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Mechanism research on fast pyrolysis of Organosolv lignin by pyrolyzer coupled with gas chromatography and mass spectrometry

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In this study, fast pyrolysis of Organosolv lignin was carried out on an analytical pyrolyzer coupled with gas chromatography and mass spectrometry detectors. The pyrolytic products included phenols, furans, linear acids, or esters, as well as a small amount of alcohol and acetic acid. Phenolic compounds were main products, whose yields changed not obviously at different temperature with holding time increasing. But the successive tests showed that the fast pyrolysis with rapid condensation extensively favored the formation of phenolic compounds. The breakage of propane side chain at different positions led to various formations of products. The C_{α} - C_{β} bond was easiest to break and formed aldehyde group, which produced the most abundant products of vanillin and syringaldehyde. The breakage of C_4 - C_{α} bond to form guaiacol and syringol was the most difficult reaction in the aromatic skeleton degradation. © 2015 AIP Publishing LLC.

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I. INTRODUCTION

Lignin is regarded as an abundant renewable and sustainable source for the production of aromatic polymers, water reducing agent, dispersant and additive, etc.^{1,2} And it is polymerized by three *p*-hydroxycinnamyl alcohol precursors, *p*-coumaryl, coniferyl, and sinapyl alcohols, resulting in the formation of three lignin units called H-lignin (*p*-hydroxyphenyl), G-lignin (guaiacyl), and S-lignin (syringyl).³ In the past, little attention was paid to the use of lignin as a chemical resource. And residue (mainly composed of lignin) in pulping industry was mostly combusted to produce heat directly. With the potential growth of cellulosic ethanol and other bio-refineries, lignin has gained new interest as a chemical resource as a result of various thermo-chemical approaches.^{4,5} Pyrolysis is one of the most promising methods for production of aromatic hydrocarbons and phenolic compounds, due to the phenyl propane structure of lignin, including guaiacol, 4-methyl guaiacol, syringol, eugenol, vanillin, etc.⁶ Analytical pyrolysis is a well-known technique for the rapid characterization of pyrolytic products with high levels of repeatability.⁷ Many researches have reported results using an analytical pyrolyzer coupled with gas chromatography and mass spectrometry (Py-GC/MS) to investigate the composition of biomass and components.^{8,9} This method also allows for the evaluation of the relative ratio of H-, G-, and S-lignin.¹⁰ Rodrigues and Meier¹¹ measured the S-lignin and G-lignin ratios of wood lignin by identifying S- and G-derived compounds and then by summation to form a total for the two kinds of compounds. Recently, this method is also frequently used in catalytic pyrolysis of lignin. The researches include the qualitative and quantitative analysis of catalytic products from pyrolysis of lignin extracted from different biomass,¹² and the effect of various catalysts on the conversion of phenolic compounds to aromatic hydrocarbons during lignin

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pyrolysis.^{13,14} Although several studies have been published for catalytic fast pyrolysis of lignin, relatively few report the influence of basic factors on pyrolytic products formation, such as residence time and temperature. Their effects cannot be ignored.

In a recent study,¹⁵ we made the characterization of Organosolv lignin and obtained the distribution of functional groups, which was considered to be representative of natural lignin.^{16–19} Building on the findings of that study, we report the influence of residence time and temperature on the fast pyrolysis of lignin which carried on Py-GC/MS, and then try to deduce the formation mechanism of typical pyrolytic products in this paper.

II. MATERIALS AND METHOD

Organosolv lignin extracted from beech wood was purchased from Sigma for the tests. The carbon, hydrogen, nitrogen, and oxygen contents were 62.60, 6.00, 0.23, and 31.17 wt. %, respectively, from an elemental analysis. The characterization results in our previous study showed that guaiacyl and syringyl units, and methoxyl were the primary functional groups, which agreed well with other reported result.²⁰ And the average C₉ formula of Organosolv lignin was C₉H_{8.098}O_{2.601}(OCH₃)_{1.214}; the content of free aliphatic and phenolic hydroxyl groups per C₉ unit was 1.710 and 2.613.¹⁵ The reactivity of lignin was essentially affected by the free phenolic hydroxyl group, due to its activation of the aromatic ring in the ortho-position and the possibility of forming intermediates that were susceptible to nucleophilic reaction at the benzylic carbon atom.²¹

Fast pyrolysis of Organosolv lignin was carried out on the analytical pyrolyzer and the volatiles obtained were analyzed by GC-MS. The pyrolyzer was a CDS5200 Pyroprobe with a platinum filament used to heat the quartz tube micro-reactor to 1400 °C. The pyrolysis tube was filled successively with some quartz wool, lignin, and more quartz wool. About 0.5 mg of Organosolv lignin was fed in by a controlled length of filled tube. Fast pyrolysis was carried out at different temperatures (400, 500, 600, and 700 °C) for 10 s and at 600 °C holding for different residence times (2 s, 5 s, 10 s, and 20 s) with the same heating rate of 10 000 °C/s. Moreover, the successive fast pyrolysis of lignin was operated. During the successive fast pyrolysis of lignin, the residue formed in a previous test was used as the sample for the continuous pyrolysis. Here lignin sample underwent a pyrolysis at 600 °C holding for 5 s first, and the formed solid residue was still remained in the reactor to be used as the sample for next pyrolysis under the same condition with the previous test. After four successive tests, the total reaction time was 20 s. The results obtained from successive tests were compared with a normal pyrolysis of lignin at 600 °C holding for 20 s. The pyrolysis vapors desorbed from the trap were immediately analyzed by GC/MS (Thermo scientific, Trace DSQ II). The injector temperature was kept at 250 °C. The chromatographic separation was performed using a DB-WAX capillary column (30 m × 0.25 mm × 0.25 μm). Helium (99.999%) was used as the carrier gas with a constant flow rate of 1 ml/min and a 1:50 split ratio was used for the injection of pyrolysis volatiles to the GC. The oven temperature was programmed from 40 °C (1 min) to 240 °C (24 min) at a heating rate of 8 °C/min. The temperature of the GC/MS interface was held at 250 °C and the mass spectrometer was operated in EI (Electron Ionization) mode at 70 eV. The mass spectra were obtained from m/z 35 to 450 with a scan rate of 2337.1 amu/s. Identification of chromatographic peaks was achieved using the NIST MS library. In addition, a mass balance with 0.01 mg accuracy was used to measure the weight of samples before and after pyrolysis, to determine any weight loss. All experiments were conducted at least three times to confirm the reproducibility of each test.

III. RESULTS

A. Experimental results

1. Distribution of pyrolytic products

Fast pyrolysis of lignin produces volatiles, char, and permanent gases. Due to limitations of the experimental device, we only discuss the observed volatile products detectable by GC/MS.

When Organosolv lignin pyrolyzed at 600 °C holding for 10 s, the analyzed result about the compounds (including the names, retention times, formulae, and relative areas of pyrolytic products) is listed in Table I. In this experimental condition, the final residue yield was 38.08%, which mainly composed of char. The high char yield was also described in a review. It summarized that the char yield from fast pyrolysis of lignin was in the range of 30%–50%.²² A study on the pyrolysis of milled wood lignin also obtained a char yield of 40.69%, which was very close to our study.²³ The high char yield was mainly ascribed to the polymerization of the abundant aromatic radicals produced during lignin degradation.

The main products were oxygenates, which were divided into three kinds of compounds, phenolic compounds, furan compounds, and linear acids or esters with a large carbon number. The total peak area of furan compounds was about 16.16%, including 5-methyl-furfural, furfural, and 5-hydroxymethyl-furfural. Generally, furans are mainly degraded from cellulose or hemicellulose structure. Both furfural and acetic acid are representative of typical products of xylan. Therefore, furan compounds can be attributed to the decomposition of residue xylan and carbohydrates in lignin, which was discovered in previous structure characterization. However, the origin of small molecular weight compounds ethyl alcohol and acetic acid is not very clear, as their formation can be through various ways. The yield of linear acids or esters, such as hexadecanoic acid, ethyl ester, 9, 12-octadecadienoic acid, n-hexadecanoic acid, was about 22.53%. They are rarely reported as the products of lignin pyrolysis. Their production is probably caused by the degradation of lipophilic extracts.^{24,25}

Phenolic compounds are primary pyrolytic products, whose yield was about 45.2%. Based on the kinds of lignin units, phenolic compounds were divided into phenol, guaiacols (G-phenols), and syringols (S-phenols).^{26,27} In this study, guaiacols predominately consisted of guaiacol, guaiacol, 4-propenyl, vanillin, guaiacol, 4-vinyl, and guaiacylacetone; syringols were mainly composed of syringol, syringol, 4-propenyl, and syringaldehyde. The yield of phenol

TABLE I. Main pyrolytic products of Organosolv lignin at 600 °C and holding for 10 s.

RT (min)	Compounds	Formula	Area (%)
3.64	Ethyl alcohol	C ₂ H ₆ O	3.53
11.79	Acetic acid	C ₂ H ₄ O ₂	1.56
12.12	Furfural	C ₅ H ₄ O ₂	11.62
13.91	5-methyl-furfural	C ₆ H ₆ O ₂	3.47
18.03	Guaiacol (2-methoxy-phenol)	C ₇ H ₈ O	2.46
19.88	Phenol	C ₆ H ₆ O	1.88
20.28	Guaiacol, 4-vinyl	C ₉ H ₁₀ O ₂	2.69
22.35	Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	1.14
22.77	Hexadecanoic acid, ethyl ester	C ₁₈ H ₃₆ O ₂	3.68
23.08	Syringol (2,6-dimethoxy-phenol)	C ₈ H ₁₀ O ₃	5.41
24.05	Guaiacol, 4-propenyl	C ₁₀ H ₁₂ O ₂	3.52
25.03	Ethyl heptadecanoate	C ₁₉ H ₃₈ O ₂	1.88
25.30	Octadecenoic acid ethyl ester	C ₂₀ H ₃₈ O ₂	1.20
25.49	8,11-Octadecadienoic acid, methyl ester	C ₁₉ H ₃₄ O ₂	1.97
25.71	5-Hydroxymethyl-furfural	C ₆ H ₆ O ₃	1.07
25.89	9,12-Octadecadienoic acid, ethyl ester	C ₂₀ H ₃₆ O ₂	7.76
26.66	Vanillin	C ₈ H ₈ O ₃	8.28
27.97	Guaiacylacetone	C ₁₀ H ₁₂ O ₃	1.61
29.07	Syringol, 4-propenyl	C ₁₁ H ₁₄ O ₃	5.45
32.72	n-hexadecanoic acid	C ₁₆ H ₃₂ O ₂	2.65
34.10	Syringaldehyde	C ₉ H ₁₀ O ₄	12.73
35.64	4-Hydroxy-3,5-dimethoxy-acetophenone	C ₁₀ H ₁₂ O ₄	1.17
44.08	9,12-Octadecadienoic acid	C ₁₈ H ₃₂ O ₂	2.25

(1.88%) was much lower than that of guaiacols (18.56%) and syringols (24.76%). In addition, the proportion of G-/S-lignin unit was 3:4. And it indicated that the amount of syringyl unit was more than that of guaiacyl unit and *p*-hydroxyphenyl unit in beech wood.

In view of many researches on fast pyrolysis of lignin, Table II is obtained after comparison. Every lignin has its typical pyrolytic product distribution, but the main products are nearly all phenolic compounds, such as phenol, guaiacols, and syringols. Windt *et al.*¹⁹ compared the pyrolysis behaviors of different lignins extracted from hardwood and found that phenol, guaiacols, and syringols were also formed during the pyrolysis of Organosolv lignin. But major differences were observed when the feedstock was ALM lignin from non-woody plants and ETEK lignin from softwood.²⁸ It is because the kinds of lignin units contained in non-woody biomass are very different from softwood and hardwood. Moreover, the analytical method also has obvious effect on the yields of pyrolytic products.

2. Effect of residence time and temperature on the product yields

Residence time and temperature have important influence on the fast pyrolysis of biomass and its three main components. They are obviously weaker in fast pyrolysis of lignin than that of cellulose and hemicellulose, but the effect cannot be ignored. With the residence time and temperature increasing, the yield of furan compounds always decreased, and the yield of linear acids or esters was almost constant. Furfural was the most abundant product in furan compounds, with a production of 13.56%, 12.31%, 11.62%, and 10.67% for the pyrolysis at 600 °C holding for 2 s, 5 s, 10 s, and 20 s, respectively; and its production was 12.78%, 12.04%, 11.62%, and 10.52% for the pyrolysis at 400 °C, 500 °C, 600 °C, and 700 °C holding for 10 s. This change tendency agrees well with the properties of their origin structures. Lipophilic extracts are unstable and will be decomposed rapidly at low temperature holding for short time. The xylan or carbohydrate structures are relatively stable, which will be degraded gradually as the reaction progresses.

As the main products, the yields of phenolic compounds changed relatively obvious. Their yields are shown in Fig. 1 at different temperature with residence time increasing. Vanillin and syringaldehyde were the most abundant products from the decomposition of guaiacyl and syringyl units, and their maximum yields were obtained at 700 °C and 500 °C holding for 20 s, respectively. It reveals that aldehyde group in broken propyl-side chain is easiest to form and strong reaction intensity (high temperature and long holding time) is in favor of their formation. Guaiacol, 4-propenyl and syringol, 4-propenyl were the second abundant compounds in guaiacols and syringols. And their yields decreased first and then increased roughly. The formation of 4-propenyl presented a competition with that of aldehyde group. Guaiacol, 4-vinyl was formed but syringol, 4-vinyl disappeared. Guaiacol and syringol were both existed as the simplest product with relatively low yield. The yield of guaiacol changed specially compared with other products. When holding for 2 s and 5 s, guaiacol was only formed at 700 °C and 600 °C,

TABLE II. Comparison of different studies on Organosolv lignin pyrolysis.

Item	This study	Reference 19	Reference 28	
Lignin	Organosolv	Organosolv	ALM	ETEK
Nature	Hardwood	Hardwood	Non-woody	Softwood
Pyrolyzer	Online	Offline	Online	
Detector	GC/MS	GC-MS/FID	GC/MS	
Method	Qualitative	Semi-quantitative	Qualitative	
Unit	% relative area	wt. %	% relative area	
Phenol	1.88	1.21	10.15	3.79
Guaiacols	16.10	2.03	57.81	51.62
Syringols	24.76	3.44	17.54	0

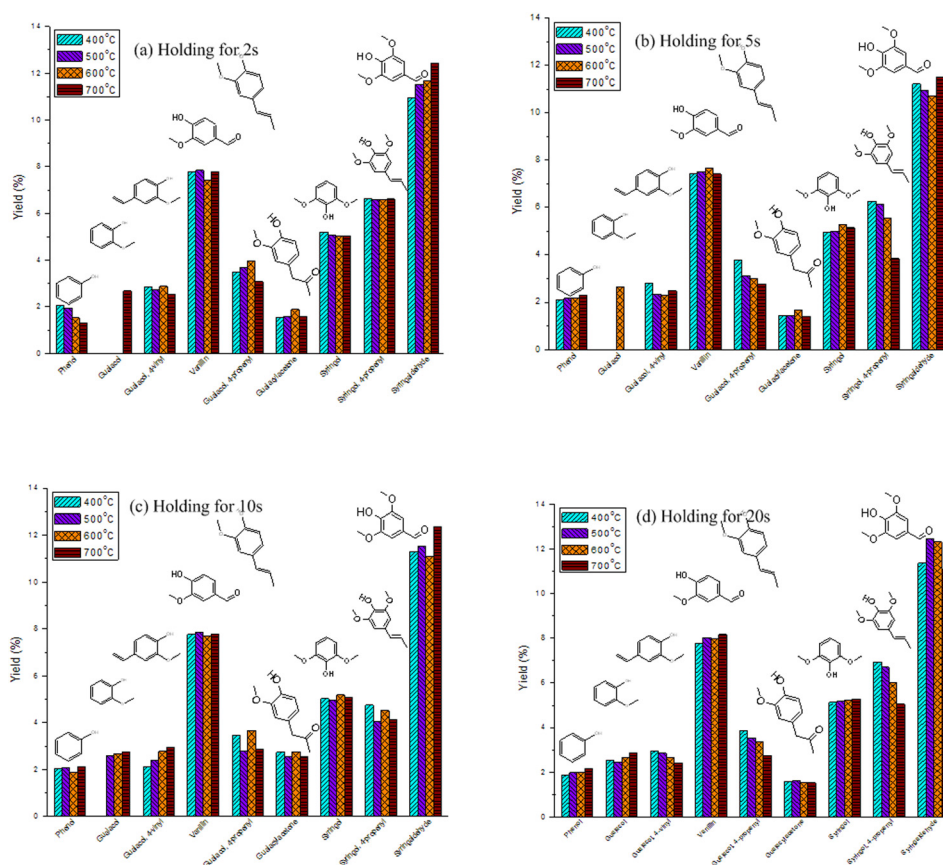


FIG. 1. Yield changes of phenolic compounds at different temperatures: (a) holding for 2 s, (b) holding for 5 s, (c) holding for 10 s, and (d) holding for 20 s.

respectively. When holding for 10 s and 20 s, it was formed in all conditions except for at 400°C holding for 10 s. And the highest yield of guaiacol (2.88%) was obtained at 700°C holding for 20 s. This result shows that residence time and temperature have similar effect on the formation of guaiacol, and the performance of residence time is more sensitive. In addition, the yield of phenol decreased with temperature increasing holding for 2 s, but it increased nearly when temperature increasing holding for 5 s, 10 s, and 20 s. Therefore, it is identified that the effect of residence time and temperature is not completely consistent.

3. Results from successive reactions

In order to well study the influence of residence time on the gradual degradation of lignin, successive test was operated. The comparison of product distributions between successive tests and test at 600°C holding for 20 s is shown in Table III. Though the total residence time was 20 s for both, the yields of product varied obviously. It was confirmed that the formation of acetic acid and furans compounds were caused by the decomposition of non-lignin structure (mainly xylan structure), which degraded rapidly within 5 s.

The successive tests were in favor of the formation of phenolic compounds. First, saturated guaiacols, like guaiacol, 4-methyl, and guaiacol, 4-ethyl were formed, which were not discovered in normal test; second, typical products of guaiacols and syringols in normal test were all formed in step 1 and continued to produce in step 2–step 4; third, shorter residence time inhibited the subsequent decomposition of formed products, which was observed by the low yield of

TABLE III. Yields of typical products obtained from the successive tests (%).

Compounds	Normal	Successive tests (holding for 20 s totally)			
	20 s	Step 1(5 s)	Step 2(5 s)	Step 3(5 s)	Step 4(5 s)
Ethyl alcohol	3.25	3.27	2.3	1.62	1.34
Acetic acid	1.63	1.96	0	0	0
Furfural	14.67	15.31	0	0	0
Furfural, 5-methyl	3.45	4.09	0	0	0
Furfural, 5-hydroxymethyl	1.21	1.02	0.96	0	0
Phenol	2	2.19	0	0	0
Guaiacol	2.66	2.66	1.07	1.11	1.29
Guaiacol, 4-methyl	0	0	0	1.24	1.63
Guaiacol, 4-ethyl	0	0	0	0.89	1.09
Eugenol	0	0	0	0.77	0.76
Guaiacol, 4-vinyl	2.64	2.31	3.46	3.25	3.29
Guaiacol, 4-propenyl	3.37	3.77	0.36	0	0
Vanillin	7.98	7.65	6.7	3.88	2.54
Guaiacylacetone	1.52	1.66	2.52	1.87	1.56
Syringol	5.23	5.26	4.98	4.94	5.57
Syringol, 4-propenyl	6.02	5.55	17.24	10.81	22.47
Syringaldehyde	12.33	10.7	14.73	14.21	12.38
3,5-Dimethoxy-4-hydroxyphenylacetic acid	0	0	1.1	1.17	1.21
Ethanone,4-hydroxy-3,5-dimethoxyphenyl	0	1.12	1.73	2.16	2.47

ethyl alcohol. Therefore, large amount of phenolic compounds, especially for vanillin and syringaldehyde, could be produced by multiple fast pyrolysis with rapid condensation.

B. Deduced formation pathways of phenolic compounds

The phenyl propane structure is the basic unit in lignin and much more thermo-stable than the cross-linked structure of carbohydrate. And the decomposition of lignin produces various phenolic compounds. In order to improve the extraction of phenols from lignin by fast pyrolysis, the formation pathways of phenolic compounds are deduced as Fig. 2. They all are related to the breakage of propane side chain. Vanillin and syringaldehyde were the most abundant products, which both contained aldehyde group in side chain. So lignin units are easiest to degrade by the breakage of the C_α - C_β bond and subsequent formation of the aldehyde group. Next is the breakage of C_γ -OH bond to produce 4-propenyl group. And the breakage of the C_4 - C_α bond from aromatic skeleton was the most difficult, which leads to the formation of guaiacol and syringol.

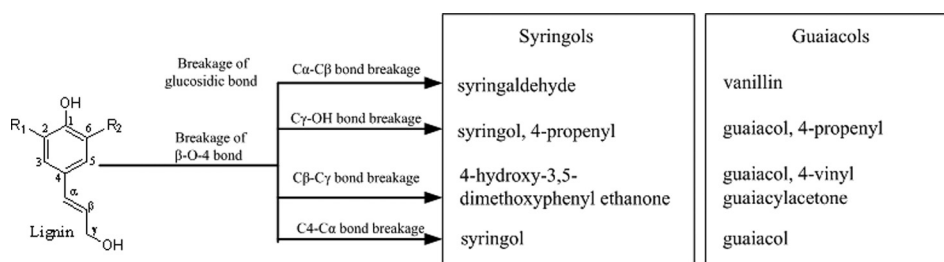


FIG. 2. Possible breakage of lignin unit to form phenolic compounds.

IV. CONCLUSIONS

The structure of lignin was stable and had linkage with the residual xylan units from extraction. Fast pyrolysis of lignin produced furans, linear acids or esters, and phenolic compounds, mainly by the degradation of xylan fragment, lipophilic extractives, and phenyl propane units, respectively. Phenolic compounds, such as phenol, guaiacols, and syringols, were the primary products with the total yields of about 45% at different conditions. Vanillin and syringaldehyde were the most abundant products, and guaiacol, syringol, and phenol were less formed. The effect of residence time and temperature cannot be ignored, though it is not obvious. And multiple fast pyrolysis with rapid condensation was in favor of the formation of phenolic compounds. The breakage of side chain was the most important reaction to form various phenolic compounds. And the stabilities of different bonds followed $C_{\alpha}-C_{\beta} > C_{\gamma}-OH > C_{\beta}-C_{\gamma}$ and C_4-C_{α} .

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