Catalytic Stepwise Pyrolysis of Technical Lignin

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The stepwise pyrolysis of technical lignin with and without a catalyst was investigated by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Lignin was first pyrolyzed at 260 or 360 °C, and then the residue was subsequently pyrolyzed at 650 °C. It was found that stepwise pyrolysis of lignin concentrated the phenolic compounds in lignin-derived bio-oil. In a stepwise 260 to 650 °C process, the maximum total phenolic compounds were 86.2%. Among the phenolic compounds, guaiacol-type and phenol-type phenolic compounds were predominant. Further addition of a catalyst (HZSM-5) in the stepwise pyrolysis process enhanced control over the product distribution through conversion of phenolic compounds into aromatic hydrocarbon products. The aromatic hydrocarbons achieved the highest yield of 30.4% in the catalytic stepwise 260 to 650 °C process.

Keywords: Lignin; Catalyst; Pyrolysis; Stepwise; Py-GC/MS

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INTRODUCTION

Lignocellulose, which includes forest materials, agricultural residues, or energy crops, is the cheapest and most abundant form of biomass. Biomass is a promising alternative to petroleum for the production of fuels and chemicals (Brebu *et al.* 2013). It consists of approximately 35% to 45% cellulose, 25% to 30% hemicellulose, and 20% to 35% lignin (Custodis *et al.* 2015). Lignin, nature's dominant aromatic polymer, is found in most terrestrial plants and provides structural integrity (Ragauskas *et al.* 2014). Lignin is a complex amorphous copolymer in which guaiacyl (G), p-hydroxyphenyl (H), and syringyl (S) units are interconnected by various ether bonds and carbon-carbon linkages (Shen *et al.* 2015). The majority of interunit linkages are *β*-*O*-4, *β*-5, and *β*–*β* (Yue *et al.* 2017). *β*-*O*-4 bonds especially are the most frequent coupling linkage and comprise 50% to 60% of the total linkages (Chu *et al.* 2013). Lignin as a by-product of the pulp and paper industry and the bioethanol industry is very underutilized because of its inherent heterogeneity, low reactivity, and recalcitrance. Most lignin has been traditionally employed for heat and power purposes through combustion (Xu *et al.* 2014). However, lignin is a potential source for fuel and chemical production because of its rich aromatic structures. The use of lignin as a substitute for crude oil to produce petrochemicals can reduce the reliance on fossil fuel resources or replace it to some extent in the future. Therefore, efficient transformation of lignin is necessary.

Pyrolysis has been identified as one of the primary thermochemical conversion technologies for lignin transformation (Liu *et al.* 2016). During pyrolysis, lignin can be rapidly converted into gaseous products, volatiles, and solid residue, in which the volatiles are known as bio-oil (Liu *et al.* 2016). Bio-oil is a high-energy content transportable liquid for subsequent processing for heat, hydrocarbon fuels, and valuable chemicals (Ma *et al.* 2016). The properties of bio-oil are greatly affected by the reaction conditions, such as the chemical structure of lignin and temperature (Li *et al.* 2015). Py-GC/MS is widely employed to explore the effect of reaction conditions on the proportion and yield of bio-oil from lignin pyrolysis. For instance, Wang *et al.* (2015) demonstrated that the structure of lignins from a different isolation process greatly influenced the pyrolysis behavior, and a high phenols yield in the pyrolysis process was found for alkaline lignin and milled wood lignin. During the pyrolysis process, the cleavage of different bonds in lignin occurs at different temperatures. Ether bonds are readily cleaved to form condensable volatile products at low temperatures. Methoxyl groups are more resistant to thermal degradation than the ether linkages. C-C bonds are the most stubborn bonds in lignin structures, and their cleavage only appears at high temperatures (Li *et al.* 2015). Jiang *et al*. (2010) studied the effect of temperature on the composition of lignin pyrolysis products and concluded that the maximum yield of phenolic compounds was obtained at 600 °C. However, pyrolysis oil obtained from the direct fast pyrolysis process also had some adverse properties, such as high acidity, high oxygen content, and the inherent complexity related to being a multicomponent mixture (Garcia-Perez *et al.* 2007). Upgrading processes are needed to improve the quality of bio-oil.

Modification of the pyrolysis process could be a candidate to improve the quality of bio-oil. Based on the thermal stability of the material, a stepwise pyrolysis process is proposed to obtain various chemicals, in which the raw material is pyrolyzed or torrefied at low temperatures, followed by pyrolysis of the solid residue at high temperatures. Zheng *et al.* (2013) investigated the effect of first-step pre-treatment temperature on the yield and composition of bio-oil during the stepwise pyrolysis of corncobs. They found that the content of acetic acid and furfural decreased when pre-treatment was applied, while the yield of most phenolic compounds increased. The heating value and pH of bio-oil also increased. These results confirmed that the quality of bio-oil was improved by two-stage pyrolysis of corncob. Westerhof *et al.* (2012) reported the stepwise pyrolysis of pine wood and concluded that light compounds and guaiacols could be more concentrated in the first-step liquid compared with that in the direct fast pyrolysis process. However, most studies have investigated the influence of two-stage pyrolysis on the products from biomass, and less attention has been paid to the effect of stepwise pyrolysis temperature on the product distribution from the lignin fraction.

Catalysis is another technology extensively used to improve the properties of bio-oil. Different kinds of catalysts have been adopted in the pyrolysis reactor, such as metal chlorides, metal oxide catalyst, and zeolites (Mullen and Boateng 2010; Neumann and Hicks 2012; Asadieraghi *et al.* 2015; Chen *et al*. 2015b). Zeolites are the most commonly used catalysts in the literature for catalytic pyrolysis of lignin because of their special pore structure and acid sites that can induce oligomerization, dehydration, deoxygenation, demethoxylation, and aromatization reactions (Ma and van Bokhoven 2012; Ma *et al.* 2012). Yu *et al.* (2012) investigated the inherent mechanism between lignin pyrolysis product distribution and the effective pore size of four zeolites, suggesting that ZSM-5 was the optimal catalyst for achieving satisfactory deoxygenation and aromatic production simultaneously.

The main goal of this paper is to evaluate the effect of stepwise pyrolysis with and without a catalyst on the product distribution of lignin-derived bio-oil to maximize the properties of bio-oil. The structures of technical lignin were also characterized to define the thermal stability.

EXPERIMENTAL

Materials

Biorefinery technical lignin from corncob, obtained from Shandong Longlive Bio-Technology Co., Ltd, China, was used as the feedstock. The general production process for lignin is as follows: first, the corncob was treated hydrothermally to transform the hemicelluloses into oligosaccharides. Then, the residue was treated with an alkaline solution to dissolve lignin and obtain a cellulose-rich residue. The solid residue from this step was used to produce bio-ethanol, while the effluent was adjusted to acidic conditions to precipitate the lignin (Yang *et al.* 2014). The purity of technical lignin was determined according to laboratory analytical procedures developed by the National Renewable Energy Laboratory (Sluiter *et al.* 2008). The technical lignin had a purity of 94% (calculated by Klason lignin and acid-soluble lignin content). The molecular weights of the technical lignin were performed using an Agilent 1200 gel permeation chromatograph (Agilent, Santa Clara, CA) with a refraction index detector (RID). HZSM-5 zeolite was used as the catalyst in this study. It was purchased from the Catalyst Plant of Nankai University, China. The properties of HZSM-5 are listed as follows: Si/Al mole ratio-25; crystallinity-95%; surface area: 365 m^2/g; cation type-H. The catalyst was calcined at 550 °C for 5 h in air in a muffle furnace with a heating rate of 10 °C/min.

Elemental Analysis

Elemental analysis (C, H, N, and O) of technical lignin was accomplished with an elemental analyzer (Vario EL III, Elementar Analysensysteme, Germany) (You *et al.* 2014). The contents of C, H, and N were measured directly and the O content was calculated by difference. The molecular formula was determined from the molar ratio of C, H, and O.

FTIR Spectroscopy

The FTIR measurement of lignin was carried out using a VERTEX70 (Bruker, Karlsruhe, Germany). The sample was prepared according to the potassium bromide pellet method, in a proportion of 1:100 (approximately 200 mg of KBr). The spectrum was scanned in the range from 400 to 4000 cm^{-1}.

Thermal Stability

The thermal stability of lignin with and without HZSM-5 was investigated using a TA Q50 thermogravimetric analyser (TA Instruments, USA). Approximately 8 mg of lignin was loaded in a platinum crucible and heated from ambient temperature to 750 °C with a heating rate of 20 °C/min. High-purity nitrogen was used as purge gas with a flow rate of 60 mL/min. Thermogravimetry was used to estimate the appropriate temperature for a two-stage pyrolysis process.

Py-GC/MS

Fast pyrolysis experiments, with and without catalyst, were conducted in a CDS 5200 pyrolyzer coupled with GC/MS (Agilent Technologies 7890A/5975, USA) to obtain the distribution of products from lignin pyrolysis with respect to temperature. The sample (0.3 mg) and catalyst (0.3 mg) were weighed accurately and mixed in a quartz tube, which was wrapped by a Pt filament. In the direct pyrolysis process, the pyrolysis temperature was set at 260, 360, and 650 °C at a heating rate of 20 °C/ms. The residence time was set at 15 s. The pyrolysis products were directly carried into the GC/MS by helium carrier gas and then detected. For stepwise pyrolysis process, the sample was first pyrolyzed at 260 or 360 °C with a heating rate of 20 °C/ms and residence time of 20 s. After detecting the pyrolysis products by GC/MS, the pyrolyzer was subsequently heated to 650 °C with the same heating rate and residence time described above. This process was defined as stepwise from 260 to 650 °C or stepwise from 360 to 650 °C. Then, the products were analyzed by the GC/MS.

The conditions for GC/MS were set as follows: the injector temperature was maintained at 270 °C and the injection split ratio was 50:1 with a carrier gas flow rate of 50 mL/min. The pyrolysis products were separated using an Agilent HP-5MS (30 m × 0.25 mm × 0.25 m) capillary column. The oven temperature was initially maintained at 50 °C for 2 min, increased to 250 °C at a heating rate of 10 °C/min, then held for another 5 min. An ion trap mass spectrometer was used for the detection of compounds, with a mass scan range of m/z from 45 to 650 (EI 70 eV). The pyrolysis products were identified based on the database of the NIST 14 mass library, chemical standards, and literature (Brebu *et al.* 2013; Shen *et al.* 2015; Ma *et al.* 2016).

When lignin undergoes fast pyrolysis, it produces permanent gases, volatiles, and char. Because of the limitations of the experimental setup, this study only discusses the volatile products (Zhang *et al.* 2014). For each sample, the experiment was conducted three times to confirm the repetition. The average values of peak area and peak area% obtained by TIC were used for discussion (Dong *et al.* 2012; Shen *et al.* 2015; Ma *et al.* 2016).

RESULTS AND DISCUSSION

Structural Analysis of Technical Lignin

The elemental composition of the technical lignin is shown in Table 1. According to the molar ratio of the elements C, H, and O, the molecular formula of the lignin was $C_9H_{12.339}O_{3.697}$. Compared with the elemental composition of corncob (Worasuwannarak *et al.* 2007), the content of carbon increased, while the oxygen content decreased in this technical lignin. From the results of elemental analysis, we calculated the effective hydrogen-to-carbon ratio (H/C_{eff}) defined by Chen *et al.* (1986) with the following equation (1), where H, C, and O were the moles of hydrogen, carbon, and oxygen, respectively.

$$H/C_{eff} = (H - 2O)/C \qquad (1)$$

The H/C_{eff} ratio was used to describe whether the economic conversion from a feedstock into hydrocarbons is possible. Accordingly, samples with higher H/C_{eff} ratios signify easier conversion into hydrocarbons. As shown in Table 1, the H/C_{eff} of technical lignin and corncob were 0.55 and 0.09, respectively. It can be inferred that the bio-oil from the technical lignin may be easier to upgrade to hydrocarbons (Zhang *et al.* 2012). The weight-average molecular weight (M_w) of the lignin was determined to be 3260 g/mol with a polydispersity (M_w/M_n) of 1.44.

Table 1. Elemental Composition of Samples

Sample	Elemental composition (%)				Molar Ratio		
	C	H	N	O	O/C	H/C	H/C$_{eff}$
Lignin	59.5	6.8	0.9	32.8	0.41	1.37	0.55
Corncob[a]	45.5	6.2	1.3	47.0	0.77	1.64	0.09

[a]Data from reference Worasuwannarak *et al.* (2007).

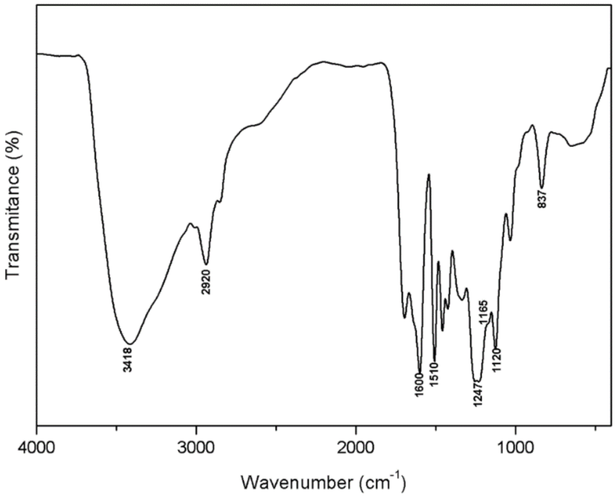

Fig. 1. FTIR spectrum of lignin

The FTIR spectrum of lignin is presented in Fig. 1. The absorbance peak located at 3418 cm^{-1} represents O-H stretching vibration in aromatic and aliphatic OH groups. The absorbance peak at 2920 cm^{-1} is assigned to C-H stretching vibration in methyl and methylene groups. The peak at 1700 cm^{-1} corresponds to the unconjugated carbonyl groups in ketone or aldehyde groups. Peaks located at 1600 and 1510 cm^{-1} indicate the existence of typical aromatic rings in lignin (Pasquali and Herrera 1997). The stretching signal at 1247 cm^{-1} indicates the existence of the guaiacyl (G) unit of lignin, whereas signals at 1120 and 1330 cm^{-1} are derived from the syringyl (S) unit of lignin. The absorbance peak at 1165 cm^{-1} corresponding to conjugated ester-based C=O stretching vibration represents typical characteristics of H-G-S-type lignin (Yan *et al.* 2016). It can be inferred that this technical lignin belongs to the H-G-S-type lignin.

Thermogravimetric Analysis

The mass loss (TG) and mass loss rate (DTG) curves of lignin with and without HZSM-5 are shown in Fig. 2. As can be seen from Fig. 2(a), the decomposition of lignin can be divided into three stages. In the initial weight loss stage (before 260 °C), the mass loss (11.2 wt%) was primarily caused by the release of water and some organic constituents. The primary weight loss stage happened at the middle temperature ranges (260 to 650 °C) because of the intensive evolution of volatiles, at which stage the mass loss rate reached its maximum value at 360 °C. Approximately 49.7 wt% of technical lignin was converted into volatiles in this active pyrolysis stage, and this part would become bio-oil using condensation technology. The third stage happened at higher temperatures (above 650 °C) and was recognized as the passive pyrolysis stage (Liang *et al.* 2015). In this stage, the mass loss was only 1.8 wt% and char was the main product. The final solid residue from pyrolysis of technical lignin was approximately 37.3 wt%. According to the primary weight loss stage, we chose 260 °C or 360 °C as the first-step pyrolysis temperature and 650 °C as the second-step pyrolysis temperature. As can be seen from Fig. 2(b), the residue was reduced with the addition of HZSM-5. The maximum rate of mass loss happened at 480 °C. This phenomenon indicated that HZSM-5 had a promoting effect on the degradation of lignin.

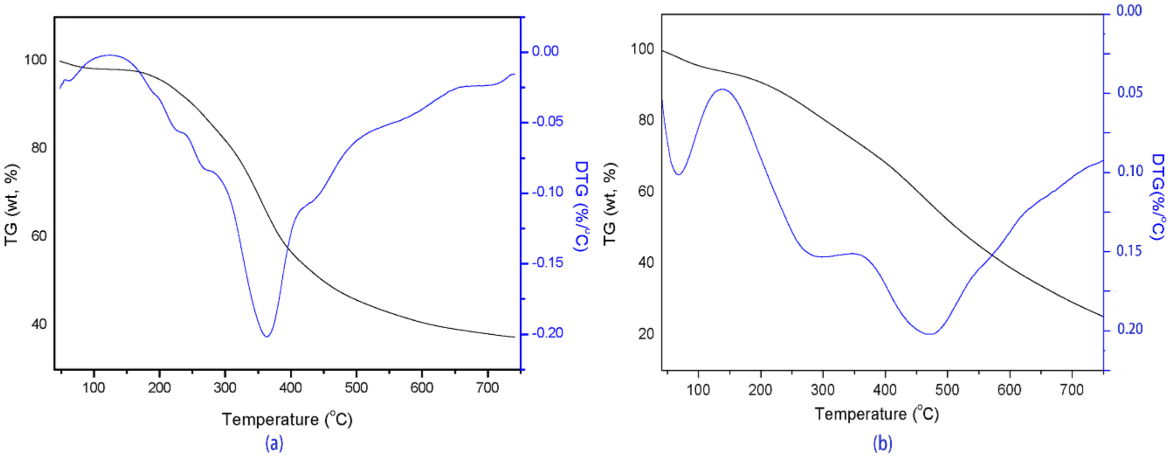

Fig. 2. TG/DTG curves of lignin. (a): without catalyst (b): with catalyst

Non-Catalytic Stepwise Pyrolysis of Lignin

The total ion current (TIC) chromatograms of lignin pyrolysis at various temperatures with and without catalyst are shown in Fig. 3.

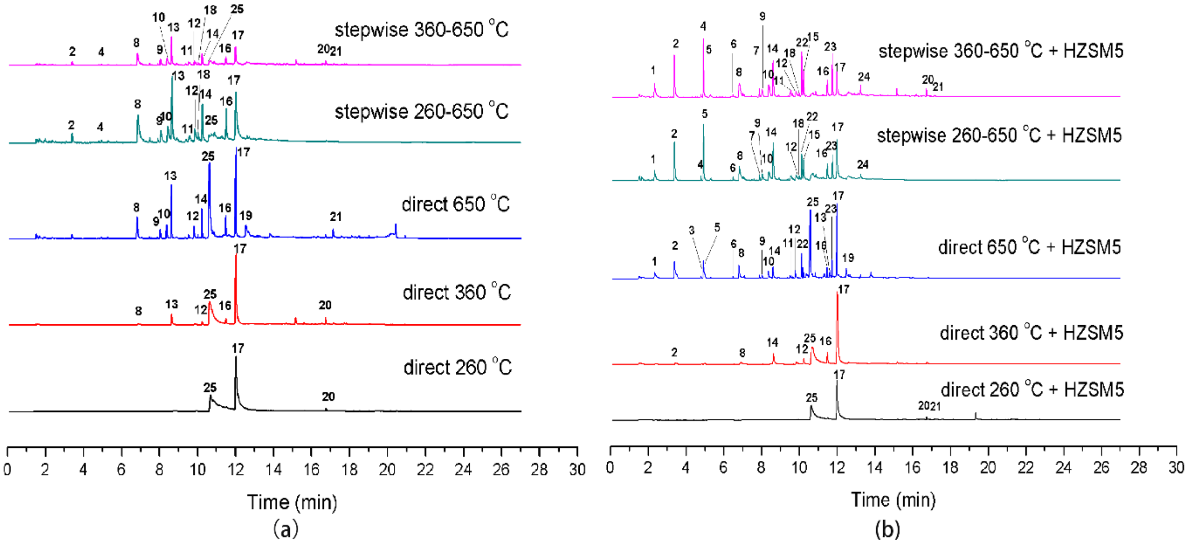

Fig. 3. Total ion current (TIC) chromatograms of lignin pyrolysis under different pyrolysis conditions. (a) without catalyst, (b) with catalyst

The products corresponding to each signal peak were identified based on the TIC chromatograms and the NIST library. The peak area and peak area% of the identified chemicals were obtained from the TIC chromatograms. The chemicals obtained from lignin pyrolysis were mostly aromatic compounds, which were divided into six categories according to the aromatic substituent groups: guaiacol-type compounds (G), syringol-type compounds (S), phenol-type compounds (H), aromatic hydrocarbons (AH), naphthalene-type compounds (N), and 2,3-dihydrobenzofuran (DHBF) (Ma *et al.* 2016).

Figure 4 shows the effect of pyrolysis process on the product distribution at various temperatures. The values of peak area% of identified product at different temperatures varied similarly to the peak area. According to the previous references (Chen *et al.* 2015a; Ma *et al.* 2016), the peak area% is chosen to study yield of pyrolysis product, and the results are summarized in Table 2.

During the direct pyrolysis process, the G-type, H-type, and DHBF compounds were the predominant products at various pyrolysis temperatures. The number of types of pyrolysis products increased with elevated temperature, and no aromatic hydrocarbon compounds were detected. The relative content of G-type compounds decreased from 54.3% at 260 °C to 40.8% at 650 °C, while H-type compounds increased from 2.6% at 260 °C to 14.0% at 650 °C during the direct pyrolysis process. *β*-*O*-4 linkages are readily cleaved to form condensable volatile products at low temperatures. Most methoxyl phenols, such as G-type phenols, are contained in the pyrolysis products due to the fact that the methoxyl groups are more resistant than the ether linkages during the thermal degradation. As temperatures increased, the demethoxylation reaction was enhanced. Hence, the content of G-type phenols decreased, while content of H-type phenols increased as temperature rose up (Li *et al.* 2015). The yield of DHBF at 650 °C was the lowest, and the relative content was 31.5%. During the stepwise pyrolysis process, the relative content of G-type compounds (55.4%) from 260 to 650 °C was higher than that (38.8%) from 360 to 650 °C. The main reason was that different chemical bonds broke at different temperatures. For example, guaiacol is mainly produced by the direct breaking of *β*-*O*-4 bond (Wang *et al.* 2015). The degree of breakage among chemical bonds was higher at 360 °C than that at 260 °C. The stepwise pyrolysis process from 260 to 650 °C can produce more G-type compounds.

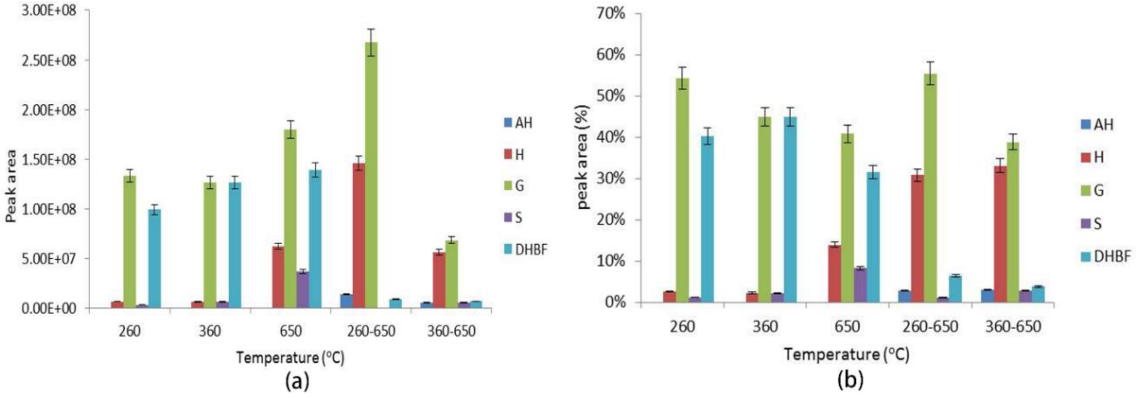

Fig. 4. Peak area (a) and peak area% (b) of pyrolytic products without catalyst under different pyrolysis conditions

Table 2. Products from Pyrolysis of Technical Lignin without Catalyst

Peak	Compounds	RT (min)	Relative content (peak area%)				
			260°C	360°C	650°C	260 to 650°C	360 to 650°C
AH-type							
2	Toluene	3.397	-	-	-	2.3	2.3
4	o-Xylene	4.927	-	-	-	0.6	0.7
H-type							
8	Phenol	6.810	-	1.3	6.1	13.2	13.5
9	2-Methylphenol	8.040	2.0	-	1.6	3.9	4.6
10	4-Methylphenol	8.369	-	-	3.4	6.6	7.4
11	2,5-Dimethylphenol	9.524	-	-	-	2.1	4.0
12	4-Ethylphenol	9.796	0.6	1.0	2.9	5.0	3.6
G-type							
13	2-Methoxyphenol	8.624	-	4.8	9.4	18.2	15.8
14	2-Methoxy-4-methylphenol	10.223	-	1.2	4.1	7.5	5.7
16	4-Ethyl-2-methoxyphenol	11.482	-	3.1	4.0	6.3	4.1
17	2-Methoxy-4-vinylphenol	12.002	54.3	35.9	23.3	21.6	12.0
18	2-Methoxy-3-methylphenol	10.016	-	-	-	1.8	1.2
S-type							
19	2,6-Dimethoxyphenol	12.499	-	-	6.6	-	-
20	4-Allyl-2,6-dimethoxyphenol	16.744	1.2	2.1	-		2.0
21	Acetosyringone	17.160	-	-	1.7	-	0.9
DHBF							
25	2,3-Dihydro-benzofuran	10.581	40.3	45	31.5	6.4	3.8

AH: aromatic hydrocarbons; H: phenol-type compounds; G: guaiacol-type compounds;
S: syringol-type compounds; DHBF: 2,3-dihydrobenzofuran

Comparing the products of direct pyrolysis (650 °C) and stepwise pyrolysis (first step: 260 or 360 °C; second step: 650 °C) of lignin in Table 2, the number of types of pyrolysis products noticeably increased in the stepwise pyrolysis process. The pyrolysis process produced predominantly phenolic compounds, and only trace amounts of aromatic hydrocarbons were detected in the stepwise pyrolysis process, possibly because of the secondary pyrolysis cracking of the methoxyl group and phenolic hydroxyl group from the benzene unit.

Approximately 2.9% and 3.0% aromatic hydrocarbons were found in stepwise pyrolysis from 260 to 650 °C and from 360 to 650 °C, respectively. Similar to the direct pyrolysis, G-type and H-type compounds were also the predominant products during the stepwise pyrolysis process. The production of DHBF decreased greatly, from 31.5% in direct pyrolysis at 650 °C to 6.4% in stepwise pyrolysis from 260 to 650 °C and 3.8% in stepwise from 360 to 650 °C. These results indicate that DHBF was primarily produced at low temperatures. As temperature increased, secondary decomposition of DHBF occurred easily. The production of H-type compounds in stepwise pyrolysis was remarkably higher than that in direct pyrolysis. The yield of total phenolic compounds also increased in the stepwise pyrolysis process, and the maximum relative content was 86.2% in stepwise pyrolysis from 260 to 650 °C.

Comparing the product distributions in different pyrolysis process reveals that the process of stepwise pyrolysis, especially from 260 to 650 °C, can yield more phenolic compounds in bio-oil. During the stepwise pyrolysis process, the secondary cracking reactions (especially the demethoxylation reaction) of those products were intensively promoted. This can explain why the H-type content increased in the stepwise pyrolysis process. At the same time, more DHBF were removed at the first step and the relative content of phenolic compounds in bio-oil increased throughout the whole stepwise pyrolysis process.

Catalytic Stepwise Pyrolysis of Lignin with HZSM-5

The relative content of the identified aromatic compounds is summarized in Table 3, and product distributions from various pyrolysis processes are shown in Fig. 5. For both direct 650 °C and stepwise 650 °C (from 260 to 650 °C and from 360 to 650 °C) processes, the composition of pyrolysis products changed dramatically in the presence of HZSM-5 zeolite catalyst compared with that of non-catalytic pyrolysis of lignin. The amount of aromatic hydrocarbons obviously increased when HZSM-5 catalyst was added, and the content of products produced in the stepwise pyrolysis process was higher than that in the direct pyrolysis process.

As shown in Fig. 5, the maximum value of aromatic hydrocarbons was 30.4% in stepwise pyrolysis from 260 to 650 °C. As the temperature increased, naphthalene-type compounds appeared, and their relative content was 7.9% in direct pyrolysis at 650 °C, 10.7% in stepwise pyrolysis from 260 to 650 °C, and 15.7% in stepwise pyrolysis from 360 to 650 °C, respectively. It is also apparent from Fig. 5 that catalytic stepwise pyrolysis led to a decrease in the content of DHBF, and even no DHBF was detected in stepwise pyrolysis from 360 to 650 °C. As shown in Figs. 4 and 5, the content of total phenolic compounds (including H-type, G-type, and S-type compounds) notably decreased in catalytic stepwise pyrolysis compared with the non-catalytic stepwise pyrolysis process.

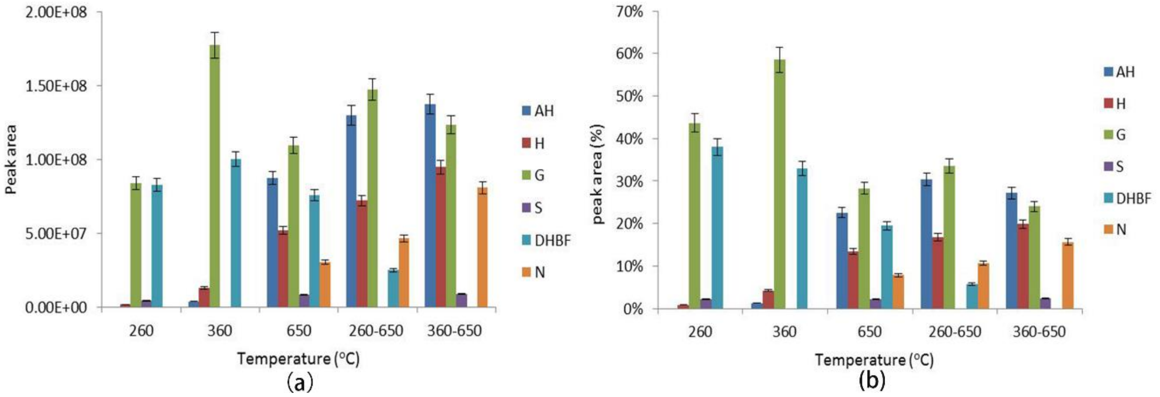

Fig. 5. Peak area (a) and peak area% (b) of pyrolytic products with HZSM-5 catalyst under different pyrolysis conditions

Table 3. Products from Pyrolysis of Technical Lignin using HZSM-5 as Catalyst

Peak	Compounds	RT (min)	Relative content (peak area%)				
			260°C	360°C	650°C	260 to 650°C	360 to 650°C
AH-type							
1	Benzene	2.346	-	-	4.2	3.9	5.0
2	Toluene	3.397	-	1.3	9.0	11.0	10.2
3	Ethylbenzene	4.800	-	-	0.8	-	-
4	o-Xylene	4.927	-	-	-	1.0	9.6
5	1,3-Dimethylbenzene	4.933	-	-	6.8	12.2	0.4
6	2-Methyl-ethylbenzene	6.504	-	-	0.8	0.9	0.5
7	1-propynylbenzene	7.902	-	-	1.0	1.4	1.5
H-type							
8	Phenol	6.810	-	2.4	4.9	7.0	7.0
9	2-Methylphenol	8.040	-	-	1.4	2.7	2.5-
10	4-Methylphenol	8.369	-	-	2.6	4.4	4.8
11	2,5-Dimethylphenol	9.524	-	-	0.8	-	3.5
12	4-Ethylphenol	9.796	0.9	1.8	2.3	2.7	2.1
13	2-Allylphenol	11.627	-	-	1.4	-	-
G-type							
14	2-Methoxyphenol	8.624	0.7	5.6	3.6	10.6	8.4
15	2-Methoxy-4-methylphenol	10.223	-	2.3	2.0	4.5	4.9
16	4-Ethyl-2-methoxyphenol	11.482	-	4.3	2.1	3.7	3.2
17	2-Methoxy-4-vinylphenol	12.002	43.0	46.3	20.6	14.0	6.9
18	2-Methoxy-3-methylphenol	10.016	-	-	-	0.7	0.6
S-type							
19	2,6-Dimethoxyphenol	12.499	-	-	2.2	-	-
20	4-Allyl-2,6-dimethoxyphenol	16.744	1.5	-	-	-	1.7
21	Acetosyringone	17.160	0.7	-	-	-	0.7
N-type							
22	Naphthalene	10.131	-	-	4.5	4.7	7.1
23	2-Methyl-naphthalene	11.748	-	-	2.7	4.6	6.8
24	1,3-Dimethyl-naphthalene	13.250	-	-	0.7	1.4	1.8-
DHBF							
25	2,3-Dihydro-benzofuran	10.581	38.0	33.0	19.5	5.7	-

AH: aromatic hydrocarbons; H: phenol-type compounds; G: guaiacol-type compounds;
S: syringol-type compounds; N: naphthalene-type compounds; DHBF: 2,3-dihydrobenzofuran

The most important reason that the catalyst HZSM-5 plays an important role in lignin pyrolysis is because of its specific pore structure and acid sites (Ma *et al.* 2012). The volume in the pores can prevent repolymerization and coke formation. The acid sites can promote the cleavage of C-O and C-C bonds and catalytic transformation of intermediates through reactions like dealkylation, dehydroxylation, demethoxylation, aromatization, dehydration, cracking, isomerization, and oligomerization (Mullen and

Boateng 2010; Neumann and Hicks 2012; Yu *et al.* 2012). Therefore, the relative content of aromatic hydrocarbons increased while the relative content of total phenolic compounds decreased in the catalytic stepwise pyrolysis process. The presence of more aromatic hydrocarbons in bio-oil can undoubtedly improve its heating value.

CONCLUSIONS

1. For non-catalytic stepwise pyrolysis, phenolic compounds, especially the G-type and H-type phenolic compounds, were the predominant products in lignin-derived bio-oil. The relative content of the total phenolic compounds increased in the stepwise pyrolysis process compared with the direct pyrolysis process. A maximum relative content of 86.2% was obtained in stepwise pyrolysis from 260 to 650 °C.
2. For catalytic stepwise pyrolysis of lignin, the composition of pyrolysis products changed dramatically in the presence of HZSM-5 zeolite catalyst compared with the non-catalytic pyrolysis process. The total phenolic compounds and DHBF decreased in the catalytic stepwise pyrolysis process. In contrast, in stepwise pyrolysis from 260 to 650 °C, aromatic hydrocarbons increased and achieved a maximum value of 30.4%.
3. The results indicated that stepwise pyrolysis of lignin without a catalyst could concentrate the phenolic compounds in bio-oil. Adding a catalyst like HZSM-5 in stepwise pyrolysis could noticeably improve the content of aromatic hydrocarbons in bio-oil.

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REFERENCES CITED

Asadieraghi, M., Daud, W. M. A. W., and Abbas, H. F. (2015). "Heterogeneous catalysts for advanced bio-fuel production through catalytic biomass pyrolysis vapor upgrading: A review," *RSC Adv.* 5(28), 22234-22255. DOI: 10.1039/C5RA00762C

Brebu, M., Tamminen, T., and Spiridon, I. (2013). "Thermal degradation of various lignins by TG-MS/FTIR and Py-GC-MS," *J. Anal. Appl. Pyrolysis* 104, 531-539. DOI: 10.1016/j.jaap.2013.05.016

Chen, N. Y., Degnan, T. F., and Koenig, L. R. (1986). "Liquid fuel from carbohydrates," *Chemtech* 16(8), 506-511.

Chen, L., Wang, X., Yang, H., Lu, Q., Li, D., Yang, Q., and Chen, H. (2015a).“Study on pyrolysis behaviors of non-woody lignins with TG-FTIR and Py-GC/MS,” *J. Anal. Appl. Pyrolysis* 113, 499-507. DOI: 10.1016/j.jaap.2015.03.018

Chen, J., Liu, C., and Wu, S. (2015b). “Catalytic fast pyrolysis of Alcell lignin with nano-NiO,” *BioResources* 11(1), 663-673 DOI: 10.15376/biores.11.1.663-673

Chu, S., Subrahmanyam, A. V., and Huber, G. W. (2013). "The pyrolysis chemistry of a *β-O*-4 type oligomeric lignin model compound," *Green Chem.* 15(1), 125-136. DOI: 10.1039/C2GC36332A

Custodis, V. B., Bährle, C., Vogel, F., and van Bokhoven, J. A. (2015). "Phenols and aromatics from fast pyrolysis of variously prepared lignins from hard-and softwoods," *J. Anal. Appl. Pyrolysis* 115, 214-223. DOI: 10.1016/j.jaap.2015.07.018

Dong, C. Q., Zhang, Z. F., Lu, Q., and Yang, Y. P. (2012). "Characteristics and mechanism study of analytical fast pyrolysis of poplar wood, " *Energy Convers. Manage.* 57, 49-59. DOI:10.1016/j.enconman.2011.12.012

Garcia-Perez, M., Chaala, A., Pakdel, H., Kretschmer, D., and Roy C. (2007). "Characterization of bio-oils in chemical families," *Biomass Bioenerg.* 31(4), 222-242. DOI: 10.1016/j.biombioe.2006.02.006

Jiang, G., Nowakowski, D. J., and Bridgwater, A. V. (2010). "Effect of the temperature on the composition of lignin pyrolysis products," *Energy Fuel.* 24(8), 4470-4475. DOI: 10.1021/ef100363c

Li, C., Zhao, X., Wang, A., Huber, G. W., and Zhang, T. (2015). "Catalytic transformation of lignin for the production of chemicals and fuels," *Chem. Rev.* 115(21), 11559-11624. DOI: 10.1021/acs.chemrev.5b00155

Liang, J., Lin, Y., Wu, S., Liu, C., Lei, M., and Zeng, C. (2015). "Enhancing the quality of bio-oil and selectivity of phenols compounds from pyrolysis of anaerobic digested rice straw," *Bioresour. Technol.* 181, 220-223. DOI: 10.1016/j.biortech.2015.01.056

Liu, C., Hu, J., Zhang, H., and Xiao, R. (2016). "Thermal conversion of lignin to phenols: Relevance between chemical structure and pyrolysis behaviors," *Fuel* 185, 864-870. DOI: 10.1016/j.fuel.2016.05.104

Ma, Z., and van Bokhoven, J. A. (2012). "Deactivation and regeneration of H-USY zeolite during lignin catalytic fast pyrolysis," *ChemCatChem* 4(12), 2036-2044. DOI: 10.1002/cctc.201200401

Ma, Z., Troussard, E., and van Bokhoven, J. A. (2012). "Controlling the selectivity to chemicals from lignin via catalytic fast pyrolysis," *Appl. Catal. A* 423, 130-136. DOI: 10.1016/j.apcata.2012.02.027

Ma, Z., Sun, Q., Ye, J., Yao, Q., and Zhao, C. (2016). "Study on the thermal degradation behaviors and kinetics of alkali lignin for production of phenolic-rich bio-oil using TGA–FTIR and Py–GC/MS," *J. Anal. Appl. Pyrolysis* 117, 116-124. DOI: 10.1016/j.jaap.2015.12.007

Mullen, C. A., and Boateng, A. A. (2010). "Catalytic pyrolysis-GC/MS of lignin from several sources," *Fuel Process. Technol.* 91(11), 1446-1458. DOI: 10.1016/j.fuproc.2010.05.022

Neumann, G. T., and Hicks, J. C. (2012). "Novel hierarchical cerium-incorporated MFI zeolite catalysts for the catalytic fast pyrolysis of lignocellulosic biomass," *ACS Catal.* 2(4), 642-646. DOI: 10.1021/cs200648q

Pasquali, C. L., and Herrera, H. (1997). "Pyrolysis of lignin and IR analysis of residues," *Thermochim. Acta* 293(1-2), 39-46. DOI: 10.1016/S0040-6031(97)00059-2

Ragauskas, A. J., Beckham, G. T., Biddy, M. J., Chandra, R., Chen, F., Davis, M. F., Davison, B. H., Dixon, R. A., Gilna, P., and Keller, M., *et al*. (2014). "Lignin valorization: Improving lignin processing in the biorefinery," *Science* 344(6185), 1246843. DOI: 10.1126/science.1246843

Shen, D., Liu, G., Zhao, J., Xue, J., Guan, S., and Xiao, R. (2015). "Thermo-chemical conversion of lignin to aromatic compounds: Effect of lignin source and reaction temperature," *J. Anal. Appl. Pyrolysis* 112, 56-65. DOI: 10.1016/j.jaap.2015.02.022

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2008). *Determination of Structural Carbohydrates and Lignin in Biomass* (NREL/TP-510-42618), National Renewable Energy Laboratory, Golden, CO.

Wang, S., Ru, B., Lin, H., Sun, W., and Luo, Z. (2015). "Pyrolysis behaviors of four lignin polymers isolated from the same pine wood," *Bioresour. Technol.* 182, 120-127. DOI: 10.1016/j.biortech.2015.01.127

Westerhof, R. J., Brilman, D. W. F., Garcia-Perez, M., Wang, Z., Oudenhoven, S. R., and Kersten, S. R. (2012). "Stepwise fast pyrolysis of pine wood," *Energy Fuel.* 26(12), 7263-7273. DOI: 10.1021/ef301319t

Worasuwannarak, N., Sonobe, T. and Tanthapanichakoon, W. (2007). "Pyrolysis behaviors of rice straw, rice husk, and corncob by TG-MS technique," *J. Anal. Appl. Pyrolysis* 78(2), 265-271. DOI: 10.1016/j.jaap.2006.08.002

Xu, C., Arancon, R. A. D., Labidi, J., and Luque R. (2014). "Lignin depolymerisation strategies: Towards valuable chemicals and fuels," *Chem. Soc. Rev.* 43(22), 7485-7500. DOI: 10.1039/C4CS00235K

Yan, K., Liu, F., Chen, Q., Ke, M., Huang, X., Hu, W., Zhou, B., Zhang, X., and Yu, H. (2016). "Pyrolysis characteristics and kinetics of lignin derived from enzymatic hydrolysis residue of bamboo pretreated with white-rot fungus," *Biotechnol. Biofuel.* 9(1), 76. DOI: 10.1186/s13068-016-0489-y

Yang, S., Wen J., Yuan T., and Sun, R. (2014). "Characterization and phenolation of biorefinery technical lignins for lignin-phenol-formaldehyde resin adhesive synthesis," *RSC Adv.* 4(101), 57996-58004. DOI: 10.1039/C4RA09595B

You, T., Zhou, S., Wen J., Ma, C., and Xu. F. (2014). "Chemical composition, properties, and antimicrobial activity of the water-soluble pigments from *Castanea mollissima* shells," *J. Agric. Food Chem.* 62(8), 1936-1944. DOI: 10.1021/jf4045414

Yu, Y., Li, X., Su, L., Zhang, Y., Wang, Y., and Zhang, H. (2012). "The role of shape selectivity in catalytic fast pyrolysis of lignin with zeolite catalysts," *Appl. Catal. A* 447, 115-123. DOI: 10.1016/j.apcata.2012.09.012

Yue, F., Lu, F., Regner, M., Sun, R., and Ralph, J. (2017). "Lignin-derived thioacidolysis dimers: reevaluation, new products, authentication, and quantification," *ChemSusChem* 10(5), 830-835. DOI: 10.1002/cssc.201700101

Zhang, M., Resende, F. L., Moutsoglou, A. and Raynie, D. E. (2012). "Pyrolysis of lignin extracted from prairie cordgrass, aspen, and kraft lignin by Py-GC/MS and TGA/FTIR," *J. Anal. Appl. Pyrolysis* 98, 65-71. DOI: 10.1016/j.jaap.2012.05.009

Zhang, M., Resende, F. L., and Moutsoglou, A. (2014). "Catalytic fast pyrolysis of aspen lignin via Py-GC/MS," *Fuel* 116, 358-369. DOI: 10.1016/j.fuel.2013.07.128

Zheng, A., Zhao, Z., Chang, S., Huang, Z., Wang, X., He, F., and Li, H. (2013). "Effect of torrefaction on structure and fast pyrolysis behavior of corncobs," *Bioresour. Technol.* 128, 370-377. DOI: 10.1016/j.biortech.2012.10.067

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