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Maximizing Anhydrosugar Production from Fast Pyrolysis of Eucalyptus Using Sulfuric Acid as an Ash Catalyst Inhibitor

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Abstract: Anhydrosugars, such as levoglucosan (LG), are high value-added chemicals which are mainly derived from fast pyrolysis of pure cellulose. However, fast pyrolysis of raw lignocellulosic biomass usually produces a very low amount of levoglucosan, since alkali and alkaline earth metals (AAEM) present in the ash can serve as the catalysts to inhibit the formation of levoglucosan through accelerating the pyranose ring-opening reactions. In this study, eucalyptus was impregnated with H_2SO_4 solutions with varying concentrations (0.25–1.25%). The characteristics of ash derived from raw and H₂SO₄-impregnated eucalyptus were characterized by X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD). The pyrolysis behaviors of raw and H₂SO₄-impregnated eucalyptus were performed on the thermogravimetric analysis (TGA) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). TG analysis demonstrated that the H₂SO₄-impregnated eucalyptus produced less char than raw eucalyptus. Py-GC/MS analysis showed that even small amounts of H₂SO₄ can obviously improve the production of anhydrosugars and phenols and suppressed the formation of carboxylic acids, aldehydes, and ketones from fast pyrolysis of eucalyptus. The rank order of levoglucosan yield from raw and impregnated eucalyptus was raw < 1.25% H₂SO₄ < 1% $H_2SO_4 < 0.75\%$ $H_2SO_4 < 0.25\%$ $H_2SO_4 < 0.5\%$ H_2SO_4 . The maximum yield of levoglucosan (21.3%) was obtained by fast pyrolysis of eucalyptus impregnated with 0.5% H₂SO₄, which was close to its theoretical yield based on the cellulose content. The results could be ascribed to that H₂SO₄ can react with AAEM (e.g., Na, K, Ca, and Mg) and lignin to form lignosulfonate, thus acting as an inhibitor to suppress the catalytic effects of AAEM during fast pyrolysis of eucalyptus.

Keywords: eucalyptus; fast pyrolysis; acid impregnation; H₂SO₄; inhibitor; anhydrosugar

1. Introduction

The growing consumption of fossil fuels and the resulting environmental issues demand renewable resources to partly replace fossil fuels for the production of power, heat, liquid fuels, and chemicals [1–4]. Lignocellulosic biomass, as the only renewable carbonaceous resource, is being studied worldwide for the production of liquid fuels and chemicals from both academia and industry.



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Technologies for using biomass to produce liquid fuels and chemicals include pyrolysis, gasification, fermentation, catalytic conversion, and their hybrid processes [5]. One of the most promising technologies is fast pyrolysis due to its highest yield of pyrolysis liquid and lowest production cost [6–8]. Fast pyrolysis of biomass usually requires middle temperatures (400–600 °C), a high heating rate (>1000 °C/s), short vapor residence time (<2 s), inert atmosphere, and rapid quenching of the pyrolysis vapors, forming three fractions: char, permanent gas, and bio-oil [9–11]. The objective of fast pyrolysis is to minimize secondary reactions such as cracking, condensation, and polymerization for maximizing the yield of bio-oil. The yield of bio-oil can reach up to 50–75 wt% on a dry basis, depending upon biomass species and operating conditions. Bio-oil mainly comprises of water and hundreds of organic oxygenates, such as anhydrosugars, carboxylic acids, aldehydes, alcohols, ethers, ketones, esters, and oligomeric lignin [12–14].

Anhydrosugars are important platform molecules for the synthesis of pharmaceuticals, petrochemicals, polymers, and plastics. It is widely accepted that fast pyrolysis of pure cellulose can get a high yield of levoglucosan [15,16]. However, fast pyrolysis of raw lignocellulosic biomass typically generates a very low yield of levoglucosan when compared with the theoretical yield based on its cellulose content. Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin [17,18]. In addition, it also contains moisture and minor amounts of extractives and ash. The complicated compositions of biomass intensely affect the production distribution from fast pyrolysis. Considerable studies have been focused on the effect of chemical structure and composition on the product distribution from fast pyrolysis of biomass and its components [19–22]. It is found that alkali and alkaline earth metals (AAEM) in the ash is the most powerful factor in determining the yields of anhydrosugars. The alkali and alkaline earth metals, especially Na, K, Ca, and Mg, can act as catalysts for accelerating pyranose ring fragmentation resulting in the decrease in the yields of anhydrosugars and the increase in the yields of low molecular compounds (e.g., aldehydes and ketones) [23–25].

To date, many methods for removing or passivating the AAEM in biomass have been reported for enhancing the production of anhydrosugars from fast pyrolysis of biomass. Mourant and coworkers demonstrated that the removal of AAEM present in mallee wood by water washing and acid washing did not cause obvious changes in the yields of bio-oil and bio-char from fast pyrolysis. However, the removal of AAEM can significantly improve the yield of anhydrosugars and reduce the yields of water and low molecular compounds [26]. Zheng and co-workers found that microwave treatment of corncobs in glycerol can effectively remove the AAEM in raw corncobs, thus significantly improving the yield of levoglucosan in subsequent fast pyrolysis [27]. Brown and Garcia-Perez demonstrated that the passivation of AAEM using mineral acid can significantly enhance the yield of levoglucosan from fast pyrolysis of biomass [28,29]. Sui and co-workers showed that fast pyrolysis of bagasse impregnated with sulfuric acid or phosphoric acid at low temperature favored the formation of levoglucosenone [30]. Blasi suggested that H_2SO_4 can catalyze the selective pyrolysis of corncobs into furfural. However, there is still a lack of in-depth insight into the functions of H₂SO₄ during fast pyrolysis of acid-impregnated biomass. Hence, in this study, the effects of different H_2SO_4 concentrations on the product distributions from fast pyrolysis of H₂SO₄-impregnated eucalyptus were systematically investigated, especially the variation trends of anhydrosugars, furans phenols, carboxylic acids, aldehydes, and ketones. The functions of H₂SO₄ during fast pyrolysis were further explored by comparing the production distribution from fast pyrolysis of cellulose mixed with H₂SO₄ and ash derived from H₂SO₄-impregnated eucalyptus.

2. Results and Discussion

2.1. X-Ray Fluorescence Spectroscopy (XRF) and XRD Analysis of Ash from Raw and H₂SO₄-Impregnated Eucalyptus

The contents of selected elements in the ash were determined by XRF. As shown in Table 1, potassium (K), calcium (Ca), Sodium (Na), magnesium (Mg), sulfur (S), and chlorine (Cl) are the

major elements in the two ashes. The ash from 0.5% H₂SO₄-impregnated eucalyptus has a very high S content of 15.02 wt% and a relative low Cl content of 0.40 wt%, while the other ashes exhibited opposite trends, indicating that the thermally stable sulfur-containing compounds were formed, and the chlorine-containing compounds were evaporated during pyrolysis of 0.5% H₂SO₄-impregnated eucalyptus. After H₂SO₄ impregnation and washing, the contents of AAEM (K, Ca, Na, and Mg,) in ash were slightly reduced due to the effect of washing by solutions and the dilution by S.

Flomont	Elemental Analysis (wt%)			
Element	Α	SA		
K	21.20	18.60		
Ca	13.64	9.50		
Na	5.61	5.11		
Mg	3.30	3.22		
Mn	1.70	1.44		
Fe	1.42	1.62		
Р	1.31	1.29		
S	0.77	15.02		
Cl	4.09	0.40		

Table 1. Elemental analysis of ash.

A: Ash from raw eucalyptus. SA: Ash from 0.5 wt% H₂SO₄-impregnated eucalyptus.

The XRD patterns of the two ashes are shown in Figure 1. The diffraction peaks found at $2\theta = 28.4^{\circ}$, 40.6° , 50.3° , 58.8° , 66.5° , and 73.9° in ash from raw eucalyptus corresponded to the (200), (220), (222), (400), and (422) crystal planes of KCl (JCPDS 41-1476). It is worthy of noting that the ash from 0.5 wt% H₂SO₄-impregnated eucalyptus showed a very different diffraction pattern. Its diffraction peaks were well matched with the standard JCPDS 74-0398 for K₃Na(SO₄)₂. The results demonstrated that K was predominantly in the form of KCl and K₃Na(SO₄)₂ in the ashes from raw and 0.5% H₂SO₄-impregnated eucalyptus, respectively. It was consistent with the result of XRF.



Figure 1. XRD patterns of the two ashes. A: Ash from raw eucalyptus. SA: Ash from 0.5 wt% H_2SO_4 -impregnated eucalyptus.

2.2. Thermogravimetric Analysis of Raw and H₂SO₄-Impregnated Eucalyptus

The pyrolysis behaviors of raw and H_2SO_4 -impregnated eucalyptus are examined by thermogravimetric analysis. The thermogravimetric (TG)/differential thermal gravity (DTG) curves of raw and H_2SO_4 -impregnated eucalyptus are given in Figure 2, and their corresponding characteristic

parameters are presented in Table 1. The DTG curve shows a small shoulder at approximately 285 °C, which could be mainly described as the degradation of hemicellulose. The sharp peak that appears at a higher temperature is probably due to the thermal decomposition of cellulose [31]. As the H_2SO_4 concentrations increased, the maximum weight loss rates (D_{max}) first changed slightly and then gradually decreased. At the same time, the peak temperature (T_{max}) corresponding to the maximum weight loss rate shifted toward lower temperature. It is well accepted that AAEM could effectively catalyze the pyrolysis of cellulose, thus lowering the activation energy and improving the reaction rate. After H₂SO₄ impregnation, AAEM could react with H₂SO₄ to form thermally stable compounds without catalytic ability, resulting in the reduction in the weight loss rate and its peak temperature. The results indicated that H₂SO₄ could act as an inhibitor to suppress the catalytic activity of AAEM during pyrolysis of H₂SO₄-impregnated eucalyptus. As shown in Table 2, the rank order of char yield was HCl-washed eucalyptus < H₂SO₄-impregnated eucalyptus < raw eucalyptus. HCl washing could effectively remove the AAEM present in the raw eucalyptus. The char yield of HCl-washed eucalyptus was evidently lower than those of raw and H₂SO₄-impregnated eucalyptus, indicating that AAEM played key roles in the formation of char during pyrolysis of eucalyptus. H₂SO₄ could act as an inhibitor to suppress the catalytic functions of AAEM. The results suggested that AAEM could simultaneously catalyze the pyranose ring-opening reactions and the char formation reactions during pyrolysis of biomass. Both the removal and passivation of AAEM could reduce the formation of char [32].



Figure 2. Thermogravimetric (TG) and differential thermal gravity (DTG) analysis of raw and H_2SO_4 -impregnated eucalyptus: (**a**) TG curves of raw and H_2SO_4 -impregnated eucalyptus, (**b**) DTG curves of raw and H_2SO_4 -impregnated eucalyptus.

Feedstocks	Char Yield (at 800 °C, wt%)	T _{max} (°C)	D _{max} (wt%/°C)	
raw	23.81	340.3	1.10	
0.25% H ₂ SO ₄	15.16	338.6	1.14	
0.5% H ₂ SO ₄	17.31	319.7	0.85	
0.75% H ₂ SO ₄	18.24	316.7	0.75	
$1\% H_2SO_4$	22.83	312.1	0.69	
1.25% H ₂ SO ₄	18.21	305.7	0.57	
Demineralized	8.54	343.2	1.46	

Table 2. The pyrolysis characteristic parameters of raw and H₂SO₄-impregnated eucalyptus.

T_{max}: the corresponding temperature of the maximum weight loss rate. D_{max}: the maximum weight loss rate.

2.3. Product Distributions from Fast Pyrolysis of Raw and H₂SO₄-Impregnated Eucalyptus

The product distributions from fast pyrolysis of raw and H₂SO₄-impregnated eucalyptus are presented in Table 3. The identified compounds were classified into six groups according their main function groups: aldehydes, ketones, furans, phenols, acids, and anhydrosugars. It is evident that the product distributions from fast pyrolysis of eucalyptus were drastically altered by H₂SO₄ impregnation. As shown in Table 3, the contents of anhydrosugars, furans, and phenols were significantly improved by H₂SO₄-impregnation, whereas the contents of acids, aldehydes, and ketones was obviously reduced by H₂SO₄ impregnation. Hydroxy acetaldehyde and 1-hydroxy-2-propanone are typically considered as the products from ring-opening reactions of hemicellulose and cellulose via AAEM catalyzed retro-aldol condensation. Their contents were obviously reduced by H₂SO₄ impregnation. Additionally, their lowest contents were achieved at the H_2SO_4 concentrations of 1.25%. The results demonstrated that H₂SO₄ can serve as an inhibitor to suppress AAEM catalyzed retro-aldol condensation during fast pyrolysis of eucalyptus, thus reducing the yields of low molecular compounds, such as hydroxy acetaldehyde and 1-hydroxy-2-propanone. Furfural, levoglucosan, and levoglucosenone, are the most representative and commercially valuable products from fast pyrolysis of cellulose and hemicellulose. Furfural is usually produced from acid-catalyzed dehydration of hemicellulose. The content of furfural from eucalyptus was promoted by H₂SO₄ impregnation. The content of furfural increased from 1.90% to 2.83% when the 0.25% H_2SO_4 was impregnated with raw eucalyptus. As the H_2SO_4 concentration increased from 1.0% to 1.25%, the content of furfural was sharply raised from 2.74% to 6.83%, indicating that H₂SO₄ mainly acted as a catalyst for accelerating the dehydration reaction when H_2SO_4 concentration was greater than 1.0%. The content of levoglucosan was sharply enhanced by H_2SO_4 impregnation. As the H_2SO_4 concentration increased from 0% to 0.25%, the content of levoglucosan increased from 9.88% to 43.2% and reached the maximum value. As the H₂SO₄ concentration further increased from 0.5% to 1.25%, the content of levoglucosan gradually declined from 43.2% to 27.95%. It is speculated that H_2SO_4 first served as an inhibitor to suppress the catalytic functions of AAEM, resulting in the sharp increase in the content of levoglucosan. H₂SO₄ then acted as a catalyst for accelerating the formation of dehydrated product, leading to the enhancement in the contents of furfural and levoglucosenone and the decrease in the content of levoglucosan. The variation trend of levoglucosenone with different H_2SO_4 concentration strongly supported this speculation. Levoglucosenone is mainly generated by acid-catalyzed dehydration of levoglucosan. As shown in Table 4, the content of levoglucosenone is very low from fast pyrolysis of raw eucalyptus. Its content was also evidently improved by H_2SO_4 impregnation and reached the highest value of 2.38% at the H₂SO₄ concentration of 1.25%. Acetic acid is predominantly formed from pyrolysis of hemicellulose, particularly from the O-acetylxylan and 4-O-methylglucuronic acid units [33]. The content of acetic acid was reduced by H_2SO_4 impregnation. Phenols are mainly derived from pyrolysis of lignin. The H₂SO₄-impregnated eucalyptus produced more phenols than the raw eucalyptus, especially 2-methoxy-4-vinylphenol (MVP) and 2-methoxy-4-(1-propenyl)-phenol (MPP). As the concentration of H₂SO₄ increased, the content of MVP and MPP first increased and then dropped. The results could be

due to that both AAEM and excess H₂SO₄ could catalyze the polycondensation of lignin to form more char and less phenols.

			Content ^a /%					
Time (min)	Compounds	Davy	H ₂ SO ₄ Concentration (wt%)					
()	()		0.25	0.5	0.75	1	1.25	
4.762	Acetaldehyde		1.49	1.16	1.38	1.32	1.12	
8.306	Acetaldehyde, hydroxy-	2.82	0.84	0.98	0.55	0.59	0.3	
37.615	4-Methyl-2,5-dimethoxybenzaldehyde	2.85	0.93	1.1	0.74	0.85	0.48	
41.216	Benzaldehyde,4-hydroxy-3,5-dimethoxy-	1.53	0.67	0.71	0.54	0.62	0.48	
42.629	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	0.89	0.7	0.8	0.69	0.68	0.72	
	Total of aldehydes	10.19	4.63	4.76	3.89	4.07	3.10	
5.657	Acetone	0.58	0.42	0.29	0.39	0.38	0.48	
7.146	Methyl vinyl ketone	0.29	0.28	0.15	0.23	0.2	0.31	
7.212	2,3-Butanedione	0.75	0.44	0.34	0.38	0.35	0.32	
10.568	2-Propanone, 1-hydroxy-		0.94	0.74	0.61	0.68	0.58	
13.819	1-Hydroxy-2-butanone	0.41	0.55	0.07	0.35	0.5	0.15	
19.587	2-Cyclopenten-1-one, 2-hydroxy-	1.5	0.59	0.54	0.45	0.45	0.48	
22.668	1,2-Cyclopentanedione, 3-methyl-	1.28	0.58	0.55	0.51	0.51	0.52	
26.953	Levoglucosenone	0.05	0.25	0.31	1.16	0.8	2.38	
	Total of ketones	8.58	4.04	2.99	4.07	3.87	5.22	
15.939	Furfural	1.9	2.83	2.21	3.07	2.74	6.83	
17.334	2-Furanmethanol	0.38	0.21	0.21	0.22	0.25	0.28	
20.435	2-Furancarboxaldehyde, 5-methyl-	0.27	0.36	0.36	0.33	0.29	0.55	
21.406	2(5H)-Furanone	0.6	0.21	0.19	0.16	0.18	0.18	
31.857	5-Hydroxymethylfurfural	0.46	0.81	0.76	0.59	0.63	0.56	
	Total of furans		4.43	3.73	4.36	4.10	8.40	
23.498	Phenol	0.46	0.35	0.26	0.32	0.35	0.38	
24.129	Phenol, 2-methoxy-	0.78	0.5	0.64	0.49	0.6	0.7	
27.07	Creosol	0.41	0.32	0.36	0.3	0.42	0.41	
30.886	2-Methoxy-4-vinylphenol	1.46	2.62	3.02	3.49	3.72	2.46	
31.508	Phenol, 2-methoxy-3-(2-propenyl)-	0.27	0.12	0.11	0.11	0.1	0.2	
32.253	Phenol, 2,6-dimethoxy-	2.31	1.23	1.36	1.16	1.43	1.6	
34.204	Phenol, 2-methoxy-4-(1-propenyl)-	1.4	2.2	2.55	2.34	2.48	1.71	
39.17	(E)-2,6-Dimethoxy-4-(propenyl)phenol	0.55	0.15	0.17	0.15	0.16	0.21	
	Total of phenols	7.65	7.59	8.47	8.36	9.27	7.77	
9.323	Acetic acid		4.17	3.44	3.38	3.57	4.07	
	Total of acids	7.42	4.17	3.44	3.38	3.57	4.07	
40.179	levoglucosan	9.88	40.14	43.2	41.33	38.93	27.95	
43.45	1,6-Anhydro-β-D-glucofuranose (AGF)	1.05	5.09	4.98	5.27	5.62	5.89	
	Total of anhydrosugars	11.85	49.31	53.57	53.58	50.02	37.63	

Table 3. The product distributions from fast pyrolysis of raw and H₂SO₄-impregnated eucalyptus.

^a: The relative chromatographic area.

The yields of levoglucosan and 1,6-Anhydro- β -D-glucofuranose (AGF) from fast pyrolysis of raw and H₂SO₄-impregnated eucalyptus are illustrated in Figure 3. The yield of levoglucosan was 3.6% from fast pyrolysis of raw eucalyptus. It was found that even small amounts of H₂SO₄ can drastically improve the yield of levoglucosan due to the low content of inherent AAEM in raw eucalyptus. The yields of levoglucosan from 0.25% H₂SO₄-impregnated eucalyptus were 17.8%. The maximum yield of levoglucosan (21.3%) was achieved by fast pyrolysis of 0.5% H₂SO₄-impregnated eucalyptus. The value was close to its theoretical yield based on the cellulose content. As the H₂SO₄ concentration further increased from 0.5% to 1.25%, the yield of levoglucosan decreased from 21.3% to 9.8%. The results also supported that H₂SO₄ mainly served as an inhibitor to suppress the catalytic functions of AAEM when the H₂SO₄ concentration was less than or equal to 0.5%. The excess H₂SO₄ then served as a catalyst for accelerating the dehydration reaction, resulting in the decrease in the yield of levoglucosan. Similarly, the yield of AGF was enhanced by H_2SO_4 impregnation. However, the concentration of H_2SO_4 did not exert significant impacts on the yield of AGF. Demineralization of eucalyptus by HCl washing can effectively promote the yield of levoglucosan. It is worthy of note that the yield of levoglucosan from HCl-washed eucalyptus was evidently lower than that from 0.5% H_2SO_4 -impregnated eucalyptus. It could be attributed to that the AAEM in eucalyptus cannot be totally removed by HCl washing.



Figure 3. The yields of levoglucosan (LG) and AGF from fast pyrolysis of raw and H₂SO₄-impregnated eucalyptus.

2.4. The Possible Roles of H₂SO₄ during Fast Pyrolysis of H₂SO₄-Impregnated Eucalyptus

In order to further reveal the possible roles of H_2SO_4 during fast pyrolysis, the yield of levoglucosan from cellulose mixed with H_2SO_4 and ash is graphed in Figure 4. It is obvious that the addition of H_2SO_4 , K_2SO_4 , and ash from 0.5% H_2SO_4 -impregnated eucalyptus can cause the significant decrease in the yield of levoglucosan from fast pyrolysis of cellulose, indicating that the presence of AAEM in the form of metal sulfate (e.g., $K_3Na(SO_4)_2$ or K_2SO_4) was not the decisive reason for the increase in the yield of levoglucosan from fast pyrolysis of H_2SO_4 -impregnated eucalyptus. H_2SO_4 could react with the AAEM and organic macromolecules in eucalyptus to form a metal-organic complex. Shafizadeh found that water washing combined with H_2SO_4 impregnation was capable of maximizing the yield of anhydrosugars only when lignin was present [34]. Hence, it is speculated that H_2SO_4 first reacted with AAEM and lignin to form lignosulfonates (e.g., potassium lignosulfonate, calcium lignosulfonate.), resulting in the effective reduction in the catalytic functions of AAEM during fast pyrolysis of H_2SO_4 -impregnated eucalyptus.



Figure 4. The yield of levoglucosan from fast pyrolysis of cellulose mixed with H_2SO_4 and ash. (1: pure cellulose, 2: cellulose impregnated with 0.5% H_2SO_4 , 3: cellulose impregnated with 0.5% K_2SO_4 , 4: cellulose mixed with SA, 5: cellulose mixed with A).

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4

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3. Experimental

3.1. Materials

Eucalyptus used in this study was acquired from a local wood processing factory in Guangzhou, China. Before the experiment, the samples were ground and sieved to a particle size of 60–80 mesh, and then dried at 105 °C for 12 h. The elemental analysis of eucalyptus is listed in Table 4. Sulfuric acid (analytical grade, 98%) was purchased from Guangzhou Chemical Reagent Factory, Guangzhou, China. Pure cellulose was obtained from Fuyu Fine Chemical, Tianjin, China.

Items	Elemental Analysis (wt%) ^a							
itellis	С	Н	N	S	O ^b	Ash	H/C °	O/C ^d
Raw 44 0.5%H ₂ SO ₄ 44	8.10 7.30	5.96 5.74	0.13 0.09	0.06 0.17	45.37 46.26	0.38 0.44	0.12 0.12	0.94 0.98

Table 4. Elemental analysis of raw and acid-impregnated eucalyptus.

^a: dry basis. ^b: The oxygen content was calculated by difference. ^c:hydrogen to carbon ratio. ^d: oxygen to carbon ratio

3.2. H₂SO₄ Impregnation of Eucalyptus

The eucalyptus (10 g) was impregnated with 50 mL H_2SO_4 solutions with various concentrations (0.25 wt%, 0.5 wt%, 0.75 wt%, 1.0 wt%, and 1.25 wt% based on the dry weight of eucalyptus) in a beaker and then the beaker was put under ultrasonic irradiation for 3 h at room temperature. The H_2SO_4 -impregnated eucalyptus was then dried at 80 °C for 24 h.

3.3. Demineralization of Eucalyptus

The eucalyptus (10 g) was washed with 100 mL of 2.0 M HCl solution at room temperature with stirring for 24 h to realize demineralization and then filtered to neutral—denoted as demineralized eucalyptus. The eucalyptus (10 g) was washed with 100 mL deionized water with stirring for 24 h

for the removal of extractable ash and then filtered—denoted as water-washed eucalyptus. All the samples were dried at 80 $^\circ C$ for 24 h to remove moisture.

3.4. Thermogravimetric Analysis

Thermal degradation behaviors of raw and H_2SO_4 -impregnated eucalyptus were studied in a thermogravimetric analyzer (STA PT 1600, Linseis, Germany). In each experiment, the samples (20 mg) were conducted at a heating rate of 10 °C/min from 40 to 800 °C, and high purity nitrogen (99.99%) with a flow rate of 100 mL/min was used as the purge gas.

3.5. Fast Pyrolysis of Raw and H₂SO₄-Impregnated Eucalyptus

Fast pyrolysis of raw and H_2SO_4 -impregnated eucalyptus was conducted on a pyroprobe reactor (Pyroprobe 5200 Series, CDS Analytical, Oxford, PA, USA) coupled with a gas chromatograph (7890A, Agilent Technologies, Santa Clara, CA, USA) connected with a mass spectrometer (5975C, Agilent Technologies, Santa Clara, CA, USA). In each experiment, a sample size of approximately 0.3~0.5 mg was weighed using an electronic balance with an accuracy of 0.001 mg (XP6152, METTLER TOLEDO, Germany). The temperature, heating rate, and residence time of pyrolysis were 600 °C, 10 °C/ms and 20 s, respectively. The compounds were identified by comparison with the national institute of standards and technology (NIST) mass spectral data library. Quantitative analysis of main pyrolysis products were calculated based on the dry weight of the solid sample used in the pyrolysis experiment.

3.6. X-ray Diffractometer Analysis (XRD) and X-ray Fluorescence Analysis (XRF) of Ash

The ash from the raw and H₂SO₄-impregnated eucalyptus was prepared in a muffle furnace at 600 °C for 40 min under an air atmosphere. The XRD patterns of ash were examined by X-ray diffraction (X'Pert Pro MPD, PANalytical B.V., Almelo, The Netherlands) using Cu K α radiation (λ = 0.15406 nm) at 40 kV and 40 mA. The samples were scanned at a scanning rate of 10°/min from 20 =10° to 80° with a step of 0.1°. The contents of elements in the ash were analyzed by X-ray fluorescence spectroscopy (AxiosmAX Petro, PANalytical B.V., Almelo, The Netherlands) spectrophotometer with 2.4 kW Rh K α radiation.

4. Conclusions

It was demonstrated that H_2SO_4 impregnation is an effective method for the selective production of anhydrosugars from fast pyrolysis of eucalyptus. Even small amounts of H_2SO_4 (0.25–0.5%) can obviously improve the production of anhydrosugars and suppress the formation of carboxylic acids, aldehydes, and ketones from fast pyrolysis of eucalyptus. The maximum yield of levoglucosan (21.3%) was achieved by fast pyrolysis of 0.5% H_2SO_4 -impregnated eucalyptus. The value was close to its theoretical yield based on the cellulose content. As the H_2SO_4 concentration was further increased from 0.5% to 1.25%, the yield of levoglucosan decreased from 21.3% to 9.8%. It is speculated that H_2SO_4 first reacted with AAEM and lignin to form lignosulfonates, which can serve as an inhibitor to suppress the catalytic functions of AAEM, resulting in the sharp increase in the production of levoglucosan. As the H_2SO_4 concentration further increased, the excess H_2SO_4 can act as a catalyst for accelerating the formation of dehydrated product, leading to the decrease in the production of levoglucosan and the enhancement in the production of furfural and levoglucosenone. These findings can provide better understanding and insights into the pyrolysis behaviors of H_2SO_4 -impregnated woody biomass.

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