band at 1635 cm⁻¹ was assigned to the conjugated C=O stretching of the aromatic ring. The absorbance bands at 1605 and 1513 cm⁻¹ were assigned to C–C and C=C stretching of the aromatic ring of lignin, while the band at 1029 cm⁻¹ was due to the C–O stretching of O–CH₃ and C–OH. The bands at 1740 cm⁻¹ (belonging to C==O stretching in xylan or C==O stretching vibration of carbonyl, carboxyl, and acetyl groups in hemicellulose), 1246 cm⁻¹ (belonging to C==O stretching vibration in xylglucan), and 1056 cm⁻¹ (belonging to C–O stretching vibrations or C–OH bending in hemicellulose) were assigned to the characteristic absorbance of hemicellulose. The bands at 1378, 1165, 1117, and 896 cm⁻¹ were assigned to the characteristic absorbance of cellulose, whereas those at 1165, 1117, and 896 cm⁻¹ were assigned to C–O–C asymmetric stretching at the β-(1-4)-glycosidic linkage, stretching of the glucose ring in plane, and glucose ring stretching.

As shown in Figure 4, limited absorbance variations were observed for raw pubescens torrefied at 200 °C, which was in accordance with our previous research. The changes above indicated the effect of heat on the degradation of biomass. As for PSW-0 wt % and PS-0 wt % samples, pretreated with pure water, only a bit more changes were observed after torrefaction. The relative intensity of bands at 1246 and 1029 cm⁻¹ slightly decreased. It could be inferred that the pure water pretreatment not only favored the degradation of the easily degradable part of hemicellulose and lignin in the pretreatment process but also had an effect on further thermal degradation of hemicellulose and lignin. The variation of the band at 1378 cm⁻¹ might also be caused by the water pretreatment, which exposed more of the cellulose part.

Similar absorption variations were observed in the torrefied PSW samples as well, while the bands at 1378, 1029, and 1462 cm⁻¹ slightly changed, indicating the cleavage of aliphatic side chains or hydrogen bonds in cellulose as well as G unit variation in lignin, respectively.

However, for the torrefied PS samples, obvious variations were observed. The absorbance bands at 1635, 1605, and 834 cm⁻¹ decreased significantly, which indicated that the cleavage of C–O–C between lignin and cellulose was promoted in the presence of aluminum salts, which further affected the C==C stretching within the benzene ring, indicating the variation of the C–O–C linkage between the major components in pubescens. Moreover, the sharp decreases at 1740, 1246, and 1056 cm⁻¹ caused by AlCl₃ indicated the cleavage of C==O stretching and C–H stretching in hemicellulose, manifesting the high conversion of hemicellulose. In addition, the red shifts at 1378 and 1164 cm⁻¹ might be due to the cleavage of C–O–C and the hydrogen bond in cellulose and hemicellulose.

2.1.4. Distribution of Products in Different Phases after Torrefaction. Based on our previous work, on increasing the residence time from 2 to 4 h, the conversion of pubescens and

Figure 4. FT-IR spectra of raw *pubescens* and torrefied samples: (a) PSW samples and (b) PS samples.
yield of liquid products were almost the same as those obtained within 2 h. Thus, experimental data provided here was based on 2 h (residence time). The distribution of products in different phases and the conversion of raw *pubescens* and pretreated samples after torrefaction are shown in Figure 5. The conversion of raw *pubescens* was 5.2 wt %, where 4.2 wt % liquid product and 1.0 wt % gaseous products were obtained. For samples pretreated with pure water (PSW-0 wt % and PS-0 wt %), the conversion rate and $Y_{\text{liquid}}$ slightly increased (5.7 and 4.6 wt %, respectively), indicating that the effect of pretreatment with pure water on the structure changes, which further affected the subsequent thermal degradation. Obvious variations of product distribution in different phases and conversion rate were observed in 5–20 wt % PSW samples after torrefaction. The conversion rate varied from 5.7 to 15.5 wt % and $Y_{\text{liquid}}$ increased from 4.6 to 10.8 wt %. Significant variations of the conversion rate and $Y_{\text{liquid}}$ were observed in PS samples after torrefaction, where the conversion rate of PS samples increased from 5.7 to 15.8 wt % in the presence of residual aluminum salts (5 wt % AlCl$_3$ ·6H$_2$O aqueous solution pretreatment) and then reached up to 44.2 wt % with 20 wt % AlCl$_3$·6H$_2$O aqueous solution pretreatment, while that of the PSW sample was only 15.5 wt %. However, the $Y_{\text{liquid}}$ varied from 4.6 to 11.3 wt % in the presence of residual aluminum salts (5 wt % AlCl$_3$·6H$_2$O aqueous solution pretreatment) via torrefaction and then boosted to the maximum value of 32.9 wt % corresponding to 15 wt % AlCl$_3$·6H$_2$O aqueous solution pretreatment, while that of the PSW sample was only 10.9 wt %. Combined with the Van Soest titration and small-molecular-weight product distribution results, it was found that the degradation of hemicellulose and cellulose occurred intensely in PS samples during torrefaction at 200 °C. At the same time, the products derived from lignin had a good yield (10.52 wt % monophenols). The results further confirmed that the initial decomposition temperature of the pretreated solids moved to the lower temperature range, and the decomposition of the three main components was promoted by the structural changes caused by pretreatment and the presence of residual aluminum salts, which was more conducive to the acquisition of liquid products.

### Table 1. Variation of the Three Major Components after Torrefaction of PSW Samples

| no.   | hemicellulose | cellulose | lignin + coke |
|-------|---------------|-----------|---------------|
|       | rem. ratio (wt %) | cov. (wt %) | rem. ratio (wt %) | cov. (wt %) | rem. ratio (wt %) | cov. (wt %) |
| raw   | 20.1          | 0$^a$(b)  | 43.7          | 0$^a$(b)    | 24.4          | 0$^a$(b)    |
| raw-200 | 19.3         | 4.0(-)    | 41.1          | 6.0(-)      | 23.9          | 2.0(-)      |
| 0 wt % | 18.9          | 6.0(5.5)  | 39.9          | 8.7(6.9)    | 23.7          | 2.9(1.0)    |
| 5 wt % | 17.0          | 15.4(1.5) | 37.6          | 14.0(12.2)  | 23.4          | 4.1(2.3)    |
| 10 wt % | 16.7         | 16.9(0.3) | 35.3          | 19.2(17.4)  | 22.5          | 7.8(4.1)    |
| 15 wt % | 16.2         | 19.4(1.4) | 34.6          | 20.8(18.7)  | 22.8          | 6.6(3.2)    |
| 20 wt % | 16.0         | 20.4(1.1) | 33.7          | 22.9(20.3)  | 23.0          | 5.7(3.4)    |

$^a$Total cov. (wt %). $^b$Cov. (wt %) was based on the remaining (shortened as rem) content after pretreatment; total rem. ratio (wt %) and cov. (wt %) were calculated based on the initial weight of *pubescens*.

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2.1.5. Variation of the Three Major Components after Torrefaction. As shown in Table 1, the detailed variation of the three major components in raw *pubescens* and PSW samples after torrefaction was analyzed by Van Soest titration. It is worth noting that heavy coking caused by lignocellulosic biomass conversion might promote the formation of pseudo-lignin, which would influence the accuracy of lignin analysis. The dried raw *pubescens* was composed of 20.1 wt % hemicellulose, 43.7 wt % cellulose, and 24.4 wt % lignin. Limited conversion was observed in raw *pubescens* torrefied at 200 °C, indicating the limited thermal degradation caused by heat, which might include cleavage of C=O(R), C=O, and hydrogen bonds. For samples pretreated with pure water after torrefaction (PSW-0 wt % and PS-0 wt %), the conversion of cellulose, hemicellulose, and lignin was slightly promoted. This might be due to the structure variation caused by the pretreatment, which facilitated the conversion of the easily degradable parts and made thermal degradation easier. Obvious variation of the three major components of the PSW sample set was observed. Here, the maximum thermochemical conversion of the PSW sample could only reach 15.5 wt %, and the corresponding conversion rates of the three components were 20.6 wt % hemicellulose, 22.9 wt % cellulose, and 5.6 wt % lignin.
Significant component variation of PS samples is seen in Table 2. Obvious variation of hemicellulose was observed in the PS-5 wt % sample, where the conversion of hemicellulose increased from 6.0 to 51.2 wt % in the presence of residual aluminum salts after pretreatment during torrefaction, indicating the promotion effect on the selective conversion of hemicellulose. The maximum conversions of hemicellulose and cellulose in PS samples could reach up to 96.0 and 31.8 wt %, respectively. In addition to the high conversion of hemicellulose, conversions of cellulose and lignin were also promoted. The reason for degradation of cellulose and lignin might be due to the removal of hemicellulose, which released the lignin component and more cellulose component was exposed. Due to the coking of the sample and conversion of the cross-linked network between carbohydrates and lignin, a large amount of carbon deposition was formed, which further made it difficult to determine the actual content of lignin by Van Soest titration. The increased yields of phenols indicated the promoted conversion of lignin.

Moreover, the total conversion rate and component conversion variation of each PSW sample were far lower than those of the PS samples after torrefaction under the same conditions.

Table 2. Variation of the Three Major Components after Torrefaction of PS Samples

| no. | hemicellulose | cellulose | lignin + coke |
|-----|---------------|-----------|--------------|
|     | rem. ratio (wt %) | cov. (wt %) | rem. ratio (wt %) | cov. (wt %) | rem. ratio (wt %) | cov. (wt %) |
| raw | 20.1 | 0.0 | 43.7 | 0.0 | 24.4 | 0.0 |
| raw-200 | 19.3 | 4.0 | 41.1 | 6.0 | 23.9 | 2.0 |
| 0 wt % | 18.9 | 6.0 | 39.9 | 8.7 | 23.7 | 2.9 |
| 5 wt % | 9.8 | 51.2 | 38.8 | 11.2 | 23.9 | 2.0 |
| 10 wt % | 5.3 | 73.6 | 37.5 | 14.2 | 23.7 | 2.9 |
| 15 wt % | 1.2 | 94.0 | 31.5 | 27.9 | 23.6 | 2.9 |
| 20 wt % | 0.8 | 96.0 | 29.8 | 31.8 | 23.5 | 2.9 |

Total cov. (wt %), cov. (wt %) was based on the remaining (shortened as rem) content after pretreatment; total rem. ratio (wt %) and cov. (wt %) were calculated based on the initial weight of pubescens.

Table 3. Yields of Liquid Products Obtained from PSW Samples via Torrefaction

| no. | compound | raw-200 | 0 wt % | 5 wt % | 10 wt % | 15 wt % | 20 wt % |
|-----|----------|---------|--------|--------|---------|---------|---------|
| 1   | glucose  | 0.07    | 0.08   | 0.11   | 0.32    | 0.27    | 0.18    |
| 2   | fructose | 0.03    | 0.05   | 0.08   | 0.14    | 0.12    | 0.01    |
| 3   | xylose   | 0.03    | 0.03   | 0.04   | 0.13    | 0.11    | 0.07    |
| 4   | lactic acid | 0.02 | 0.02   | 0.04   | 0.11    | 0.15    | 0.01    |
| 5   | formic acid | 0.06 | 0.07   | 0.17   | 0.24    | 0.03    | 0.07    |
| 6   | acetic acid | 0.07 | 0.09   | 0.15   | 0.40    | 0.11    | 0.18    |
| 7   | furfural | 0.08    | 0.08   | 0.19   | 0.16    | 0.18    |         |
| 8   | 5-HMF    | 0.01    | 0.01   | 0.01   | 0.06    | 0.04    | 0.06    |
| 9   | 2-furanmethanol | 0.01 |         | 0.01   |         |         | 0.11    |
| 10  | 5-methylfurfural | 0.01 |         | 0.01   | 0.08    | 0.08    | 0.03    |
| 11  | phenol   | 0.01    | 0.01   | 0.08   | 0.09    | 0.02    | 0.09    |
| 12  | 2,3-dihydrobenzofuran | 0.02 |         | 0.02   | 0.03    | 0.03    | 0.01    |
| 13  | 4-methylphenol | 0.04 |         | 0.04   | 0.31    | 0.28    | 0.35    |
| 14  | guaiacol | 0.05    | 0.03   | 0.09   | 0.31    | 0.28    | 0.35    |
| 15  | 4-ethylphenol | 0.01  |         | 0.05   | 0.06    | 0.05    | 0.06    |
| 16  | 4-methylguaiacol | 0.01 | 0.01   | 0.07   | 0.08    | 0.03    | 0.08    |
| 17  | 4-vinylphenol | 0.15  |         | 0.21   | 0.21    | 0.25    |         |
| 18  | 4-ethylguaiacol | 0.04 |         | 0.04   | 0.08    | 0.04    |         |
| 19  | 4-vinylguaiacol | 0.01 |         |         |         |         |         |
| 20  | 5-allylguaiacol | 0.09 |         | 0.10   | 0.02    |         |         |
| 21  | 2,6-dimethoxyphenol | 0.01  | 0.02   | 0.30   | 0.43    | 0.19    | 0.23    |
| 22  | vanillin | 0.01    | 0.01   | 0.01   | 0.01    | 0.01    | 0.11    |
| 23  | 4-allyl-2,6-dimethoxyphenol | 0.01 | 0.01   | 0.02   | 0.02    | 0.02    |         |
| 24  | syringaldehyde | 0.01 |         | 0.01   |         |         |         |

The yield (wt %) was based on the weight of pubescens contained in the samples.
Vinylphenol was produced from dehydration of Cα ether bonds and inter-hydrogen bonds of lignin, 4-ethoxyphenol obtained from further dehydration as well as cleavage of acetyl degradation of carbohydrates. Carboxylic acids and furans were increased, where monosaccharides were obtained from the guaiacol, 4-vinylphenol, and 2,6-dimethoxyphenol was strongly production of monosaccharides, carboxylic acids, furans, yields showed no obvious variations with further increase of aluminum chloride hexahydrate until 10 wt %. However, the and furans increased with the increasing concentration of solution, the total yields of monosaccharides, carboxylic acids, furans, caused by pretreatment with pure water.

As for PSW samples pretreated with pure water (PS-0 wt % and PSW-0 wt %) after torrefaction, 4-methylguaiacol was first obtained, while the yields of products detected exhibited no obvious variations from those of raw-200, indicating limited structural variation caused by pretreatment with pure water.

As for PSW samples pretreated with AlCl₃·6H₂O aqueous solution, the total yields of monosaccharides, carboxylic acids, and furans increased with the increasing concentration of aluminum chloride hexahydrate until 10 wt %. However, the yield showed no obvious variations with further increase of aluminum chloride hexahydrate. As shown in Table 3, the production of monosaccharides, carboxylic acids, furans, guaiacol, 4-vinylphenol, and 2,6-dimethoxyphenol was strongly increased, where monosaccharides were obtained from the degradation of carbohydrates. Carboxylic acids and furans were obtained from further dehydration as well as cleavage of acetyl group in lignin. Guaiacol was obtained from the cracking of the major ether bonds and inter-hydrogen bonds of lignin, 4-vinylphenol was produced from dehydration of C₅-OH units of lignin into C₅-C₆β and the cracking of C₆β-C₆ bonds in alcohol side chains or in coniferyl aldehyde, and 2,6-dimethoxyphenol was obtained via cleavage of C₁-C₆α bonds.1−38 Moreover, a small quantity of other phenols was detected, including 2,3-dihydrobenzofuran, phenol derivatives, and guaiacol derivatives. Thus, structure changes and cleavage of bonds in carbohydrates and lignin caused by pretreatment could further enhance the decomposition to yield more small-molecular-weight products in torrefaction.34,35

As demonstrated in Table 4, the total yield of detected products obtained from PS samples increased significantly compared to that of PSW samples, indicating the catalytic effect of residual aluminum salts on the thermal degradation of the pretreated sample. The increase of monosaccharide and furans was due to the strong degradation of holocellulose (hemicellulose and cellulose), while the sharp increase of carboxylic acids could be attributed to the high conversion of carbohydrate with further dehydration, as well as the cleavage of the acetyl group in lignin. Moreover, the acquisition of identified monophenols might be due to the following reason: the production of 2,3-dihydrobenzofuran might lead to H-reduction of the allyl radical intermediate from cleavage of C=O bonds of quinone methide and cyclization.37,38 The acquisition of phenol, 4-methylphenol, 4-ethylphenol, and 4-vinylphenol was mainly from the degradation of H units (p-hydroxyphenyl phenols) in lignin via cracking of hydrogen bonds, aliphatic and phenolic −OH groups, and the aliphatic side chains.39,40 The yields of guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, 5-allylguaicol, and vanillin were mainly from the degradation of G units (guaiacyl phenols) in lignin via cleavage of the saturated alkyl side-chain structure, cracking of C₆α-C₆β bonds and in guaiacyl units, cleavage of C₆β-C₆γ on saturated and α-carbonyl, and cracking of C₆α-C₆β, as well as cleavage of C₆γ-OH via dehydration and cleavage of saturated alkyl side chains.15,41 The production of 2,6-dimethoxyphenol, 4-allyl-2,6-dimethoxyphenol, and syringaldehyde was due to the degradation of S units (syringyl phenols) in lignin via cracking of C₆α-C₆β bonds and C-O-H(R) in aliphatic side chains (C₆γ-OH or C₆γ-OH/R position).31,42,43 It could be easily observed that all of the paths for the formation of monoaromatic species via torrefaction involved the cleavage of β-O-4 linkage in lignin.44 Moreover, it could be easily inferred that in comparison with PSW samples, the

### Table 4. Yields of Liquid Products Obtained from PS Samples via Torrefaction

| no | compound                  | raw-200 0 wt % | 5 wt % | 10 wt % | 15 wt % | 20 wt % |
|----|---------------------------|---------------|--------|---------|---------|---------|
| 1  | glucose                   | 0.07          | 0.08   | 0.21    | 0.32    | 0.67    | 0.98    |
| 2  | fructose                  | 0.03          | 0.05   | 0.30    | 0.74    | 0.92    | 1.01    |
| 3  | xylose                    | 0.03          | 0.03   | 0.12    | 0.30    | 0.37    | 0.40    |
| 4  | lactic acid               | 0.02          | 0.02   | 1.01    | 1.20    | 1.71    | 1.75    |
| 5  | formic acid               | 0.06          | 0.07   | 0.31    | 0.64    | 0.81    | 0.97    |
| 6  | acetic acid               | 0.07          | 0.09   | 0.82    | 1.40    | 2.11    | 2.42    |
| 7  | furfural                  | 0.81          | 0.89   | 0.86    | 0.80    |
| 8  | 5-HMF                     | 0.01          | 0.01   | 0.10    | 0.12    | 0.13    | 0.16    |
| 9  | 2-furanmethanol           | 0.14          | 0.61   | 0.68    | 0.81    |
| 10 | 5-methylfurfural          | 0.02          | 0.03   | 0.80    | 0.83    |
| 11 | phenol                    | 0.08          | 0.09   | 0.12    | 0.18    |
| 12 | 2,3-dihydrobenzofuran     | 0.81          | 0.82   | 1.10    | 1.13    |
| 13 | 4-methylphenol            | 0.01          | 0.02   | 0.21    | 0.22    |
| 14 | Guaiacol                  | 0.05          | 0.03   | 0.61    | 0.71    | 1.12    | 1.15    |
| 15 | 4-ethylphenol             | 0.45          | 0.46   | 0.90    | 0.96    |
| 16 | 4-methylguaiacol          | 0.01          | 0.07   | 0.08    | 0.71    | 0.78    |
| 17 | 4-vinylphenol             | 0.52          | 1.21   | 2.69    | 2.82    |
| 18 | 4-ethylguaiacol           | 0.03          | 0.04   | 0.80    | 0.84    |
| 19 | 4-vinylguaiacol           | 0.01          | 0.01   | 1.03    | 1.01    |
| 20 | 5-allylguaicol            | 0.09          | 0.13   | 0.12    | 0.23    |
| 21 | 2,6-dimethoxyphenol       | 0.01          | 0.02   | 0.30    | 0.43    | 0.61    | 0.66    |
| 22 | vanillin                  | 0             | 0.01   | 0.11    | 0.11    |
| 23 | 4-allyl-2,6-dimethoxyphenol| 0             | 0.02   | 0.22    | 0.21    |
| 24 | syringaldehyde            | 0.01          | 0.02   | 0.21    | 0.22    |

*The yield (wt %) was based on the weight of *pubescens* contained in the samples.*
cracking of hydrogen bonds, aliphatic and phenolic −OH groups, the aliphatic side chains, C–C bonds (C–C–H and C–C–C), and the C−O−H(R) (in aliphatic side chains (C–O−H or C–C–O−H−R position) was strongly promoted by residual aluminum salts. This might be due to the Lewis acidity and accessibility of residual aluminum salts, which favor the cleavage of chemical bonds in lignin and holocellulose and further promoted the decomposition of *pubescens* to a good conversion rate.45 The results discussed here were in accordance with FT-IR and XRD analyses.

Moreover, the gaseous products obtained via torrefaction are listed in Table 5. More than 99% of gaseous products obtained from *raw pubescens* was CO₂, which might be obtained from the cracking of aliphatic side chains. Gaseous products obtained from the sample pretreated with pure water exhibited no obvious variation from that of *raw pubescens*. As for PSW samples, the yield of H₂ exhibited no variations, and a little decrease of CO and CH₄ was observed with the increasing dosage of aluminum salts used in the pretreatment process. This might be caused by the cracking of the unstable carbonyl group and demethylation of the methoxy group in lignin. Obvious variation of gaseous products was observed for PS samples. The yield of reductive gases (H₂, CO, CH₄) was promoted in the presence of residual aluminum salts.

However, the proportion of small-molecular-weight products was still low in comparison with the yield of liquid; thus, characterization and identification of oligomers were performed.

### 2.1.7. Identification of Oligomers

The variations of the average molecular weight of liquid products after torrefaction were evaluated by Acquity Advanced Polymer Chromatograph (APC, Waters) analysis. APC analysis provided detailed data on weight-averaged and number-averaged molecular weights of compounds in liquids. As shown in Figures 6 and 7, the number-averaged molecular weight (Mn) distribution in the liquid from *raw pubescens* and PSW and PS samples was classified into four regions: 200 Da ≤ Mn ≤ 500 Da, 500 Da < Mn ≤ 1000 Da, 1000 Da < Mn ≤ 2000 Da, and Mn ≥ 2000 Da (defined as others).

As shown in Figure 6, for *raw pubescens* torrefied at 200 °C, the species with Mn over the 200 Da ≤ Mn ≤ 500 Da range had the largest proportion in liquid products, which constituted 61.3%, followed by species with Mn in the range of 500 to 1000 Da, which constituted 20.8%, and those in the range of 1000 Da < Mn ≤ 2000 Da accounted for 4.3%, whereas those with Mn below 200 Da and above 2000 Da accounted for 11.6%. Combined with the yield of small-molecular-weight products obtained, APC results indicated that the liquid products were mainly in the form of oligomers. Limited variations were observed in the APC results of the sample pretreated with pure water. The proportion of the 1000–2000 Da range weakly decreased from 4.3 to 1.7%, while the proportions of 200–5000, 500–1000, and Mn ≤ 200 and Mn ≥ 2000 Da slightly increased by 1.1, 0.9, and 0.6%, respectively.

Results here indicated that a limited promotion effect of pretreatment with pure water on further thermal degradation was observed in the molecular weight distribution of liquid products than that of *raw pubescens*. Obvious variation of Mn was observed in the samples pretreated with aluminum chloride hexahydrate aqueous solutions (PSW), where the proportion of Mn in the 200 Da ≤ Mn ≤ 500 Da and 500 Da < Mn ≤ 1000 Da ranges increased obviously, while limited changes were observed in the 1000–2000 Da range. With over 10 wt % AlCl₃·6H₂O used, further weak promotion effect was observed in the Mn distribution in APC analysis of liquid products.

Significant variation of Mn distribution was observed in the liquid of PS-5 wt % (see Figure 7) in the presence of residual
aluminum salts, where the proportion of 200 Da < \( M_n \) ≤ 500 Da promptly increased from 62.4 to 70.1%, followed by the increase in the range of \( M_n \) ≤ 200 Da and \( M_n \) ≥ 2000 Da took up 16.7% than that of 14.2% (PS-0 wt %). The percentage of \( M_n \) within 500–1000 Da decreased obviously from 21.7 to 12.3%, while the percentage of \( M_n \) between 1000 and 2000 Da showed no variation. The results were mainly due to the decrease in the proportion of \( M_n \) ≥ 2000 Da accompanied by the increased proportion of \( M_n \) ≤ 200 Da, which could be confirmed by the yield variation of small-molecular-weight products. Similar variations of four \( M_n \) ranges were observed in APC analysis of the liquid obtained over 10 wt % \( \text{AlCl}_3 \cdot 6\text{H}_2\text{O} \) used in PS samples. Notably, APC results of 15 and 20 wt % were quite different from results obtained with those treated with a lower concentration of \( \text{AlCl}_3 \cdot 6\text{H}_2\text{O} \) below 10 wt %. The proportion of \( M_n \) in 200–500 Da promptly increased from about 62.4 to 75% and that of \( M_n \) in the range \( M_n \) ≤ 200 Da and \( M_n \) ≥ 2000 Da changed from about 14.2 to 20.9%, while those in the 500–1000 Da range decreased significantly from about 21.7 to 3.6%; however, limited variation was observed in the 1000–2000 Da range. The variations here indicated that the degradation of \( \text{pubescens} \) to lower-molecular-weight products might be promoted in the presence of aluminum salts, and the promotion effect showed little variation with further increase of aluminum chloride hexahydrate by 15 wt %.

To further confirm the main structures and the connecting linkages of oligomers, 2D HSQC characterization of liquids was performed, as shown in Figures S3–S8, where the peak assignments were based on the literature. The region in the 2D HSQC NMR spectra was divided into three parts: cellulose and hemicellulose were observed at \( \delta_C/\delta_H = 58–100/3.0–4.5 \) ppm, aromatic regions of lignin were assigned to \( \delta_C/\delta_H = 95–150/5.5–8.0 \) ppm, and C–H signals in aliphatic side-chain regions of lignin belonged to \( \delta_C/\delta_H = 50–95/2.5–6.0 \) ppm. Detailed information on this is provided in Tables S1 and S2. The results indicated that classical representative signals of pentoses and hexoses, linkages involving the lignin, and classical structure units derived from the decomposition of lignin were observed. As for liquids obtained from PS samples via torrefaction, characteristic signals of guaiacyl (G) \( \delta_C/\delta_H = 115.5/6.77 \) and ferulate (FA) \( \delta_C/\delta_H = 123.3/7.15 \) could be detected, which indicated the thermal degradation of pretreated samples and the formation of oligomers derived from lignin. Moreover, xylan-related signals of hemicellulose and glucan-related signals of cellulose based on carbohydrate were observed as well, suggesting that various oligomers were generated in the torrefaction process.

The ESI-MS was introduced for the structure analysis of oligomers in the liquid products in both the positive and negative ionization modes. From the spectra shown in Figures S9–S19, it could be inferred that the molecular weight of liquid products was mainly distributed in the ranges of 200–500 and 500–1000 Da, and the results were in accordance with the results from APC that the liquid products predominantly presented as oligomers.

To figure out various oligomers, characteristic units of oligomers and lignin-derived monomers had been observed (shown in Figures S20–S30). Variations of oligomers obtained from \( \text{pubescens} \), PS samples, and PSW samples are shown in Figure S31, where limited kinds of oligomers were detected in liquid products from raw \( \text{pubescens} \), indicating the weak degradation. However, more species of five kinds of oligomers were obtained from torrefaction of PSW samples, confirming the variation of liquid products caused by pretreatment. Significant variations were observed in the liquid products obtained via torrefaction of PS samples, where nearly most of the oligomers detected in liquid products from raw and PSW samples were found. In addition, a large quantity of other five kinds of oligomers was identified as well. The results obtained further confirmed the catalytic effect of residual aluminum salts on the variation of liquid products obtained. In Figure S24, lignin-derived oligomers (totally identified) are shown, including classical connection linkages, such as β-O-4, C-O-C, 4-O-S, α-O-4, β-β, and 5–5.

Based on ESI-MS and 2D HSQC results, the proposed formation routes of oligomers from liquids obtained from raw
As shown in Figure 8, smaller oligomers were obtained via cleavage of weak ether bonds such as β-O-4 and C-O-C as well as dehydration and isomerization, and consequently, those

pubescens, PSW samples, and PS samples are shown in Figures 8–10, respectively.
reactions could take place even under mild conditions, indicating the degradation of easily degradable parts. The variation of oligomers obtained from PSW samples is shown in Figure 9; compared with Figure 8, the cleavage of \( \alpha{-}\beta \), \( S{-}S \), and \( \alpha{-}\beta{-}O{-}4 \) linkages was promoted in the PS samples by the catalytic effect of residual aluminum salts, confirming the catalytic performance of residual AlCl\(_3\) in torrefaction (seen in Figure 10).

In addition to oligomers from lignin being identified, classical units of LCC oligomers derived from bamboo in accordance with the literature reported by Pan were identified as well.\(^{51}\)

Based on the results and discussions above, a schematic mechanism involving the degradation of the lignin-carbohydrate-complex–lignin cross-linked oligomers (\( m/z = 902 \), identified in liquid from raw \( \textit{pubescens} \)) via pretreatment–torrefaction was tentatively proposed. As shown in Figure 11, where the cracking of the weak ether bond \( \beta{-}\beta \), \( S{-}S \), and \( \alpha{-}\beta{-}O{-}4 \) first yields one classical LCC (\( m/z = 379 \)) and one lignin oligomer (\( m/z = 542 \)), both of them were confirmed by the ESI-MS results of liquid from PSW samples, confirming the effect of pretreatment on the conversion of raw \( \textit{pubescens} \). The cracking of the ether bond \( \beta{-}\beta \) further promoted the formation of \( C_{18}H_{20}O_{5} \) (\( m/z = 316 \), identified in liquids from PS samples with a weak intensity), indicating the additional promotion effect of residual aluminum salts on degradation of oligomers with a larger weight. Further cracking of \( C_\alpha{-}\alpha{-}C_\beta \) and the dehydration reaction were strongly promoted by the residual aluminum salts, facilitating cleavage of \( \beta{-}\beta{-}O{-}4 \) linkage in \( C_{18}H_{20}O_{5} \) yielding two smaller lignin oligomers (\( m/z = 274 \) and 256).

The \( C_{10}H_{16}O_{5} \) (\( m/z = 316 \)) went through another cracking of \( \beta{-}\beta{-}O{-}4 \) linkage to form smaller-molecular-weight compounds. Moreover, two more lignin monomers could be obtained via further dehydration and dihydroxylation of \( C_{9}H_{10}O_{3} \) (\( m/z = 168 \)).

3. CONCLUSIONS

It was found that the composition and structure changes of raw \( \textit{pubescens} \), caused by pretreatment with AlCl\(_3\) aqueous solutions, could further promote thermal degradation during torrefaction at 200 °C, favoring yielding of liquid and small-molecular-weight products. The maximum conversions of PSW and \( Y_{\text{liquid}} \) in the torrefaction could reach 15.5 and 10.8 wt %, whereas those for PS were 44.2 and 32.1 wt %, respectively. The yield of small-molecular-weight products from PS was promoted by obvious catalytic effects of residual AlCl\(_3\) on the decomposition of the three major components in the torrefaction, promoting maximum yield of monosaccharides from 0.26 to 2.39 wt %, carboxylic acids from 0.26 to 5.14 wt %, furans from 0.38 to 2.60 wt %, and phenols from 1.28 to 10.52 wt %, where the conversions of cellulose and hemicellulose increased from 22.9 to 32.1 and 20.4 to 96.0 wt %, respectively. The residual AlCl\(_3\) catalyzed the cleavage of \( \beta{-}\beta{-}O{-}4 \), \( 4{-}O{-}S \), \( \alpha{-}\beta{-}O{-}4 \), \( \beta{-}\beta \), \( S{-}S \), \( C_\alpha{-}\alpha{-}C_\beta \), \( C_\alpha{-}OH \), \( C_\beta{-}C_\alpha \), and \( C_\beta{-}C_\alpha \) linkages in lignin parts in the torrefaction, favoring the acquisition of monophenols. As last, degradation paths of identified oligomers (derived from lignin and lignin–carbohydrate complex) from raw \( \textit{pubescens} \) and PSW and PS samples via torrefaction were proposed.

4. EXPERIMENTAL SECTION

4.1. Material.

The raw biomass used was \( \textit{Phyllostachys heterocyla cv. pubescens} \) (shorten to \( \textit{pubescens} \)), collected from Anji county, Zhejiang Province, China. Prior to the experiments, \( \textit{pubescens} \) was dried and ground to 80 mesh size. Particles with a size of 0.18 mm and smaller were selected for further pretreatments and experiments. These particles were then washed with distilled water at about 50 °C three times before use. Finally, the materials were dried in an oven at 110 °C for 3 h and then at 80 °C overnight before use.

4.2. Chemicals.

All chemicals were acquired commercially and used directly without any further purification. Solvents and reagents were bought from Chengdu Chron Chemical Co., Ltd. Standard substances were purchased from TCI with at least 98% purity.

4.3. Pretreatment of \( \textit{Pubescens} \) with AlCl\(_3\) Aqueous Solutions.

The detailed process of \( \textit{pubescens} \) pretreatment with AlCl\(_3\)·6H\(_2\)O was the same as that in our previous research.\(^{13}\) A certain amount of AlCl\(_3\)·6H\(_2\)O was added into 23 mL of deionized water to obtain aqueous solutions with different AlCl\(_3\) concentrations. About 6.00 g of the \( \textit{pubescens} \) sample was soaked in the above-prepared aqueous AlCl\(_3\) solutions for 24 h at room temperature (about 16 °C) before being filtered. The obtained solids were called pretreated samples (shortened as PS). In comparison, the same procedure was performed as above. After being soaked and filtered, the pretreated samples were washed five times until no Al species remained, and the samples obtained via this operation were called pretreated sample, washed (shortened as PSWs). Afterward, the acquired PS and PSW were freeze-dried in a freeze dryer for 18 h before being stored in a desiccator. Van Soest titration was employed to analyze the variation of the three major components in \( \textit{pubescens} \).\(^{52–55}\) An inductively coupled plasma optical emission spectrometer (ICP-OES) was introduced to determine the amount of AlCl\(_3\)·6H\(_2\)O remaining in the solid. All of the data presented were average values, with three careful parallel experiments, where the relative deviation was less than ±0.5%. The conversion of the reactant (\( X \)), yield of the solid, yield of the identified compound, and the total yield of identified compounds were defined as follows:

\[
X = \frac{W_{\textit{pubescens}} - W_{\text{residue}}}{W_{\textit{pubescens}}} \times 100\%
\]

\[
Y_{\text{residue}} = \frac{W_{\text{residue}}}{W_{\textit{pubescens}}} \times 100\%
\]

\[
W_{\text{AlCl}_3 \cdot 6\text{H}_2\text{O} \text{ remained}} = \frac{W_{\text{PS or PSW}}}{W_{\text{ICP}}} \times V_{\text{ICP}} \times C_{\text{AlCl}_3} \text{ICP} \times M_{\text{AlCl}_3 \cdot 6\text{H}_2\text{O}}
\]

\[
W_{\text{Al}_2\text{O}_3 \text{ remained}} = \frac{W_{\text{solid residue}}}{W_{\text{ICP}}} \times V_{\text{ICP}} \times C_{\text{AlCl}_3} \text{ICP} \times M_{\text{Al}_2\text{O}_3}
\]

yield of identified compound = \[
\frac{\text{mass of the identified compound}}{W_{\textit{pubescens}}} \times 100\%
\]
total yield = ∑ yield of each identified compound

where $X$ is the conversion of *pubescens*, $W_{pubescens}$ represents the weight of *pubescens* contained in the samples, $W_{residue}$ represents the weight of char contained in the residue after reaction, $W_{PS\ or\ PSW}$ represents the weight of the PS or PSW sample after pretreatment, $W_{solid\ residue}$ is the weight of residue after reaction, $W_{AlCl_3\·6H_2O}$ was determined by the Al$^{3+}$ obtained from ICP-OES considering its existence as AlCl$_3$.

After each trial, the electric furnace was opened, and then the system was swept with a N$_2$ flow rate of 0.6 mL min$^{-1}$ in the outer tube and 60 mL min$^{-1}$ in the inner tube were applied, where torrefaction of samples was investigated at 200 °C for 2 h.

After each trial, the electric furnace was opened, and then the pretreated residue was cooled down to ambient temperature under a N$_2$ atmosphere at the rate of 10 mL min$^{-1}$ in both outer and inner tubes. Then, the device was taken out and weighed to calculate the yields of solid, liquid, and gaseous products. The differences in the condenser and the outer tube before and after torrefaction were recognized as the yield of liquid products, which consisted of bio-oil and water, in which the content of moisture in liquid products was measured by an automatic trace moisture meter. The yield of gaseous products was counted by the overall mass balance in the process. All of the data provided were based on the weight of the *pubescens* contained in raw *pubescens* and PS and PSW samples; besides, all of the data were average values, in which parallel experiments were performed thrice, and the parallel experiments showed that the relative deviation of the data obtained from the experiments was less than ±0.3%. In our previous research, we found that water soaking could also affect the composition of the raw sample; thus, we chose pure-water-pretreated samples as the "blank control" in our experiments to rule out the effect of water in the present work.

4.5. Characterization of the Solid Material. 4.5.1. Van Soest Titratin. The variation of the three major components in solid was analyzed by Van Soest titration. The experimental details could be obtained from refs 52–55. Every sample was tested for three parallel experiments, and the average deviation of the results was less than ±0.5%.

4.5.2. XRD. The crystallinity of cellulose in raw *pubescens* and solid residues obtained after torrefaction was characterized by X-ray diffraction on a PANalytical B.V. of EMPYREAN instrument at 2θ from 5 to 80° on Cu Ka radiation with 35 kV and 30 mA. The detailed crystallinity index (CrI) in the sample was calculated by the following equation according to the literature:

$$CrI = \frac{I_{002} - I_{AM}}{I_{002}} \times 100\%$$

where $I_{002}$ represents the peak intensity consistent with the (002) (2θ = 22°) lattice plane of the cellulose and $I_{AM}$ stands for the peak intensity observed at 2θ = 18°. $I_{002}$ represents both crystalline and amorphous cellulose, while $I_{AM}$ only represents amorphous cellulose.

4.5.3. FT-IR. The FT-IR spectra of the raw *pubescens*, treated samples, and solid residues were recorded on a Nicolet 670 Fourier transform infrared spectrometer in the range of 4000–400 cm$^{-1}$ with a minimum resolution at 2 cm$^{-1}$.

4.6. Characterization of Liquid Products. Liquid products obtained from torrefaction were dissolved and diluted to a desired volume with methanol for further analysis.

4.6.1. Characterization of Small-Molecular-Weight Products. 4.6.1.1. GC-FID. After torrefaction, the small-molecular-weight liquid products dissolved in methanol derived from lignin were quantitatively detected by GC equipped with a flame ionization detector (Fuli 9750). The GC-FID was equipped with a DB-5 column (30 m × 0.25 mm × 0.25 μm), and the temperature program was set as increasing from 50 to 250 °C at 5 °C min$^{-1}$, holding at 250 °C for 10 min. Besides, the temperature of both the detector and injector was set as 280 °C. Benzyl alcohol was used as an internal standard to quantify the content of the products obtained from the degradation of lignin.

4.6.1.2. HPLC. The small-molecular-weight products obtained from the conversion of cellulose and hemicellulose were analyzed by Dionex U-3000 high-performance liquid chromatography (HPLC) equipped with a Dionex PG-3000 pump, an Aminex HPX-87 column (Bio-Rad), and a Shodex 101 refractive index detector (RID). The temperature of the column oven was 50 °C, and that of the detector was 35 °C. A 0.005 M H$_2$SO$_4$ solution at a flow rate of 0.6 mL min$^{-1}$ was used as the mobile phase. The products, such as monosaccharides, carboxylic acids, and furans, were quantified by an external standard method.

4.6.2. Characterization of Oligomer-Based Liquid Products. 4.6.2.1. APC. The desired volume of liquid products was first treated on a rotary evaporator to remove the solvent, and the solid obtained was dissolved in tetrahydrofuran (THF; the flow phase of APC). The molecular weight distribution of liquid products formed in the process of torrefaction was analyzed by an Acquity Advanced Polymer Chromatograph (APC, Waters) equipped with a column (4.6 mm × 150 mm) and an RI detector. Here, THF was the eluent with a rate of 0.5 mL min$^{-1}$, and the column temperature was maintained at 40 °C. A calibration curve was obtained using monodisperse polystyrene standards, where the analysis error was within 5%.

4.6.2.2. ESI-MS (Shimadzu). The liquid products were analyzed by electrospray ionization mass spectrometry (ESI-MS, LCMS-IT-TOF, Shimadzu). The detailed instrument parameters are as follows: flow rate of N$_2$ was set at 1.5 L min$^{-1}$, the detector voltage was run at 1.60 kV, the flow velocity of the mobile phase (with 80% methanol and 20% water) was 0.25 mL min$^{-1}$, and the injection volume was 15 μL. Positive and negative ion modes were run simultaneously.

4.6.2.3. 2D HSQC. 2D HSQC NMR spectra of the liquid products were recorded on a Bruker Advance 600 MHz spectrometer. In short, about 50 mg of viscous samples after removing the solvent was fully dissolved in 0.5 mL of deuterated dimethyl sulfoxide (DMSO-d$_6$). The parameters...
of the instrument were chosen according to the data reported in the literature.58

4.7. Characterization of Gaseous Products. 4.7.1. GC-TCD. The content of gaseous products was analyzed by GC 9710 (Fuli) with a TCD detector, equipped with a TDX-1 carbon molecular sieve packed column (2 m × 3 mm id). The detailed parameters of the instrument were set as follows: column 120 °C, detector 160 °C, carrier gas of nitrogen was used at a rate of 20 mL min⁻¹.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.0c04426.

Frame diagram of the pyrolysis process; XRD pattern of raw pubescens and torrefied PSW samples and PS samples; assignment of lignin C–H signals in 2D HSQC NMR spectra; ESI-MS spectra of the liquid obtained from torrefaction of raw pubescens (PDF).

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Notes
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