

# Influence of Si/Al Ratio of ZSM-5 Zeolite on the Properties of Lignin Pyrolysis Products

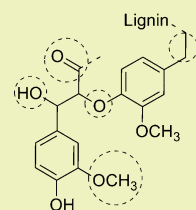
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## S Supporting Information

**ABSTRACT:** The pyrolysis of softwood (SW) kraft lignin in the presence of various H-ZSM-5 zeolites with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratios from 23/1–280/1 as additives were examined at 600 °C. Nuclear magnetic resonance (NMR), including quantitative <sup>13</sup>C, <sup>31</sup>P NMR, and heteronuclear single-quantum correlation (HSQC)-NMR, and gel permeation chromatography (GPC) were used to characterize various pyrolysis oils. On the basis of the results of the <sup>13</sup>C and <sup>31</sup>P NMR for pyrolysis oils, the use of H-ZSM-5 zeolites during the pyrolysis process caused the near complete decomposition of aliphatic hydroxyl and carboxyl groups. With the exception of carboxylic acid, the H-ZSM-5 zeolite with a relatively higher SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio was more effective at the elimination of methoxyl groups, ether bonds, and aliphatic C–C bonds, and dehydration of aliphatic hydroxyl groups during pyrolysis. However, the H-ZSM-5 zeolite with a very large SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio, such as 280, has only limited effects on the properties of upgraded pyrolysis oil. After the use of zeolite, the pyrolysis oils contain some polyaromatic hydrocarbons, the content of which decreased with an increasing SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio of zeolite. GPC results show that the molecular weight decreased by 8–16% after the use of H-ZSM-5 zeolites.

**KEYWORDS:** Pyrolysis oil, Upgrading, H-ZSM-5 zeolite, Si/Al ratio



Improved decomposition during the pyrolysis

- Cleavage of C–C bond
- Decarboxylation
- Dehydration and cleavage of ether bonds
- Cleavage of methoxyl–aromatic bond

## INTRODUCTION

The use of biomass for renewable energy production is increasingly being viewed as a promising alternative method to reduce net carbon dioxide emissions and gain long-term energy security.<sup>1</sup> Among the various conversion technologies being investigated, pyrolysis has been reported as one of the economic ways (i.e., low capital and operating costs) to utilize biomass for biofuels and biochemicals.<sup>2</sup> Lignin is the second most abundant biomass component and the primary renewable aromatic resource in nature. Lignin, however, has received much less attention than plant polysaccharides as a resource for biofuels. Kraft lignin obtained by precipitation from the cooking liquor of the kraft pulping process is abundant and has been used as a low-value material.<sup>3,4</sup> The major drawback toward commercialization of pyrolysis oils are several challenging properties, including poor volatility, high oxygen content, acidity, viscosity, corrosiveness, and cold flow problems.<sup>5</sup> Therefore, upgrading technologies that convert bio-oils to a potential substitution of diesel and gasoline fuels is necessary. Among these technologies, in situ upgrading of pyrolysis oil during the pyrolysis process appears to be pragmatic.<sup>6</sup>

Many researchers have used zeolites to upgrade the properties of pyrolysis oil during the pyrolysis process. For example, Mullen et al.<sup>7</sup> used analytical pyrolysis methods (Py-GC-MS) to pyrolyze four different lignins at 650 °C, and they indicated that H-ZSM-5 zeolite could improve the depolymerization of lignins. French et al.<sup>8</sup> used molecular-beam mass

spectrometry (MBMS) to analyze the product vapors from pyrolysis of cellulose, straw lignin, and ground aspen wood with 40 different additives at 400, 500, and 600 °C. They found that the highest yield of hydrocarbons (~16 wt %) was achieved using nickel-, cobalt-, iron-, and gallium-substituted ZSM-5 zeolite during the pyrolysis. Consistent with the results of Mullen et al.<sup>7</sup> and Zhao et al.,<sup>9</sup> they suggested that the zeolites could improve deoxygenation reactions during pyrolysis, in addition, they also indicated that the best-performing catalysts belonged to ZSM-5 zeolites. Jackson et al.<sup>10</sup> used sand, H-ZSM-5, and K-ZSM-5 zeolite as additives during the pyrolysis of lignin at 600 °C and analyzed the gas and liquid products by GC-MS. They found that H-ZSM-5 zeolite almost completely deoxygenated the liquid phase producing simple aromatics and naphthalenics. The pyrolysis of several biomasses such as, corn stalks,<sup>11,12</sup> cassava rhizome,<sup>13,14</sup> hybrid poplar wood,<sup>15</sup> rice husks,<sup>16</sup> and pine wood<sup>17–19</sup> with ZSM-5 zeolites has also been studied in recent years. All of these studies indicated that the use of zeolite during pyrolysis yielded a bio-oil that had lower oxygen content. Most of the researchers have focused on the pyrolysis of biomass,<sup>11–20</sup> while only a few have examined the behavior of lignin in the presence of additives during pyrolysis.<sup>7,8</sup> Different Si/Al ratios of zeolite have been shown to affect the cracking reactions of model compounds during

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Table 1. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Mole Ratio and Code Name Used in This Work for Each Zeolite

	CBV 2314	CBV 3020E	CBV 5524G	CBV 8014	CBV 28014
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mole ratio	23	30	50	80	280
code name	Z23	Z30	Z50	Z80	Z280

thermal treatment.<sup>21–27</sup> However, only a few researchers have investigated the influence of different Si/Al ratios of zeolite on the properties of pyrolysis products. For example, Aho et al.<sup>28</sup> pyrolyzed pine wood with various H-Beta zeolites, and they indicated that zeolites with lower Si/Al ratios formed less organic oil, more water, and polyaromatic hydrocarbons.

Our previous work<sup>29</sup> investigated the efforts of zeolites and nickel salt as pyrolysis additives for softwood kraft lignin and found that H-ZSM-5 zeolite was shown to improve the decomposition of aliphatic hydroxyl, carboxyl, and methoxyl groups and ether bonds in the lignin during the pyrolysis. To avoid the limitation of several analysis methods such as GC-MS and FTIR for pyrolysis oils, we introduced the use of nuclear magnetic resonance (NMR) including <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and heteronuclear single-quantum correlation (HSQC)-NMR to characterize various pyrolysis oils.<sup>30–32</sup> The general goal of this work was to examine the influence of Si/Al ratio of zeolite on the properties of pyrolysis products. This was accomplished by using NMR and GPC to analyze the liquid products of pyrolysis of a softwood kraft lignin with different ZSM-5 zeolite as the additives. We have done related work on the influence of different frameworks of zeolites with similar Si/Al ratios.<sup>33</sup>

## MATERIALS AND METHODS

All reagents used in this study were purchased from VWR International or Sigma-Aldrich (St. Louis, MO) and used as received. Lignin was isolated from a commercial United States softwood kraft pulping liquor. ZSM-5 (CBV 2314, CBV 3020E, CBV 5524G, CBV 8014, and CBV 28014) zeolites were purchased from Zeolyst, Inc.

**Lignin Separation and Purification.** Lignin was isolated from a commercial softwood kraft pulping liquor following published methods.<sup>31</sup> In brief, the cooking liquor was filtered through filter paper, and the filtrate was treated with EDTA-2Na<sup>+</sup> (0.50 g/100.0 mL liquor) and stirred for 1 h. The liquor was adjusted to a pH value of 6.0 with 2.0 M H<sub>2</sub>SO<sub>4</sub> and stirred vigorously for 1 h. The liquors were then further acidified to a pH of 3.0 and frozen at –20 °C. After thawing, the precipitates were collected on a medium sintered glass funnel and washed three times with cold water by suspending the precipitates in the water and stirring vigorously at 0 °C for 1 h. The precipitates were collected, air dried, and Soxhlet extracted with pentane for 24 h. The solid product was air dried and further dried under high vacuum at 45 °C for 48 h. The resulting purified kraft lignin sample was stored at –5 °C.

**Preparation of Pyrolysis Sample.** Different ZSM-5 (CBV 2314, CBV 3020E, CBV 5524G, CBV 8014, and CBV 28014) zeolites were used as additives in this work. The pyrolysis samples were mechanical stirred with a 1:1 mass ratio of lignin to zeolite. All the zeolites were preactivated in a pyrolysis tube at 500 °C under nitrogen for 6 h. The detailed information of each zeolite can be found in Table 1.

**Equipment and Process of Pyrolysis.** Pyrolysis experiments were conducted in a quartz pyrolysis tube heated with a split-tube furnace. Typically, the pyrolysis sample (4.00 g) was placed in a quartz sample boat that was then positioned in the center of a pyrolysis tube. A K-type thermal couple was immersed in the sample powder during the pyrolysis to measure the heating rate. The pyrolysis tube was flushed with nitrogen gas, and the flow rate was adjusted to a value of 500 mL/min and then inserted in the preheated (600 °C) furnace. The outflow from pyrolysis was passed through two condensers, which were immersed in liquid N<sub>2</sub>. Upon completion of pyrolysis, the reaction tube was removed from the furnace and allowed to cool to room temperature under constant N<sub>2</sub> flow. The condensers were then

removed from liquid nitrogen. The pyrolysis char and oil were collected for subsequent chemical analysis. In general, the liquid products contained two immiscible phases referred to as heavy and light oil. The light oil was acquired by decantation, and the heavy oil was recovered by washing the reactor with acetone followed by evaporation under reduced pressure. Char yields were determined gravimetrically, and gas formation was calculated by mass difference.

**Characterization of Pyrolysis Oils by GPC.** The weight average molecular weight (*M<sub>w</sub>*), number average molecular weight (*M<sub>n</sub>*), and molecular weight polydispersity of the heavy oils were determined by GPC analysis following literature methods.<sup>31</sup> Prior to GPC analysis, the heavy oil samples were dissolved in THF (1 mg/mL) and filtered through a 0.45 μm syringe filter. The samples were injected into a Polymer Standards Service (PSS) Security 1200 system featuring an Agilent HPLC vacuum degasser, isocratic pump, a refractive index (RI) detector, and UV detector (270 nm). Separation was achieved with four Waters Styragel columns (HR0.5, HR2, HR4, HR6) using THF as the mobile phase (1.0 mL/min) with injection volumes of 30 μL. Data collection and processing were performed using PSS WinGPC Unity software. Molecular weights (*M<sub>n</sub>* and *M<sub>w</sub>*) were calibrated against a calibration curve. The calibration curve was created by fitting a third-order polynomial equation to the retention volumes obtained from a series of narrow molecular weight distribution polystyrene standards (i.e., 7.21 × 10<sup>3</sup>, 4.43 × 10<sup>3</sup>, 1.39 × 10<sup>3</sup>, 5.80 × 10<sup>2</sup> Da), dioctyl phthalate (*M<sub>w</sub>* = 390 g/mol), 2,2'-dihydroxy-4,4'-dimethoxy-benzophenone (*M<sub>w</sub>* = 274 g/mol), 2-phenylhydroquinone (*M<sub>w</sub>* = 186 g/mol), phenol (*M<sub>w</sub>* = 94 g/mol), and acetone (*M<sub>w</sub>* = 58 g/mol). The curve fit had an *R*<sup>2</sup> value of 0.998.

**Characterization of Pyrolysis Oil by NMR.** *Quantitative <sup>13</sup>C NMR.* All NMR spectral data reported in this study were recorded with a Bruker Avance/DMX 400 MHz NMR spectrometer. Quantitative <sup>13</sup>C NMR were acquired using 100.0 mg heavy oil dissolved in 450 μL DMSO-*d*<sub>6</sub> employing an inverse gated decoupling pulse sequence, 90° pulse angle, a pulse delay of 5 s for heavy oils, and 6000 scans at room temperature with a line broadening (LB) of 5.0 Hz. <sup>31</sup>P The <sup>13</sup>C NMR has been reported to have a standard deviation of ±3.0%.<sup>29</sup>

*Quantitative <sup>31</sup>P NMR.* Quantitative <sup>31</sup>P NMR data were acquired after in situ derivatization of the samples using 10.0 mg of heavy oil or 4.0 mg for the light oil with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) in a solution of (1.6:1 v/v) pyridine/CDCl<sub>3</sub>, chromium acetylacetonate (relaxation agent), and endo-N-hydroxy-5-norbornene-2,3-dicarboximide (NHND, internal standard). <sup>31</sup>P NMR spectra data were acquired using an inverse gated decoupling pulse sequence, 90° pulse angle, 25 s pulse delay, and 128 scans at room temperature with a LB of 4.0 Hz.<sup>31</sup> The <sup>31</sup>P NMR data have been reported have a standard deviation of ±1.2%.<sup>29</sup>

**Characterization of Pyrolysis Oil by HSQC-NMR.** HSQC-NMR were acquired using 100.0 mg pyrolysis oil dissolved in 450 μL DMSO-*d*<sub>6</sub> employing a standard Bruker pulse sequence “hsqcetgpsi.2” with a 90° pulse, 0.11 s acquisition time, 1.5 s pulse delay, <sup>1</sup>J<sub>C–H</sub> of 145 Hz, 48 scans, and an acquisition of 1024 data points (for <sup>1</sup>H) and 256 increments (for <sup>13</sup>C). The <sup>1</sup>H and <sup>13</sup>C pulse widths are p1 = 11.30 μs and p3 = 10.00 μs, respectively. The <sup>1</sup>H and <sup>13</sup>C spectral widths are 13.02 and 220.00 ppm, respectively. The central solvent peak was used for chemical shift calibration. HSQC data processing and plots were carried out using the MestReNova v7.1.0 software's default processing template and automatic phase and baseline correction.

**Higher Heating Value (HHV) Measurement.** The higher heating values of lignin and heavy oils were measured in a Parr 1261 isoperibol bomb calorimeter according to the literature report.<sup>34,35</sup>

**Elemental Analysis.** Elemental analysis data of lignin and heavy oils were obtained by Atlantic Microlab, Inc. (Norcross, GA) utilizing

**Table 2.** HHV, Energy Yield, and Carbon Yield of Heavy Oil and Mass Yields of Light Oil, Heavy Oil, Char, and Gas for the Pyrolysis of Pure SW Kraft Lignin and Pyrolysis of SW Kraft Lignin with 1.0/1.0 ( $W_{\text{additive}}/W_{\text{lignin}}$ ) of H-ZSM-5 Zeolites as Additives at 600 °C for 10 min

pyrolysis samples <sup>a</sup>	Mass yield (%)				HHV (MJ/kg)	energy yield <sup>b</sup> (%)	carbon yield <sup>c</sup> (%)
	light oil	heavy oil	char	gas			
lignin (L)	14.47	28.97	44.21	12.35	30.78	33.11	27.52
L+Z23	17.21	23.81	44.50	14.48	31.24	27.63	23.55
L+Z30	17.60	24.47	47.02	10.91	31.55	28.68	24.33
L+Z50	15.18	27.17	46.68	10.97	31.38	31.67	26.90
L+Z80	14.74	26.53	46.57	12.16	31.27	30.81	25.96
L+Z280	17.49	25.05	48.33	9.13	30.21	28.10	24.14

<sup>a</sup>All yields are based on duplicated tests. <sup>b</sup>Energy yield = mass yield × (HHV of heavy oil/HHV of dried SW kraft lignin). HHV of dried SW kraft lignin is 26.92 MJ/kg. <sup>c</sup>Carbon yield = mass yield × (carbon% of heavy oil/carbon% of dried SW kraft lignin).

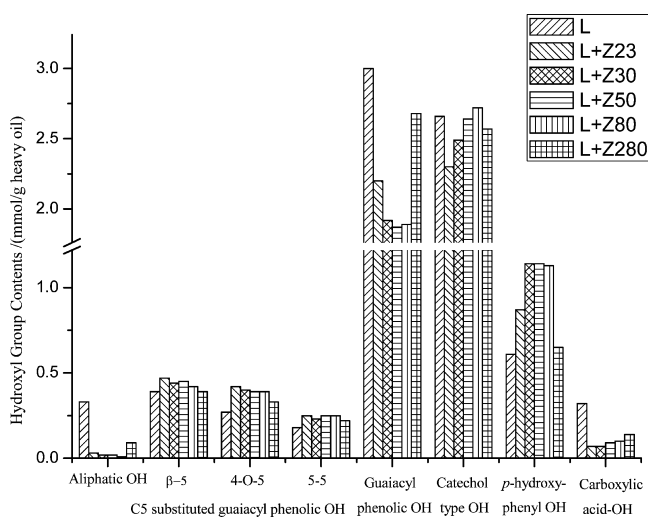
combustion to determine carbon, hydrogen, and sulfur contents, and the oxygen content was calculated by mass difference. The standard deviation is  $\pm 0.3\%$ .<sup>36</sup>

## RESULTS AND DISCUSSION

**Yields of Pyrolysis Products.** The HHV and energy, carbon, and mass yields from pyrolyzing a softwood kraft lignin

**Table 3.** Chemical Shifts and Integration Regions for Lignin Pyrolysis Oils in a Quantitative <sup>31</sup>P-NMR after Derivatization with TMDP<sup>29,31</sup>

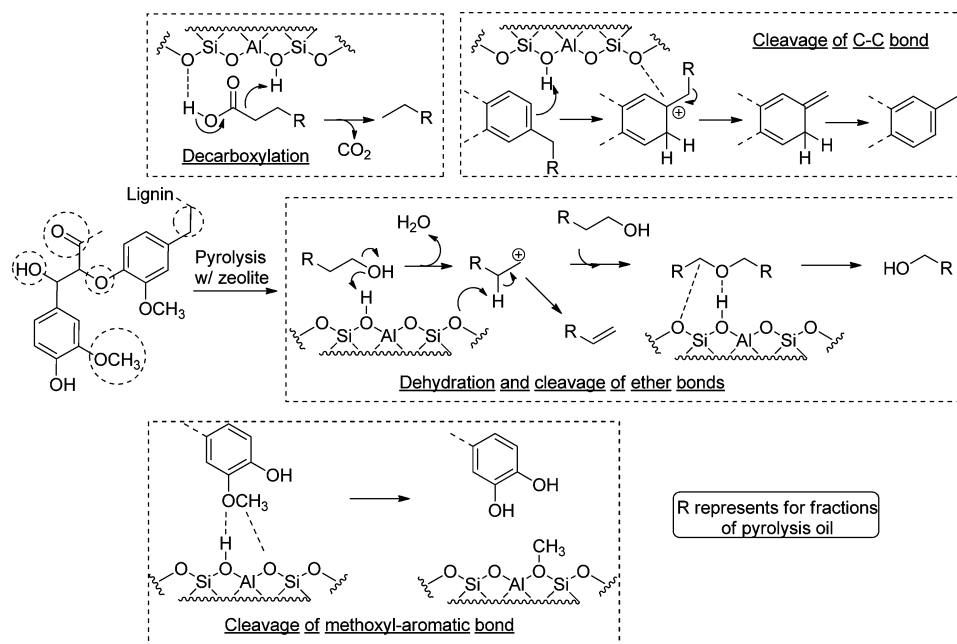
functional group	integration region (ppm)	
endo-N-hydroxy-5-norbornene-2,3-dicarboximide (NHND, internal standard)	151.0–152.8	
aliphatic OH	150.0–145.5	
C <sub>5</sub> -substituted guaiacyl phenolic OH	$\beta$ -5	144.7–142.8
	4-O-5	142.8–141.7
	5-5	141.7–140.2
guaiacyl phenolic OH	140.2–139.0	
catechol type OH	139.0–138.2	
<i>p</i> -hydroxy-phenyl OH	138.2–137.3	
carboxylic acid–OH	136.6–133.6	
water	133.1–131.3, 16.9–15.1	



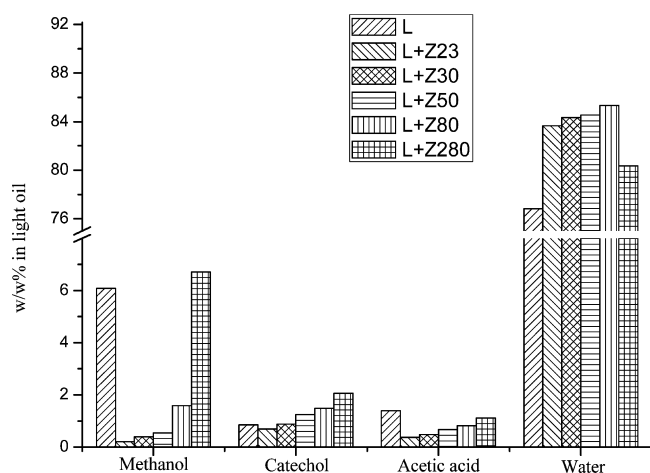
**Figure 1.** Hydroxyl group contents of different heavy oils produced by pyrolysis of pure SW kraft lignin and pyrolysis of SW kraft lignin with 1.0/1.0 ( $W_{\text{additive}}/W_{\text{lignin}}$ ) of H-ZSM-5 zeolites as additives at 600 °C for 10 min, determined by quantitative <sup>31</sup>P NMR after derivatization with TMDP.

with different ZSM-5 zeolites at 600 °C are summarized in Table 2. These results indicate that the yields of char slightly increased after the use of additives, and the char yield is almost constant for all zeolites, which suggests that the additives have very limited effects on the primary decomposition of lignin. In contrast, the yield of heavy oil decreased after the use zeolite. Correspondingly, the yield of light oil and gas increased with used zeolites. In addition, pyrolysis samples with lower Si/Al ratio zeolites formed relatively less heavy oil but more light oil. Our previous work indicated that light oil contains  $\sim 70$ – $90$  wt % of water and another 10 wt % of methanol, catechol, and acetic acid.<sup>29,31</sup> Aho et al.<sup>28</sup> pyrolyzed pine wood with various H-Beta zeolites, and they indicated that zeolites with lower Si/Al ratios formed less organic oil but more water, which supported our results. HHV data for the heavy oil upgraded by Z280 are similar with the control pyrolysis oil, which indicates that the H-ZSM-5 zeolite with a very large SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio only limitedly affects the properties of pyrolysis oil. Nevertheless, both energy and carbon yields show that Z50-upgraded pyrolysis oil retained the most energy and carbon from the SW kraft lignin, which indicates this type of zeolite is a promising candidate to upgrade the properties of pyrolysis oil.

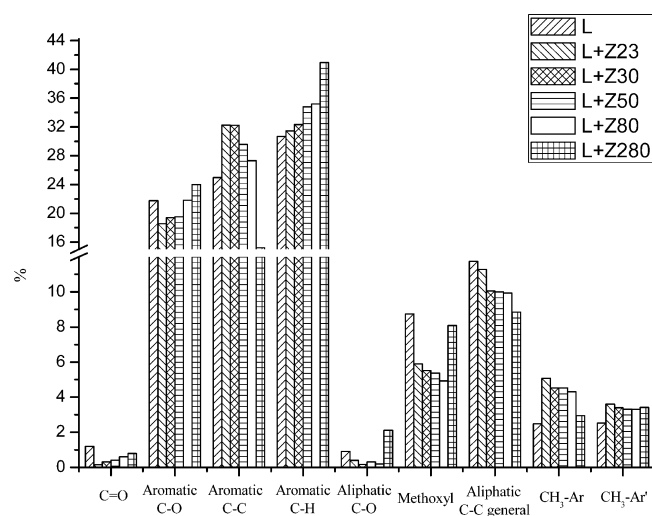
**Quantitative <sup>31</sup>P NMR Analysis of Pyrolysis Oils.** Our previous work<sup>29,31,32,37</sup> introduced quantitative <sup>31</sup>P NMR to quantitatively determine hydroxyl functional groups in pyrolysis oils. The <sup>31</sup>P NMR chemical shifts and integration regions of the phosphorylated aryl/alkyl hydroxyl groups and water with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) are summarized in Table 3. The integration results for the heavy oils are shown in Figure 1. For all the heavy oils, the integration results show that there are significant amounts (from 2–3 mmol/g of heavy oil) of guaiacyl and catechol types of hydroxyl groups. If there is only one of these two types of functional groups in each pyrolysis oil components, there should be  $>11$ – $17$  wt % of catechol and its derivatives and  $>24$ – $37$  wt % of guaiacol and its derivatives in the heavy oils. After the use of H-ZSM-5 zeolite as an additive, the aliphatic hydroxyl groups and carboxylic acid in the heavy oils are nearly completely decomposed. With the exception of those two hydroxyl groups, the heavy oil produced from pyrolysis of lignin with Z280 is similar with the control pyrolysis oil, which indicates that the H-ZSM-5 zeolite with a very large SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio has limited effects on the phenolic hydroxyl groups of pyrolysis oil during the pyrolysis process. Other than Z280, after the use of H-ZSM-5 zeolites, the contents of C<sub>5</sub>-substituted and normal guaiacyl phenolic hydroxyl groups decreased with the increasing SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio of zeolites. In contrast, the contents of catechol type and *p*-hydroxy-phenyl



**Figure 2.** Primary decomposed functional groups in lignin during the pyrolysis (circled by dashed line in lignin model structure) and possible cracking pathways on zeolite.<sup>38–48</sup>



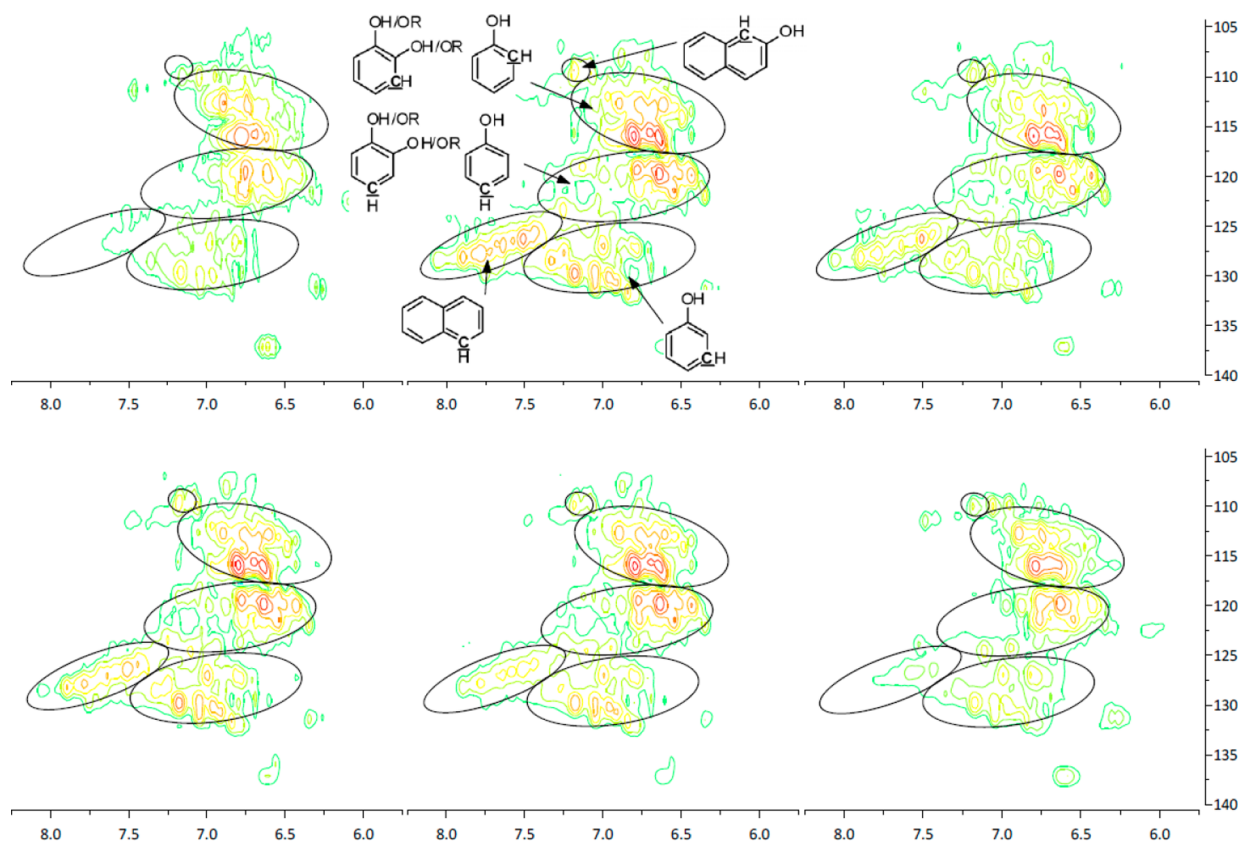
**Figure 3.** Weight percentage of four major components in light oils produced by pyrolysis of pure SW kraft lignin and pyrolysis of SW kraft lignin with 1.0/1.0 ( $W_{\text{additive}}/W_{\text{lignin}}$ ) of H-ZSM-5 zeolites as additives at 600 °C for 10 min, determined by quantitative  $^{31}\text{P}$  NMR after derivatization with TMDP.



**Figure 4.** Integration results for heavy oils produced by pyrolysis of pure SW kraft lignin and pyrolysis of SW kraft lignin with 1.0/1.0 ( $W_{\text{additive}}/W_{\text{lignin}}$ ) of H-ZSM-5 zeolites as additives at 600 °C for 10 min, detected by quantitative  $^{13}\text{C}$  NMR.

**Table 4.**  $^{13}\text{C}$ -NMR Chemical Shift Assignment Range of Lignin Pyrolysis Oil Based on the Chemical Shift Database Created in Our Previous Work.<sup>31</sup>

functional group	integration region (ppm)
carbonyl or carboxyl bond	215.0–166.5
aromatic C–O bond	166.5–142.0
aromatic C–C bond	142.0–125.0
aromatic C–H bond	125.0–95.8
aliphatic C–O bond	95.8–60.8
methoxyl–aromatic bond	60.8–55.2
aliphatic C–C bond	55.2–0.0
general	55.2–0.0
methyl–aromatic ( $\text{CH}_3\text{–Ar}$ )	21.6–19.1
methyl–aromatic at ortho position of a hydroxyl or methoxyl group ( $\text{CH}_3\text{–Ar}'$ )	16.1–15.4



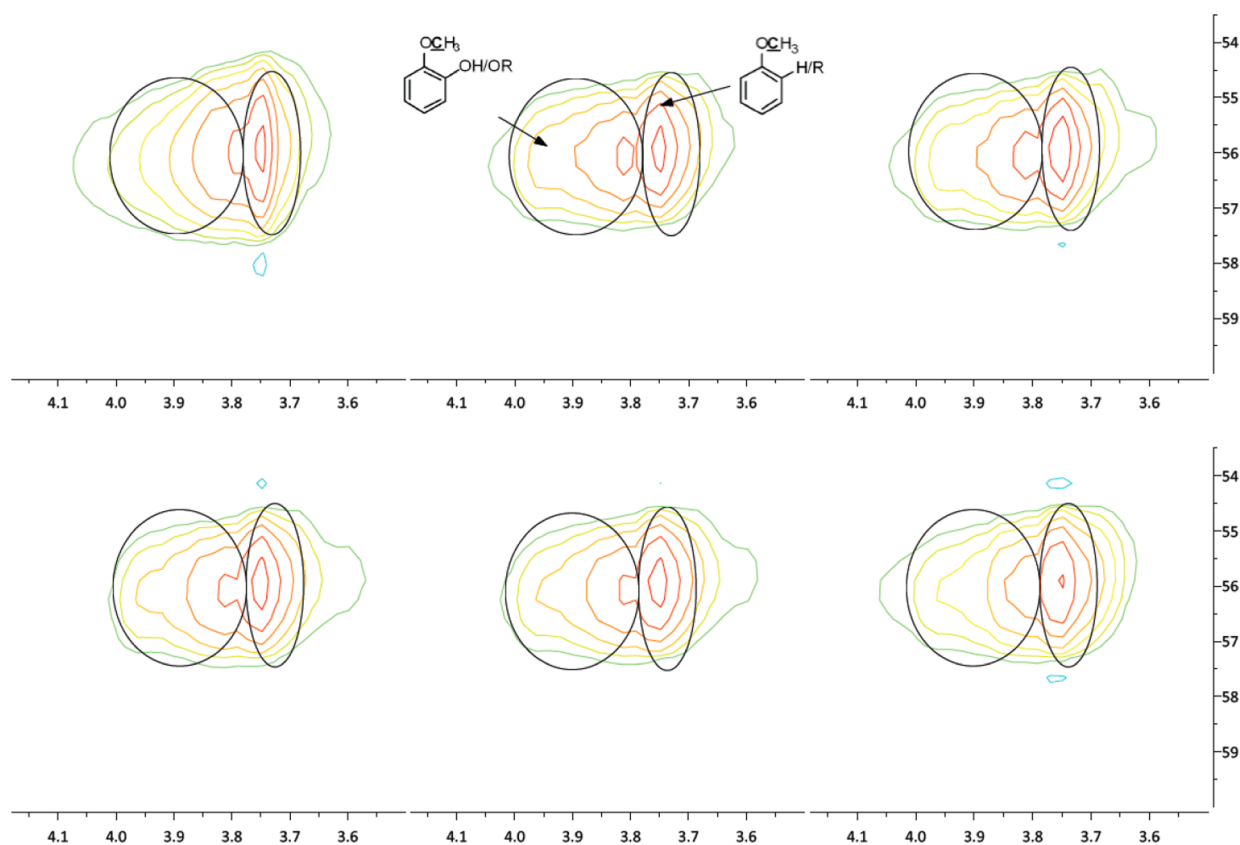
**Figure 5.** Aromatic C–H bonds in the HSQC-NMR spectra for the pyrolysis oils produced by pyrolysis of SW kraft lignin with H-ZSM-5 zeolites, from left top to right bottom is L-, Z23-, Z30-, Z50-, Z80-, and Z280-upgraded pyrolysis oil.

hydroxyl groups increased when a high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio zeolite was used. Because those two types of hydroxyl groups are the decomposition products of methoxyl aromatic bonds and ether bonds in the lignin structure,<sup>29,31</sup> this indicates that a zeolite with a relatively higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio could improve the cleavage of aromatic C–O bonds including methoxy groups and ether bonds more efficiently. Some possible degradation pathways of ether bonds and methoxyl groups on the surface of zeolite have been proposed in literatures<sup>38–40</sup> and these are summarized in Figure 2. The limited amount of aliphatic OH also decreased after the use of a high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio zeolite, which indicates an enhanced dehydration of aliphatic C–O bonds. In contrast, the content of carboxylic acid–OH increased with the increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio, which suggests that a zeolite with a lower  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio is more effective for the decomposition of carboxylic acid. Several researchers have examined the effects of zeolite on the dehydration and decarboxylation of model compounds.<sup>38,41–45</sup> The tentative mechanisms in the literatures are shown in Figure 2.

Our previous works indicated that the light oils contain more than 80 wt % of water and another 10 wt % of methanol, catechol, and acetic acid.<sup>29,31,32</sup> The integration results of those four major components in the light oils are summarized in Figure 3. The yields of methanol, catechol, and acetic acid in the light oil significantly decreased when H-ZSM-5 zeolite was used as an additive. Methanol is the major product of cleavage of methoxyl groups in lignin structure, and catechols are the further decomposition products of guaiacols.<sup>31</sup> The yields of those two components increased with an increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio of zeolite, which indicates improved decomposition

of the methoxyl group and is consistent with the  $^{31}\text{P}$  NMR results for the heavy oils. Similarly, with heavy oils, the content of the carboxylic acid–OH in light oil also increased after the use of a higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio zeolite. The concentration of water in light oil also increased after the use of zeolite. With the exception of Z280, the water contents increased after the use of a higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio zeolite. Water is the dehydration product of aliphatic C–O bonds;<sup>31</sup> the higher water content indicates an enhanced decomposition of the aliphatic hydroxyl groups, which is also supported by the  $^{31}\text{P}$  NMR results for the heavy oils.

**Quantitative  $^{13}\text{C}$  NMR Analysis of Pyrolysis Oils.** To fully characterize the functional groups in the heavy oils, a detailed analysis of heavy oils was accomplished using  $^{13}\text{C}$  NMR. The  $^{13}\text{C}$  NMR chemical shift assignment ranges are based on our previous work<sup>31</sup> and are shown in Table 4. The integration results of this analysis for the heavy oils are summarized in Figure 4. This data shows that compared to the use of other zeolites, the effects of Z280 on the heavy oil are very limited, and the product is more similar with the control heavy oil, which is consistent with  $^{31}\text{P}$  NMR results. The carbonyl groups are nearly completely eliminated, and the content increased with an increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio of H-ZSM-5 zeolite, which is additional evidence that the upgraded pyrolysis oil has lower acidity. After the use of zeolite, the content of the methoxyl groups in the heavy oil decreased by ~45%, and the decomposition of this functional group is improved when a higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio of H-ZSM-5 zeolite is used. This effect could explain the increasing contents of catechol type hydroxyl groups in the heavy and light oils detected by  $^{31}\text{P}$  NMR. The percentage of aromatic C–



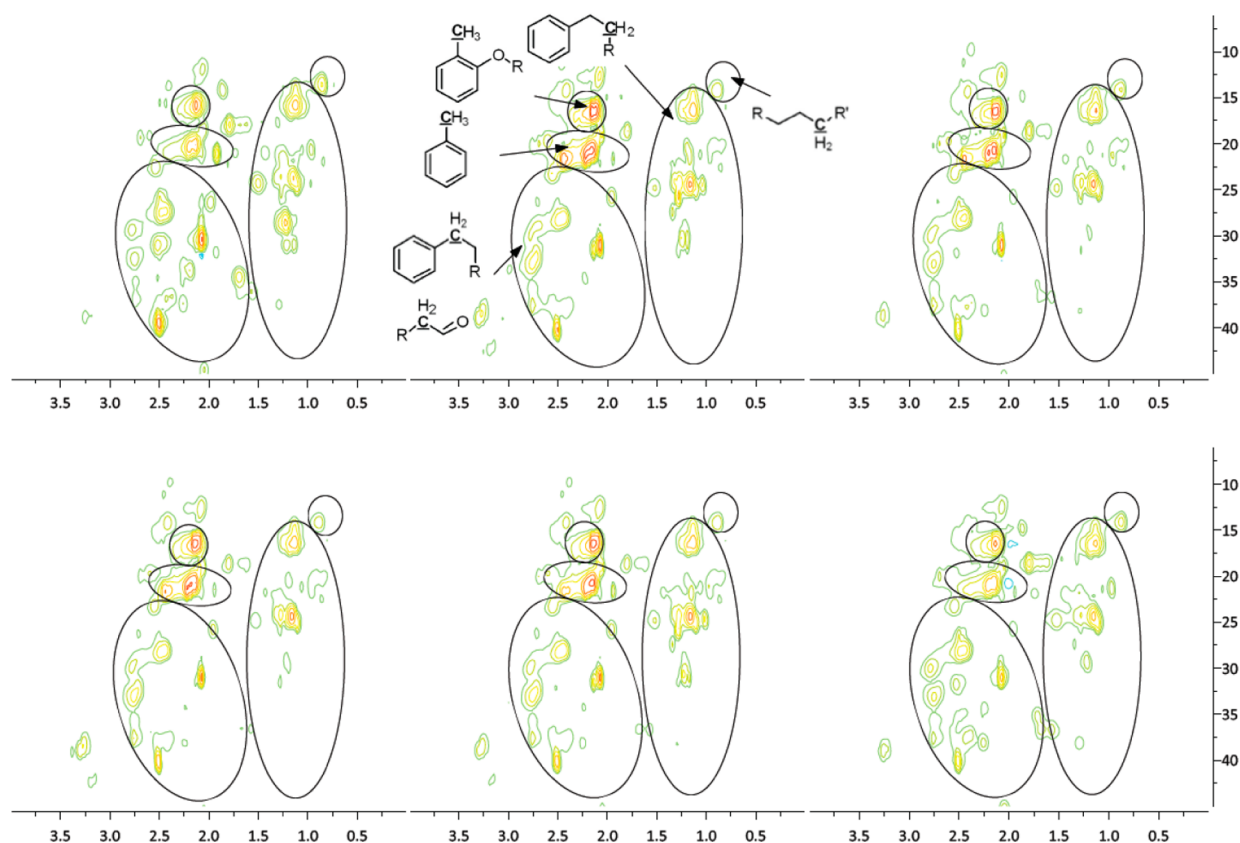
**Figure 6.** Methoxyl groups in the HSQC-NMR spectra for the pyrolysis oils produced by pyrolysis of SW kraft lignin with H-ZSM-5 zeolites, from left top to right bottom is L-, Z23-, Z30-, Z50-, Z80-, and Z280-upgraded pyrolysis oil.

C bonds decreased with the use of a higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio zeolite, which suggests that the zeolite with a higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio favors cleaving aromatic C–C bonds or prevents the formation of such bonds. There are also fewer aliphatic C–C bonds after the use of zeolite. Zeolite has been reported<sup>46–48</sup> to improve the cleavage of aliphatic C–C bonds, which could explain the reduced content of such bonds in the upgraded pyrolysis oil. The possible pathways reported in the literatures are summarized in Figure 2. The two types of methyl–aromatic bonds in the heavy oils are the rearrangement products of methoxyl groups.<sup>31</sup> Because the cleavage of methoxyl groups have been enhanced, the content of those two methyl–aromatic bonds also increased after the use of zeolite. The increased aromatic C–O bonds in the upgraded heavy oils indicate higher phenol hydroxyl groups, which is supported by <sup>31</sup>P NMR results.

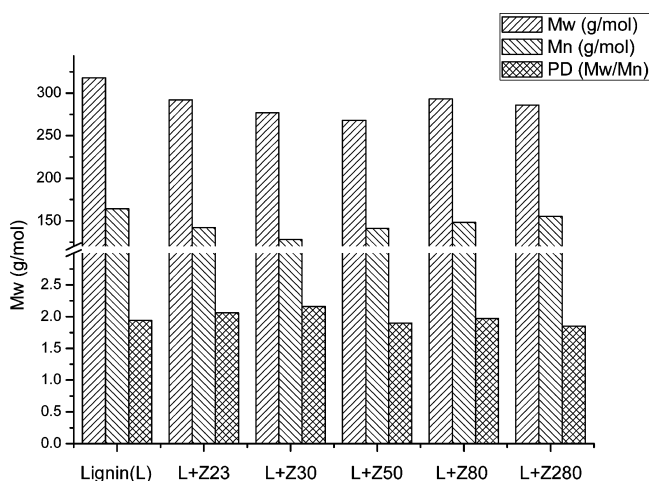
**HSQC-NMR Analysis of Pyrolysis Oils.** To solve the overlaps problem when using <sup>13</sup>C NMR to analyze pyrolysis oils, our previous work demonstrated the value of HSQC-NMR to analyze various C–H bonds presented in pyrolysis oils.<sup>30</sup> The HSQC-NMR spectra for the pyrolysis oils after the use of various H-ZSM-5 zeolites are shown in Figures 5–7. HSQC-NMR results show that after the use of zeolite as additive, the pyrolysis oils contain some polyaromatic hydrocarbons (PAH), and the content decreased with an increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio of zeolite, both of which are supported by the GC-MS analysis (see the Supporting Information for the details). The formation of PAH on the surface of zeolites was also observed by several model compound studies.<sup>49–52</sup> It has been reported that the Brønsted acid sites of H-ZSM-5 zeolites could be calculated by the unit cell formula of the zeolite

( $\text{H}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}$  for H-ZSM-5 zeolite).<sup>23</sup> Therefore, the Brønsted acid sites for H-ZSM-5 zeolites used in this work linearly decreased from 0.35 mmol/g (Z23) to 0.03 mmol/g (Z280). Figure 2 shows that the improved cracking pathways of pyrolysis oil on the zeolites always involve protons from Brønsted acid sites, which indicate the more acidic zeolites should perform better upgrading results. However, both <sup>31</sup>P and <sup>13</sup>C NMR results show that the H-ZSM-5 zeolite with a relatively higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio (~50–80) was more effective at upgrading the properties of pyrolysis oil. Because the PAH has been reported as the precursor of coke,<sup>51,52</sup> which will deactivate the zeolite, the higher contents of PAH in more acidic zeolite-upgraded pyrolysis oils provide insight into the reason why Z50 has better upgrading results than Z23. The intensity of aromatic C–H bonds increased after using zeolite, which is consistent with our <sup>13</sup>C NMR result. The native methoxyl groups (with a hydroxyl group or ether bond in the ortho position) decreased after adding zeolite during the pyrolysis, and the content decreased when a higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio zeolite was employed. After the use of zeolite, there are more methyl–aromatic bonds in the pyrolysis oil, which is also supported by our <sup>13</sup>C NMR results.

**GPC and Elemental Analysis of Pyrolysis Oils.** The number average, weight average molecular weights ( $M_n$  and  $M_w$ ), and polydispersity values for the heavy oils produced by pyrolysis of softwood kraft lignin with zeolite at 600 °C are summarized in Figure 8. This analysis indicates the molecular weight decreased by 8–16% after the use of H-ZSM-5 zeolite. The lower molecular weight of upgraded pyrolysis oil is evidence of enhanced decomposition of the methoxyl group, carboxyl acid, and dehydration of aliphatic hydroxyl groups.



**Figure 7.** Aliphatic C–H bonds in the HSQC-NMR spectra for the pyrolysis oils produced by pyrolysis of SW kraft lignin with H-ZSM-5 zeolites, from left top to right bottom is L-, Z23-, Z30-, Z50-, Z80-, and Z280-upgraded pyrolysis oil.



**Figure 8.** Molecular weight distribution and polydispersity of heavy oils produced by pyrolysis of pure SW kraft lignin and pyrolysis of SW kraft lignin with 1.0/1.0 ( $W_{\text{additive}}/W_{\text{lignin}}$ ) of H-ZSM-5 zeolites as additives at 600 °C for 10 min.

The results of elemental analysis for pyrolysis oils are shown in Table 5. After the use of zeolites, the carbon contents of heavy oils increased up to 5%. In contrast, there is up to 13% less oxygen in the upgraded pyrolysis oils, which indicates zeolite could improve the deoxygenation during the pyrolysis process. Most interestingly, the sulfur content also decreased by 50% after using Z50 as the additive, which exhibits a potential method to decrease the sulfur content in the kraft lignin pyrolysis oils.

**Table 5.** Elemental Analysis for the Pyrolysis of Pure SW Kraft Lignin and Pyrolysis of SW Kraft Lignin with 1.0/1.0 ( $W_{\text{additive}}/W_{\text{lignin}}$ ) of H-ZSM-5 Zeolites as Additives at 600 °C for 10 min

pyrolysis samples <sup>a</sup>	C (wt %)	H (wt %)	O (wt %)	S (wt %)
lignin (L)	70.64	6.80	21.31	1.25
L+Z23	73.53	6.68	18.90	0.89
L+Z30	73.93	6.67	18.49	0.91
L+Z50	73.61	6.71	19.05	0.63
L+Z80	72.75	6.79	19.59	0.87
L+Z280	71.65	6.78	20.74	0.83

<sup>a</sup>Dried SW kraft lignin contains 74.35 wt % of carbon, 6.60 wt % of hydrogen, 17.79 wt % of oxygen, and 1.26 wt % of sulfur.

## CONCLUSION

The pyrolysis of softwood kraft lignin with various H-ZSM-5 zeolites as additives was accomplished at 600 °C. The yields of char slightly increased after the use of the additives, and the char yield is almost constant for all zeolites, which suggests that the additives have very limited effects on the primary decomposition of lignin. The yield of heavy oil decreased, but the yield of light oil and gas increased after the use of zeolite. In addition, pyrolysis samples with lower Si/Al ratio zeolites formed relatively less heavy oil but more light oil. After the use of H-ZSM-5 zeolite, the aliphatic hydroxyl groups and carboxylic acid in the heavy oils are nearly completely decomposed, which represents a more suitable precursor for the biofuel. With the exception of those two hydroxyl groups, the heavy oils produced from pyrolysis of lignin with Z280 are

similar with the control pyrolysis oil, which indicate that the H-ZSM-5 zeolite with very large SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio has limited effects on the properties of pyrolysis oil. The results of <sup>13</sup>C and <sup>31</sup>P NMR for the heavy oils indicate that the H-ZSM-5 zeolite with a relatively higher SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio is more effective to improve the cleavage of methoxyl groups, ether bonds, and aliphatic C–C bonds, and dehydration of aliphatic hydroxyl groups. In contrast, the content of carboxylic acid–OH in both heavy and light oil increased with increasing SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio, which suggests that the zeolite with lower SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio is more effective for the decomposition of carboxylic acid. HSQC-NMR results show that after the use of the additive, the pyrolysis oils contain some polyaromatic hydrocarbons (PAH), and the content decreased with the increasing SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio of zeolite. GPC results show that the molecular weight decreased by 8–16% after the use of various H-ZSM-5 zeolites.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

GC-MS analysis data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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