Effects of Ultrasound Pretreatment on Eucalyptus Thermal Decomposition Characteristics As Determined by Thermogravimetric, Differential Scanning Calorimetry, and Fourier Transform Infrared Analysis

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ABSTRACT: Samples were pretreated by ultrasound at 300 W and 28 kHz in three different solutions. The thermal degradation characteristics of the samples were then characterized via thermogravimetric, differential scanning calorimetry, and Fourier transform infrared analysis in a nitrogen environment. The characteristic of gas product release, the formation mechanisms of the main products, and the mechanistic basis for the effects of ultrasound on wood components were studied. The results showed that the gaseous products are the same with ultrasound pretreatment but the amounts are changed. The gaseous products mainly constitute of CO, H2O, CO2, CH4, and CH3COOH, and more gaseous products were produced at 361 °C than at 308 °C. The reaction rates for specimens pretreated in aqueous soda solution proceeded faster than specimens pretreated in aqueous acetic acid solution and distilled water. Moreover, the maximum FTIR spectra absorbance appeared around 341 °C for specimens pretreated in aqueous soda solution but appeared around 369 °C for the control sample and samples pretreated in distilled water or acetic acid solution. The heat flows for specimens pretreated in aqueous soda solution, compared to control group, was much lower. Additionally, hydroxyl and hydroperoxy radicals provided by ultrasound cavitation in alkaline conditions act to intensify the overall rates of reactions.

1. INTRODUCTION

Wood, as one kind of renewable biomass resource, can be used to solve the energy shortage in worldwide.1,2 At present, a significant amount of timber is used in the wood industry, and much wood waste is generated during furniture manufacturing and by the building industries. However, most wooden waste, at present, is combusted or abandoned directly, which contribute to rather severe environmental pollution. To solve such problem, wood waste could be converted to cellulosic material and thus improve its value. However, the structure of wood, which mainly consist of cellulose, hemicellulose, and lignin,3 is very complex,4 and it is difficult to process wood waste with low cost in a short time period.5 Wooden waste pretreatment is one of the best ways to modify wood structure and change the characteristics of cellulose, hemicellulose, and lignin.6,7 At present, many pretreatments were used to facilitate the thermal conversion of wooden material, such as acid pretreatment,8 hot water pretreatment,9 torrefaction pretreatment,10 ionic liquid pretreatment,11 and so on. However, the existing methods could not be applied widely considering the cost and efficiency. Ultrasound with the characteristics of cavitation, sponge effect, and so on can generate high temperature and high pressure in liquid medium and induce wood chemical and physical transformation.12,13 Ultrasound pretreatment also can break down the lignin, remove hemicelluloses, and allow pretreatment chemicals to reach and increase cellulose nanocrystal accessibility.15,16 Thus, ultrasonic treatment is an interesting option for lignocellulosic pretreatment to facilitate the thermal conversion.15,16 Moreover, the choice of medium also has significant influence on wood ultrasound pretreatment.15 Therefore, it is necessary to discuss the effects of ultrasound pretreatment on wood thermal decomposition characteristics under different conditions.

Additionally, thermal decomposition of biomass is the fundamental process of biomass thermal conversion and can be quantitatively measured by thermogravimetric, differential scanning calorimetry, and Fourier transform infrared (TG–DSC–FTIR) analysis. This provides useful data on the gas-product-evolution process and to elucidate the mechanism of wood pyrolysis.18–21 In this study, TG–DSC–FTIR analysis was used to determine the effects of ultrasound pretreatment
on wood thermal decomposition characteristics under different conditions.

2. RESULTS AND DISCUSSION

2.1. Materials Characterization. The proximate analysis as dry basis (db) and ultimate analysis as dry ash-free (daf) basis of the samples were measured as shown in Table 1. The control and pretreated specimens were grind to smaller than 100-mesh and dried at 105 °C for at least 2 h before analysis. The C, H, and N contents were calculated by an Elementar Vario EL III. The O content was obtained by the difference. A muffle furnace was used to measure the content of volatile matter, fixed carbon, and ash. All analyses were performed in triplicate.

2.2. Gas Product Release Characteristics of Wood Samples. The differential thermogravimetric (DTG) curves of specimens pretreated by ultrasound under different conditions are shown in Figure 1. It indicates that the peak of decomposition for specimens pretreated by ultrasound in aqueous soda solution is around 341 °C and those for the control sample and samples pretreated in distilled water or acetic acid solution are around 308 and 361 °C.

An FTIR spectrometer was used to analyze the volatile emission characteristic during the thermal degradation process. On the basis of the widely used Lambert–Beer law and the existing research studies,22–24 the absorption spectrum intensity at a specific wavenumber is linearly dependent on gas concentration.25 Thus, the variation of absorbance during thermal degradation reflects the concentration trend of the gas species.26 Figure 2 demonstrates the FTIR spectra of the thermal degradation gases of wood pretreated in different solutions at the indicated temperatures. For all specimens, the absorption bands of volatile appeared at the same wave-numbers, but there were some differences in the absorbance peaks. It means that the different thermal degradation products vary in amounts but not in identity. Qualitative analysis indicates that the production of compounds could be classified into two kinds. The noncondensable gases contain CO (2183 cm⁻¹), CO₂ (2360, 669 cm⁻¹), and CH₄ (2183 cm⁻¹), and the condensable gases contain water (3964–3500 cm⁻¹ and 1650–1300 cm⁻¹), mainly generated by the evaporation of free water and absorbed water in material and the cracking of aliphatic hydroxyl groups in the lateral chains,27 ketones (1260–1145 cm⁻¹) and acids, or CH₃COOH in the IR spectra data-base.26,28 Additionally, HCN and NH₃ were also found in the FTIR spectra,20,29 but at low amounts. The formation of gaseous products at 361 °C was much stronger than that at 308 °C, perhaps because when thermal degradation progresses into the first stage, more gaseous products are released.27 Additionally, compared to the control group, specimens pretreated in acetic acid solution or in distilled water showed little effect of pretreatment time and conditions on the amount of gaseous products. However, more gaseous products were produced for specimens pretreated in the aqueous soda solution, these results are likely because in alkaline solutions, the sodium can catalyze devolatilization reactions,30,31 and physical and chemical effects of ultrasound on wood component.

2.3. Formation Mechanisms of Main Products. Different gases are detected in different FTIR zones according to their main FTIR spectra. The evolution profiles of CH₃COOH, CO, CO₂, and CH₄ are shown in Figure 3. The gas products varied with temperature for specimens pretreated in different solutions. CH₃COOH, which is most likely generated by cellulose and hemicellulose pyrolysis,30 appears starting at 250 °C and peaks around 343 °C for specimens pretreated in aqueous soda solution. In contrast, in the control samples and the samples pretreated in distilled water or acetic acid solution, the CH₃COOH appeared around 250 °C and peaked around 366 °C. The lower temperature for samples pretreated in aqueous soda solution might be for the reason of the removal of alkali metals such as calcium and magnesium, which have negligible influence on the thermal degradation of cellulose and hemicellulose and the addition of sodium carbonate, which can catalyze devolatilization reactions.23,15 The temperature range of CO₂ production was from 200 to 400 °C for all conditions and with a peak at 345 °C for specimens pretreated in aqueous soda solution and with two peaks at 296 and 366 °C, respectively, for the control one and specimens pretreated in distilled water and acetic acid solution. Additionally, the evolution of CO starting at 250 °C is higher than that of CO₂. The maximum absorbance appeared around 336 °C for specimens pretreated in aqueous soda solution but appeared at 200 °C and peaked around 369 °C for the control sample and samples pretreated in distilled water or acetic acid solution. This suggests that the CO₂ produced in biomass pyrolysis is mainly due to hemicellulose thermal decomposition and the breaking of lateral C–C bonds,27 but CO is most likely generated by cellulose pyrolysis and by the breaking of lateral chains in lignin polymers, such as the aliphatic hydroxyl group and C–C bond.15,16 Our data agreed well with previous results.7 CH₄ is formed from the cracking of methyl radicals in lignin15 and weakly bonded methoxy groups,30 and was evident starting at 200 °C and concentration around 341 °C.

2.4. DSC Analysis. The DSC curves for specimens pretreated in different solutions are shown in Figure 4. There was a significant endothermic process for all specimens, and the reaction of specimens pretreated in aqueous soda
solution occurred in a lower temperature region (309–400 °C) than for specimens pretreated in aqueous acetic acid (328–428 °C), distilled water (321–424 °C), or the control group (312–442 °C). Additionally, the data also shows that,
compared to the control group, the heat flow for specimens pretreated in aqueous soda solution was much lower. Moreover, the reaction rates for specimens pretreated in aqueous soda solution was faster than the specimens pretreated in aqueous acetic acid and distilled water, and there were no significant differences for specimens pretreated for different amounts of time (0.5, 1.0, and 1.5 h). These results are likely because in alkaline solutions both physical and chemical effects of ultrasound and cavitation can promote delignification.32 Additionally, sodium carbonate was able to enter samples33 and the sodium can catalyze devolatilization reactions.3,7,34

2.5. Influencing Mechanism of Ultrasound on Wood. Our findings show that ultrasound pretreatment in different solutions has a significant effect on the wood thermal decomposition characteristics, especially for wood pretreated in aqueous soda solution. Wood consists mainly of cellulose, hemicellulose, and lignin, and we propose the following mechanism for the effects of wood pretreatment by hydrodynamic cavitation in alkaline conditions, and the mechanism also is shown in Figure 5.

Ultrasound cavitation generates high pressure and temperature during the pretreatment process,13 promoting the decomposition of water molecules into OH\(^-\) and H\(^+\).35 These OH\(^-\) radicals are highly reactive and may facilitate the oxidation of cellulose, hemicellulose, and lignin molecules.

Figure 3. FTIR spectrum of the pyrolysis gaseous products of wood pretreated in different solutions.

Figure 4. DSC curves for pretreated and control specimens.

Figure 5. Influencing mechanism of ultrasound on wood.
Under alkaline conditions, the oxidation potential (reactivity) of the hydroxyl radicals decreases and recombination occurs between hydroxyl radicals to form hydrogen peroxide (H$_2$O$_2$), and this H$_2$O$_2$ can be separated to generate hydroperoxy radical under alkaline conditions, and HOO$^-$ can react again with the residual H$_2$O$_2$ to generate highly reactive superoxide (O$_2^-$) and OH$^*$. The cellulose, hemicellulose, and lignin molecules react with themselves or with the hydroperoxy (HOO$^-$) and hydroxyl (OH$^*$) radicals formed during ultrasound cavitation to form carbon dioxide, organic acids, and other low molecular weight organic products by side chain elimination, ring opening, and other processes.$^{3,36–39}$

3. CONCLUSIONS

Ultrasound pretreatment is an effective technique to modify the thermal decomposition characteristics of wood. The peak of decomposition for specimens pretreated by ultrasound in aqueous soda solution is around 341 °C, while those for the control sample and samples pretreated in distilled water or acetic acid solution are around 308 and 361 °C. Ultrasound pretreatment influences the amounts, but not the kinds, of gaseous products: the absorption bands of volatile species are at the same wavenumbers for all the specimens. The gaseous products mainly constitute of CO, H$_2$O, CO$_2$, CH$_4$, CH$_3$COOH, and ether, and more gaseous products were produced at 361 °C than at 308 °C. Pretreatment time and conditions showed little effect on the amount of gaseous products for specimens pretreated in acetic acid solution or in distilled water, but a higher amount of gaseous products were produced for specimens pretreated in aqueous soda solution. Additionally, gaseous products varied with temperature, with different production patterns of CH$_3$COOH for the different samples. The process was endothermic for all the specimens, and the specimens pretreated in aqueous soda solution reacted over lower temperatures ($309–400$ °C) than specimens pretreated in aqueous acetic acid ($328–428$ °C), distilled water ($321–424$ °C), or the control group ($312–442$ °C). The reaction rate was faster for the specimens pretreated in aqueous soda solution compared to those with other pretreatment conditions. Additionally, compared to the control group, the heat flow for specimens pretreated in aqueous soda solution was much lower. Finally, the treatment of wood using alkaline conditions combined with hydrodynamic cavitation provides additional hydroxyl and hydroperoxy radicals to promote the degradation reaction and intensity the overall rates of reactions.

4. MATERIAL AND METHODS

4.1. Material. Eucalyptus (Eucalyptus grandis $\times$ Eucalyptus urophylla), a fast-growing wood in China that was provided by YuXiang Wood Products Co., Ltd, GuangXi, China, was taken as specimen. The samples were grinded to less than 0.5 mm in diameter in a grinder and then dried at the temperature of 100 °C and this H$_2$O$_2$ can be separated to generate hydroperoxy radical under alkaline conditions, and HOO$^-$ can react again with the residual H$_2$O$_2$ to generate highly reactive superoxide (O$_2^-$) and OH$^*$. The cellulose, hemicellulose, and lignin molecules react with themselves or with the hydroperoxy (HOO$^-$) and hydroxyl (OH$^*$) radicals formed during ultrasound cavitation to form carbon dioxide, organic acids, and other low molecular weight organic products by side chain elimination, ring opening, and other processes.$^{3,36–39}$

washed, and then dried at the temperature of $100 \pm 3$ °C to the oven dry.$^{40}$

4.3. TG–DSC–FTIR Analysis. A TG analyzer (Netzsch STA449F3, Germany) coupled with a differential scanning calorimeter and a Fourier transform infrared spectrometer (a TG–DSC–FTIR system) was used to compare the decomposition, gas release, and thermal characteristics of the untreated and treated eucalyptus powder samples using a heating rate of 10 °C/min and a final temperature of 900 °C in a nitrogen environment.$^{40}$

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**Notes**

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