

Article

Fast Pyrolysis of Four Lignins from Different Isolation Processes Using Py-GC/MS

Xiaona Lin ¹, Shujuan Sui ¹, Shun Tan ¹, Charles U. Pittman, Jr. ², Jianping Sun ^{1,3} and Zhijun Zhang ^{1,*}

¹ MOE Key Laboratory of Bio-based Material Science and Technology, Northeast Forestry University, Harbin 150040, Heilongjiang, China; E-Mails: linxiaona1120@163.com (X.L.); 15945180240@163.com (S.S.); shuntannefu@163.com (S.T.); sunjp1977@163.com (J.S.)

² Department of Chemistry, Mississippi State University, Mississippi State, MS 39762, USA; E-Mail: cpittman@chemistry.msstate.edu

³ School of Municipal and Environmental Engineering, Shenyang Jianzhu University, Shenyang 110168, Liaoning, China

* Author to whom correspondence should be addressed; E-Mail: zzj_1003@163.com; Tel./Fax: +86-451-8219-1993.

Academic Editor: Thomas E. Amidon

Received: 6 April 2015 / Accepted: 22 May 2015 / Published: 1 June 2015

Abstract: Pyrolysis is a promising approach that is being investigated to convert lignin into higher value products including biofuels and phenolic chemicals. In this study, fast pyrolysis of four types of lignin, including milled Amur linden wood lignin (MWL), enzymatic hydrolysis corn stover lignin (EHL), wheat straw alkali lignin (AL) and wheat straw sulfonate lignin (SL), were performed using pyrolysis gas-chromatography/mass spectrometry (Py-GC/MS). Thermogravimetric analysis (TGA) showed that the four lignins exhibited widely different thermolysis behaviors. The four lignins had similar functional groups according to the FTIR analysis. Syringyl, guaiacyl and p-hydroxyphenylpropane structural units were broken down during pyrolysis. Fast pyrolysis product distributions from the four lignins depended strongly on the lignin origin and isolation process. Phenols were the most abundant pyrolysis products from MWL, EHL and AL. However, SL produced a large number of furan compounds and sulfur compounds originating from kraft pulping. The effects of pyrolysis temperature and time on the product distributions from corn stover EHL were also studied. At 350 °C, EHL pyrolysis mainly produced acids and alcohols, while phenols became the main products at

higher temperature. No obvious influence of pyrolysis time was observed on EHL pyrolysis product distributions.

Keywords: lignin; fast pyrolysis; phenolic compounds; Py-GC/MS

1. Introduction

Concerns over future fossil fuel depletion and current global warming have led to an increasing interest in converting biomass into biofuels [1]. Biomass-derived fuels are renewable because the CO₂ released from their combustion can be recycled into the replacement plants by photosynthesis [2]. Lignin is a major component of biomass. It is a three-dimensional amorphous polymer consisting of methoxylated phenylpropane structures [3]. It is the major renewable aromatic resource and its chemical structure and abundance varies with its source species [4]. Abundant industrial lignin is obtained as by-product from pulping and enzymatic hydrolysis or fermentation processes [5]. However, these lignin residues are disposed of as waste or burned to generate steam as a low-grade fuel. This is a low value use. A minor fraction is used to produce low value products such as dispersants and adhesives, while most lignin has not been used more profitably because of its complex structure [6]. Fast pyrolysis converts biomass into gas, liquid and solid biofuels using intermediate temperatures and short residence times in the absence of oxygen [7,8]. Lignin has a higher carbon and lower oxygen content than bulk plant (lignocellulosic) biomass, so fast pyrolysis may lead to biofuels with lower oxygen content or useful phenolic chemicals [9].

Thermogravimetric analysis (TGA) demonstrates that lignin is the most thermally resistant biomass organic component of plants, gradually decomposing over a wide temperature range of 300–800 °C [10,11]. The relative composition and product distribution from pyrolysis depend on the heating rate, reaction temperature, residence time, plant species and age, isolation methods, *etc.* [12–14]. Generally, lignins from hardwoods contain guaiacyl- and syringyl-type compounds as major components, while lignins from softwoods only contain guaiacyl-type compounds as major constituents. Their pyrolysis products reflect this chemistry [15]. The pyrolysis of lignin is mainly a free-radical decomposition mechanism, leading to the formation of monomeric phenolic compounds [10].

Various types of lignin are derived from different isolation methods, such as Björkmann lignin, Klason lignin, Organosolv lignin and Alkali lignin [16]. The structure of milled wood lignin (MWL) isolated by the Björkmann method is considered to produce a product most similar to the native lignin versus the compositions of other extracted lignins [14]. Kraft lignin contains sulfur originating from Kraft pulping. This leads to the existence of sulfur compounds in Kraft lignin's pyrolytic products [17]. Lignin residue from ethanol production contains cellulose and hemicellulose degradation products.

Recently, Nowakowski *et al.* [18] demonstrated that the lignin feedstock's origin has a significant effect on the pyrolysis-derived bio-oil products. The lignin's thermal behavior and product yields vary with the process by which the lignin was derived. However, only one or two types of lignins were investigated in most publications [19]. This makes it difficult to compare data for different lignins because of the varying conditions used and analytic methods employed. Therefore, systematic investigations and comparisons of the pyrolysis behavior of various types of lignins could help to

better understand the effects of both lignin separation method and origin on their pyrolysis behaviors. Additionally, Lignins from large industrial processes need to be targeted for detailed optimized fast pyrolysis studies to determine if specific process conditions can be identified to produce useful product fractions. In this study, the pyrolysis of four types of lignin obtained by different processes, including Amur linden lignin MWL, corn stover lignin EHL, wheat straw lignin AL and wheat straw lignin SL, were carried out using TGA and pyrolysis gas-chromatography/mass spectrometry. The differences in pyrolysis behavior and product distribution of the four lignins were investigated under the same pyrolytic conditions systematically. The effects of different pyrolysis temperatures and times on the product compositions of the EHL were also studied.

While the three biomass sources (Amur linden, corn stover and wheat straw lignins) chemically differ and the methods of isolation used also differ, we have not studied lignin thermolysis from each biomass source where the lignin was isolated by all four of the separation methods (Björkmann, EHL, AL and SL). Instead we have only used the commercially available sources of lignin. This was focus of this work rather than developing the isolation methods for each species.

2. Results and Discussion

2.1. Thermogravimetric Analysis

The TGA and derivative thermogravimetric analysis (DTG) curves of the four selected lignins are shown in Figure 1. The DTG curves' peak temperatures, and maximum decomposition rates and the TGA residue percents are given in Table 1. When the temperature was <120 °C, the weight loss of the four lignins involved free water evaporation. Most decomposition occurred over a wide temperature 150–500 °C range. There are two small DTG peaks between 200 °C and 250 °C in MWL, attributed to the loss of some gaseous products from the cleavage of lignin side chains [20]. Major decomposition of MWL occurred at higher temperatures. The MWL was isolated by the Björkmann method, which leaves the lignin less decomposed than other methods (and with the highest molecular wt.). Thus, it takes more total bond cleavages and bond breaking to vaporize MWL. This, in turn, requires higher temperatures. EHL has the lowest decomposition rate and lowest absolute weight loss, leading to the highest residue yield (57.8%). The TGA of wheat straw AL also has a slow weight loss and about the same residue yield as corn stover EHL. The wheat straw AL has two major mass loss peaks appearing at 232 °C and 404 °C. The fragmentation of many major chain linkages occurred between 150–300 °C and the residue further reacted to form char in the temperature range from 350 to 500 °C. The low decomposition temperature of wheat straw AL was most likely promoted by the catalytic effect of sodium derived from the isolation process [21]. The Wheat Straw SL lignin shows a vast weight decrease at relatively low temperatures due to its high sulfur and carboxylic group content, which can both readily decompose to form gases (e.g., SO₂ and CO₂). These four lignin types displayed markedly different thermal degradation behaviors, a result of their different structures and compositions when isolated by different processes.

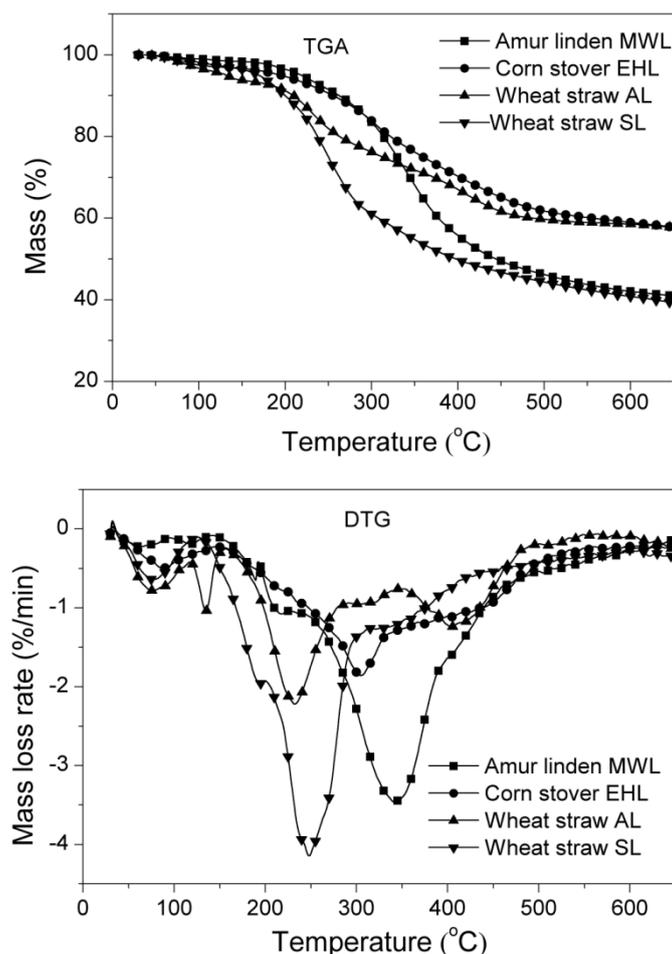


Figure 1. Curves of TGA and DTG for four different lignins, all at a heating rate of 10 °C/min. MWL: milled wood lignin; EHL: enzymatic hydrolysis lignin; AL: alkali lignin; SL: sulfonate lignin.

Table 1. Characteristic points on the TGA and DTG curves of the four lignins used in pyrolysis studies.

Lignin ^a	T _{max} ^b (°C)	MDR ^c (°C/min)	Residue (%)
MWL	342	3.5	41.0
EHL	305	1.9	57.8
AL	232	2.2	57.6
SL	248	4.1	39.2

^a MWL: milled Amur linden wood lignin; EHL: enzymatic hydrolysis corn stover lignin; AL: alkali lignin from wheat straw black liquor; SL: sulfonate lignin from wheat straw black liquor. ^b The peak temperature of DTG curve. This is where the mass loss occurs at the highest rate under the DTG conditions used. ^c The maximum decomposition rate.

2.2. FTIR Analysis

The FTIR spectra of the four lignins and their pyrolytic residues are presented in Figure 2, and their main adsorption peaks are assigned in Table 2. All four lignins exhibited similar characteristic absorptions for the functional groups identified in Figure 2. Hydroxyl (3571–3037 cm⁻¹), methoxyl

(1210 cm^{-1} , 1028 cm^{-1}) and aromatic ring (1600, 1515 and 1420 cm^{-1}) vibration bands are present in all four lignins. However, the aromatic ring absorption peaks in AL exhibited higher intensities than those in the other three lignins. The MWL absorption peaks in fingerprint region were the most abundant and its non-conjugated carbonyl absorption at 1710 cm^{-1} was detected. MWL exhibited the highest molecular weight (18,000, Table 3), in agreement with this lignin having a structure closer to what occurs in the plant. Thus, one would expect more of the aliphatic regions between aromatics rings would survive. MWL also showed the strongest sp^3 C-H stretching absorptions at 2932 and 2835 cm^{-1} among the four types of lignin, in accord with this view. This suggests that MWL might generate more hydrocarbons during pyrolysis [9]. The FTIR spectrum of EHL was similar that of MWL, but the absorption peaks were weaker from 1700 cm^{-1} to 1250 cm^{-1} . A broad-absorptive band was found between 1180 cm^{-1} and 880 cm^{-1} in EHL, and two broad bands appeared in AL at 1527–1241 cm^{-1} and 1190–910 cm^{-1} . These broad bands occur due to the overlap of many different peaks. The S=O symmetric stretching vibration was found at 1030 cm^{-1} in the spectrum of SL. The FTIR spectra of the pyrolytic residues of all four lignins are shown in Figure 2. The intensities of most absorption peaks are weakened, indicating that many syringyl, guaiacyl and p-hydroxyphenylpropane structural units and the three carbon units connecting such units into the lignin crosslinked structure were broken down in pyrolysis.

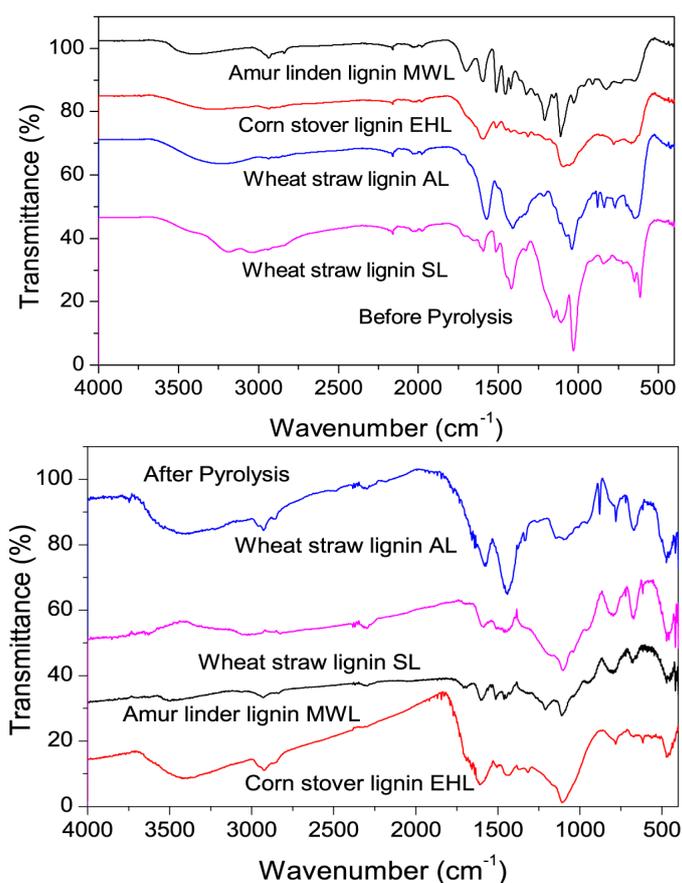


Figure 2. FTIR spectra of the four lignins before and after pyrolysis. MWL: Amur linden milled wood lignin; EHL: corn stover enzymatic hydrolysis lignin; AL: wheat straw alkali lignin; SL: wheat straw sulfonate lignin.

Table 2. The FTIR analysis of lignin microstructure.

Wave number (cm ⁻¹)	Band origin
2932, 2835	C–H stretching vibrations of alkyls
1710	C=O non-conjugate stretching vibration
1600	C=O stretching vibration conjugated to the aromatic ring, aromatic ring vibration
1510	Aromatic ring vibrations
1455	C-H bending vibration, asymmetric vibration of CH ₃ and CH ₂
1420	Aromatic ring vibrations and C–H in plane deformation
1322	Syringyl ring and C–O stretching vibration
1270	Guaiacyl ring and C–O stretching vibration
1210	C–C and C–O stretching vibrations
1148	C–H in plane deformations of guaiacyl units
1108	C–H in plane deformations of syringyl units
1028	C–H in plane deformation of aromatic ring, S=O symmetrical stretching vibration
910	C–H out-of-plane deformation of aromatic ring
836	C–H out-of-plane in positions 2 and 6 of syringyl units
827	C–H out-of-plane in positions 2, 5 and 6 of guaiacyl units

2.3. Results of Py-GC/MS

2.3.1. Pyrolysis of the Four Lignins

Pyrolyses of all lignins were carried out using Py-GC/MS at 450 °C with a 30 s pyrolysis time. Since the heating rate was 20 °C/ms, only 21–22 ms are required for a sample to reach 450 °C from room temperature. Thus, for essentially all 30 s the sample experiences 450 °C. The detected products can be roughly classified into acids, alcohols, aldehydes, ketones, furans, phenols, esters and hydrocarbons as summarized in Figure 3a. Phenols are the most abundant products among the MWL, EHL and AL pyrolysis products, and the second most abundant group for SL. Large numbers of furans and sulfur compounds are formed in the pyrolysis of SL. Furans are the most abundant products from SL. The highest phenolic content, 58.4 area % of all GC peaks, was obtained from AL pyrolysis. This was consistent with the FTIR analysis, which showed the most intense adsorption peaks associated with aromatic ring vibrations (1600 and 1420 cm⁻¹) and C-H out-of-plane deformations of aromatic rings at 800–900 cm⁻¹. Amen-Chen *et al.* [22] and Zakzeski *et al.* [23] suggested that free-radical depolymerization/fragmentation reactions during lignin pyrolysis resulted in monomeric phenolic compound formation.

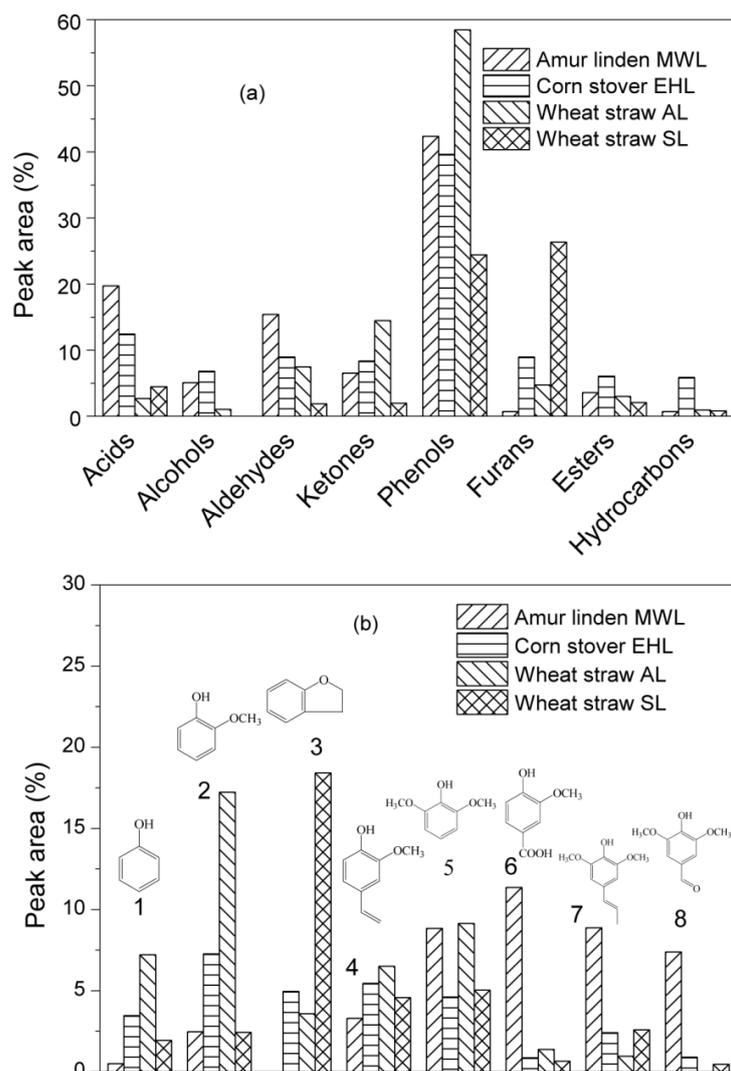


Figure 3. (a) Comparison of the product distributions from the pyrolysis of the four lignins. (b) Specific typical compounds produced by pyrolyzing the four lignins. MWL: milled wood lignin; EHL: enzymatic hydrolysis lignin; AL: alkali lignin; SL: sulfonate lignin.

The composition and distribution of phenolic products are influenced by the types of lignin as readily illustrated in Figure 3b. Guaiacyl (G)- and syringyl (S)-type compounds were the predominant products of Amur linden MWL, and the peak area ratio of G/S was 1.1. Small amounts of phenol and alkyl phenols were identified in MWL pyrolysis products indicating that few methoxyl groups were removed from the lignin monomeric unit at 450 °C. The main Guaiacyl- and syringyl-type products were 2-methoxyphenol, 2-methoxy-4-vinylphenol, 4-hydroxy-3-methoxybenzoic acid, 2,6-dimethoxyphenol, 2,6-dimethoxy-4-(2-propenyl)phenol and 4-hydroxy-3,5-dimethoxybenzaldehyde as shown in Figure 3b. Other guaiacyl- and syringyl-type compounds were also observed, such as 2-methoxy-4-methylphenol, 4-ethyl-2-methoxyphenol, eugenol, vanillin, 2-methoxy-4-(1-propenyl)phenol and 1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone. As expected, the guaiacyl-, syringyl- and p-hydroxyphenyl-type (H) compounds were all identified in the products of corn stover EHL and wheat stalk AL and wheat stalk SL. The peak area ratio of G/S/H was 1.7/1/0.8 for EHL, 2.3/1/0.9 for AL and 0.8/1/0.4 for SL. The primary H-type products were 4-methylphenol and 4-ethylphenol.

Guaiacyl-type compounds were the most abundant phenols in the AL pyrolysate, accounting for 31.1% of the total peak area. However, in SL pyrolysis products, the total peak area of syringyl-type compounds was slightly higher than those of guaiacyl-type compounds. Above all, it is clear that the fast pyrolysis products depend strongly on the lignin's origin and isolation process.

The yield of furans in the SL pyrolysate was higher, up to 26.3%, than for the other three lignins. 2,3-Dihydrobenzofuran was the most abundant furan accounting for 18.4%. According to Lou *et al.* [24], the lignin pyrolysis mechanism proceeds through an o-quinonemethide intermediate with an allylmethyl group. This intermediate then cyclized followed by hydrogen abstraction to produce 2,3-dihydrobenzofuran. Furan compounds such as furfural and 5-methoxy-2-furancarboxaldehyde are well known to arise from the pyrolysis of cellulose and hemicellulose or their oligomers. These constituents were found in EHL, AL and SL, confirming that these three feedstocks were not pure lignins. Levoglucosan was identified in the EHL, AL and SL pyrolysis products (1.4%, 0.9%, and 0.3%, respectively), which confirmed this point.

MWL generated the largest amounts of acids and aldehydes indicating the presence of large amounts of carbonyl functions in MWL. This is in good agreement with the relatively higher adsorption in about 1710 cm^{-1} (characteristic absorption of C=O stretching vibration) in FTIR spectrum of MWL. Moreover, the peak areas of 4-hydroxy-3-methoxybenzoic acid (11.3%), 4-hydroxy-3,5-dimethoxybenzaldehyde (7.4%), and vanillin (3.3%) in MWL pyrolysate were significantly higher than those in other three lignins. This further agrees with our postulate that large amounts of carbonyl and carboxyl functional groups were present in the structure of MWL. Acetic acid and aldehydes (mainly acetaldehyde) detected in the pyrolysate of four lignins were derived from the side-chain cleavage from lignin as well as the decomposition of residual cellulose, hemicellulose or their oligomers remaining in the lignin. AL had the highest ketone yield, composed mainly of 2-hydroxy-3-methyl-2-cyclopenten-1-one, 2-methyl-2-cyclopenten-1-one and 2-butanone. Large amounts of sulfur-containing compounds including sulfur dioxide, methanethiol, carbon disulfide and dimethyl sulfide were detected in the pyrolysis products of SL. The yield of methanethiol in SL pyrolysate reached 14.0 GC area %. These sulfur-containing compounds may originate during kraft pulping as well as from thermochemical reactions occurring during pyrolysis [25]. Pyrolysis char residues have higher C/H ratios than the original lignins (Table 3), indicating the degree of carbonization of lignin that occurred during its pyrolysis.

2.3.2. The Effects of Pyrolysis Temperature and Time

The effect of different pyrolysis temperatures (350, 450, 550 and 650 °C) on the corn stover EHL product compositions and distributions was studied. The pyrolysis products derived from EHL were classified into eight categories: acids, alcohols, aldehydes, ketones, phenols, furans, esters and hydrocarbons as given in Figure 4a. At 350 °C, EHL pyrolysis mainly produced alcohols and acids including 5.1% acetic acid, 14.1% 2-hydroxypropanoic acid, 3.4% 2-octanol, 4.8% glycerin and 2.3% 1,2,3-butanetriol (in GC area percents). These products were mainly derived from the pyrolysis of cellulose, hemicellulose and the side-chain cleavages from lignin's guaiacyl rings. The yields of acids and alcohols decreased as the pyrolysis temperature increased. Ben *et al.* also found that the concentration of acetic acid and methanol in light oil produced by lignin pyrolysis decreased as

temperature rose [26]. The 13.3% yield of phenols indicated that only a fraction of the EHL decomposition pathway occurred at 350 °C. At higher temperature (450 °C), the amounts of phenolic compounds increased from 13.3% to 40.0% as greater structural fragmentation occurred. The yields of some typical phenols varied using different pyrolysis temperatures as shown in Figure 4b. All phenolic products increased distinctly as the temperature increased from 350 °C to 450 °C. This demonstrated that more β -O-4, α -O-4, C-C lignin linkages were cracked to produce a large amount of single ring phenolic structures at higher temperature. As 550 °C, the amount of phenols slightly decreased. The yields of aldehydes, ketones and furans rose in contrast to acids and alcohols at higher temperatures. These results are similar to the report of Lou *et al.* [13]. He found that the lower temperature (250–400 °C) pyrolysis products of enzymatic/mild acidolysis lignin were mainly 2,3-dihydrobenzofuran, while at 400–800 °C, phenols were the main products.

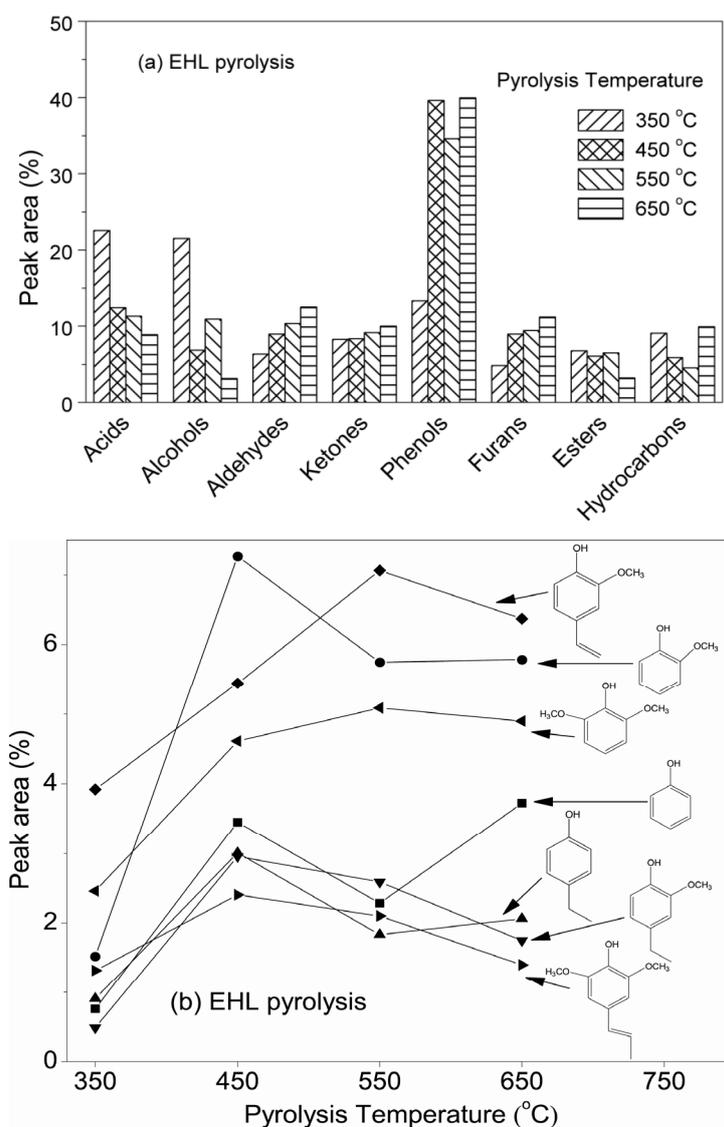


Figure 4. (a) Comparison of the product distributions. (b) typical compounds from corn stover EHL pyrolysis at different temperatures. The pyrolysis time holding for 30 s. ■: phenol, ●: 2-methoxyphenol, ▲: 4-ethylphenol, ▼: 4-ethyl-2-methoxyphenol, ◆: 2-methoxy-4-vinylphenol, ◀: 2,6-dimethoxyphenol, ▶: 2,6-dimethoxy-4-(2-propenyl)phenol.

The influence of pyrolysis time (15, 30 and 60 s) at 450 °C on corn stover EHL was also studied. As presented in Figure 5, pyrolysis time had little effect on product distribution. The yields of aldehydes, ketones, furans, esters and hydrocarbons fluctuated versus pyrolysis times within a fairly narrow range. Alcohol production increased to 15.5% going from 30 s to 60 s. The maximum yield of phenols occurred in 30 s.

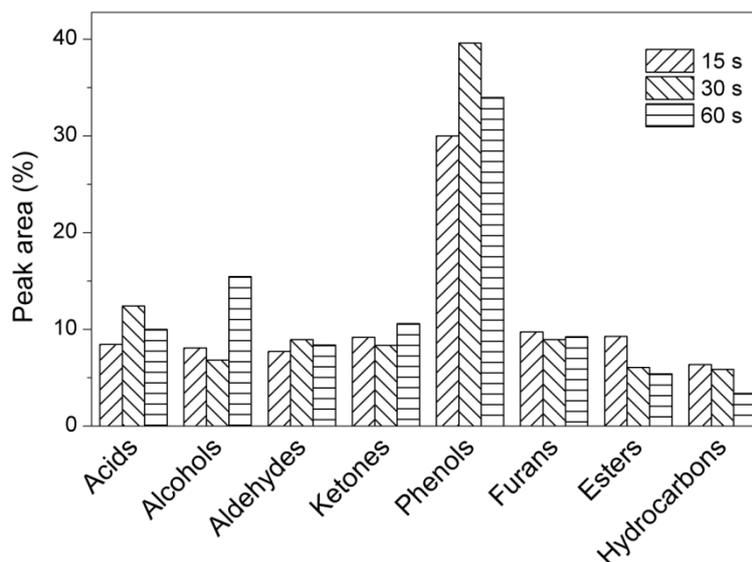


Figure 5. The effect of pyrolysis times from 15 to 60 s at 450 °C on the product distributions of corn stover EHL pyrolysis.

2.4. Comparability between TGA and Py-GC/MS

It is well known that the weight loss behavior and product composition depend on the lignin isolation processes. In this study, TGA was used to determine degradation behaviors of the four lignins. Py-GC/MS was used to detect the product compositions of the four lignins. TGA and Py-GC/MS are not directly comparable because of the significantly differences of sample dosage and heating rates. Different sample dosages and heating rates would play different effects on both heat and mass transfer rate which would clearly produce different and varying product distributions. Actually, we studied the effect of heating rate on the pyrolysis product composition of EHL. The peak area % of phenols and carbonyls were decreased while the peak area % of acids, esters and aromatics were slightly increased with the heating rate decrease from 20 °C/ms to 2 °C/s. It indicated that different heating rates result in different product distribution.

Table 3. Comparison char yields by using Py-GC/MS and TGA at 450 °C ^a.

Lignin sample	Char yield (%)	
	Py-GC/MS	TGA
MWL	52.2	49.5
EHL	66.7	65.1
AL	62.7	61.7
SL	45.2	46.7

^a The heating rates of Py-GC/MS and TGA are 20 °C/ms and 10 °C/min, respectively.

Table 3 shows the comparison of char yields obtained separately by Py-GC/MS and TGA at the same pyrolysis temperature (450 °C). We can see from Table 3 that, weight losses from Py-GC/MS and TGA, which employed both varying sample dosages and heating rates, show a close relationship. This implies that weight loss from the TG analysis would be reflected in the fast pyrolysis to a considerable extent. In fact, extent of this rather close correspondence is rather surprising given the enormous differences in heating rates.

3. Experimental Section

3.1. Materials

Milled wood lignin was isolated after extensive milling of Amur linden (*Tilia amurensis Rupr.*) wood flour in a ball mill prior to extraction with dioxane-water according to the Björkman method [27]. Enzymatic hydrolysis lignin, provided by Tianguan Company (Henan, China), was extracted from corn stover residue, a byproduct derived from the production of bioethanol. We didn't determine the content of protein in enzymatic hydrolysis corn stover lignin (EHL). But, cellulose-isolated lignin is known to have protein impurities. The higher nitrogen content of EHL (1.1%) *versus* the other lignins (0.5–0.8%) determined by an elemental analyzer agrees with the existence of some nitrogenous compounds, protein most likely. Both alkali lignin (AL) and sulfonate lignin (SL) were purchased from Feihuang Chemical Company (Xinyin, China). AL was produced by treating the wheat straw black liquor from the NaOH pulping process with acid. SL was recovered from the spent wheat straw pulping liquids (red or brown liquor) from sulfite pulping. The four original lignins are characterized in Table 4. All the four types of lignin were used for experiments without further treatment except drying to constant weight at 105 °C.

Table 4. Characterization of the four lignin types used for pyrolysis.

Analyses	Lignin ^a			
	MWL	EHL	AL	SL
Average Mol. Wt.	18,000	1,200	9,000	5,400
Ash content (%)	<0.1	<3.0	13.1	11.8
Particle size (Mesh)	120	120	120	120
Residual sugar (%)	<0.5	< 5.0	UT ^b	UT ^b
C (%)	58.1	60.5	31.0	19.4
H (%)	5.7	6.5	4.4	3.2
O (%) ^c	35.7	31.9	64.0	71.0
N (%)	0.5	1.1	0.6	0.8
S (%)	0	0	0	5.6
C/H ratio ^d	0.9 (1.0)	0.9 (1.4)	0.6 (0.7)	0.5 (0.8)
O/C ratio ^e	0.6 (6.4)	0.5 (3.1)	2.1 (5.1)	3.7 (11.3)

^a MWL: milled Amur linden wood lignin; EHL: enzymatic hydrolysis corn stover lignin; AL: alkali lignin from wheat straw black liquor; SL: sulfonate lignin from wheat straw black liquor. ^b Untested. ^c Determined by difference. ^d The corresponding C/H ratios of the four lignins after pyrolysis at 450 °C for 30 s are shown in parentheses as bold type. ^e The corresponding O/H ratios of the four lignins after pyrolysis at 450 °C for 30 s are shown in parentheses as bold type.

3.2. Methods

The carbon, hydrogen, nitrogen and sulfur content of the samples were determined using an elemental analyzer (Flash EA 1112, Thermo Electron SPA, Waltham, MA, USA). The thermogravimetric behaviors of four lignins were performed in a thermogravimetric analyzer manufactured by Perkin-Elmer Company. TGA samples were heated from room temperature to 650 °C at a heating rate of 10 °C/min under nitrogen (99.99%). The main chemical functional groups of these four lignins were analyzed by Nicolet6700 FTIR spectroscopy (Thermo Fisher Nicolet, Waltham, MA, USA) with high performance diamond ATR. Their pyrolytic residues were characterized using a MAGNA-IR560E.S.P. FTIR spectrometer (Nicolet Instr., Madison, WI, USA) in KBr pellets, between 400–4000 cm^{-1} at a resolution of 4 cm^{-1} .

Fast pyrolysis experiments were carried out in a CDS 5200 pyroprobe directly connected to an Agilent 6890N gas chromatograph (GC) mated to an Agilent 5973i mass spectrometer (MS). Samples (0.5 mg) were placed in quartz tube and between quartz wool packed on each side and then the tubes were inserted into the pyroprobe. The sample in the pyroprobe was pyrolysed at a set point temperature range between 350 °C and 650 °C at a ramp rate of 20 °C/ms with the final dwell time of 30 s. The pyroprobe was operated in trap mode under a He atmosphere. The valve oven and transfer lines were maintained at 300 and 285 °C, respectively. Separation of volatile pyrolysis products was achieved on an Agilent DB-17ms capillary column (30 m \times 0.25 mm \times 0.25 μm film thickness). The split ratio was 50:1 with helium carrier gas flow of 1 mL/min. The GC oven temperature was held at 40 °C for 4 min and then programmed to 230 °C (2 min) at 5 °C/min, and then heated further to 280 °C (5 min) at 10 °C/min. The mass spectrometer was operated in EI mode at 70eV over the m/z range from 40 to 500 amu. The ion source was kept at 230 °C. The inlet and auxiliary lines were both maintained at 300 °C. Peak identification was carried out using both the NIST mass spectral library and relevant literature. Pyrolytic experiments were replicated two times under identical conditions, including using the same controlled amounts. The total ion chromatograms exhibited good reproducibility. The average values were used in plots of Py-GC/MS figures and standard deviations were less than 0.2.

4. Conclusions

The four lignins studied exhibited widely different thermal degradation behaviors at both slow and fast heating rates. The maximum weight loss rate regions in DTG were especially different and distinct. It is attributed to the different chemical structures of the lignins isolated by different processes. The same characteristic FTIR absorptions for the main lignin functional groups including both sp^2 and sp^3 C–O, –OH and aromatic ring breathing vibration were all identified in the four lignins, although with different intensities. The syringyl, guaiacyl and p-hydroxyphenyl structural units were partially broken down after pyrolysis.

The fast pyrolysis volatile products depend strongly on the lignin origin and isolation process. Phenols are the predominant products in the four lignins except for wheat straw SL which produces furans as the major products and large amounts of sulfur-containing compounds originating from kraft pulping. Corn stover MWL exhibited a guaiacyl-syringyl structure with the G/S peak area ratio of 1.1. Other three lignins exhibited guaiacyl-syringyl-p-hydroxyphenyl structure with different G/S/H ratios.

Pyrolysis of corn stover-derived EHL at lower temperature (350 °C) mainly caused side-chain cleavage to produce abundant acids and alcohols while at higher temperature (≥ 450 °C) phenolic compounds became the predominant products. Pyrolysis time has no obvious effect on the EHL pyrolysis product distribution.

This work represents a first step in understanding how fast pyrolysis could be used to optimize product distribution ranges for isolation and further use or for upgrading. A thorough study of pyrolysis heating rates, temperatures and holding periods is needed at both atmospheric pressure and under vacuum to further explore the potential of various commercial lignins. Huge amounts of various types of lignin from different plant species are available. Each species is unique and each lignin isolation process is different. Hence, lignins from large industrial processes need to be targeted for detailed optimized fast pyrolysis studies to determine if specific process conditions can be identified to produce useful product fractions. Mixtures of products in all fractions are likely. Fast pyrolytic co-thermolysis of lignin with other organic feeds (waste polymers, bio-oil, hydrocarbon fractions, etc.), both in the presence and absence of catalysts, are future challenges.

Acknowledgments

This material is based upon work performed at the MOE Key Laboratory of Bio-based Material Science and Technology at Northeast Forestry University. This work was supported by the Fundamental Research Funds for the Central Universities under the Project Number 2572015BB02, and by the Academic Research Fund Project of Education Bureau of Liaoning Province, China (No.12012209). Mississippi State University supported Charles U. Pittman Jr.'s contribution to this work.

Author Contributions

Shu-juan Sui and Zhi-jun Zhang conceived and designed the experiments; Xiao-na Lin performed the experiments and wrote the paper; Shun Tan and Jian-ping Sun analyzed the data; Charles U. Pittman Jr. polished the article.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Butler, E.; Devlin, G.; Meier, D.; McDonnell, K. A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renew. Sust. Energ. Rev.* **2011**, *15*, 4171–4186.
2. Zhang, Q.; Chang, J.; Wang, T.J.; Xu, Y. Review of biomass pyrolysis oil properties and upgrading research. *Energy Convers. Manag.* **2007**, *48*, 87–92.
3. Chakar, F.S.; Ragauskas, A.J. Review of current and future softwood kraft lignin process chemistry. *Ind. Crop. Prod.* **2004**, *20*, 131–141.
4. Mu, W.; Ben, H.; Ragauskas, A.; Deng, Y. Lignin Pyrolysis Components and Upgrading-Technology Review. *Bioenerg. Res.* **2013**, *6*, 1183–1204.

5. Windt, M.; Meier, D.; Marsman, J.H.; Heeres, H.J.; de Koning, S. Micro-pyrolysis of technical lignins in a new modular rig and product analysis by GC-MS/FID and GC×GC-TOFMS/FID. *J. Anal. Appl. Pyrolysis* **2009**, *85*, 38–46.
6. Brebu, M.; Cazacu, G.; Chirila, O. Pyrolysis of lignin—a potential method for obtaining chemicals and/or fuels. *Cellul. Chem. Technol.* **2011**, *45*, 43–50.
7. Pittman, C.U., Jr.; Mohan, D.; Eseyin, A.; Li, Q.; Ingram, L.; Hassan, E.B.M.; Mitchell, B.; Guo, H.; Steele, P.H. Characterization of bio-oils produced from fast pyrolysis of corn stalks in an auger reactor. *Energy Fuels* **2012**, *26*, 3816–3825.
8. Mohan, D.; Pittman, C.U., Jr.; Steele, P.H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* **2006**, *20*, 848–889.
9. Zhang, M.; Resende, F.L.P.; Moutsoglou, A.; Raynie, D.E. Pyrolysis of lignin extracted from prairie cordgrass, aspen, and Kraft lignin by Py-GC/MS and TGA/FTIR. *J. Anal. Appl. Pyrolysis* **2012**, *98*, 65–71.
10. Patwardhan, P.R.; Brown, R.C.; Shanks, B.H. Understanding the fast pyrolysis of lignin. *ChemSusChem* **2011**, *4*, 1629–1636.
11. Shen, D.K.; Gu, S.; Luo, K.H.; Wang, S.R.; Fang, M.X. The pyrolytic degradation of wood-derived lignin from pulping process. *Bioresour. Technol.* **2010**, *101*, 6136–6146.
12. Sharma, R.K.; Wooten, J.B.; Baliga, V.L.; Lin, X.H.; Chan, W.G.; Hajaligol, M.R. Characterization of chars from pyrolysis of lignin. *Fuel* **2004**, *83*, 1469–1482.
13. Lou, R.; Wu, S.B.; Lv, G.J. Effect of conditions on fast pyrolysis of bamboo lignin. *J. Anal. Appl. Pyrolysis* **2010**, *89*, 191–196.
14. Wang, S.R.; Wang, K.G.; Liu, Q.; Gu, Y.L.; Luo, Z.Y.; Cen, K.F.; Fransson, T. Comparison of the pyrolysis behavior of lignins from different tree species. *Biotechnol. Adv.* **2009**, *27*, 562–567.
15. Obst, J.R. Analytical pyrolysis of hardwood and softwood lignins and its use in lignin-type determination of hardwood vessel elements. *J. Wood Chem. Technol.* **1983**, *3*, 377–397.
16. Pandey, M.P.; Kim, C.S. Lignin depolymerization and conversion: A review of thermochemical Methods. *Chem. Eng. Technol.* **2011**, *34*, 29–41.
17. Beis, S.H.; Mukkamala, S.; Hill, N.; Joseph, J.; Baker, C.; Jensen, B.; Stemmler, E.A.; Wheeler, M.C.; Frederick, B.G.; Heiningen, A.V.; *et al.* Fast pyrolysis of lignins. *BioResources* **2010**, *5*, 1408–1424.
18. Nowakowski, D.J.; Bridgwater, A.V.; Elliott, D.C.; Meier, D.; de Wild, P. Lignin fast pyrolysis: Results from an international collaboration. *J. Anal. Appl. Pyrolysis* **2011**, *88*, 53–72.
19. Jiang, G.Z.; Nowakowski, D.J.; Bridgwater, A.V. A systematic study of the kinetics of lignin pyrolysis. *Thermochim. Acta* **2010**, *498*, 61–66.
20. Jakab, E.; Faix, O.; Till, F.; Szekely, T. Thermogravimetry/mass spectrometry study of six lignins within the scope of an international round robin test. *J. Anal. Appl. Pyrolysis* **1995**, *35*, 167–179.
21. Wang, J.; Zhang, M.X.; Chen, M.Q.; Min, F.F.; Zhang, S.P.; Ren, Z.W.; Yan, Y.J. Catalytic effects of six inorganic compounds on pyrolysis of three kinds of biomass. *Thermochim. Acta* **2006**, *444*, 110–114.
22. Amen-Chen, C.; Pakdel, H.; Roy, C. Production of monomeric phenols by thermochemical conversion of biomass: A review. *Bioresour. Technol.* **2001**, *79*, 277–299.

23. Zakzeski, J.; Bruijninx, P.C.A.; Jongerius, A.L.; Weckhuysen, B.M. The catalytic valorization of lignin for the production of renewable chemicals. *Chem. Rev.* **2010**, *110*, 3552–3599.
24. Lou, R.; Wu, S.B.; Lv, G.J. Fast pyrolysis of enzymatic/mild acidolysis lignin from moso bamboo. *BioResources* **2010**, *5*, 827–837.
25. Brebu, M.; Tamminen, T.; Spiridon, I. Thermal degradation of various lignins by TG-MS/FTIR and Py-GC-MS. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 531–539.
26. Ben, H.; Ragauskas, A.J. NMR Characterization of Pyrolysis Oils from Kraft Lignin. *Energy Fuels* **2011**, *25*, 2322–2332.
27. Björkmann, A. Studies on finely divided wood. Part 1: Extraction of lignin with neutral solvents. *Svensk Papperstidn* **1957**, *59*, 477–485.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).