Synergy of Hydrothermal and Organic Acid Washing Treatments in Chinese Fir Wood Vinegar Preparation

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ABSTRACT: Pretreatment is an effective method to change the pyrolysis behavior and improve the product properties of biomass. In this study, the effects of hydrothermal treatment (HTT) and hydrothermal treatment combined with organic acid washing (HTT-A) on Chinese fir waste (CF) pyrolysis and preparation of wood vinegar (WV) were investigated. The results indicated that HTT promoted the decomposition of hemicellulose and disrupted the chemical structure, while HTT-A partly removed the lignin as well as hemicellulose. HTT-A showed a more effective removal efficiency of alkali/alkaline earth metals (AAEMs) than HTT. Both HTT and HTT-A delayed the initial decomposition temperature but promoted the pyrolysis process. The yields of WVs increased after HTT and HTT-A, while the moisture contents reduced, obviously. HTT increased the relative contents of phenols from 47.04 to 59.85% but reduced the relative contents of acids from 24.31 to 18.38%, whereas HHT-A reduced the relative contents of phenols but increased those of aldehydes. In addition, HTT and HTT-A showed the different effects on chemical compositions of WVs, especially for phenolic and acid compounds. This study indicated that HTT and HTT-A were the efficient methods to produce WVs with target chemical components, which would be conducive to the efficient application of WVs.

1. INTRODUCTION

With the growing demand for energy, renewable energy has become of growing interest. Biomass, due to the abundance and renewability, has been considered as an important renewable resource to overcome the energy crisis and eliminate dependence on fossil energy.1 Biomass can be processed into high-grade energy and fuel via thermochemical conversion technologies such as gasification, pyrolysis, and liquefaction.2 Among those conversion technologies, pyrolysis is regarded as a promising method to convert the biomass to generate the products of gaseous, biochar and bio-oil, which can be used to produce power for heating or the high-value products.3,4

Wood vinegar (WV) is a major product of biomass via slow pyrolysis. In general, WV accounts for about 30–50% of production from a biomass pyrolysis process. WV is a mixture liquid of water and more than 200 chemical compounds, such as phenols, acids, ketones, aldehydes, and esters.5 Consisting of abundant organic compounds, WVs have been used as the value-added chemicals in sustainable agriculture and environment management. The ongoing works showed that WVs have the antimicrobial, pesticidal, antioxidant, and plant growth enhancing effects, which can be used as bactericides, pesticides, soil amendments, food additives, plant growth regulators, and so on.6 Therefore, the preparation and application of WVs are beneficial to the efficient and comprehensive utilization of biomass.

Recently, the research studies on the application of WVs were quite intensive. Li et al. found that the antioxidant activities of WVs were contributed to the phenolic compounds,
but the acids compounds inhibited the antioxidant activities of phenolic compounds. Li et al. studied the antiviral activity of phenolic derivatives in WVs. The results indicated that antiviral activities of phenolic compounds were affected by the number of hydroxyl groups and the kinds of substituent groups.8 Lu et al. found that WVs exhibited the regulation performance on the growth of a plant root, which was relevant to the acids and phenolic compounds via a synergy effect.9 The synergy effect can be described as acids that caused the intercellular acidification and increased root activity, while phenols caused the oxidative stress and inhibited the root growth. Those research studies indicated that the application efficiency of WVs were closely related to the chemical properties. Hence, the oriented preparation of WVs and pyrolysis behavior of biomass. To achieve this target, the HTT under different temperature and chemical pretreatment agents. Combining HTT with organic acid washing could change the chemical structure, constitute the metal spice content of biomass, and cause the changing in biomass pyrolysis behavior and chemical compounds of products. Moreover, organic acid has less pollution to the environment than inorganic acids and alkalis. Nevertheless, the organic acids, especially acetic acid, which exist in the liquid from HTT and pyrolysis, also can be used as chemical pretreatment agents. Combining HTT with organic acid washing could change the chemical structure, constitute the metal spice content of biomass, and cause the changing in biomass pyrolysis behavior and chemical compounds of products. Moreover, organic acid has less pollution to the environment than inorganic acids and alkalis. Therefore, HTT combined with organic acid washing is an efficient and environmental friendly pretreatment method.

Pretreatment is an efficient method used for biomass pyrolysis to improve the pyrolysis product quality and produce the target chemicals.10,11 Physical and chemical pretreatment methods have been employed to disrupt the fiber structure, decrease the crystallinity, and change the contents of metallic elements.12–14 Hydrothermal treatment (HTT) is one of the thermal treatments used in biomass modification, which has great advantages of low energy input and mild reaction conditions.15 The previous studies found that HTT was effective to change the chemical compositions of biomass and influence the pyrolysis behavior. During the HTT, some complex reactions occurred, including hydrolysis, decarboxylation, dehydration, condensation, and aromatization, leading to the changes in chemical compositions of biomass.16 In addition, some researchers reported that chemical pretreatment could remove most of the metallic species from biomass and improve the product quality. Zhang et al. investigated the effects of HCl washing on the pyrolysis of a walnut shell, which found that acid washing obviously reduced the metallic species and achieved the higher selectivity of value-added chemicals, such as furfural, levoglucosan, and 2-methoxy-4-methyl phenol.17 Chen et al. found that HCl washing has removed nearly 94.25% of the metals and significantly enhanced the relative contents of ketones and D-allose in bio-oil.18 The reagents selected for chemical pretreatment mainly focused on inorganic acids and alkalis. Nevertheless, the organic acids, especially acetic acid, which exist in the liquid from HTT and pyrolysis, also can be used as chemical pretreatment agents. Combining HTT with organic acid washing could change the chemical structure, constitute the metal spice content of biomass, and cause the changing in biomass pyrolysis behavior and chemical compounds of products. Moreover, organic acid has less pollution to the environment than inorganic acids and alkalis. Therefore, HTT combined with organic acid washing is an efficient and environmental friendly pretreatment method.

To date, most of the works focus on the individual effects of HTT and chemical pretreated on the biomass pyrolysis and the properties of bio-oil. However, no research has been explored to investigate the synergistic effect of the HTT-combined organic acid washing on the biomass pyrolysis behavior. Moreover, the effects of pretreatment on the properties of WVs were also lacking. Hence, this study aimed to investigate the synergistic effect of HTT and organic acid washing on the preparation of WVs and pyrolysis behavior of biomass. To achieve this target, the HTT under different temperature and HTT combined with organic acid washing (HTT-A) were

| samples | C      | H      | O      | VM   | FC   | ash   | mass yields(%) |
|--------|--------|--------|--------|------|------|-------|----------------|
| CF     | 47.76 ± 0.25 | 5.66 ± 0.13 | 46.58 ± 0.38 | 85.76 ± 1.03 | 13.39 ± 0.86 | 0.85 ± 0.18 | 100          |
| LHCFL  | 48.79 ± 0.20 | 5.80 ± 0.11 | 45.41 ± 0.10 | 84.83 ± 0.84 | 14.43 ± 0.93 | 0.74 ± 0.09 | 95.96 ± 1.28 |
| MHCF   | 49.94 ± 0.17 | 5.85 ± 0.11 | 44.21 ± 0.28 | 81.95 ± 1.08 | 17.35 ± 0.99 | 0.70 ± 0.10 | 95.26 ± 2.31 |
| SHCF   | 51.88 ± 0.11 | 5.89 ± 0.09 | 42.23 ± 0.03 | 80.98 ± 0.64 | 18.35 ± 0.75 | 0.67 ± 0.11 | 93.50 ± 1.68 |
| LHCFA  | 49.13 ± 0.06 | 5.88 ± 0.08 | 44.99 ± 0.14 | 85.78 ± 1.15 | 13.94 ± 1.07 | 0.28 ± 0.08 | 90.16 ± 1.07 |
| MHCF-A | 50.08 ± 0.03 | 5.92 ± 0.04 | 44.00 ± 0.03 | 83.91 ± 1.12 | 15.91 ± 1.06 | 0.18 ± 0.07 | 89.07 ± 1.52 |
| SHCF-A | 52.10 ± 0.10 | 5.99 ± 0.09 | 41.91 ± 0.13 | 81.88 ± 0.91 | 17.96 ± 0.96 | 0.16 ± 0.05 | 87.09 ± 1.43 |

Figure 1. Contents of metallic species in (a) samples and (b) removal efficiency.
performed and the synergistic effects were evaluated by TG and GC–MS analysis. The obtained results can be helpful for further utilization of biomass waste via the pyrolysis process.

2. RESULTS AND DISCUSSION

2.1. Effects of Pretreatment on the Physicochemical Characteristics of Samples. The basic characteristics of the samples are shown in Table 1. Compared with raw CF (47.76%), the carbon contents of the samples after HTT increased to 48.79% of LHCf (hydrothermal-treated at 120 °C), 49.94% of MHCF (hydrothermal-treated at 150 °C), and 51.88% of SHCF (hydrothermal-treated at 180 °C). After organic acid washing, the carbon contents increased slightly compared with hydrothermal-treated samples. In general, the carbon content of components in biomass follows the order of lignin > cellulose > hemicellulose. The results indicated that HTT was likely to promote the decomposition of hemicellulose, and the removal effect was related with the severity of HTT. Meanwhile, HTT-A exhibited the indistinctive effects on the decomposition of hemicellulose. According to proximate analysis, the increasing of HTT severity caused the increase of the fixed carbon content and the decrease of the volatile content, which were due to the dehydroxylation, decarboxylation, and dehydration reactions during the HTT process.19 With the subsequent acid washing process, the changes in the volatile and fixed carbon content were not significant. For the ash content, it slightly decreased from 0.85 to 0.67% after HTT but obviously reduced to 0.16% after HTT-A, indicating that acid washing reduced the ash content, obviously. In addition, the mass yields of pretreated samples decreased to 93.50% after HTT and further decreased to 87.09% after acid washing. It may be due to the fact that HTT changed the constituents and the structure of biomass, and the acid washing treatment process removed a small amount of organic and inorganic matter of biomass.

2.1.2. The Contents of Metallic Species in Samples. The contents of metallic species and removal efficiency are presented in Figure 1. As shown in Figure 1a, Ca, K, Mg, and Na were the main alkali/alkaline earth metals (AAEMs) in raw CF with the values of 1200, 779, 185, and 56.2 mg/kg, respectively. The removal effects of HTT on K were more obvious than those of Ca, Mg, and Na, which were attributed to the fact that K was more easily dissolved in water with the ionic form and led to a higher solubility in water. Furthermore, the contents of Ca and Mg first decreased and then increased with the increasing of HTT severity. This might be due to the HTT process promoting the dissolution of the low solubility metals. However, under high HTT temperature, more volatiles have been released and most metals remained, resulting in the increase of contents.20 Moreover, HTT-A resulted in a significant decrease of metallic species concentrations in hydrothermal-treated samples, especially for K. The removal efficiencies of metallic species within the samples by HTT and HTT-A are presented in Figure 1b. For HTT, the removal efficiencies of Ca, K, Mg, and Na were 24.24, 80.37, 43.26, and 42.39%, respectively. After a subsequent acid washing process, the removal efficiencies further increased to 71.08, 97.19, 85.18, and 53.19%, respectively. This indicated that acid washing promoted the removal of metallic species and exhibited the obvious removal efficiency. The acid washing process could remove a mass of metallic species because the metallic species were dissolved in the form of soluble salts. For HTT samples, the removal efficiencies of metallic species were gradually enhanced with the increasing of HTT severity. For Ca and Mg, the increasing trends of removal efficiencies were more obvious than those of K and Na. This might be due to the changes in the association of metallic species within the biomass during the thermal treatment, which affected the dissolution and the removal efficiency.

2.1.3. FTIR Analysis. The chemical structure changes of CF during the treatment process can be characterized by Fourier transform infrared (FTIR) analysis. The FTIR spectra of raw CF and treated samples are shown in Figure 2. The possible assignments to main bands were shown to be 3400 cm\(^{-1}\) (1) for the \(-OH\) stretching vibration, 2900 cm\(^{-1}\) (2) and 1640 cm\(^{-1}\) (3) for the \(-C\equiv O\) stretching vibration, 1506 cm\(^{-1}\) (4) for the aromatic skeletal vibration in lignin, 1460 cm\(^{-1}\) (5) and 1420 cm\(^{-1}\) (6) for the C–H deformation in lignin and carbohydrates, 1370 cm\(^{-1}\) (7) for C–H in CH\(_2\) in lignin, 1330 cm\(^{-1}\) (8) for the C–H vibration in cellulose and C\(_1\)–O vibration in syringyl derivatives, 1250 cm\(^{-1}\) (9) for the syringyl ring and C–O stretch in lignin and xylan, 1160 cm\(^{-1}\) (10) for the C–O–C vibration in cellulose and hemicellulose, 1120 cm\(^{-1}\) (11) for the aromatic skeletal and C–O stretch, 1040 cm\(^{-1}\) (12) for the C–O ester stretching vibration in methoxy
groups, and aromatic C–H and β–O–4 linkages in lignin.\textsuperscript{21,22} The band at 2900 cm\textsuperscript{-1} (2) changed slightly after HTT, but it became smooth after HTT-A. The relative intensity of the band at 1640 cm\textsuperscript{-1} (3) decreased after HTT and HTT-A, which was attributed to the deacetylation reaction of hemicellulose. The relative intensity of bands at 1506 (4), 1420 (6), and 1250 cm\textsuperscript{-1} (9), which were assigned to the aromatic structure of lignin, were enhanced with the increasing of HTT severity, indicating that the other components in biomass have degraded but lignin has not decomposed totally under the HTT, resulting in the increase of lignin fraction. Compared with HTT samples, these bands decreased slightly after acid washing, which indicated the partial decomposition of lignin during the acid washing process. The similar trends were observed in bands at 1370 (7) and 1330 cm\textsuperscript{-1} (8). Furthermore, the bands at 1040 cm\textsuperscript{-1} (12) increased by HTT and then decreased by subsequent acid washing pretreatment, which might be due to the aromatic structure conversion during the HTT and the breaking of β–O–4 linkages in lignin by acid washing.\textsuperscript{23} These results indicated that HTT degraded the hemicellulose/cellulose and enhanced the relative fraction of lignin, while HTT-A promoted the removal of lignin.

2.2. Effect of Pretreatment on Pyrolysis Behavior. The effects of pretreatment on the pyrolysis behavior of the samples were analyzed by a TG analyzer. The TG and DTG data of the samples are displayed in Figure 3. In general, hemicellulose, cellulose, and lignin are the major constituents in biomass, and the thermal degradation temperature ranges are considered to be 150–350 °C for hemicellulose, 275–350 °C for cellulose, and 250–500 °C for lignin. As shown in Figure 3a, it can be seen that HTT and HTT-A changed the pyrolysis behavior of CF. The residual mass ($M_r$) decreased gradually from 19.14% of raw CF to 17.43% of SHCF, and the decreased trend was related to the severity of HTT. After subsequent acid washing pretreatment, the $M_r$ further reduced to 17.08, 16.14, and 15.74%. This was attributed to the removal of inorganic species during the washing process and resulted in the decrease of residual mass. In Figure 3b, the DTG curves in a temperature range of 250–400 °C slightly shifted to the right compared to those of CF, while the peaks with the maximum amplitude shifted from 365.5 to 378.3 °C.

The characteristic parameters from TG analysis are presented in Table 2. It can be seen that HTT and HTT-A exhibited the significant effects on the pyrolysis characteristics of CF. The values of the maximum mass loss rate (DTG\textsubscript{max}) increased from 9.64%/min of CF to 11.45%/min of SHCF. This was due to HTT changing the compositions of biomass and made the sample structure more homogeneous, resulting in the reduction of the temperature range of volatile release.\textsuperscript{24} After the acid washing process, the values of DTG\textsubscript{max} were 10.42, 11.73, and 11.53%/min, which were higher than those of HTT samples. The initial decomposition temperature ($T_i$) increased from 313.7 °C of CF to 331.4 °C of SHCF, which could be considered as the indication of hemicellulose degradation during the HTT.\textsuperscript{25} Meanwhile, the temperature of DTG\textsubscript{max} ($T_{max}$) increased from 365.5 °C of CF to 376.6 °C of MHCF and then decreased to 370.3 °C of SHCF, and it further increased after acid washing. These results indicated that HTT and HTT-A delayed the initial decomposition temperature but promoted the pyrolysis process. The hemicellulose, a low thermal stability composition in biomass, was easier to degrade than the other two compositions during the HTT. Therefore, the fraction of hemicellulose in HTT samples was much lower than that of CF, resulting in the increase of $T_i$ and $T_{max}$.\textsuperscript{26} However, the higher HTT temperature led to the formation of covalent cross-linking and delayed the pyrolysis. After HTT-A, the $T_i$ and $T_{max}$ further increased to 334.7 and 378.3 °C, respectively, which were higher than those of HTT samples.

Table 2. Pyrolysis Characteristic Parameters of Raw CF and Pretreated Samples

| samples  | $M_i$ (wt %) | $M_r$ (wt %) | DTG\textsubscript{max} (wt %/min) | $T_i$ (°C) | $T_{max}$ (°C) |
|---------|-------------|-------------|------------------------------|-----------|----------------|
| CF      | 19.14       | 80.86       | −9.64                        | 365.5     | 313.7          |
| LHCF    | 18.86       | 81.14       | −10.53                       | 376.0     | 325.2          |
| MHCF    | 17.99       | 82.11       | −10.78                       | 376.6     | 326.6          |
| SHCF    | 17.43       | 82.57       | −11.45                       | 370.3     | 331.4          |
| LHCF-A  | 17.08       | 82.92       | −10.42                       | 375.8     | 331.5          |
| MHCF-A  | 16.14       | 83.86       | −11.73                       | 378.1     | 334.7          |
| SHCF-A  | 15.74       | 84.26       | −11.53                       | 378.3     | 334.3          |
effectively removed during the acid washing process. These AAEMs exhibited the catalytic effects on the pyrolysis process and caused the movement of pyrolysis temperature to the lower district. As a result of AAEMs being removed by acid washing, the catalytic effects were weakened, and the values of $T_e$ and $T_{max}$ increased.27

2.3. Effects of Pretreatment on Preparation of WVs.

2.3.1. Basic Properties of WVs. The effects of pretreatment on basic properties of WVs are shown in Table 3. The values of pH and density gradually increased from 2.65 and 1.011 g/mL of CF to 3.05 and 1.025 g/mL of SHCF. Compared with HTT samples, subsequent acid washing further enhanced the values of pH and density. This was attributed to HTT and HTT-A changing the components of biomass that resulted in the alteration of chemical compositions of WVs. The moisture contents decreased from 56.13 to 44.28% by HTT pretreatment and further decreased to 43.49% by HTT-A pretreatment, suggesting that HTT and HTT-A reduced the moisture contents and increased the organic compound contents of WVs. After HTT, the yields based on pretreated samples increased to 29.86, 28.21, and 27.44%. HTT made the structure of the sample more homogeneous and promoted the volatile release, resulting in the increase of WVs yields. However, with the increasing of HTT severity, the yields decreased, which might be due to the HTT changing the sample structure by formation of cross-linking and making it difficult to pyrolyze.28 Moreover, the subsequent acid washing process slightly increased the yields of WVs, indicating that HTT-A showed no obvious effects on increasing the yields of WVs.

2.3.2. Relative Contents of Different Groups of Chemicals. The chemical compositions of WVs were further studied using GC–MS. The relative contents of pyrolysis products and the chemical compositions distribution are tabulated in Figure 4. It can be seen that the identified chemical compounds in WVs from pyrolysis of CF were classified into six groups, including phenols, acids, aldehydes, ketones, alcohols, and esters. HTT decreased the relative contents of acids, ketones, and esters, which gradually decreased from 24.31, 13.07, and 1.65% of CF to 18.38, 9.64, and 0.99% of SHCF with the increasing severity of HTT. The relative contents of aldehydes decreased after HTT. For alcohols, the relative contents increased from 3.31% of CF to 3.73% of LHCF and then decreased to 3.10% of SHCF. The relative contents of phenols gradually increased from 47.04% of raw CF to 59.85% of SHCF, obviously. During the HTT process, hemicellulose and cellulose partly decomposed, which decreased the formation of compounds derived from hemicellulose or cellulose (such as acids, ketones, aldehydes, etc.) in the subsequent pyrolysis step. Moreover, the cross-linking and carbonization reactions that occurred in the HTT led to the condensation of hemicellulose, cellulose, and lignin, which significantly affected the generation of volatiles in the pyrolysis process, whereas the lignin has no obvious mass loss and its fraction enhanced by HTT, resulting in the increase of relative contents of phenols.29,30 After the HTT-A process, the relative contents of phenols reduced obviously, while the relative contents of aldehydes, alcohols, and esters increased slightly. This may be due to the fact that acid washing partly removed the lignin, which reduced the lignin fraction in biomass and caused the decrease of phenols. On the other hand, the removal of AAEMs by acid washing affected the cellulose depolymerization and caused the changes on the contents of chemical compounds.31 It was clear that phenols were the major compounds in WVs responsible for the antioxidant, antiviral, and antimicrobial activities. Furthermore, it has been revealed by Li et al. that acids exhibited inhibition effects on the antioxidant activity of phenols. HTT and HTT-A enhanced the phenols content and reduced the acid content of WVs, which would be beneficial to promote the antioxidant, antiviral, and antimicrobial activities of WVs.

2.3.3. Relative Contents of Key Chemical Compounds. The relative contents of phenols in WVs are presented in Figure 5. Phenols are produced by the fracture of C–C and ether bonds in lignin during the biomass pyrolysis. Phenols have high antioxidant and antiviral activities, such as phenol, 3-methyl phenol, 2-methoxy-4-propyl phenol, 2-methoxy-4-ethyl phenol, 1,2-benzenediol, and 2-methoxy methyl phenol. As shown, phenols were the most abundant chemical compounds in WVs, which could be classified into the guaiacol type, including 2-methoxy-4-methyl phenol, 2-methoxy-4-ethyl phenol, 2-methoxy phenol, and 2-methoxy-4-propenyl phenol. This indicated that the major units of lignin in CF were the guaiacol type.26 It can be seen that HTT and HTT-A had the obvious effects on the phenol formation. The relative content of 2-methoxy-4-ethyl phenol increased obviously from 8.57 to 18.98% by HTT but decreased sharply after the subsequent

| samples   | pH     | density (g/mL) | moisture content (%) | yield (%)  |
|-----------|--------|----------------|----------------------|------------|
| CF        | 2.65 ± 0.05 | 1.011 ± 0.07   | 56.13 ± 1.02           | 26.24 ± 1.17 |
| LHCF      | 2.81 ± 0.09 | 1.018 ± 0.04   | 51.24 ± 0.56           | 30.86 ± 0.95 |
| MHCF      | 2.99 ± 0.03 | 1.023 ± 0.02   | 48.39 ± 0.34           | 29.21 ± 1.06 |
| SHCF      | 3.05 ± 0.17 | 1.025 ± 0.05   | 44.28 ± 0.61           | 27.44 ± 0.73 |
| SHCF-A    | 2.93 ± 0.11 | 1.020 ± 0.05   | 49.07 ± 0.83           | 31.35 ± 0.84 |
| MHCF-A    | 3.06 ± 0.06 | 1.025 ± 0.03   | 46.16 ± 0.16           | 30.24 ± 1.16 |
| SHCF-A    | 3.09 ± 0.13 | 1.026 ± 0.04   | 43.49 ± 0.50           | 28.23 ± 1.01 |

Table 3. Basic Properties of WVs
acid washing, whereas the relative content of 2-methoxy-4-methyl phenol increased slightly by HTT but enhanced markedly to 20.60% after HTT-A. This was due to the fact that the efficiency removal of the K element by acid washing had a promotion effect on the formation of 2-methoxy-4-methyl phenol.\textsuperscript{33} HTT-A reduced the relative contents of 2-methoxy-4-vinyl phenol and 2-methoxy-4-propyl phenol, which could be attributed to the breaking of $\beta-O-4$ and demethoxylation in lignin.\textsuperscript{34} Both of HTT and HTT-A promoted the production of 3-methyl phenol, 2-methoxy methyl phenol, eugenol, and 2-methoxy-4-propenyl phenol. This indicated that HTT and HTT-A exhibited the different enrichment effects on phenolic compounds, which could influence antioxidant and antiviral activities of WVs.

The relative contents of acids are presented in Figure 5b. The major kinds of acids were pentanoic, acetic, 3-methoxy-4-hydroxybenzoic, and propanoic acid. It can be observed that all kinds of acids decreased by HTT. Compared with HTT samples, the acid washing process enhanced the relative contents of acetic and 3-methoxy-4-hydroxybenzoic acid but reduced the contents of pentanoic and propanoic acid. During the pyrolysis of biomass, acids were mainly obtained from the pyrogenic decomposition of hemicellulose. HTT partly degraded hemicellulose and changed the composition of biomass, resulting in the decrease of acid contents. With the subsequent acid washing process, some of the lignins have been removed and the fraction of hemicellulose increased, which promoted the increase of acid contents. However, acid washing also removed most of AEEMs, reduced the organic extractives of HTT samples, and inhibited on the formation of fatty acids such as pentanoic and propanoic acid.\textsuperscript{35} Therefore, the contents of acetic and 3-methoxy-4-hydroxybenzoic acid increased, while the contents of pentanoic and propanoic acid decreased.

Figure 5c,d shows the relative contents of ketones and aldehydes. 1,2-Cyclopentanedione and 3-methyl-1,2-cyclopentanedione were the major organic compounds of ketones. During the pyrolysis process, the volatile releases were conducive to the dehydration of oligosaccharides and secondary reactions, which promoted the formation of cyclopentadione.\textsuperscript{36} HTT and HTT-A removed the volatile releases from CF and decreased the formation of cyclopentadione. The major aldehydes were furfural and its derivatives (5-methyl-2-furfural and 5-hydroxymethyl furfural). In general, the furfural and its derivatives are obtained from the ring-open reaction and the oligosaccharide dehydration of hemicellulose or cellulose. Hemicellulose/cellulose decomposed partly during HTT and resulted in the reduction of
aldehydes. Compared with HTT samples, HTT-A enhanced the aldehydes contents, especially for furfural and its derivatives with a relative content of 14.00%. This indicated that acid washing promoted the ring scissions and oligosaccharide dehydration and increased the contents of furfural and its derivatives.

3. CONCLUSIONS

In this study, the synergy effects of HTT and HTT-A on the preparation of WVs from CF were investigated. The results indicated that HTT promoted the decomposition of hemi-cellulose and increased the fraction of lignin, while HTT-A could partly remove the lignin. Moreover, the removal efficiencies of metallic species were obviously increased by the subsequent acid washing process. HTT and HTT-A showed the significant effects on changing the pyrolysis behavior of CF. Both HTT and HTT-A increased the yields of WVs and reduced the moisture contents of WVs. The chemical compositions of the WVs were also analyzed. HTT increased the relative contents of phenols while reducing the relative contents of acids, ketones, and aldehydes, whereas HTT-A reduced the relative contents of phenols but increased the relative contents of aldehydes. Some antioxidant and antiviral activities phenolic compounds were enriched with different levels by HTT and HTT-A pretreatments, such as 2-methoxy-4-ethyl phenol, 3-methyl phenol, 2-methoxy-4-propyl phenol, and 2-methoxy-4-methyl phenol. Those results present a guidance to prepare WVs with high antioxidant and antiviral activities for applying in the field of food preservation and medicine.

4. MATERIALS AND METHODS

4.1. Materials. Chinese fir (CF) wastes were used as the raw materials, which were the residues generated in the utilization process (especially the furniture industry) and obtained from a furniture industry in Jiangxi of China. Prior to the treatment experiment, the CF was smashed into 0.5−2.0 mm and dried at 100 °C for 5 h.

4.2. Pretreatment Experiment. The HTT was operated via a Teflon-lined stainless steel autoclave reactor. Twenty grams of raw CF and 200 mL of deionized water were added into a 500 mL autoclave reactor and treated at a desired temperature for 1 h. The high purity nitrogen was used to provide an inert atmosphere during the HTT. Three different hydrothermal temperatures of 120, 150, and 180 °C corresponding to light, mild, and severe HTT conditions, respectively, were selected in this study. When the treatment was finished, the autoclave was placed in the air to cool naturally to room temperature and the mixture was separated. The solid product was dried at 100 °C for 6 h. The samples were marked as CF for raw material, LHCF for treated at 120 °C, MHCF for treated at 150 °C, and SHCF for treated at 180 °C.

HTT-A was performed as the hydrothermal-treated samples were washed with organic acid solution (solid/solution ratio = 1:10) at 30 °C and stirred for 3 h. Acetic acid solution (2%, wt %) was used as the agent to simulate the hydrothermal liquid. After acid washing, the solid sample was isolated and washed to neutral pH and then dried. The acid washing samples were marked as LHCF-A, MHCF-A, and SHCF-A. Three parallel experiments were used to ensure reproducibility and consistency.

4.3. Pyrolysis Experiment. The pyrolysis experiment was carried out in a fixed bed reactor (vacuum tube furnace, VTL 1200, China) at 450 °C for 30 min. The pyrolysis schematic diagram was according to our previous study.37 N2 (100 mL/min) that guaranteed an inert atmosphere and 20 g of the sample was used for each experiment. The pyrolysis volatile matters flowed through two condensers to collect WVs. The yields of WVs were calculated based on the dry weight of the solid samples. For each pyrolysis condition, three parallel experiments were used to ensure reproducibility and consistency.

4.4. Analysis for Physicochemical Characteristics of Samples. The proximate analysis of the sample was tested, according to the National Standard in China GB/T 28731−2012. The elemental analysis was carried out using an element analyzer (PerkinElmer 2400, Germany), and the O content was determined by difference. The chemical structure was investigated using FTIR spectroscopy (FTIR, IS10, Niko, USA). The metallic species contents of the samples were determined using a nitric acid− perchloric acid digestion method and inductively coupled plasma atomic emission spectroscopy (ICP-OES; Optima 7000 DV, PerkinElmer Corporation, USA). Thermogravimetric (TG) analysis was carried out by a thermogravimetric analyzer (TG-DTG, 409PC, Netzsch, Germany). The water content, density, and pH of WVs were tested by the Karl Fischer titration, an optical density meter, and a pH meter (PHS-3CS, Inesa, China), respectively. For analysis of the chemical compositions, the WV was extracted by diethyl ether with a ratio of 1:1 followed by gas chromatography−mass spectrometry (GC−MS; 7890A−5975C, Agilent, USA). The column used was HP-5 (0.05 μm × 0.32 nm) of 30 m. The sample (0.2 μL) was injected into the column at 50 °C and held for 2 min, then heated by 5 °C/min to 280 °C, and kept for 20 min. A split ratio of 100:1 was used. The MS analysis was obtained under 230 °C at 70 eV. The chromatograms and mass spectra were identified based on the database of ChemStation and the NIST-MS library.

The removal efficiency of metallic species in sample was calculated as follows

\[
\text{removal efficiency} = \frac{C_i - C_p}{C_r} \times 100\%
\]

where \( C \) is the content of metallic species in the sample and the subscripts of "r" and "p" stand for the raw and pretreated sample, respectively.

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Notes

The authors declare no competing financial interest.

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