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Abstract: Boric acid is recently proved to be a good substitute for conventional acidic catalytic materials. However, few studies used boric acid as a catalyst in biomass pyrolysis. This study focused on the catalytic effects of boric acid (BA) on pyrolysis behaviors of woody biomass. The birch wood flour (WF) was used as feedstock and treated by impregnation of boric acid solution. Both untreated and boric acid-treated samples (BW) were characterized by FTIR and SEM. Thermogravimetry (TG) and pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) techniques were used for studying mass loss, composition, and distribution of evolved volatiles formed from pyrolysis process. Additionally, a small fixed-bed pyrolyzer with an amplificated loading amount was used to prepare liquid products, and further, GC/MS were used to analyze the composition of these liquid products. Different pyrolysis temperatures and boric acid/wood flour mass ratios were also studied. The main results are as follows. Boric acid infiltrated into both cell cavity and cell wall through impregnation treatment. FTIR analysis showed that boric acid reacted with wood flour to form B-O-C bond during the treatment. After the treatment of boric acid, the initial degradation temperatures and residual carbon contents were increased, while the maximum weight loss rates were decreased. Boric acid significantly altered the composition and distribution of volatile pyrolysis products of wood flour. It significantly increased the contents of small molecule compounds such as acetic acid and furfural but, decreased the contents of phenol derivatives with high molecular weights. And these changes became more pronounced as the temperature increased. When mass ratio of boric acid (BA) to wood flour (WF) was 2, the acetic acid accounted for 91.28% of the total product in the pyrolysis liquid, which was 14 times higher than that of untreated wood flour. Boric acid effectively catalyzed fast pyrolysis of woody biomass to selectively produce acetic acid

Keywords: woody biomass; fast pyrolysis; boric acid; acetic acid; pyrolysis characteristics

## 1. Introduction

Environmental pollution and energy shortage have become the main contradictions restricting the sustainable development of economy and society. Biomass has attracted people's attention for its renewability, availability, carbon neutrality, less dependency on fossil fuels, and other advantages [1–4]. Woody biomass derived from trees is a vital biomass resource since new forests can be regenerated through afforestation and appropriate maintenance [5]. The construction scrap wood is almost completely utilized in construction materials. However, only a small amount of the wood wastes generated in wood products and paper industries, such as wood chips, lumber, and furniture mill sawdust were recycled to produce heat and electricity in power plants [6–8]. It is very important to make full use of the existing wood resources, especially waste wood. In fact, besides the direct combustion (burning) to produce heat, as the only renewable carbon resource, woody biomass also can be recycled to produce materials such as scrimber, fiberboards, and composites to produce solid, gaseous, and liquid fuels and to produce high value-added chemicals [9–12]. Thermochemical conversion processes, especially fast pyrolysis technology has been considered



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as a typical and promising method for effectively converting biomass into high-value chemicals and bio-fuels in a short time by rapid heating [2,13,14]. However, owing to the complexity of biomass structure and various pyrolysis reaction pathways, the bio-crude produced from biomass pyrolysis contains a large number of oxygenated compounds such as acids, aldehydes, ketones, dehydrated sugars and phenols, which make it difficult to be directly used as liquid fuel or chemicals [15,16]. Frequently, in order to promote the yield of desired chemicals, appropriate catalysts were used to adjust the composition and distribution of pyrolysis products via selectively enhancing some specific reactions that occur in the pyrolysis for this purpose [4,21–24]. HZSM-5 improves the acid and furan yields at low temperature by promoting dehydration and retro-aldol fragmentation during the in-bed catalytic pyrolysis of hemicellulose monosaccharide [19,25,26]. Zinc chloride promotes the formation of furfural by catalyzing the dehydration, depolymerization, and ring opening reactions of biomass [27].

Boric acid is recently proved to be a good substitute for conventional acidic catalytic materials [28–35]. It successfully catalyzed various types of reactions such as fructose dehydration, salicylic acid esterification, and condensation between aldehyde and ketone [28,29,31,32,35]. Additionally, it has been proved that boric acid can react with methanol and polyhydroxy compounds such as D-Mannitol, D-glucose, and D-fructose to form boric acid esters [32,33]. However, boric acid is rarely used as catalyst for biomass pyrolysis.

In fact, for several decades, boric acid, owing to its easy commercial availability and environmentally friendly characteristics, has been primarily used as a bactericide and flame retardant for wood biomass [5,36,37]. Boric acid could reduce the maximum degradation temperature and increase the residual char amount of wood biomass [38,39]. It is generally assumed that boric acid mainly plays a role in the inhibition of both heat and mass transfer during the biomass pyrolysis processes [33]. Moreover, some researchers stated that boric acid can act as a catalyst for some specific reactions, such as dehydration, isomerization, etc. [28,30,31,34,35]. Wang et al. presented that boric acid not only catalyzes dehydration and deoxidation reactions of wood at 100–300 °C but also catalyzes isomerization of newly formed intermediates to finally form aromatic structure and char [33]. Zhang et al. discovered that complexation and esterification reactions occur between wood fiber and boric acid, which promoted the char formation [34]. However, there are few reports about the preparation of chemicals from biomass catalyzing over boric acid.

Thus, this study aimed to catalytically convert woody biomass into chemicals such as acetic acid and furfural via fast pyrolysis over the boric acid. Acetic acid is often used as a solvent and raw material in agriculture, medicine, and the dyestuff industry, while furfural is a fundamental raw material of fine chemicals and widely applied in synthetic rubber, plastics, medicine, pesticides, and other industries [40,41]. In this study, birch wood flour (WF) was used as the feedstock and treated by impregnation with boric acid solution. The mass loss, composition, and distribution of evolved volatiles formed from pyrolysis process were studied by using thermogravimetry (TG) and Py-GC/MS techniques. Additionally, the pyrolysis liquid products were prepared by a small fixed-bed pyrolyzer and further analyzed by a GC/MS technique. Different pyrolysis temperatures and boric acid/wood flour mass ratios were also studied.

## 2. Results and Discussion

### 2.1. Feedstock Characterization

The feedstock used in this study was birch wood powder. The elemental analysis and proximate analysis as well as the chemical composition of birch feedstock are presented in Table 1.

Birch	Elemental (wt. %)						Proximate (wt. %)		
	С 44.52	Н 6.06	O   N   S   Volatile matter     6   45.71   3.16   0.55   79.43		<b>Volatile matter</b> 79.43	<b>Ash</b> 4.15	Fixed carbon 16.42		
	Chemical composition (wt. %)								
	Holocellulose 75.76			<b>Lignin</b> 23.02		<mark>α-cellulose</mark> 48.87		Extract 2.23	

Table 1. The proximate, elemental and compositional analyses of the birch feedstock.

### 2.2. FTIR Characteristics

Figure 1a displays the FTIR spectra of the untreated wood flour (WF), boric acid (BA), and BA/WF mixtures with different mass ratios (0.1:1, 0.5:1, 1:1, 2:1). Compared with those untreated samples and pure boric acid, new infrared absorption peaks appeared at 3200, 1375, 1340, 1195, 945, and 815 cm<sup>-1</sup> in the infrared spectrum of BA-treated wood flour. This not only proved the successfully loading of BA on wood flour, but also implied some reactions occurred after BA treatment. This is in accord with other research results showing that boric acid could react with wood fiber to form boron complex [34].



**Figure 1.** (a) FTIR spectra of wood flour (WF), boric acid (BA) and BA/WF mixtures with different ratios (0.1:1, 0.5:1, 1:1, 2:1 wt/wt); (b) Raman spectra of boric acid aqueous solution (with different concentrations).

In Raman spectra (Figure 1b), strong Raman scattering characteristic peaks can be observed at 601, 811, 988, 1118, and 1449  $\text{cm}^{-1}$ . The IR peak at 3200  $\text{cm}^{-1}$  was ascribed to the stretching vibration–OH in boric acid. The IR absorption peak at 1375 cm<sup>-1</sup> was attributed to the unsymmetrical stretching vibration of the B-O bond in B(OH)<sub>3</sub>. The absorption peak at 1340 cm<sup>-1</sup> was attributed to the bridge stretching vibration of the B-O-C bond [42], corresponding to the scattering characteristic peak at 1338  $\text{cm}^{-1}$  in the Raman spectrum. The flexural vibration of the B-O bond observed at  $1195 \text{ cm}^{-1}$  was in line with the Raman scattering peak at 1183 cm<sup>-1</sup> [42,43]. The weak infrared absorption peak at 945 cm<sup>-1</sup> indicated the existence of the -BO<sub>4</sub> bond. The peak at 1118 cm<sup>-1</sup> in the Raman spectrum was related to the B-O symmetric stretching vibration. Polyborate anions formed in the concentrated boric acid solution. The absorption peak at  $1270 \text{ cm}^{-1}$ belonged to the stretching vibration of the B-O bond in cyclic boride. It demonstrated that boric acid polymerize in aqueous solution [43,44]. The characteristic scattering vibrations of  $[B_6O_7(OH)_6]^{2-}$  can be observed at 967 cm<sup>-1</sup>. The symmetrical pulse vibration of  $[B_4O_5(OH)_4]^{2-}$  appeared at 554 cm<sup>-1</sup>. The Raman scattering at 732 cm<sup>-1</sup> was identified as the symmetric pulse vibration of  $[B(OH)_4]^-$ . The scattering characteristic vibration of  $[B_3O_3(OH)_4]^-$  appeared at 840 cm<sup>-1</sup>, and the symmetric pulse vibration of  $[B_3O_3(OH)_4]^$ appeared at 988 cm<sup>-1</sup>. These results suggest that self-polymerization reactions of boric

acid occur, forming boric acid trimer, tetramer, and hexamer in the processes of boric acid pretreatment and pyrolysis initial stage where approximated conditions existed.

### 2.3. Scanning Electron Microscopy

Figure 2 shows the SEM micrographs of different samples (the corresponding original images are shown in Figure S2 in the Supplementary Materials). Compared with untreated wood flour, the surface morphology of wood flour treated by boric acid changed significantly. The surface of untreated wood fiber was clean (Figure 2a), and it became uneven after treatment. In Figure 2b,c, the pits on the cell wall were blocked by boric acid, and in Figure 2d, boric acid filler was obviously seen in ray tracheid. Boric acid exists as solid sediments deposited in/on the cell cavity and cell wall of wood. This is in accord with the point that inorganic modifier with a small molecular weight could infiltrate into both cell cavity and cell wall through impregnation treatment [5]. With the increase of BA/WF ratio, the surface depositions of boric acid particles on wood fiber were increased. A glassy heterogeneous film of BA formed on the surface of wood fiber (Figure 2d,e). Figure 3 shows the electron energy spectrum of BW–1.0. It indicates the presence and uniform distribution of boron element.



**Figure 2.** The SEM images of (**a**) wood flour (WF) and BA/WF mixtures with different mass ratios ((**b**) BA/WF = 0.1; (**c**) BA/WF = 0.5; (**d**) and (**e**) BA/WF = 2.0;  $\times$ 1000).



Figure 3. The SEM and EDX images of the BW-1.0 sample (mass ratio of BA/WF is 1) (×1000).

#### 2.4. Pyrolysis Characteristics of Samples

Figure 4 shows the TG-DTG profiles of boric acid and boric acid-treated and untreated wood flour. Table 2 lists the pyrolysis characteristic parameters of all these samples. Boric acid initially decomposes into H<sub>2</sub>O (g) and metaboric acid (HBO<sub>2</sub>) at around 160 °C. Metaboric acid melts at about 236 °C and dehydrates to form pyroboric acid when heated above 300 °C. Further heating (about 330 °C) leads to boron trioxide [45]. The whole pyrolysis processes of all the samples except BA can be divided into approximately three stages. The mass loss at the first stage (50–200 °C) was mainly related to removal of water, CO<sub>2</sub>, CO, and other small molecule volatile compounds. The mass loss in the second stage (200–400 °C) was ascribed to the degradation of cellulose, hemicellulose, and lignin. Conversion of non-volatile and noncombustible parts of wood into tar or coke mainly occurred in the third stage (400–700 °C).



**Figure 4.** Thermogravimetry (TG) curves (**a**) and differential thermogravimetric (DTG) curves (**b**) from the thermal decomposition of wood flour (WF), boric acid (BA), and BA/WF mixtures with different ratios (0.1:1, 0.5:1, 1:1, 2:1 wt/wt).

(	т	т	Temperature Range of Most Weight Loss	Residual Mass (%)			
	₁ <sub>i</sub> (°C)	ι <sub>max</sub> (°C)		Experimental Value	Adjust Value	Theoretical Value	
WF	268.3	319.1	268.3-356.4	22.05	_	-	
BA	114.9	123.1	114.9-128.4	54.94	_	_	
BW-0.1	286.6	319.6	286.6-349.9	27.29	21.80	25.33	
BW-0.5	287.2	320.9	287.2-365.9	38.80	20.49	33.01	
BW-1.0	288.5	321.1	288.5-376.1	50.51	23.04	38.50	
BW-2.0	292.5	324.6	292.5-378.1	58.09	21.46	43.97	

Table 2. Pyrolysis parameters of all samples.

 $T_i$  (initial degradation temperature),  $T_{max}$  (the temperature corresponding to the maximum mass loss rate), and residual mass (in %) of BA impregnated WF measured at 700 °C; adjusted value was obtained by proportionally subtracting the residue mass value of boric acid from the related experimental value; theoretical value was acquired by simple mathematical summation of respective residue masses of both wood and BA components.

Boric acid treatment affected the thermochemical properties of wood flour significantly. The initial degradation temperatures ( $T_i$ ) and the temperature corresponding to the maximum mass loss rate ( $T_{max}$ ) as well as the residual carbon contents were increased, while the maximum weight loss rate was decreased. Compared with the untreated sample, the  $T_i$  values of the BA-treated samples (BW-0.1, BW-0.5, BW-1.0, and BW-2.0) increased by 6.82%, 7,04%, 7.53%, and 9.02%, respectively. It proved that boric acid remarkably improves the thermal stability of wood. The residual masses were increased by 23.76%, 83.54%, 129.07%, and 163.45%, respectively. These were consistent with Wang's results [33]. However, it is worth mentioning that besides the coke (fix carbon) and ash that originated

from the wood, boron trioxide that formed from BA dehydration was also included in the pyrolysis residue. An adjusted value for the real residue mass derived from wood was obtained by proportionally subtracting the residue mass value of boric acid from the related experimental value (Table 2). It is based on the hypotheses that, in the BA-treated wood samples, boric acid could dehydrate fully as it decomposes alone, generating a boron trioxide that exists in a form of glassy nonvolatile liquid substance in the temperature range from 450 °C (melting point) to 1860 °C (boiling point). In this case, boric acid had little impact on the residue formation of wood. Nevertheless, when comparing the experimental value of residue with its related theoretical value acquired by simple mathematical summation of respective residue masses of both wood and BA components, the values of all the formers were higher than those of the latters. This implied that there exists a chemical interaction between wood and boric acid. Wood may inhibit dehydration of BA from releasing water. In another words, some incompletely dehydrated products, such as tetraborate and boron triborate remained in the residue. BA may catalytically change the pyrolysis path of wood, presenting varied thermal stabilities and pyrolysis products. This is in accord with the views that boric acid can react with alcohols to form borate esters, especially, with polyols containing cis-vicinal diols, such as glycerol and mannitol, to form a boron-containing chelate [32].

### 2.5. Py-GC/MS Analysis of Samples

Py-GC/MS was used to investigate the composition and distribution of evolved volatiles formed from the pyrolysis process. Figure 5 shows the total ion chromatograms of pure wood flour and boric acid/wood flour mixtures with different mass ratios (0.1:1, 0.5:1, 1:1, 2:1) obtained by Py-GC/MS at 500 °C for 60 s. The main pyrolysis volatile's compositions and distributions of these samples were shown in Figure 6. Apparently, BA treatment simplified the product composition of the wood flour samples. Eighty-three kinds of compounds were detected in the volatile pyrolysis products of untreated wood powder. However, 80, 44, 28, and 9 kinds of compounds were detected for BA-treated wood samples with varied BA/WF mass ratios from 0.1:1, 0.5:1, 1:1, and 2:1, respectively (Figure 5). This finding indicates that boric acid selectively inhibits the formation of some products and promotes the formation of other products. These pyrolysis products were mainly divided into 11 categories: aldehydes, furans, ketones, acids, esters, alcohols, phenols, saccharides, benzenes, hydrocarbons, and nitrogenous compounds. Compounds like furfural, 5-hydroxymethylfurfural, methylglyoxal, and hydroxyacetaldehyde were mainly formed from pyrolysis of glucose-based carbohydrates. This is because the glycosidic bond in cellulose is relatively weak, and it was easy to crack under acidic or high temperature conditions, largely generating furans and levoglucosan [4,46,47]. Additionally, furans, ketones, acetic acid, and anhydrosugars were derived from hemicellulose pyrolysis [18,48,49]. Lignin is composed of phenylpropane units. The main pyrolysis products of lignin are phenol derivatives, acetic acid, methanol, and other small molecular compounds [50].

With the increase of the BA/WF ratio, the contents of ketones and phenols were decreased, while the contents of acids, furans and lipids were increased significantly. When the BA/WF mass ratio was 2.0, a small number of ketones and aldehydes were detected, while acids, furans, and esters became the main compounds in the pyrolysis products. Especially, acetic acid was the main compound, and its content reached about 39.66% (percentage of area). These results show that boric acid treatment varied the decomposition paths of cellulose and hemicellulose, while it inhibited the decomposition of lignin to form phenols.

### 2.6. Small Fixed-Bed Pyrolysis Study of Samples

The loading amount of sample required in the Py-GC/MS test is about 0.5 mg. It is difficult to calculate the mass change before and after pyrolysis. In order to figure out the mass balance, a serial of bench-scale pyrolysis experiments were carried out on a small fixed-bed pyrolysis reactor, of which the sample amount was about 0.2 g. Table 3 lists

the mass balance (yields of volatiles and non-volatile residues) obtained from pyrolysis of pure wood powder and BA-treated wood powders with different mass ratios. BA-treatment lowered the yields of volatile but improved the yields of solid products to some extent. Additionally, with the increase of boric acid usage, this trend became even more pronounced. As described in Section 2.3, the increasing residue yields were mainly attributed to the mixing of the increasing pyrolysis residues of boric acid.







**Figure 6.** The main classification of pyrolysis volatiles of wood flour (WF) and boric acid /wood flour mixtures (BW) with different mass ratios (0.1:1, 0.5:1, 1:1, 2:1) obtained by Py-GC/MS at 500 °C for 60 s.

<b>Table 3.</b> Volatile and solid	product y	yield of all	samples <sup>a</sup>
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	WF	BW-0.1	BW-0.5	BW-1.0	BW-2.0
$w_{(v)}\%$	$76.4\pm2.0$	$66.9 \pm 1.8$	$63.1\pm1.5$	$61.9 \pm 1.7$	$56.3\pm1.6$
$w_{(s)}\%$	$23.6\pm3.0$	$33.1\pm2.0$	$36.9\pm2.1$	$38.2 \pm 2.4$	$43.7\pm2.6$

<sup>a</sup> Experimental conditions: sample amount, 0.2 g; temperature, 500 °C.

Figure 7a compares the different total ion chromatograms of liquid products of untreated wood obtained by a small fixed-bed at varied pyrolysis temperatures of 400 °C, 450 °C, 500 °C, 550 °C, and 600 °C. In sequence, a similar chromatogram comparison of BA-treated wood samples with a BA/WF mass ratio of 0.1, 0.5, 1.0, and 2.0 are shown in Figure 7b–e. The total number of pyrolysis products of untreated wood, especially those compounds with high relative molecular weight (refers to long retention times) increased with the increasing of pyrolysis temperature. Whereas the relative contents of each product obtained at all the temperatures were very low, it implies that complex reactions occurred in the pyrolysis processes (Figure 7a). Compared with untreated wood sample, obvious changes were observed on the compositions and distributions of pyrolysis liquid products of BA-treated wood samples (Figure 7a–e). Boric acid treatment significantly increased the contents of small molecule compounds, such as acetic acid and furfural, but decreased the contents of phenol derivatives with high molecular weights. For the sample with a BA/WF mass ratio of 0.1, the product's composition and distribution changed obviously, the contents of boric acid and furfural were increased to some extent, but the composition of their pyrolysis products was still very complex. With the further increase of the boric acid dosage, especially when the mass ratio of boric acid/wood flour was over 0.1, the total types of pyrolysis products were reduced. Meanwhile, the content of single compound was increased obviously. Remarkably, acetic acid and furfural almost became the main compounds when the mass ratio of BA/WF was 2.0. It implies that boric acid changes the distributions and relative contents of pyrolysis products by effectively inhibiting the formation of phenol derivatives and promoting the formation of acetic acid, furfural, and other small molecular compounds. For all the BA-treated samples, the temperatures studied in this study (from 400 to 600 °C) had little effect on the distributions and compositions of the main products. In order to acquire a high liquid product's yield and low energy consumption, a modest temperature (500 °C) was fitted and selected for further study.



**Figure 7.** Gas chromatography and mass spectrometry (GC-MS) total ion chromatograms of liquid products from pyrolysis of (**a**) wood flour; (**b**) BA/WF = 0.1; (**c**) BA/WF = 0.5; (**d**) BA/WF = 1.0; (**e**) BA/WF = 2.0 at 400, 450, 500, 550, and 600 °C; (**f**) comparison of the contents of both boric acid and furfural produced by pyrolysis of untreated wood and BA-treated wood samples with varied BA/WF ratios at 500 °C.

Table 4 shows the typical pyrolysis product compositions and distributions of untreated sample and BA-treated samples with varied BA/WF ratios at 500 °C. The comparison of the contents of both boric acid and furfural, the main compounds among these products are shown in Figure 7f. Apparently, boric acid treatment significantly improved the content of acetic acid in pyrolysis products of wood sample. With the increasing of BA/WF ratio, the content of acetic acid increased gradually. When BA/WF ratio was 2.0, acetic acid content reached the maximum, accounting for 91.28% of the total content of all the detected products. This value was about 14 times higher than that of untreated wood sample. Conversely, the contents of phenol and its derivatives were decreased after boric acid treatment. The content of furfural in the pyrolysis liquid products of untreated wood sample was only 0.18%. After boric acid treatment, its content first rose with the increase of BA/WF value and reached the maximum, accounting for 16.79% of the liquid pyrolysis products before it descended gradually when BA/WF ratio was over 0.5.

**Table 4.** Peak area % of the typical pyrolysis products of wood flour (WF) and boric acid / wood flour mixtures (BW) with different mass ratios (0.1:1, 0.5:1, 1:1, 2:1) obtained by a small fixed-bed pyrolysis reactor at 500 °C.

Time tmin)   Compounds   WF   BW-0.1   BW-0.5   BW-1.0   BW-2.0     225   1.2-Ethanediol   -   -   11.47   -   -     297   Acetic acid   6.56   27.19   46.24   84.48   91.28     3.55   Propanoic acid   1.06   1.29   1.54   1.41   -     6.44   Methyl acetic acid ester   -   -   2.09   -   -     7.01   1-Hydroxy-3-methyl-2-butanone   1.44   0.067   -   -   -     7.72   Furfunal   0.18   4.19   0.679   10.57   2.81     7.99   2-Cyclopenten-1-one   1.43   1.48   1.75   0.64     8.38   5-Methyl-2(3H)-furanone,   0.74   0.78   -   -     9.00   1.2Acetryloxy-2methyl-anone,   0.74   0.76   -   -     9.35   2-Cyclopentene-1-one,   1.14   2.0   0.25   -   -     10.42   Buthyl-2-furanore   1.35 <th>Retention</th> <th></th> <th colspan="6">Peak Area (%)</th>	Retention		Peak Area (%)					
225   1.2-Ebhanediol   -   1.42   8.48   91.28     237   Acetia caid   6.56   27.19   1.64.24   84.48   91.28     355   Propanoic acid   1.06   1.29   1.54   1.41   -     470   H-Hydroxy-5-methyl-2-butanone   -   2.10   -   -     644   Methyl acetic acid ester   -   0.06   0.57   -   -     701   1-Hydroxy-2-propanone   1.48   0.96   0.57   -   -     717   3-Furaldehyde   -   -   0.74   -   -     722   Furfural   0.18   4.19   1.67   0.64     8.38   5-Methyl-2(3H)-furanone,   0.34   1.56   0.22   -   -     9.00   1.2(-Euranyl)-tehnone,   0.74   0.59   0.32   -   -     9.95   2.6(-Dihydro-2H-piran-2-one,   0.52   0.67   -   -     9.95   2.6(-Dihydro-2H-piran-2-one,   1.56   3.33	Time (min)	Compounds	WF	BW-0.1	BW-0.5	BW-1.0	BW-2.0	
2.97 Acetic acid 6.56 27.19 46.48 84.48 91.28   3.55 Propanoic acid 1.06 1.29 1.54 1.41 -   4.70 4-Hipdroxy-3-methyl-2-butanone - 2.00 - -   6.44 Methyl acetic acid ester - - 2.01 - -   7.01 1-Hydroxy-2-propanone 1.48 0.96 0.57 - -   7.17 3-Furaldehyde - - 0.03 0.32 - -   7.99 2-Cyclopenten-1-one 1.43 1.48 1.75 0.64   8.36 5-Methyl-2-cyclopenten-1-one, 0.74 0.59 0.32 - -   9.00 2-Methyl-2-cyclopenten-1-one, 0.44 0.74 0.79 0.32 - -   9.93 5.6-Dihydro: 2-Hypran-2-one, - 0.52 0.33 - - -   9.94 Phenol 12.68 8.44 4.30 - - -   9.95 2-Cyclopenten-1-one, 1.41 2.0 0.25 -	2.25	1,2-Ethanediol	-	-	11.47	-	-	
3.55 Propanoic acid 1.06 1.29 1.54 1.41 -   4.70 HHydroxy-3-methyl-2-butanone - 2.39 - -   6.44 Methyl acetic acid ester - - 2.01 - -   7.01 1-Hydroxy-3-repropanone 1.48 0.96 0.57 - -   7.27 Furfural 0.18 4.19 1.67 0.64   8.38 5-Methyl+2(3H)-furanone, - 0.36 0.32 - -   9.00 2-Methyl+2(3H)-furanone, 0.34 1.56 2.16 - -   9.09 1-(2-Furanyl)-teptana-cone, 0.34 1.56 2.16 - -   9.99 5.6-Dihydro-2H-pyran-2one, 0.52 0.33 - - - -   9.98 Phenol 12.26 8.44 4.30 2.6 2.0   10.47 3-Methyl-2-trunnarboxaldehyde, - 3.5 - - -   10.42 Butyrolactone 1.67 0.40 - - - -	2.97	Acetic acid	6.56	27.19	46.24	84.48	91.28	
4.70 4-Hydroxy-3-methyl-2-butanone - 2.00 - -   7.01 1-Hydroxy-2-propanone 1.48 0.96 0.57 - -   7.17 3-Furaldehyde - - 0.74 - -   7.22 Furfural 0.18 4.19 16.79 0.57 2.81   7.99 2-Cyclopenten-1-one 1.43 1.48 1.75 0.64   8.38 5-Methyl-2:syclopenten-1-one, 0.74 0.59 0.32 -   9.00 2-Methyl-2:syclopenten-1-one, 0.74 0.59 0.32 - -   9.00 1-42-Furanyl-fethanone, 0.34 1.56 2.16 - -   9.09 1-42-Furanyl-peran-2one, - 0.57 - - -   9.12 5.6-Dihydro:2-Hypran-2one, 1.48 2.6 2.0 -	3.55	Propanoic acid	1.06	1.29	1.54	1.41	-	
6.44 Methyl acetic acid ester - - 2.01 - -   7.01 1-Hydroxy-2-propanone 1.48 0.96 0.57 - -   7.17 3-Furaldehyde - - 0.74 - -   7.22 Furfural 0.18 4.19 16.79 10.57 2.81   7.99 2-Cyclopenten-1-one 1.43 1.48 1.75 0.64   8.36 5-Methyl-2/31/J furanone, 0.44 0.74 0.78 - -   9.00 2-Methyl-2/32 propanone, 0.44 0.74 0.78 - -   9.09 1-2/4 Furanyl-dychanene, 0.34 1.56 2.16 - -   9.93 5.6-Dihydro-2H-pyran-2one, - 0.52 0.33 - - -   10.42 Butyrolactone 1.67 0.40 - - - -   10.42 Butyrolactone 1.60 3.3 0.95 - - -   10.42 Stephyl-2-tyranone 1.03 3.095 - - -	4.70	4-Hydroxy-3-methyl-2-butanone	-	-	2.39	-	-	
7.01 1-Hrydroxy-2-propanone 1.48 0.96 0.57 - -   7.17 3-Furaidehyde - 0.74 - 0.74 - -   7.79 2-Cyclopenten-1-one 1.43 1.48 1.75 0.64   8.38 5-Methyl-2-gropanone, - 0.36 0.32 - -   9.00 2-Methyl-2-gropanone, 0.44 0.74 0.78 - -   9.00 2-Methyl-2-gropanone, 0.34 1.56 2.16 - -   9.09 1-(2-Furanyl)-ethanone, - 0.34 1.56 2.16 - -   9.98 Phenol 12.86 8.44 4.30 2.6 2.0   10.20 5-Methyl-2-gropanote, 1.14 2.0 0.57 - - -   10.47 3-Methyl-2-gropanote, 1.14 2.0 0.25 -	6.44	Methyl acetic acid ester	-	-	2.10	-	-	
7.17 $3$ -Furaidehyde - - 0.74 - -   7.72 Furfural 0.18 4.19 16.79 10.57 2.81   7.99 2-Cyclopenten-1-one 1.43 1.48 1.75 0.64   8.38 5-Methyl-2(31)-furanone, 0.44 0.74 0.78 - -   9.00 2-Methyl-2-cyclopenten-1-one, 0.34 0.56 2.16 - -   9.09 1.(2-Furanyl)-bethanone, 0.34 1.56 2.16 - -   9.39 5.6-Dilydro-2H-pyran-2-one, - 0.67 - - - 0.67 - -   9.98 Phenol 12.86 8.44 4.30 2.6 2.0   10.20 5-Methyl-2-furanorboxaldehyde, - 3.55 4.12 - -   10.47 3-Methyl-2-cyclopenten-1-one, 1.14 2.0 0.25 - -   10.47 3-Methyl-2-cyclopenten-1-one 1.30 0.35 - - -   11.42 2.3-Dimethyl-2-cyclopenten-1-one 1.73 0.57	7.01	1-Hydroxy-2-propanone	1.48	0.96	0.57	-	-	
7.72 Furfural 0.18 4.19 16.79 10.57 2.81   7.99 2-Cyclopenten-1-one 1.43 1.48 1.75 0.64   838 5-Methyl-2(3H)-furanone, - 0.36 0.32 -   9.00 2-Methyl-2-yclopenten-1-one, 0.74 0.59 0.32 - -   9.00 1-(2-Furanyl)-ethanone, 0.34 1.56 2.16 - -   9.39 5.6-Dihydro-2H-pyran-2-one, - 0.52 0.33 - - -   9.98 Phenol 12.86 8.44 4.30 2.6 2.00   10.20 5-Methyl-2-cyclopenten-1-one, 1.14 2.0 0.25 - -   10.47 3-Methyl-2-cyclopenten-1-one, 1.14 2.0 0.25 - -   11.17 2.5-Dihydro-3.5-furanone, 0.33 0.23 - - -   11.25 2.Hydroxy-3-methyl-2-cyclopenten-1-one 4.44 1.33 - - -   11.12 2.3-Dimethyl-2-cyclopenten-1-one 1.73 0.57 - - <td>7.17</td> <td>3-Furaldehyde</td> <td>-</td> <td>-</td> <td>0.74</td> <td>-</td> <td>-</td>	7.17	3-Furaldehyde	-	-	0.74	-	-	
7.992-Cyclopenten-1-one1.431.481.750.648.885-Methyl-2(3H)-furanone,0.360.329.002-Methyl-2-cyclopenten-1-one,0.740.590.329.091-(2-Furanyl)-ethanone,0.341.562.169.395,6-Dihydro-2H-pyran-2-one,-0.520.339.98Phenol12,868.444.302.62.010.205-Methyl-2-furancarboxaldehyde,-3.554.1210.42Butyrolactone1.670.4010.473-Methyl-2-furancarboxaldehyde,-3.30.2511.252.FHydroxy-3-methyl-2-cyclopenten-1-one,1.142.00.2511.252.Hydroxy-3-methyl-2-cyclopenten-1-one1.730.7711.422,3-Dimethyl-2-cyclopenten-1-one1.730.5711.422,3-Dimethyl-2-cyclopenten-1-one1.730.5711.422,3-Dimethyl-2-cyclopenten-1-one1.730.5711.253.Methyl-Phenol,1.221.1512.443.Vethyl-2-cyclopenten-1-one0.730.3912.453.Ethyl-2-hydroxy-2-cyclopenten-1-one1.730.5712.453.Methyl-2-cyclopenten-1-one <td< td=""><td>7.72</td><td>Furfural</td><td>0.18</td><td>4.19</td><td>16.79</td><td>10.57</td><td>2.81</td></td<>	7.72	Furfural	0.18	4.19	16.79	10.57	2.81	
838 5-Methyl-2(2H)-furnanone, - 0.36 0.32 -   846 1-(Acetyloxy)-2-propanone, 0.44 0.74 0.79 0.32 -   9.00 2-Methyl-2-cyclopenten-1-one, 0.74 0.59 0.32 -   9.09 1-(2-Furanyl)-ethanone, 0.34 1.56 2.16 -   9.33 5.6-Dihydro-2-Hypran-2-one, - 0.67 - -   9.98 Phenol 12.86 8.44 4.30 2.6 2.0   10.20 5-Methyl-2-cyclopenten-1-one, 1.14 2.0 0.25 - -   10.47 3-Methyl-2-cyclopenten-1-one, 1.14 2.0 0.25 - -   10.52 2(5H)-Furanone 1.50 3.3 0.95 - -   11.17 2.5-Dihydro-3.5-Methyl-2-cyclopenten-1-one 4.44 1.33 - - -   11.42 2.3-Dimethyl-2-cyclopenten-1-one 1.73 0.57 - - -   12.05 Methyl-2-cyclopenten-1-one, 0.79 1.06 - - -	7.99	2-Cyclopenten-1-one	1.43	1.48	1.75		0.64	
8.46 1-(Acetyloxy)-2-programone, 0.44 0.74 0.78 -   9.00 2-Mettyl-2-cyclopenten-1-one, 0.74 0.59 0.32 -   9.39 5.6-Dihydto-2H-pyran-2-one, - 0.52 0.33 - -   9.98 Phenol 12.86 8.44 4.30 2.6 2.0   10.20 5-Methyl-2-furancarboxaldehyde, - 3.55 4.12 - -   10.47 3-Methyl-2-cyclopenten-1-one, 1.14 2.0 0.25 - -   11.47 3-Methyl-2-cyclopenten-1-one 1.67 0.40 - - -   11.17 2.5-Dihydro-35-dimethyl-2-cyclopenten-1-one 1.44 2.0 0.25 - -   11.12 2-Hydroxy-3-methyl-2-cyclopenten-1-one 1.33 0.27 - - -   11.42 2.3-Dimethyl-2-cyclopenten-1-one 1.44 1.33 - - -   11.42 2.3-Dimethyl-2-cyclopenten-1-one 1.70 0.40 0.48 -   12.26 Methyl-phenol, 0.27 0.45 - -<	8.38	5-Methyl-2(3H)-furanone,	-	0.36	0.32	-	-	
9.00   2-Methyl-2-cyclopenten-1-one,   0.74   0.59   0.32   -   -     9.99   1-(2-Furanyl)-ethanone,   0.34   1.56   2.16   -   -     9.39   5,6-Dihydro-2H-pyran-2-one,   -   0.52   0.33   -   -     9.98   Phenol   12.86   8.44   4.30   2.6   2.0     10.20   5-Methyl-2-cyclopenten-1-one,   1.14   2.0   0.25   -   -     10.47   3-Methyl-2-cyclopenten-1-one,   1.14   2.0   0.25   -   -     10.52   2 (5H)-Furanone   1.50   3.3   0.95   -   -     11.17   2.5-Dihydro-3.5-dimethyl-2-cyclopenten-1-one   4.44   1.33   -   -   -     11.25   2-Hydroxy-3-methyl-2-cyclopenten-1-one   4.44   1.33   -   -   -   -     11.24   2,3-Dimethyl-2-cyclopenten-1-one   4.44   1.33   -   -   -   -     12.05   Methyl-phenol,   1.22   1.15	8.46	1-(Acetyloxy)-2-propanone,	0.44	0.74	0.78	-	-	
9.09 $1-(2^{2} \mu canyl)$ -ethanone,0.341.562.169.39 $5,6$ -Dihydro-2H-pyran-2-one,-0.520.339.95 $2$ -Cyclopentene-1,4-dione0.679.98Phenol12.868.444.302.62.010.42Butyrolactone1.670.4010.42Butyrolactone1.670.4010.473-Methyl-2-cyclopenten-1-one,1.142.00.2511.252.1flyforxy-3-methyl-2-cyclopenten-1-one1.330.2311.252.1flyforxy-3-methyl-2-cyclopenten-1-one1.730.5711.252.4flyforxy-3-methyl-2-cyclopenten-1-one1.730.5711.252.4flyforxy-3-methyl-2-cyclopenten-1-one1.730.5712.05Methyl benzoic acid ester0.230.3112.442.Methoxy-phenol,4.562.100.400.4812.553-Ethyl-2-hydroxy-2-cyclopenten-1-one,0.791.0612.893-Methyl-phenol,0.360.3913.052.2-Dihydroxy-2-cyclopenten-1-one,0.791.0613.052.2-Dihydroxy-2-cyclopenten-1-one,0.79 <td>9.00</td> <td>2-Methyl-2-cyclopenten-1-one,</td> <td>0.74</td> <td>0.59</td> <td>0.32</td> <td>-</td> <td>-</td>	9.00	2-Methyl-2-cyclopenten-1-one,	0.74	0.59	0.32	-	-	
9.39 5,6-Dihydro-2H-pyran-2-one, - 0.52 0.33 - -   9.55 2-Cyclopenteme-1,4-dione - - 0.67 - -   9.98 Phenol 12.86 8.44 4.30 2.6 2.0   10.20 5-Methyl-2-furancarboxaldehyde, - 3.55 4.12 - -   10.47 3-Methyl-2-cyclopenten-1-one, 1.14 2.0 0.25 - -   10.52 2.6HlyHoray-Sidimethyl 2-furanone, 0.33 0.23 - - -   11.17 2.5-Dihydro-3.5-dimethyl 2-cyclopenten-1-one 4.44 1.33 - - -   11.25 2-Hydroxy-3-methyl-2-cyclopenten-1-one 1.73 0.57 - - -   11.42 2.3-Dimethyl-2-hydrono, 4.25 2.10 0.40 0.48 -   12.05 Methyl benzoic acid ester 0.23 0.31 - - - -   12.24 3-(2-Furanyl)-2-propenal, - - 0.27 - - -   12.28 3-Ethyl-2-hydroxy-2-cyclopente	9.09	1-(2-Furanyl)-ethanone,	0.34	1.56	2.16	-	-	
9.55 2-Cyclopentene 1,4-dione - - 0.67 -   9.98 Phenol 12.86 8.44 4.30 2.6 2.0   10.42 Butyrolactone 1.67 0.40 - - -   10.42 Butyrolactone 1.67 0.40 - - -   10.47 3-Methyl-2-cyclopenten-1-one, 1.14 2.0 0.25 - -   11.25 2.Hydroxy-3-relepten-1-one 1.33 0.95 - - -   11.25 2.Hydroxy-3-methyl-2-cyclopenten-1-one 1.44 1.33 - - -   11.42 2.3-Dimethyl-2-cyclopenten-1-one 1.73 0.57 - - -   12.05 Methyl benzoic acid ester 0.23 0.31 - - - -   12.05 Methyl benzoic acid ester 0.23 0.31 - - - -   12.24 3(2-Furmehyl-phenol, 0.72 0.45 0.81 - - -   12.30 2.4-Dimethyl-phenol, 0.36 0.39 -	9.39	5,6-Dihydro-2H-pyran-2-one,	-	0.52	0.33	-	-	
9.98   Phenol   12.86   8.44   4.30   2.6   2.0     10.20   5-Methyl-2-furancarboxaldehyde,   -   3.55   4.12   -   -     10.47   Butyrolactone   1.67   0.40   -   -   -     10.52   2(5H)-Furanone,   1.14   2.0   0.23   -   -     11.17   2,5-Dihydro-3,5-dimethyl 2-furanone,   0.33   0.23   -   -   -     11.12   2-Hydroxy-3-methyl-2-cyclopenten-1-one   4.44   1.33   -   -   -   -     11.12   2-Methyl-Pacyclopenten-1-one   1.73   0.57   -   -   -     12.05   Methyl-Pacyclopenten-1-one   1.73   0.57   -   -   -     12.05   Methyl-Pacyclopenten-1-one   0.73   0.47   -   -   -     12.14   2-Methyl-Pacyclopenten-1-one,   0.79   1.06   -   -   -     12.24   3-(2-Furanyl)-2-propenal,   -   -   0.27   -	9.55	2-Cyclopentene-1,4-dione	-	-	0.67	-	-	
10.205-Methyl-2-furancarboxaldehyde, Butyrolactone-3.554.1210.42Butyrolactone1.670.4010.473-Methyl-2-cyclopenten-1-one, (11171.142.00.2511.252.Hydroxy-3-furnanne,0.330.9511.252.Hydroxy-3-methyl-2-cyclopenten-1-one1.141.3311.422.3-Dimethyl-2-cyclopenten-1-one1.730.5711.422.3-Dimethyl-2-cyclopenten-1-one1.730.5712.05Methyl benzoic acid ester0.230.3112.142-Methoxy-phenol,4.562.100.400.48-12.253-Ethyl-2-hydroxy-2-cyclopenten-1-one,0.791.0612.893-Methyl-phenol,0.470.4513.002.4-Dimethyl-phenol,0.360.3913.46Levoglucosenone-2.6213.45Ethoxy-cyclohexane,-2.6214.442.3-Dimethoyl-phenol,0.760.3713.652-Methoxy-4-methyl-phenol,0.760.3714.442.3-Dimethoyr-phenol,0.760.3713.652-Met	9.98	Phenol	12.86	8.44	4.30	2.6	2.0	
10.42Butyrolactone1.670.4010.473-Methyl-2-cyclopenten-1-one,1.142.00.2510.522.(5H)-Furanone,1.300.330.9511.172.5-Dinydro-3.5-dimethyl 2-furanone,0.330.2311.422.3-Dimethyl-2-cyclopenten-1-one1.730.5711.422.3-Dimethyl-2-cyclopenten-1-one1.730.5712.05Methyl-benzoic acid ester0.230.3112.142-Methoxy-Phenol,4.562.100.400.48-12.253-Ethyl-2-hydroxy-2-eyclopenten-1-one,0.791.0612.893-Methyl-cyclohexanone,0.720.450.8113.052.5-Dimethyl-phenol,0.470.4513.46Levoglucosenone-2.6713.46Levoglucosenone-2.6714.764-Ethyl-2-methoxy-phenol,2.480.3615.562-Methoxy-4-methyl-phenol,0.760.3715.872-Methoxy-4-tropyl-phenol,0.760.3715.851.23-Timethoxy-phenol,0.760.3715.851.24-Hydroxy-3-methoxy-phenol,0.750.21<	10.20	5-Methyl-2-furancarboxaldehyde,	-	3.55	4.12	-	-	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10.42	Butyrolactone	1.67	0.40	-	-	-	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10.47	3-Methyl-2-cyclopenten-1-one,	1.14	2.0	0.25	-	-	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10.52	2(5H)-Furanone	1.50	3.3	0.95	-	-	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	11.17	2,5-Dihydro-3,5-dimethyl 2-furanone,	0.33	0.23	-	-	-	
11.422,3-Dimethyl-2-cyclopenten-1-one1.730.5711.723-Methyl-phenol,1.221.1512.05Methyl benzoic acid ester0.230.3112.142-Methoxy-phenol,4.562.100.400.4812.243-(2-Furanyl)-2-propenal,0.2712.553-Ethyl-2-hydroxy-2-cyclopenten-1-one,0.790.450.8113.052,5-Dimethyl-phenol,0.470.4513.052,5-Dimethyl-phenol,0.470.45 <td>11.25</td> <td>2-Hydroxy-3-methyl-2-cyclopenten-1-one</td> <td>4.44</td> <td>1.33</td> <td>-</td> <td>-</td> <td>-</td>	11.25	2-Hydroxy-3-methyl-2-cyclopenten-1-one	4.44	1.33	-	-	-	
11.723-Methyl-phenol, Methyl benzoic acid ester1.221.1512.05Methyl benzoic acid ester0.230.3112.142-Methoxy-phenol,4.562.100.400.48	11.42	2.3-Dimethyl-2-cyclopenten-1-one	1.73	0.57	-	-	-	
12.05Methyl benzor acid ester0.230.3112.142-Methoxy-phenol,4.562.100.400.48-12.243-(2-Furanyl)-2-propenal,-0.2712.553-Ethyl-2-hydroxy-2-cyclopenten1-one,0.791.0612.893-Methyl-cyclohexanone,0.720.450.8113.052,5-Dimethyl-phenol,0.470.4513.202,4-Dimethyl-phenol,0.360.3913.612-Methoxy-4-methyl-phenol,2.091.8313.612-Methoxy-4-methyl-phenol,2.091.8313.64Levoglucosenone-2.6214.442,3-Dimethoxy-toluene0.150.0615.562-Methoxy-4-tonyl-phenol4.802.3615.572-Methoxy-4-tonyl-phenol,0.760.3715.872-Methoxy-phenol,9.851.9917.054-Ethoxy-openzeneacetic acid,0.2717.362-Methoxy-4-(1-propenyl)-phenol,4.233.8117.362-Methoxy-4-(1-propenyl)-phenol,0.6817.362-Methoxy-4-(1-propenyl)-phenol,0.6819.13<	11.72	3-Methyl-phenol.	1.22	1.15	-	-	-	
12.142-Methoxy-phenol, $3-(2-Furanyl)-2-propenal,$ 4.562.100.400.48-12.24 $3-(2-Furanyl)-2-propenal,$ 0.2712.55 $3-Ethyl-2-hydroxy-2-cyclopenten-1-one,$ 0.791.0612.89 $3-Methyl-cyclohexanone,$ 0.720.450.8113.05 $2,5$ -Dimethyl-phenol,0.470.4513.20 $2,4$ -Dimethyl-phenol,0.360.3913.46Levoglucosenone-2.6713.85Ethoxy-cyclohexane,-2.6214.442,3-Dimethoxytoluene0.150.0614.442,3-Dimethoxytoluene0.150.0615.562-Methoxy-4-vinyl-phenol,2.480.3615.872-Methoxy-4-trinyl-phenol,0.760.3715.852.6-Dimethoxy-phenol,9.851.9915.872-Methoxy-4-(1-propenyl)-phenol,0.890.3517.362-Methoxy-4-(1-propenyl)-phenol,4.233.8117.724-Hydroxy-3-methyl-benzene,3.1719.132-(4-Guaiacyl)-ethanol0.6819.28(E)-Stilbene6.593.36 <td>12.05</td> <td>Methyl benzoic acid ester</td> <td>0.23</td> <td>0.31</td> <td>-</td> <td>-</td> <td>-</td>	12.05	Methyl benzoic acid ester	0.23	0.31	-	-	-	
12.243-(2-Furanyl)-2-propenal, 3-Ethyl-2-hydroxy-2-cyclopenten-1-one, 0.790.791.0612.553-Ethyl-2-hydroxy-2-cyclopenten-1-one, 0.720.791.0612.893-Methyl-cyclohexanone, 0.25-Dimethyl-phenol,0.470.450.8113.052.5-Dimethyl-phenol, 0.24-Dimethyl-phenol,0.360.3913.46Levoglucosenone-2.6713.612-Methoxy-4-methyl-phenol, 2.352.091.8314.442.3-Dimethoxytoluene0.150.0614.764-Ethyl-2-methoxy-phenol, 2-Methoxy-4-vinyl-phenol4.802.3615.872-Methoxy-4-vinyl-phenol, Eugenol0.760.3715.852.5-Dimethoxy-bhenol, 2-Methoxy-4-vinyl-phenol,9.851.9915.862.401.900.2715.851.2,3-Trimethoxy-benzoic acid, 2-Methoxy-4-(1-propenyl)-phenol,4.233.8117.362-Methoxy-4-(2-propenyl)-phenol, 2-Methoxy-4-(2-propenyl)-phenol,0.6817.724-Hydroxy-3-methoxy-benzoic acid, 2-2.52.750.2119.132-(4-Guaiacyl)-ethanol 0.68<	12.14	2-Methoxy-phenol.	4.56	2.10	0.40	0.48	-	
12.553-Ethyl-2-hydroxy-2-cyclopenten-1-one, 3-Methyl-cyclohexanone,0.791.0612.893-Methyl-cyclohexanone, (2,5-Dimethyl-phenol,0.470.450.8113.052,5-Dimethyl-phenol,0.360.3913.202,4-Dimethyl-phenol,0.360.3913.46Levoglucosenone-2.6713.85Ethoxy-cyclohexane,-2.6214.764-Ethyl-2-methoxy-phenol,2.480.3615.562-Methoxy-4-vinyl-phenol4.802.3615.872-Methoxy-4-propyl-phenol,0.760.3715.862-Methoxy-4-propyl-phenol,0.760.3715.872-Methoxy-4-propyl-phenol,9.851.9917.054-Ethoxy-benzeneacetic acid,0.2717.724-Hydroxy-3-methoxy-benzoic acid,2.750.2119.132-(4-Guaiacyl)-phenol,4.6819.28(E)-Stilbene6.593.3617.724-Hydroxy-3,5-dimethoxy-benzoic acid,0.550.9919.132-(4-Guaiacyl)-phenol,10.6412.2719.28(E)-Stilbene6.59<	12.24	3-(2-Furanyl)-2-propenal.	_	_	0.27	-	-	
12.893-Methyl-cyclohexanone, 2,5-Dimethyl-phenol,0.720.450.8113.052,5-Dimethyl-phenol,0.470.4513.202,4-Dimethyl-phenol,0.360.3913.46Levoglucosenone-2.6713.612-Methoxy-4-methyl-phenol,2.091.8313.85Ethoxy-cyclohexane,-2.6214.442,3-Dimethoxytoluene0.150.0614.764-Ethyl-2-methoxy-phenol,2.480.3615.562-Methoxy-4-vinyl-phenol4.802.3615.872-Methoxy-4-propyl-phenol,0.760.3715.95Eugenol0.890.3517.054-Ethoxy-benzeneacetic acid,0.2717.724-Hydroxy-3-methoy-benzene,3.1719.132-(4-Guaiacyl)-ethanol0.6819.28(E)-Stilbene6.593.3619.28(E)-Stilbene0.550.9921.26n-Hexadecanoic acid0.550.9921.281-(2,4,6-Trihydroxyphenyl)-2-pentanone0.8922	12.55	3-Ethyl-2-hydroxy-2-cyclopenten-1-one,	0.79	1.06	-	-	-	
13.052,5-Dimethyl-phenol,0.470.4513.202,4-Dimethyl-phenol,0.360.3913.46Levoglucosenone-2.6713.612-Methoxy-4-methyl-phenol,2.091.8313.85Ethoxy-cyclohexane,-2.6214.442,3-Dimethoxytoluene0.150.0614.764-Ethyl-2-methoxy-phenol,2.480.3615.562-Methoxy-4-vinyl-phenol4.802.3615.872-Methoxy-4-propyl-phenol,0.760.3716.662,6-Dimethoxy-phenol,9.851.9917.054-Ethoxy-benzeneacetic acid,0.2717.724-Hydroxy-3-methoxy-benzoic acid,2.750.21 <td>12.89</td> <td>3-Methyl-cyclohexanone.</td> <td>0.72</td> <td>0.45</td> <td>0.81</td> <td>-</td> <td>-</td>	12.89	3-Methyl-cyclohexanone.	0.72	0.45	0.81	-	-	
13.202,4-Dimethyl-phenol,0.360.3913.46Levoglucosenone-2.6713.612-Methoxy-4-methyl-phenol,2.091.8313.85Ethoxy-cyclohexane,-2.6214.442,3-Dimethoxytoluene0.150.0614.764-Ethyl-2-methoxy-phenol,2.480.3615.562-Methoxy-4-vinyl-phenol4.802.3615.872-Methoxy-4-propyl-phenol,0.760.3715.95Eugenol0.890.3516.662,6-Dimethoxy-phenol,9.851.9917.362-Methoxy-4-(1-propenyl)-phenol,4.233.8117.724-Hydroxy-3-methoxy-benzoic acid,2.750.2119.132-(4-Guaiacyl)-ethanol0.6819.28(E)-Stilbene6.593.3621.741-(4-Hydroxy-3,5-dimethoxy-phenyl)-phenol,10.6412.2721.741-(4-Hydroxy-3,5-dimethoxy-phenyl)-ethanone0.8221.741-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone0.8922.92Dibutyl phthalate0.370.27	13.05	2,5-Dimethyl-phenol,	0.47	0.45	-	-	-	
13.46Levoglucosenone-2.6713.612-Methoxy-4-methyl-phenol,2.091.8313.85Ethoxy-cyclohexane,-2.6214.442,3-Dimethoxytoluene0.150.0614.764-Ethyl-2-methoxy-phenol,2.480.3615.562-Methoxy-4-vinyl-phenol4.802.3615.872-Methoxy-4-propyl-phenol,0.760.3715.95Eugenol0.890.3516.662,6-Dimethoxy-phenol,9.851.9917.054-Ethoxy-benzeneacetic acid,0.2717.724-Hydroxy-3-methoxy-benzoic acid,2.750.2119.132-(4-Guaiacyl)-phenol,4.6819.28(E)-Stilbene6.593.3621.26n-Hexadecanoic acid0.550.9921.741-(4-Hydroxy-3,5-dimethoxy-phenyl)-phenol,10.6412.2721.741-(2,4,6-Trihydroxyphenyl)-ethanone0.8922.92Dibutyl phthalate0.370.27	13.20	2,4-Dimethyl-phenol,	0.36	0.39	-	-	-	
13.61 2-Methoxy-4-methyl-phenol, 2.09 1.83 - - -   13.85 Ethoxy-cyclohexane, - 2.62 - - -   14.44 2,3-Dimethoxytoluene 0.15 0.06 - - -   14.76 4-Ethyl-2-methoxy-phenol, 2.48 0.36 - - -   15.56 2-Methoxy-4-vinyl-phenol 4.80 2.36 - - -   15.87 2-Methoxy-4-propyl-phenol, 0.76 0.37 - - -   15.95 Eugenol 0.89 0.35 - - - -   16.66 2,6-Dimethoxy-phenol, 9.85 1.99 - - - -   17.05 4-Ethoxy-benzeneacetic acid, 0.27 -	13.46	Levoglucosenone	-	2.67	-	-	-	
13.85 Ethoxy-cyclohexane, - 2.62 - - -   14.44 2,3-Dimethoxytoluene 0.15 0.06 - - -   14.76 4-Ethyl-2-methoxy-phenol, 2.48 0.36 - - -   15.56 2-Methoxy-4-vinyl-phenol 4.80 2.36 - - -   15.87 2-Methoxy-4-propyl-phenol, 0.76 0.37 - - -   15.95 Eugenol 0.89 0.35 - - -   16.66 2,6-Dimethoxy-phenol, 9.85 1.99 - - -   17.05 4-Ethoxy-benzeneacetic acid, 0.27 - - - -   17.05 4-Ethoxy-smethoxy-benzeneacetic acid, 0.27 - - - -   17.72 4-Hydroxy-3-methoxy-benzeneacic acid, 0.27 - - - -   18.55 1,2,3-Trimethoxy-5-methyl-benzene, 3.17 - - - -   19.13 2-(4-Guaiacyl)-ethanol 0.68 - - - - <td>13.61</td> <td>2-Methoxy-4-methyl-phenol.</td> <td>2.09</td> <td>1.83</td> <td>-</td> <td>-</td> <td>-</td>	13.61	2-Methoxy-4-methyl-phenol.	2.09	1.83	-	-	-	
14.442,3-Dimethoxytoluene0.150.0614.764-Ethyl-2-methoxy-phenol,2.480.3615.562-Methoxy-4-vinyl-phenol4.802.3615.872-Methoxy-4-propyl-phenol,0.760.3715.95Eugenol0.890.3516.662,6-Dimethoxy-phenol,9.851.9917.054-Ethoxy-benzeneacetic acid,0.2717.362-Methoxy-4-(1-propenyl)-phenol,4.233.8117.724-Hydroxy-3-methoxy-benzoic acid,2.750.2118.551,2,3-Trimethoxy-5-methyl-benzene,3.1719.132-(4-Guaiacyl)-ethanol0.6819.28(E)-Stilbene6.593.3620.222,6-Dimethoxy-4-(2-propenyl)-phenol,10.6412.2721.26n-Hexadecanoic acid0.550.9921.741-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone0.8222.181-(2,4,6-Trihydroxyphenyl)-2-pentanone0.8922.92Dibutyl phthalate0.370.27	13.85	Ethoxy-cyclohexane,	-	2.62	-	-	-	
14.764-Ethyl-2-methoxy-phenol,2.480.3615.562-Methoxy-4-vinyl-phenol4.802.3615.872-Methoxy-4-propyl-phenol,0.760.3715.95Eugenol0.890.3516.662,6-Dimethoxy-phenol,9.851.9917.054-Ethoxy-benzeneacetic acid,0.2717.724-Hydroxy-3-methoxy-benzoic acid,2.750.2118.551,2,3-Trimethoxy-5-methyl-benzene,3.1719.132-(4-Guaiacyl)-ethanol0.6819.28(E)-Stilbene6.593.3620.222,6-Dimethoxy-4-(2-propenyl)-phenol,10.6412.2721.741-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone0.8221.741-(2,4,6-Trihydroxyphenyl)-ethanone0.8922.92Dibutyl phthalate0.370.27	14.44	2,3-Dimethoxytoluene	0.15	0.06	-	-	-	
15.562-Methoxy-4-vinyl-phenol4.802.3615.872-Methoxy-4-propyl-phenol,0.760.3715.95Eugenol0.890.3516.662,6-Dimethoxy-phenol,9.851.9917.054-Ethoxy-benzeneacetic acid,0.2717.362-Methoxy-4-(1-propenyl)-phenol,4.233.8117.724-Hydroxy-3-methoxy-benzoic acid,2.750.2118.551,2,3-Trimethoxy-5-methyl-benzene,3.1719.132-(4-Guaiacyl)-ethanol0.6819.28(E)-Stilbene6.593.3620.222,6-Dimethoxy-4-(2-propenyl)-phenol,10.6412.2721.26n-Hexadecanoic acid0.550.9921.741-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone0.8222.181-(2,4,6-Trihydroxyphenyl)-2-pentanone0.8922.92Dibutyl phthalate0.370.27	14.76	4-Ethyl-2-methoxy-phenol.	2.48	0.36	-	-	-	
15.872-Methoxy-4-propyl-phenol, Eugenol0.760.3715.95Eugenol0.890.3516.662,6-Dimethoxy-phenol, 4-Ethoxy-benzeneacetic acid,9.851.9917.054-Ethoxy-benzeneacetic acid, 2-Methoxy-4-(1-propenyl)-phenol, 17.724.233.8117.724-Hydroxy-3-methoxy-benzoic acid, 2-(4-Guaiacyl)-ethanol2.750.2119.132-(4-Guaiacyl)-ethanol0.6819.28(E)-Stilbene6.593.3620.222,6-Dimethoxy-4-(2-propenyl)-phenol, 10.6410.6412.2721.26n-Hexadecanoic acid0.550.9921.741-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone0.8222.181-(2,4,6-Trihydroxyphenyl)-2-pentanone0.8922.92Dibutyl phthalate0.370.27	15.56	2-Methoxy-4-vinyl-phenol	4.80	2.36	-	-	-	
15.95 Eugenol 0.89 0.35 - - -   16.66 2,6-Dimethoxy-phenol, 9.85 1.99 - - -   17.05 4-Ethoxy-benzeneacetic acid, 0.27 - - - -   17.36 2-Methoxy-4-(1-propenyl)-phenol, 4.23 3.81 - - -   17.72 4-Hydroxy-3-methoxy-benzoic acid, 2.75 0.21 - - -   18.55 1,2,3-Trimethoxy-5-methyl-benzene, 3.17 - - - -   19.13 2-(4-Guaiacyl)-ethanol 0.68 - - - -   19.28 (E)-Stilbene 6.59 3.36 - - -   20.22 2,6-Dimethoxy-4-(2-propenyl)-phenol, 10.64 12.27 - - -   21.26 n-Hexadecanoic acid 0.55 0.99 - - -   21.74 1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone 0.82 - - - -   22.18 1-(2,4,6-Trihydroxyphenyl)-2-pentanone 0.89 - -	15.87	2-Methoxy-4-propyl-phenol,	0.76	0.37	-	-	-	
16.66 2,6-Dimethoxy-phenol, 9.85 1.99 - - -   17.05 4-Ethoxy-benzeneacetic acid, 0.27 - - - -   17.36 2-Methoxy-4-(1-propenyl)-phenol, 4.23 3.81 - - -   17.72 4-Hydroxy-3-methoxy-benzoic acid, 2.75 0.21 - - -   18.55 1,2,3-Trimethoxy-5-methyl-benzene, 3.17 - - - -   19.13 2-(4-Guaiacyl)-ethanol 0.68 - - - -   19.28 (E)-Stilbene 6.59 3.36 - - -   20.22 2,6-Dimethoxy-4-(2-propenyl)-phenol, 10.64 12.27 - -   21.26 n-Hexadecanoic acid 0.55 0.99 - - -   21.74 1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone 0.82 - - - -   22.18 1-(2,4,6-Trihydroxyphenyl)-2-pentanone 0.89 - - - -   22.92 Dibutyl phthalate 0.37 0.27 -	15.95	Eugenol	0.89	0.35	-	-	-	
17.05 4-Ethoxy-benzeneacetic acid, 0.27 - - - -   17.36 2-Methoxy-4-(1-propenyl)-phenol, 4.23 3.81 - - -   17.72 4-Hydroxy-3-methoxy-benzoic acid, 2.75 0.21 - - -   18.55 1,2,3-Trimethoxy-5-methyl-benzene, 3.17 - - - -   19.13 2-(4-Guaiacyl)-ethanol 0.68 - - - -   19.28 (E)-Stilbene 6.59 3.36 - - -   20.22 2,6-Dimethoxy-4-(2-propenyl)-phenol, 10.64 12.27 - -   21.26 n-Hexadecanoic acid 0.55 0.99 - - -   21.74 1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone 0.82 - - -   22.18 1-(2,4,6-Trihydroxyphenyl)-2-pentanone 0.89 - - - -   22.92 Dibutyl phthalate 0.37 0.27 - - - -	16.66	2.6-Dimethoxy-phenol.	9.85	1.99	_	-	-	
17.36 2-Methoxy-4-(1-propenyl)-phenol, 4.23 3.81 - - -   17.72 4-Hydroxy-3-methoxy-benzoic acid, 2.75 0.21 - - -   18.55 1,2,3-Trimethoxy-5-methyl-benzene, 3.17 - - - -   19.13 2-(4-Guaiacyl)-ethanol 0.68 - - - -   19.28 (E)-Stilbene 6.59 3.36 - - -   20.22 2,6-Dimethoxy-4-(2-propenyl)-phenol, 10.64 12.27 - -   21.26 n-Hexadecanoic acid 0.55 0.99 - - -   21.74 1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone 0.82 - - -   22.18 1-(2,4,6-Trihydroxyphenyl)-2-pentanone 0.89 - - - -   22.92 Dibutyl phthalate 0.37 0.27 - - - -	17.05	4-Ethoxy-benzeneacetic acid.	0.27	_	-	-	-	
17.72 4-Hydroxy-3-methoxy-benzoic acid, 2.75 0.21 - - -   18.55 1,2,3-Trimethoxy-5-methyl-benzene, 3.17 - - - -   19.13 2-(4-Guaiacyl)-ethanol 0.68 - - - -   19.28 (E)-Stilbene 6.59 3.36 - - -   20.22 2,6-Dimethoxy-4-(2-propenyl)-phenol, 10.64 12.27 - -   21.26 n-Hexadecanoic acid 0.55 0.99 - - -   21.74 1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone 0.82 - - - -   22.18 1-(2,4,6-Trihydroxyphenyl)-2-pentanone 0.89 - - - -   22.92 Dibutyl phthalate 0.37 0.27 - - - -	17.36	2-Methoxy-4-(1-propenvl)-phenol.	4.23	3.81	_	-	-	
18.55 1,2,3-Trimethoxy-5-methyl-benzene, 3.17 - - - -   19.13 2-(4-Guaiacyl)-ethanol 0.68 - - - -   19.28 (E)-Stilbene 6.59 3.36 - - -   20.22 2,6-Dimethoxy-4-(2-propenyl)-phenol, 10.64 12.27 - -   21.26 n-Hexadecanoic acid 0.55 0.99 - - -   21.74 1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone 0.82 - - - -   22.18 1-(2,4,6-Trihydroxyphenyl)-2-pentanone 0.89 - - - -   22.92 Dibutyl phthalate 0.37 0.27 - - -	17.72	4-Hydroxy-3-methoxy-benzoic acid,	2.75	0.21	-	-	-	
19.13 2-(4-Guaiacyl)-ethanol 0.68 - - - -   19.13 2-(4-Guaiacyl)-ethanol 0.68 - - - -   19.28 (E)-Stilbene 6.59 3.36 - - -   20.22 2,6-Dimethoxy-4-(2-propenyl)-phenol, 10.64 12.27 - -   21.26 n-Hexadecanoic acid 0.55 0.99 - - -   21.74 1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone 0.82 - - - -   22.18 1-(2,4,6-Trihydroxyphenyl)-2-pentanone 0.89 - - - -   22.92 Dibutyl phthalate 0.37 0.27 - - -	18.55	1.2.3-Trimethoxy-5-methyl-benzene.	3.17	-	-	-	-	
19.28 (E)-Stilbene 6.59 3.36 - - -   20.22 2,6-Dimethoxy-4-(2-propenyl)-phenol, 10.64 12.27 - - -   21.26 n-Hexadecanoic acid 0.55 0.99 - - -   21.74 1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone 0.82 - - - -   22.18 1-(2,4,6-Trihydroxyphenyl)-2-pentanone 0.89 - - - -   22.92 Dibutyl phthalate 0.37 0.27 - - -	19.13	2-(4-Guajacyl)-ethanol	0.68	-	_	-	-	
20.22 2,6-Dimethoxy-4-(2-propenyl)-phenol, 10.64 12.27 - - -   21.26 n-Hexadecanoic acid 0.55 0.99 - - -   21.74 1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone 0.82 - - - -   22.18 1-(2,4,6-Trihydroxyphenyl)-2-pentanone 0.89 - - - -   22.92 Dibutyl phthalate 0.37 0.27 - - -	19.28	(E)-Stilbene	6.59	3.36	-	-	-	
21.26n-Hexadecanoic acid0.550.9921.741-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone0.8222.181-(2,4,6-Trihydroxyphenyl)-2-pentanone0.8922.92Dibutyl phthalate0.370.27	20.22	2.6-Dimethoxy-4-(2-propenyl)-phenol.	10.64	12.27	-	-	-	
21.741-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone0.8222.181-(2,4,6-Trihydroxyphenyl)-2-pentanone0.8922.92Dibutyl phthalate0.370.27	21.26	n-Hexadecanoic acid	0.55	0.99	_	-	-	
22.181-(2,4,6-Trihydroxyphenyl)-2-pentanone0.8922.92Dibutyl phthalate0.370.27	21.20	1-(4-Hydroxy-3.5-dimethoxyphenyl)-ethapone	0.82	-	-	_	-	
22.92 Dibutyl phthalate 0.37 0.27	21.7 1	1-(2 4 6-Trihydroxyphenyl)-2-pentanone	0.89	_	-	_	-	
	22.10	Dibutyl phthalate	0.37	0.27	-	_	-	
10tal 96.23 98.13 99.27 99.54 96.73	Total		96.23	98.13	99.27	99.54	96.73	

"-" refers to "not detected".

It is worth noting that BA pre-treatment of woody samples change the morphology and the nature of the samples (confirmed by the SEM analyses) to some extent. This indicates that BA pre-treatment leads to some chemical transformation, for instance, partial hydrolysis of a wood sample. In order to find out whether the catalytic effect in the pyrolysis process or the structural change in the pretreatment process leads to the change of the pyrolysis products, the sample treated with boric acid was pyrolyzed after removal of boric acid, and its pyrolytic products were compared with those of untreated sample and boric acid treated sample (Figure 8a). Figure 8 shows their product distributions (a) and acetic acid contents (b) obtained at 500 °C. The results show that both of them had an effect on the composition of the pyrolysis products, and that the latter was more significant. The acetic acid content of the BA-treated sample was about 6 times that of the untreated sample, but after removing boric acid, the value was about 2 times that of the untreated sample. Apparently, boric acid treatment has a positive effect on the formation of acetic acid while inhibiting the production of phenols, which were mainly derived from lignin pyrolysis. Both catalytic effects in the pyrolysis process and structural change in the pretreatment process are responsible for this.



**Figure 8.** (a) Total ion chromatograms and (b) acetic acid contents of WF (wood flour), BW-1 (BA/WF mixture with a mass ratio 1) and BW-0 (BA-treated wood sample after removing boric acid) obtained by a small fixed-bed pyrolysis reactor at 500  $^{\circ}$ C.

Acetic acid is mainly produced by pyrolysis of cellulose and hemicellulose [4,51]. In the pyrolysis process of hemicellulose, O-acetyl group was released by both fracture of the  $C_2$ -O bridged bond and ring-opening of the intermediates to produce acetic acid [52,53]. Secondary cracking of pyrolysis intermediates of cellulose may produce acetic acid too. Besides, acetic acid may form by further cracking of the acetyl group in the aliphatic chain of lignin components. Furfural and its derivative were the primary products of pyrolysis of cellulose and hemicellulose. Furfural compounds may form in two ways: (1) direct decomposition of oligosaccharides and (2) first, after oligosaccharides are converted to levoglucosan (LG) and levoglucosenone (LGO), and then LG/LGO is converted to furfural [4,54]. Additionally, the increase of furfural content may also be due to a decrease in the crystallinity of cellulose by boric acid impregnation (Figure S1). The cellulose with low crystallinity more easily formed furfural compounds [4]. Boric acid is a weak, monobasic Lewis acid of boron. However, some of its behavior toward some chemical reactions suggests it to be tribasic acid in the Brønsted sense as well. Therefore, although the detail mechanism of boric acid on wood pyrolysis is not completely clear, it is supposed that boric acid, like other acid catalysts, may fuction as an acid catalyst in promoting the ring-opening and cracking of cellulose, hemicellulose, and monosaccharides, resulting in an increase in the content of acetic acid, furfural, and other small molecule compounds. Besides, the converse variation trends for the contents of furfural and acetic acid at the high boric acid dosage imply that a competition exists between the formation of furfural and acetic acid. Moreover, furfural may convert into acetic acid in some form under these conditions.

#### 3. Materials and Methods

## 3.1. Sample Preparation

White birch wood was used as raw material for woody biomass in all experiments. It was obtained from Heilongjiang Province, China. The as-received birch wood was ground in a high-speed rotary cutting mill (DC 3-1, Benchen Technology Co, Ltd., Shenzhen, China) and screened to with a particle size of 180~250 µm using a standard vibrating screen (BZS-200, CHINT, Jinan, China). The obtained sample (WF) was then dried at 105 °C for 48 h. Boric acid (BA), with a AR grade, purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd. (Dongli District, Tianjin, China), was oven-dried at 103 °C overnight before use.

The boric acid treated wood flour samples (BW) were prepared by impregnating the wood flour with boric acid aqueous solution. Samples with varying mass ratios of BA to WF (0.1, 0.5, 1.0, and 2.0 were marked as BW-0.1, BW-0.5, BW-1.0, and BW-2.0 separately) were obtained by adjusting the BA concentration. For example, first, to get BW-1.0 sample, 2.0 g of boric acid was added into a beaker that with about 100 mL of distilled water. Secondly, the beaker was heated in a water bath pot (preheated at 50 °C) and stirred often until the BA completely dissolved in the water. Third, 2.0 g of wood powder was added into the BA aqueous solution, stirred fully with a glass rod for about 30 min. Then the beaker was sealed with plastic wrap, kept in a dry place for 24 h to ensure that the wood flour was fully impregnated by boric acid solution. Finally, the sample was placed in an oven (set at  $103 \pm 2$  °C) for 24–48 h until the sample's weight remained unchanged.

### 3.2. Sample Characterization

The proximate analysis including volatile matter (VM %), moisture, and ash (%) of the samples was performed in accordance with standard procedures delineated in American Society Standard Test Method (ASTM E870-82 (2013)). The fixed carbon (FC %) was specified through subtracting VM %, M %, and ash % from 100%. The ultimate analyses of C, H, N, and S in the samples were done using an elemental analyzer (Vario MACRO cube, Elementar, Hanau, Germany), and O was calculated by the difference of C, H, N, and S results from 100%. The content of synthetic cellulose was determined according to GB/T 2677.10-1995, the content of a-cellulose was determined according to GB/T 744-1989, the content of lignin was determined according to GB/T 2677.8-1994, and the content of extract was determined by ethanol method.

### 3.3. Scanning Electron Microscopy

The sample was attached to a conductive adhesive on the sample table. The microstructures of the samples were observed through a S3400 scanning electron microscope (SEM, Thermo Fisher Scientific, Waltham, MA, USA) after being sprayed gold. The microconsolidation state of boric acid and distribution in the wood was analyzed by scanning the boron element using the energy dispersive X-ray (EDX) spectrometer combined with the SEM.

## 3.4. FTIR and Raman Spectroscope

The FTIR analysis of sample was determined at room temperature by using an FTIR instrument (Nicolet FTIR 6700, Thermo Fisher Scientific, Waltham, MA, USA). FTIR data were collected in the region between 4000 cm<sup>-1</sup> and 600 cm<sup>-1</sup> with 32 scans at a spectral resolution of 4 cm<sup>-1</sup> via an ATR mode (Ge crystal) by using MCT detector with which liquid nitrogen was used as a refrigerant.

Raman spectra of liquid samples were recorded in the ranges of  $100-3200 \text{ cm}^{-1}$  on a Raman spectrometer (Renishaw inVia, Renishaw, London, UK) by using the following test conditions: laser: 532 nm, exposure time: 10 s, laser power (%): 50; accumulative times: 10. The liquid samples were kept on glass slides.

### 3.5. Py-GC/MS Experiment

Py-GC/MS experiment was performed on a Pyroprobe pyrolyzer (5200 series, CDS, USA) connected with GC/MS instrument (6890 GC/5973N MSD, Agilent, Palo alto, CA, USA). First, a 0.40 mg  $\pm$  2 mg amount of sample was fed into the quartz tube with quartz wool on both sides and then placed into the pyroprobe. The pyroprobe was initially set for 40 °C and then ramped at 20 °C/ms to the final temperature of 500 °C for 60 s. Then, the pyrolytic volatile products were transferred to the GC system and separated on the Agilent 122-4732 DB-17MS capillary column (30.0 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m film thickness). The split ratio was 10:1 with helium carrier gas flow of 1 mL/min. The injector temperature was kept at 250  $^{\circ}$ C, and the transfer line temperature was 285  $^{\circ}$ C to avoid condensation or adsorption of semi-volatile products. The GC oven temperature was programmed at initial 40 °C for 4 min, and then increased to 270 °C (5 min) with a heating rate of 10 °C/min, finally to 280 °C (5 min) with the heating rate of 10 °C/min. MS was operated under the electron ionization of 70 eV with a full scan mass/charge (m/z) range of 20–550. The temperatures of MS ion source and quadrupole were 230 °C and 150 °C, respectively. Py-GC/MS analysis for each sample was repeated twice and found with proper repeatability. The compounds obtained through GC/MS were identified via The National Institute of Standards and Technology (NIST) database by closet match in NIST MS Search 2.3 using identify type searching. The relative percentage content of a product was semi-quantified by comparing the peak area of the product with the total peak area of all detected products.

### 3.6. TGA Experiment

Thermogravimetric analysis, showing the loss in sample weight in response to increasing reaction temperature, was conducted at heating rates of 10 °C / min using TGA instrument (TG 209 F1 Libra, NETZSCH, Selb, Germany) from 30 °C to 700 °C. Small amounts of biomass samples about  $5 \pm 0.2$  mg) were used in alumina pans in each analysis. The scavenging air was O<sub>2</sub>, the protective air was Ar, and the airflow was 50 and 30 mL/min, respectively.

### 3.7. A Bench-Scale Fixed-Bed Pyrolysis Experiment

The series of bench-scale pyrolysis experiments were carried out on a small fixedbed pyrolysis reactor. First, an amount of sample (0.2 g) was fed into the quartz tube with quartz wool on both sides. Then, the tube was rapidly placed into the pyroprobe (Pyrojector II, SGE, Ringwood, Australian) and kept for 5 min to full pyrolysis of the sample when the expected temperature (500  $^{\circ}$ C) in the pyrolyzing furnace was ready. Almost simultaneously, the pyrolytic volatiles were swept out by purged gas (nitrogen), condensed, and further collected as the liquid products. The as-received liquid products were diluted in methanol for immediate GC-MS analysis (6890 GC/5973N MSD, Agilent, Palo alto, CA, USA). The sample was injected into the gas injection port with a manual GC syringe needle of 1 µL. The temperature of the injection port was 250 °C. The sample was separated on a Agilent 122-4732 DB-17MS capillary column (30.0 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m) using helium (1 mL/min) as the carrier gas with the split ratio of 30:1. The GC oven temperature was programmed at initial 40 °C for 4 min and then increased to 270 °C (5 min) with a heating rate of 10 °C/min, finally to 280 °C (5 min) with the heating rate of 10 °C/min. MS was operated under the electron ionization of 70 eV with a full scan mass/charge (m/z) range of 20-550.

For material balance, all the input weight and coke weight were obtained by weighing on a balance with a precision of 0.1 mg. The desired input weight ( $m_{\text{feed}}$ ) was obtained by weighing the tube before and after sample loading. The weight of non-volatile solid residue ( $m_s$ , including coke and tar) was acquired by weighing the pyrolysis tube (loaded with starting material) before and then again after reaction. The weight of the pyrolysis volatiles ( $m_v$ , volatile substance includes the condensable liquid products and all non-condensable gas and vaporized chemicals) was acquired by deducting the non-volatile coke weight from the input weight (amount of starting material). Based on it, the yields of volatiles  $(w_v\%)$  and solid residue  $(w_s\%)$  are calculated by Equations (1) and (2), respectively.

$$w_{\rm s}\% = m_{\rm s}/m_{\rm feed} \times 100\% \tag{1}$$

$$w_{\rm v} \% = m_{\rm v} / m_{\rm feed} \times 100\%$$
 (2)

where  $m_s$  refers to the weight of non-volatile solid residue,  $m_v$  refers to the weight of pyrolysis volatiles, and  $m_{feed}$  refers to the input weight of the starting materials.

# 4. Conclusions

Via impregnation treatment, boric acid successfully infiltrated into wood cell cavity and deposited on the cell wall evenly, helping boric acid function effectively in pyrolysis processes. FTIR analysis not only indicated that boric acid successfully deposited on wood flour, moreover it implied that some reactions occurred after BA treatment. TG-DTG analysis implied that there was a chemical interaction between boric acid and wood. Boric acid catalytically changed the pyrolysis path of wood, improving the thermal stabilities of wood remarkably; while wood may inhibit the BA dehydration from releasing water, it maintained some polyborate anions (incompletely dehydrated products of boric acid) in the residues. BA treatment simplified the product compositions of the wood flour samples. Specifically, it varied the decomposition paths of cellulose and hemicellulose to form acetic acid as the main product, while it inhibited the decomposing of lignin to form phenols. With the increasing of the BA/WF ratio, the content of acetic acid was increased gradually. Conversely, the contents of phenol and its derivatives were decreased after boric acid treatment. Converse variation trends for the contents of furfural and acetic acid at the high boric acid dosage implied that a competitive mechanism existed between them. Boric acid treatment significantly promoted the formation of acetic acid from biomass. It was mainly related to the catalytic effect of boric acid during the pyrolysis process and the partial hydrolysis of wood flour during the pretreatment process. The study provides a promising route for the preparation of acetic acid from woody biomass.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/2073-434 4/11/4/494/s1, Figure S1: X-ray diffraction pattern of boric acid (BA), cellulose, boric acid-treated cellulose (BA/Cellulose = 1.0), Figure S2: The original SEM figures of (a) wood flour (WF) and BA /WF mixtures with different mass ratios ((b) BA/WF = 0.1; (c) BA/WF = 0.5; (d) and (f) BA/WF = 1.0; (e) BA/WF = 2.0).

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