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Effect of the Fast Pyrolysis Temperature on the Primary and Secondary Products of Lignin

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S Supporting Information

ABSTRACT: This paper presents results on the primary pyrolysis products of organosolv lignin at temperatures between 360 and 700 °C. To study the primary products, a vacuum screen heater (heating rate of 8000 °C/s, deep vacuum of 0.7 mbar, and very fast cooling at the wall temperature of −100 °C) was used. The effect of the temperature on the primary and secondary lignin products was studied with a fluidized-bed pyrolysis reactor (T_{reactor} between 330 and 580 °C) with pine wood. The results obtained with the screen heater show that the primary products of lignin were oligomers. Between 450 and 700 °C, the yield of these oligomers was very high, between 80 and 90%. After formation, the oligomers left the particle by evaporation or thermal ejection. Monophenols and other light compounds were formed by secondary reactions inside the particle or in the vapor phase. In the fluidized-bed reactor, significant quantities of lignin oligomers were formed along with monophenols, water, and other light compounds. The changes on the yield and composition of the lignin-derived oligomers as a function of the pyrolysis temperature are reported. The lignin oligomers were isolated by cold-water precipitation and analyzed with thermogravimetry (TG), Fourier transform infrared (FTIR) spectroscopy, pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS), electrospray ionization–mass spectrometry (ESI–MS), gel permeation chromatography (GPC), and proton nuclear magnetic resonance (¹H NMR). The yield of lignin-derived oligomers reached a maximum between 450 and 580 °C. The differential thermogravimetry (DTG) results show the existence of three major peaks, which were maximal between 450 and 480 °C, indicating that not only the yield but also the structure of the lignin oligomers changed at higher pyrolysis temperatures. Py–GC/MS and ¹H NMR results indicated that, as the temperature increased, the content of methoxylated phenols decreased and the content of alkylated phenols increased. FTIR spectroscopy revealed an increase in carbonyl groups produced by carbonylation reactions, from the hydroxyl groups or the cleavage of ether bonds. Both ESI–MS and GPC results show a negligible effect of the pyrolysis temperature on the molar weight distribution. This result differs with the increase in the molecular weight observed for organosolv lignin pyrolyzed in the screen heater and highlights the importance of secondary reactions on the outcome of fast pyrolysis reactors.

1. INTRODUCTION

Pyrolysis is considered one of the most promising processes to convert lignocellulosic materials into transportation fuels and chemicals, because it is one of the few techniques that offers the opportunity to use nearly all of the biomass (cellulose, hemicelluloses, and lignin).¹ In the pyrolysis process, lignin is mainly converted into monophenols, oligomeric phenols [also known as pyrolytic lignin (PL)], char, water, and gases.² The aromatic compounds of lignin are an interesting source for bio-based materials, such as resins and fuel additives.³ The monophenols are an interesting source for the production of chemicals. Unfortunately, many different monophenols are formed, and the sum of them are still low in yield (3–8% on a biomass dry basis).² In contrast, lignin-derived oligomers are typically produced at yields up to 15% (on a biomass dry basis).^{2,4,5}

Parametric studies on the effect of alkalines,⁶ pyrolysis temperature,^{7–9} pretreatment temperature,^{10,11} particle size,^{12,13} secondary reactions in the vapor phase,¹⁴ and use of sulfuric acid as an additive^{5,15} have been published recently. Surprisingly,

in all of these studies, the lignin oligomeric fraction was the fraction most severely affected by the changes in operational parameters. These results highlight the importance of lignin thermochemical reactions on the outcome of biomass pyrolysis and the important role lignin-derived oligomers play as intermediates in lignin pyrolysis reactions. It is not clear whether the lignin oligomers are products of primary reactions or if they are formed from the oligomerization of the monomeric products of primary reactions.

Radlein et al.¹⁶ first studied the lignin-derived fraction of bio-oils obtained from fast pyrolysis of poplar wood. On the basis of analysis of the lignin content in wood, it was calculated that this fraction accounted for 80% of the lignin. The chemical composition of lignin-derived oligomers has been extensively studied.^{17–20} According to Bayerbach and Meier,²⁰ oligomeric

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lignin is formed from biphenyl, phenyl coumarin, diphenyl ethers, stilbene, and resinol structures formed by cracking, recombination, and thermal ejections. The most common units of lignin isolated from pyrolysis oils are dimers and trimers.²¹

The pyrolysis temperature is a critical factor affecting the yield and quality of bio-oils.²² The temperature at which a maximum yield of bio-oil is obtained (around 500 °C) coincides with the temperature at which maximum yields of lignin-derived oligomers are produced.^{7,8,10} Thus, current fast pyrolysis processes are operated under conditions that maximize the production of this fraction. Although the effect of the pyrolysis temperature on the production of monophenols has been a subject of intensive research, the effect of the pyrolysis temperature on the composition of lignin oligomers is yet unknown.

Lignin thermochemical reactions responsible for the formation of monomers are typically studied by pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) and micro-pyrolyzers.^{23–31} Both techniques can achieve high heating rates and allow for the quantification of (i) water, (ii) light organic compounds, (iii) gases, (iv) char,^{23,28} and (v) various monophenols.^{29–31} Lignin oligomers cannot be analyzed with these techniques because of their high boiling points. Char is often formed in high yields, typically 37²³–60%, which could point toward secondary reactions because of heat-/mass-transfer limitations. In general, it is not clear whether the monophenols identified by Py–GC/MS are produced by primary pyrolysis reactions or if they are the products of the secondary cracking of lignin oligomers produced by the primary pyrolysis reactions.

Thus, the objective of this paper is to better understand the mechanism by which PLs are formed and degraded during fast pyrolysis. To do so, a vacuum screen heater (also referred as a wire-mesh reactor) is used for studying the inner-particle processes closest to “primary pyrolysis reactions”. It is closest to primary pyrolysis reactions because the vacuum rapidly removes pyrolysis products, presumably before they can undergo secondary reactions. The screen heater allows for very high heating rates (8000 °C/s), a deep vacuum at 0.07 mbar, and extremely fast cooling (wall temperature of –100 °C). To gain a better understanding of the secondary reactions, the effect of pyrolysis temperatures on the yield and composition of PL was studied in a fluidized-bed reactor. The combination of knowledge on primary and secondary reactions could lead to new process insights for enhanced production of monophenols for fuels and chemicals.

2. MATERIALS AND METHODS

2.1. Pyrolysis of Organosolv Lignin. **2.1.1. Screen Heater.** The reactions in a very early stage of pyrolysis (hereafter referred as primary reactions) were studied in a specially designed vacuum screen heater that is described in detail elsewhere.³² Organosolv lignin {Sigma-Aldrich [371017 (CAS registry number 8068-03-9)]} was used as the feedstock. Briefly, the screen heater consists of two preweighed wire meshes pressed together with the lignin sample (approximately 50 mg) equally distributed between them. In a previous study by Hoekstra et al.,³² it was shown that there was a negligible difference between liquid, char, and gas yields when sample sizes between 10 and 100 mg were used. The pressed screens were clamped between copper rods to close the electrical circuit. Two 12 V batteries were used to supply the power to heat the mesh and sample. A glass vessel (5 cm diameter) was mounted around the wire mesh in such a way that it was airtight. Nitrogen was used to flush the vessel of air. A vacuum as low as 0.3 mbar was achieved using a continuously monitored vacuum pump. Liquid nitrogen was used to cool the outside wall of the glass tube to –100 °C. An electric pulse resulted in a heating rate of the mesh of 8000 °C/s. The holding time of 3 s is more than enough for the

pyrolysis reactions to complete. The temperature on the screen was measured with a pyrometer (180 μ s response time), and the temperature difference over the screen was not more than 35 °C.³²

During the screen-heater experiment, product vapors condense rapidly on the glass reactor wall to form a very thin oil layer. After the experiment, a gas sample was taken and subsequently analyzed by gas chromatography (GC). The reactor vessel, including the copper clamps, was carefully weighed before and after the experiment. The weight difference was the produced oil. The oil product was extracted from the reactor wall with acetone and immediately stored in a freezer at –20 °C to prevent secondary reactions. The screens with the char were weighed after the experiment to provide the char yield. The mass-balance closures were between 89 and 103%. The coefficient of variation for three identical experiments was 20% for char and 5% for oil.

2.1.2. Gel Permeation Chromatography (GPC) Analysis. The molecular weight distribution of the oil from the screen-heater and fluidized-bed experiments were measured with a gel permeation chromatograph [GPC, Agilent Technologies, 1200 series refractive index detector (RID), eluent at 1 mL/min] (columns: 3 PLgel 3 μ m MIXED-E placed in series). The solvent used was tetrahydrofuran (THF; 10 mg of pyrolysis oil/mL of THF). GPC was calibrated with polystyrene standards (M_w = 162–30 000).⁴

2.1.3. Py–GC/MS Studies of Organosolv Lignin. Py–GC/MS studies of organosolv lignin were performed on a CDS pyroprobe 5000 series (CDS Analytical, Inc.), which is connected to a GC/MS system (6890N Network GC System, 5975B inert XL MSD, Agilent Technologies) equipped with a HP-5MS capillary column (30 m \times 0.25 mm, Agilent Technologies). The CDS interface temperature was set at 250 °C to avoid condensation of the vapors. The filament was heated to 500 °C to pyrolyze the organosolv lignin and PLs obtained from oils produced in the fluidized-bed reactor. The GC inlet temperature was set to 250 °C. The temperature program was set from 40 °C (1 min) to 280 °C (15 min) at a rate of 6 °C/min. Helium was used as carrier gas (1 mL/min) in split mode (50:1). The identity of the compounds was confirmed by their retention times, mass spectra, comparison to authentic standards, and National Institute of Standards and Technology (NIST) library matching.¹⁹

2.2. Pyrolysis Studies in a Fluidized Bed. **2.2.1. Pyrolysis of Pine Wood in a Fluidized-Bed Reactor.** Pine wood was pyrolyzed in a 1 kg/h fluidized-bed fast pyrolysis reactor at temperatures between 330 and 580 °C at the University of Twente. The reactor temperature could be controlled accurately within 10 °C difference over the bed. Silica sand was used as the heating media in the fluidized-bed reactor. Nitrogen was used as the fluidization gas. The fluidized-bed reactor was equipped with an overflow to remove most of the char from the bed. A knockout vessel and two cyclones collected the remaining char and sand fines entrained from the reactor. The average residence time of the vapors inside the reactor bed was estimated between 0.44 and 0.55 s and an additional vapor residence time of 1 s outside the bed but still in the hot part of the setup ($T_{\text{outside the bed}}$ = 420 °C). The product vapors were condensed at 20 °C in a countercurrent spray column. This oil fraction, representing more than 90% of the oil and containing all PL, was used for further research. A more detailed description of the experimental setup and used procedures can be found elsewhere.⁴ An important feature of the setup is that a good mass balance closure between 94 and 101% could be obtained and that an acceptable coefficient of variation for the main fractions was as follows: char, 8%; gas, 4%; organics, 4%; and produced water, 11%, on the basis of three repeated identical experiments.

2.2.2. Isolation of PL. PL was isolated from the bio-oils using a cold-water precipitation method described elsewhere.¹⁷ Briefly, bio-oil (~10 g) was dissolved in methanol (5 g) and added dropwise into a vessel, filled with cold water (1 L) at 1 °C, surrounded by an ice bath. The water-soluble fractions, including sugars, monophenols, and small organic molecules, were dissolved in water, while the lignin oligomers precipitated. The lignin oligomers were collected on 42-grade Whatman filter paper and dried under vacuum. After vacuum drying, the PL was further dried in an oven at 100 °C. The yields were determined gravimetrically.⁵

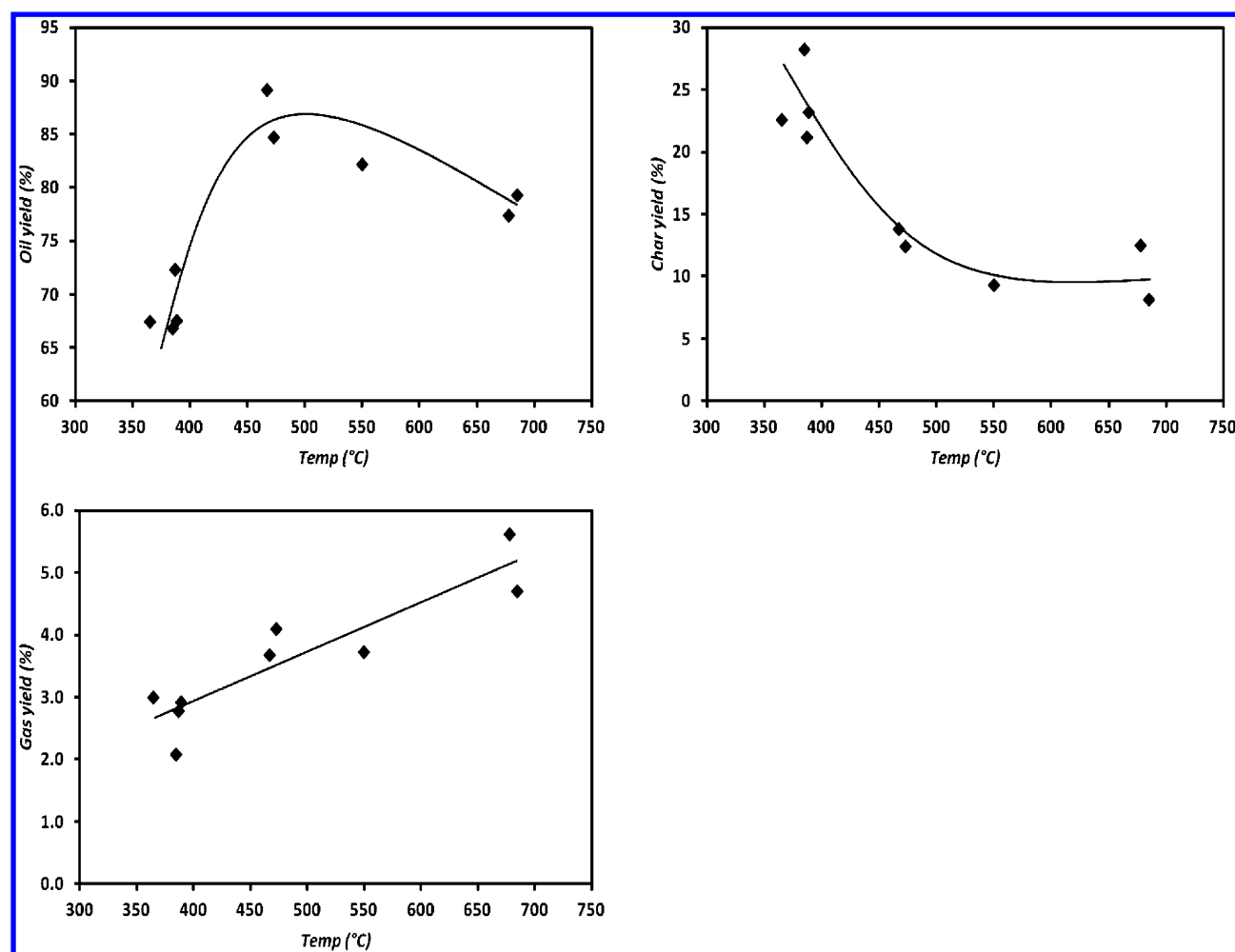


Figure 1. Organosolv lignin oil, char, and gas yields at different temperatures obtained in a vacuum screen heater (wire-mesh reactor).

2.2.3. Differential Thermogravimetry (DTG) Analysis. Thermogravimetric analysis (TGA) experiments were performed with a thermogravimetric analyzer (TGA/SDTA851e, Mettler Toledo) following a procedure described elsewhere.⁵ PL samples (6–8 mg) were loaded into an alumina crucible and heated from 25 to 600 °C at 10 °C/min under nitrogen (20 mL/min).

2.2.4. Py–GC/MS Analysis. For semi-quantitative results, approximately 500 µg of the PL sample was weighed in the TGA balance (Mettler Toledo). The areas of the chromatogram peaks were obtained by integrating the area of representative ions.

2.2.5. Fourier Transform Infrared (FTIR) Spectroscopy Analysis. The FTIR spectra of PL were recorded with an IRPrestige21 spectrometer in the attenuated total reflection (ATR) mode (Shimadzu, Ge crystal; IRSolution software). The spectra (64 scans) were baseline- and ATR-corrected and then normalized. The software Omnic 8.0 was used to analyze the data and to fit the curves; the band height ratios were compared between different samples.⁵

2.2.6. Proton Nuclear Magnetic Resonance (¹H NMR) Analysis. ¹H NMR analysis was conducted according to a method described elsewhere.³⁶ Briefly, a Varian 500 NMR spectrometer (pulse angle with 1 s relaxation delay) was applied for the ¹H NMR analysis. PL samples (25 mg) were dissolved in DMSO-*d*₆ (0.7 mL), and 64 scans were recorded for each sample.

2.2.7. Electrospray Ionization–Mass Spectrometry (ESI–MS) Analysis. As described elsewhere, negative-ion ESI–MS (*m/z* 90–2000) was performed on a LCQ-Deca (Thermo Finnigan) instrument and the *M_w* and *M_n* were calculated by the molecular weights of all negative ions detected.⁵ PL samples were dissolved in methanol containing 1% acetic acid and injected into the ESI source at 10 µL min^{−1}.²⁴ The ion source and capillary voltages were 4.48 kV and 47 V, respectively, and the

temperature was 275 °C. The number average molecular weight (*M_n*) was calculated as $M_n = \sum M_i N_i / \sum N_i$, and the weight average molecular weight (*M_w*) was calculated by $M_w = \sum M_i^2 N_i / \sum M_i N_i$, where *M_i* is the *m/z* and *N_i* is the intensity of the *i*th ion.³⁴

3. RESULTS AND DISCUSSION

3.1. Primary Products of Organosolv Lignin.

3.1.1. Yields of Oil, Char, and Gas. Figure 1 shows bio-oil, biochar, and gas yields obtained with the vacuum screen heater. Important features of the screen heater are (i) very fast heating rates (8000 °C/s) and (ii) very fast cooling of the vapors at −100 °C. Thus, the yields measured can be considered close to the theoretically achievable values and are a result of primary reactions or at least reactions in a very early stage of pyrolysis. It cannot be excluded that the obtained char is partly recondensed lignin oligomers on the meshes. It can be seen that the oil yield reached a maximum (close to 90%) at around 450 °C. At higher temperatures, the oil yield decreased but was still very high. The high oil yield of almost 75% was obtained even at below 400 °C. The existence of a maximum oil yield from organosolv lignin at 450 °C coincides with that reported by Hoekstra et al.³² It is worth noting that the lignin oil yield obtained under fast pyrolysis conditions in a fluidized bed, Py–GC/MS, and specially designed microfurnaces is lower, typically between 30 and 60%,³² indicating the importance of secondary reactions inside the particle/sample or vapor phase in this kind of reactor and the high reactivity of lignin when

heated. The char yield decreased first until 450 °C and then remained relatively constant as the temperature increased. The gas yield was low but increased with an increasing temperature over the whole temperature range studied. It seems that part of the gases comes directly from the lignin in a very early stage of pyrolysis.

3.1.2. GPC Analysis. The lignin-derived oil from the screen-heater experiments was completely soluble in acetone. The acetone solution was analyzed by GPC. Although GPC is typically used to determine molecular weight changes, this technique has intrinsic limitations; therefore, the actual values obtained can only be used relative to other samples. The results obtained for low (380 °C), middle (470 °C), and high (670 °C) temperatures were plotted in Figure 2. With an increasing

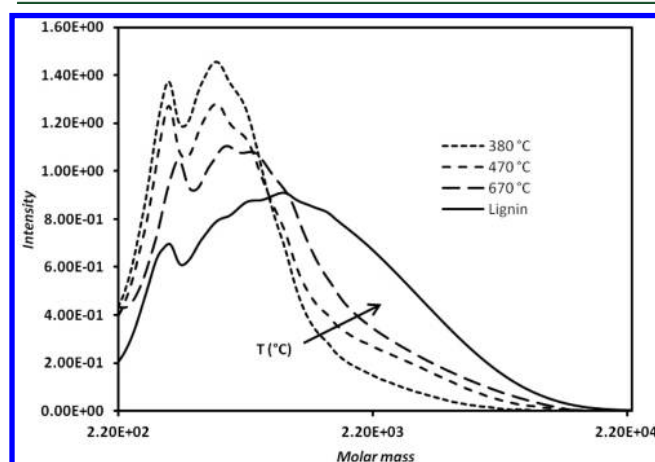


Figure 2. GPC analysis of organosolv lignin pyrolysis oil at different reaction temperatures.

temperature, the molar mass of the oil increased possibly because organosolv lignin molecules can be evaporated or thermally ejected more easily under complete vacuum before undergoing further reactions inside the particle. For comparison, the molecular size distribution of the starting organosolv lignin dissolved in acetone is also plotted. The molar mass decreased significantly after pyrolysis in the screen heater, indicating that depolymerization reactions (and not only evaporation or thermal ejection) are responsible for the obtained oil, gas, and char yields and oil composition studied.

In separate GC/MS studies of the acetone fraction (not shown), only very small traces of eugenol and vanillin were detected (<0.1%). It is also logical that a very small amount of monophenols is collected because a bond at the border of the structure (between a monophenol and the rest of the large structure) could brake as well in first primary reactions, which results in the release of a monophenol. Statistically, this should happen. However, only in a small amount especially compared to the basic large oligomers. By far, most of the monophenols are formed secondarily, especially in the presence of ash. No formic acid, acetaldehyde, acetic acid, or 2-furaldehyde was found. This means that the oligomers were removed fast enough from the hot zone to prevent further depolymerization to these smaller molecules in the solid, liquid, and gas phases. From this result, it can be concluded that PL is the main product of lignin primary reactions and that the small molecules reported in Py-GC/MS²⁶ and fluidized-bed reactors¹⁸ are produced by secondary reactions. The formation of oligomers in the liquid phase stuck on the glass vessel wall can be neglected in our case

because compounds were collected directly at −100 °C in a very thin layer. Washing with acetone (dilution 100 times) was performed at 0 °C to prevent secondary liquid-phase reactions. The acetone solution was directly frozen again. GPC analysis of the lignin/acetone solution was performed directly after the experiment and a day later at room temperature. The results did not show any change in the molecular weight distribution.

3.1.3. Py-GC/MS Analysis of Organosolv Lignin. Py-GC/MS of organosolv lignin was conducted to confirm the formation of monophenols with this technique. Figure S1 in the Supporting Information (SI) shows a typical chromatogram observed. Large quantities of monophenols were observed. This result suggests that monophenols were formed by the secondary cracking reaction of primary products (lignin oligomers) during Py-GC/MS. Thus, studying the effect of the pyrolysis temperature on the production of lignin oligomers in the presence of secondary reactions is critical to understand the mechanism of these pyrolysis reactions.

3.2. Fast Pyrolysis of Pine Wood. **3.2.1. PL Yields.** The PL produced in the fluidized-bed reactor at temperatures between 330 and 580 °C was isolated from the bio-oils following the procedure described in section 2.2.2. The yields obtained are shown in Table 1.²² The results clearly show that

Table 1. Yield of PL as a Function of the Pyrolysis Temperature (Dry Biomass Basis)

temperature (°C)	PL yields (mass fraction)
330	0.025
340	0.029
360	0.037
400	0.063
450	0.082
480	0.094
530	0.096
580	0.082

the optimum temperature for PL production is between 480 and 530 °C, which is also the optimum temperature range for bio-oil production and close to the optimum temperature found in the vacuum screen heater. Note that, in the fluidized-bed reactor test, lignin monomers were also formed.³⁵

3.2.2. DTG Analysis. The DTG curves of PLs are shown in Figure 3a. The DTG data were multiplied by the yield of PL taken from Table 1. At around 150 °C, the PL samples started to lose weight. At 500 °C, most of the volatile fractions were removed. Three points, A, B, and C (300, 336, and 369 °C) were selected in the DTG curve to follow the effect of the pyrolysis temperature. The peak heights were plotted versus the pyrolysis temperature (Figure 3b). The loss rate of peak A increased as the pyrolysis temperature increased, but after 450 °C, the weight loss rate was constant. Peaks B and C increased much faster compared to peak A from 330 to 450 °C and reached a maximum at 480 °C and decreased at higher temperatures. At higher temperatures (over 480 °C), lignin oligomers seem to undergo more intense cracking and, as a consequence, have less volatile compounds. Figure 4 confirms the formation of higher solid residues from PL collected at temperatures over 500 °C. The increase in fixed carbon could be due to the removal of ether bonds in the side chains and the formation of more stable C–C bonds as the pyrolysis temperature increased. It is difficult to attribute these changes in yield to the primary or

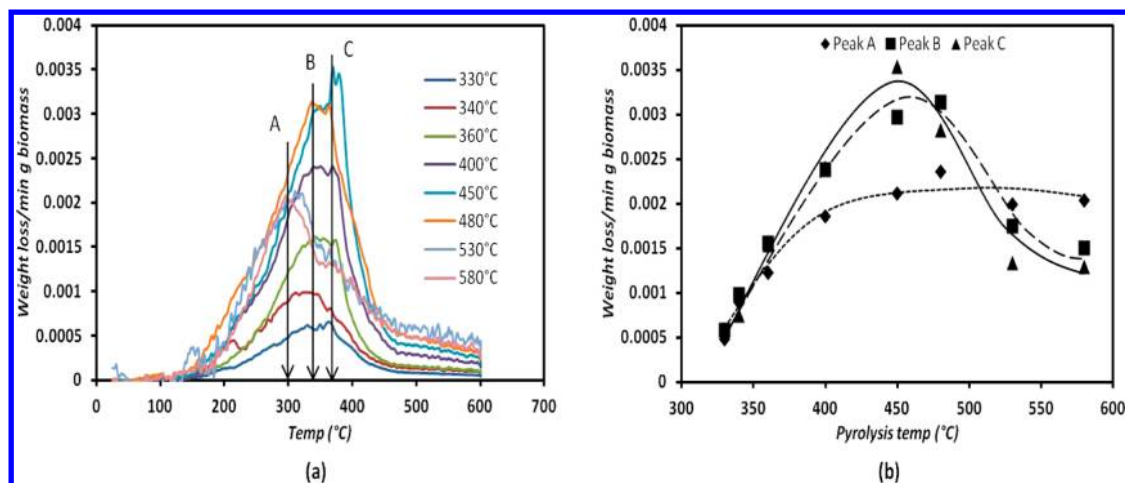


Figure 3. (a) DTG curve of PL obtained at different pyrolysis temperatures and (b) weight loss rate of selected DTG peaks (DTG data were multiplied by the PL yield listed in Table 1). The weight loss rate was expressed as the weight loss per minute per gram of PL.

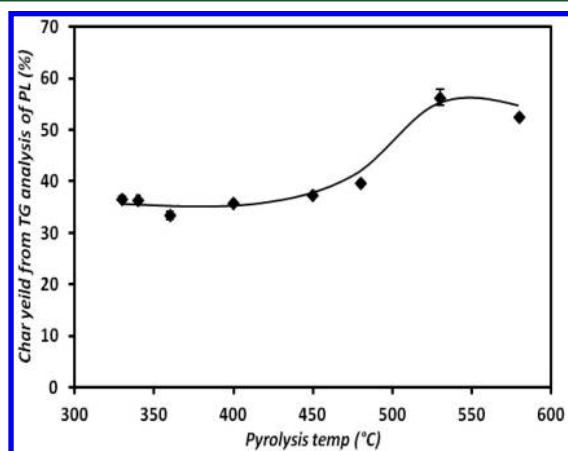


Figure 4. Char yield from the TG analysis of PLs obtained at different pyrolysis temperatures.

secondary reactions in the vapor phase. However, it has been recently proven that secondary reactions in the vapor phase, responsible for the decrease in the yield of PL, intensify at temperatures over 500 °C and are important even at the very low residence times used in our studies (around 0.44–0.55 s).²⁷

The yield of char residues from PL by TG analysis (slow pyrolysis) was plotted in Figure 4. From 330 to 480 °C, the char yield was nearly constant. From 530 to 580 °C, more char was formed, meaning the PL had fewer volatiles and more fixed carbon in the form of polyaromatic ring structures. The larger PL oligomers (peaks B and C) were responsible for the increase in char yield. Note that the high char yield from PL was mainly because of the relatively low heating rate in TGA, which facilitated the formation of this fraction. Thermal ejection, fast evaporation, and recombination reactions in fluidized beds resulted in shorter residence times of PL inside the hot particles. This could explain the presence of these “potential” char formers in the PL samples analyzed by TGA.

3.2.3. Py-GC/MS Analysis. The peak areas of pyrolytic products per microgram of the sample from the Py-GC/MS experiments were plotted in Figures 5–7 versus the pyrolysis temperature. According to the peak assignments described elsewhere,³⁶ Figure 6 shows the yield of small molecules derived from PL. The yields of CO₂ and acetone decreased as the pyrolysis temperature increased. The small molecules are generated from the decarboxylation and side-chain cleavage, which indicates that, at higher temperatures, the PL produced contains fewer carbonyl groups.

Figure 6 shows the yields of six methoxylated phenols. Clearly, the methoxyl groups were cleaved as the pyrolysis

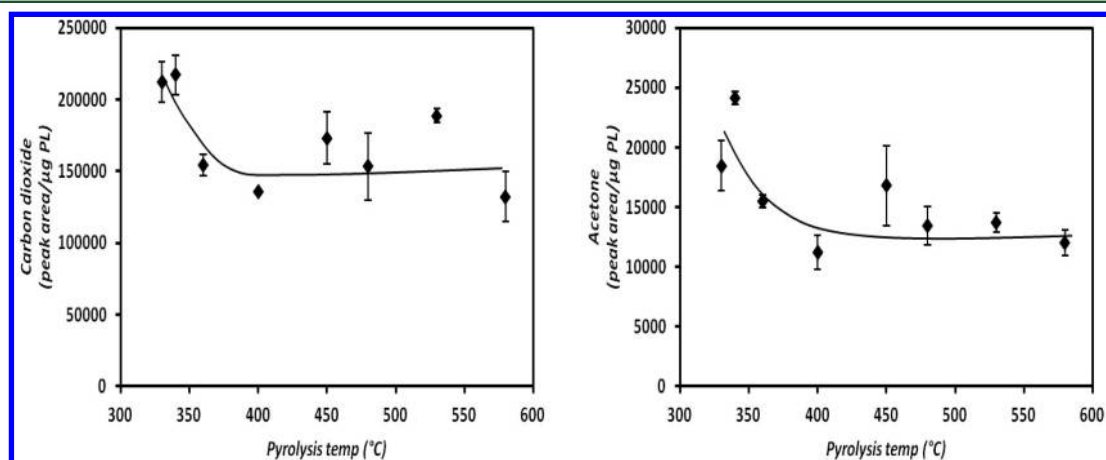


Figure 5. Effect of the pyrolysis temperature on the production of CO₂ and acetone from the pyrolysis of PL.

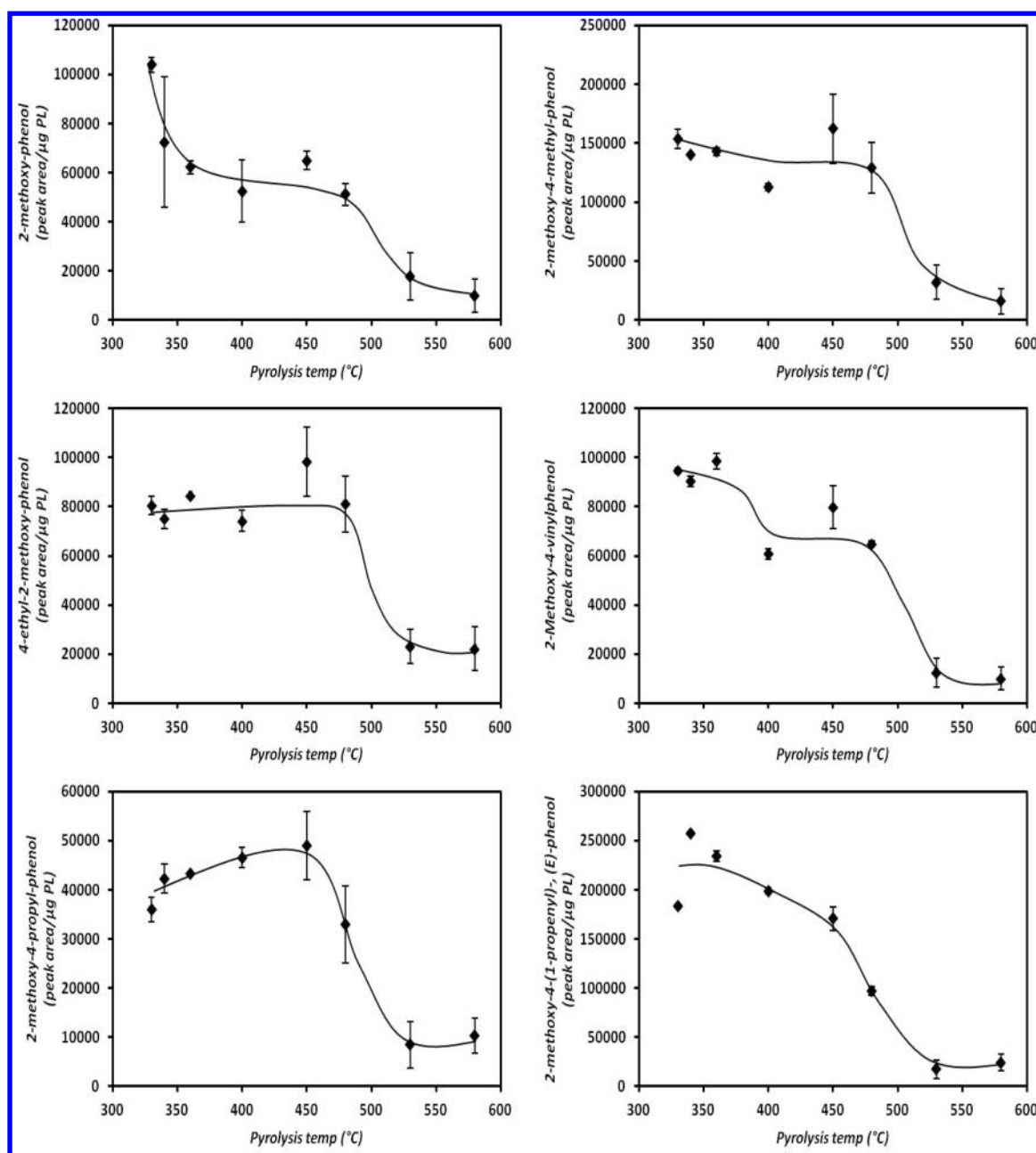


Figure 6. Effect of the pyrolysis temperature on the yield of methoxylated phenols from PL.

temperature increased. For 2-methoxy-phenol, from 330 to 400 °C, its yield decreased dramatically; between 400 and 480 °C, the changes were not significant. Above 480 °C, the concentration of all of these methoxylated phenols decreased dramatically, perhaps because of the acceleration of secondary reactions in the vapor phase or (partly) in the solid phase.²⁷ This result indicates that the methoxyl group is the most reactive and temperature-sensitive functional group in PL. For temperatures between 360 and 450 °C, the elimination reaction rates were not changed significantly. 2-Methoxy-4-methyl-phenol and 2-methoxy-4-vinylphenol had similar trends to 2-methoxy-phenol. For 2-methoxy-4-(1-propenyl)-, (E)-phenol, the yields decreased constantly as the temperatures increased.

For 4-ethyl-2-methoxy-phenol and 2-methoxy-4-propyl-phenol, from 330 to 480 °C, the temperature did not affect their yields. However, above 480 °C, the yields decreased dramatically.²⁷ Methoxylated phenolic monomers with

side chains at the 4 position of the aromatic ring are released when methoxyl groups are being cleaved. These results suggest that the reduction in the PL yield at around 500 °C is mainly due to the demethoxylation of phenolic monomers.

Figure 7 shows the yields of alkylated phenols obtained from the PL. All of these compounds were affected by the pyrolysis temperature. At temperatures from 330 to 400 °C, the yields of 2-methyl-phenol, 4-methyl-phenol, and 2,4-dimethyl-phenol first decreased and then increased above 530 °C. Above this temperature, their yields remained constant.

The temperature range can be separated into three temperature stages. At the first temperature stage, from 330 to 400 °C, the demethoxylation of PL was very slow and, consequently, the content of demethoxylated phenols was also very low. At the second stage, from 400 to 530 °C, relatively high fractions of aliphatic side chains were produced as the demethoxylation

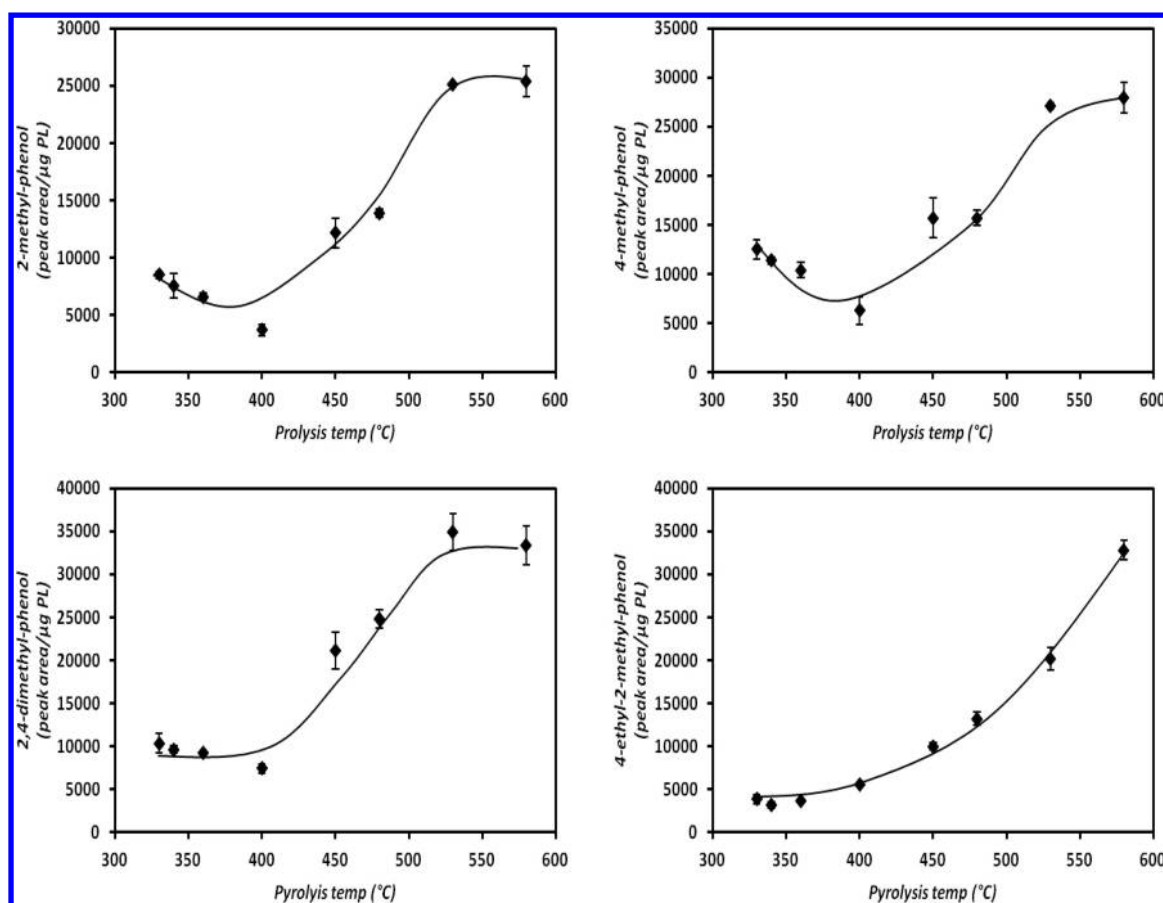


Figure 7. Effect of the pyrolysis temperature on the production of alkylated phenols from PL.

reactions accelerated. In the third stage, from 530 to 580 $^{\circ}\text{C}$, the yields were relatively constant because all of the methoxylated phenols have been converted. The yield of 4-ethyl-2-methyl-phenol increased as the pyrolysis temperature increased, suggesting that this compound is a product of secondary reactions.

3.2.4. FTIR Spectroscopy Analysis. The solid PL samples were analyzed by FTIR spectroscopy. The bands were fitted, and the band heights were collected. The spectra (expanded region of 900–1900 cm^{-1}) of PL obtained at different temperatures (330, 400, 480, and 580 $^{\circ}\text{C}$) are shown in Figure S2 of the SI.

The band at 1505 cm^{-1} indicates the aromatic skeletal vibrations, and the six other bands (1030, 1210, 1270, 1355, 1600, and 1700 cm^{-1}) are assigned to C–O, C=O, and OH groups.^{33,37–41} The ratios of the fitted band heights of these six bands to 1505 cm^{-1} were plotted versus the pyrolysis temperatures in Figure 8.

In Figure 8, the band at 1030 cm^{-1} indicates C–O in primary alcohol. Its band height ratio decreased as the pyrolysis temperature increased, implying that at a higher temperature, the C–O bonds were removed; this band could originate from the terminal $-\text{CH}_2\text{OH}$ group in the aliphatic side chain of the guaiacyl ring. The band at 1210 cm^{-1} shows the appearance of the guaiacyl C–O group; the cleavage of C–O–C ether bonds could contribute to the formation of this band at higher pyrolysis temperatures. The band at 1270 cm^{-1} indicates the existence of C=O of a guaiacyl ring. The height ratio of this band to the band at 1505 cm^{-1} increased as the temperature increased, revealing that the C=O group were formed at

higher pyrolysis temperatures. The band at 1355 cm^{-1} was affected by the pyrolysis temperature significantly; this indicates that the phenolic OH groups were released at higher pyrolysis temperatures. The band at 1600 cm^{-1} shows the aromatic skeletal vibration plus C=O stretch. The band at 1700 cm^{-1} implies either a conjugated or an unconjugated C=O stretch. The height ratios of these two bands (1600 and 1700 cm^{-1}) to the band at 1505 cm^{-1} increased as the temperature increased and implies that cleavage of the aliphatic side chains and the condensation reaction occurred.

3.2.5. ^1H NMR Analysis. The protons on the aliphatic side chains and the methoxyl functional groups are studied by ^1H NMR.¹⁹ The ^1H NMR spectra of PLs at four different temperatures of 330, 400, 480, and 580 $^{\circ}\text{C}$ are selected and plotted in Figure S3 of the SI. The protons at 0–1.5 ppm are assigned to the β position of the propyl side chain; at 1.5–3.0 ppm, the protons are assigned to the α position of the propyl side chain; the protons in the γ position are assigned to the peak at 3–3.45 ppm; the methoxyl protons are assigned to the peak at 3.45–4.2 ppm; and the aromatic protons are assigned in the region of 5.5–8.0 ppm.⁵

The ratios between aromatic protons and the protons from the propyl side chain ($-\text{CH}_2\text{CH}_2\text{CH}_3$) and methoxyl functional group ($-\text{OCH}_3$) were plotted versus the pyrolysis temperature in Figure 9. Clearly, the ratio increased as the temperature increased. This could be explained by the removal of side chains (e.g., methoxy groups forming methane and methanol), and as a result, the aromaticity of PL increases with an increasing pyrolysis temperature.

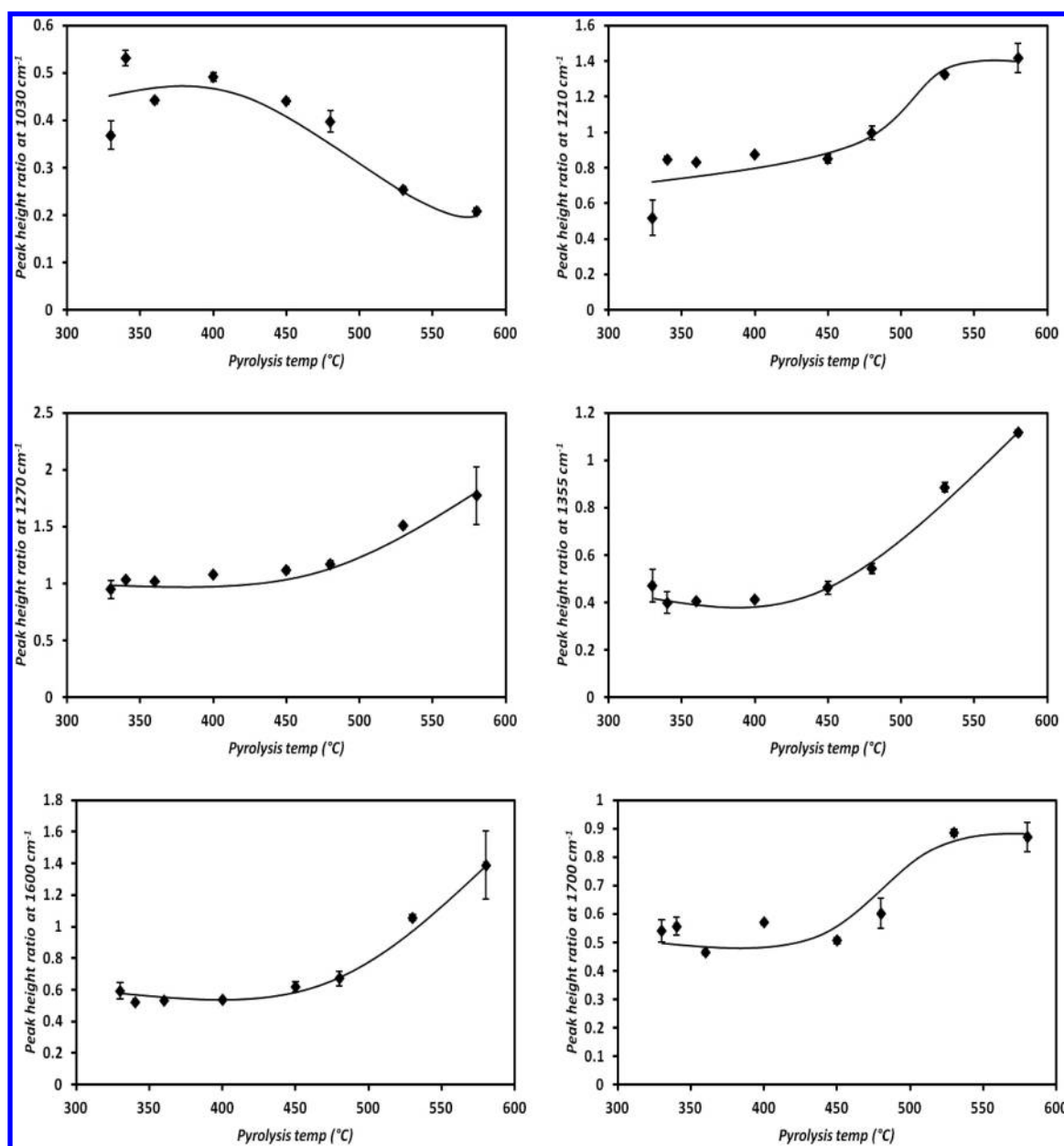


Figure 8. Effect of the pyrolysis temperature on the band height ratios (1030, 1210, 1270, 1355, 1600, and 1700 cm^{-1}).

The ratios of the propyl side chain and methoxyl protons to the aromatic protons as a function of the pyrolysis temperature are shown in Figure 10. The protons in β and γ positions decreased as the temperature increases because the aliphatic side chains are reactive during the pyrolysis. The hydroxymethyl side chain ($-\text{CH}_2\text{OH}$) could be dehydrogenated to form a carbonyl group ($-\text{CH}=\text{O}$) and could be cleaved. The proton in the α position is not significantly changed at different temperatures. The protons in methoxyl groups decreased in proportion at higher temperatures as demethylation occurred.

3.2.6. Molar Mass Analysis. The molar mass (M_w and M_n) was measured by ESI-MS and GPC. In Figures 11 and 12, no clear effect was observed for both M_w and M_n as the temperature increased. This result differs with the GPC finding for organosolv lignin in the vacuum screen heater (increase in the molecular weight when the temperature increased; see Figure 2). This apparent contradiction can be explained by the effect that

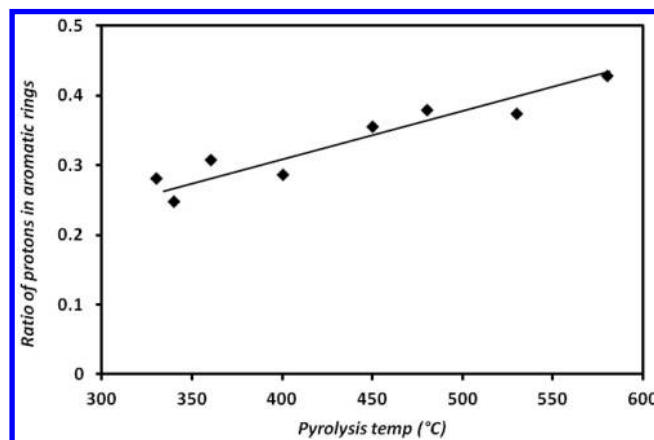


Figure 9. Effect of the pyrolysis temperature on the aromatic protons of PL.

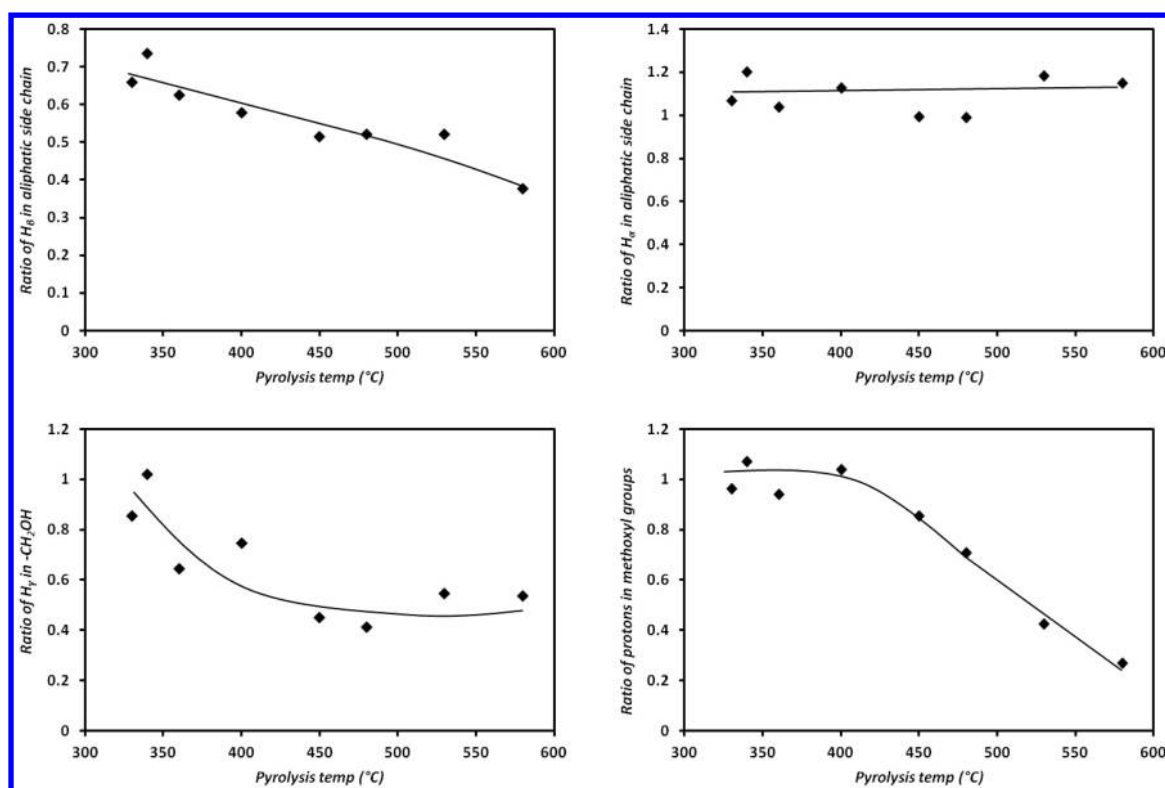


Figure 10. Effect of the pyrolysis temperature on the aliphatic side chain and methoxyl protons of PL.

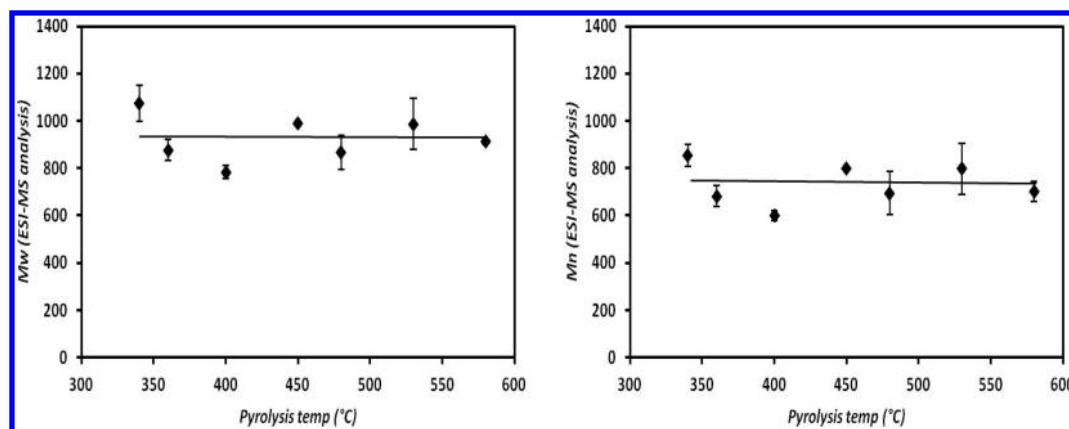


Figure 11. ESI-MS analysis of PL collected at different pyrolysis temperatures.

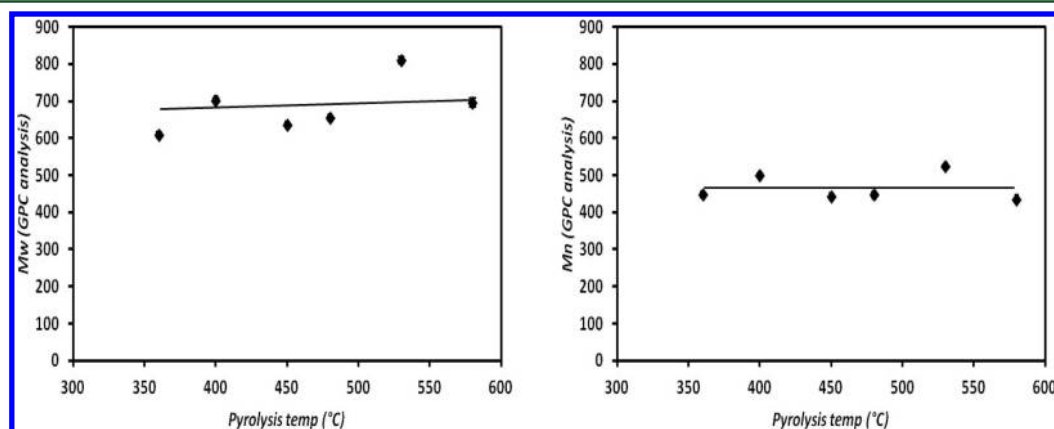


Figure 12. GPC analysis of PL collected at different pyrolysis temperatures.

secondary reactions could have on the PL molar mass. As the temperature increased, larger PL could be formed by primary reactions (some of the PL was thermally ejected); as they left the pyrolysis reactor, secondary reactions were accelerated, resulting in a decrease in the overall molar mass as the pyrolysis temperature increased. During secondary reactions in the vapor phase, the lignin bonds were cracked to form smaller oligomers or could also react with other PL molecules and polycondense into larger structures.^{19,36}

4. CONCLUSION

Vacuum screen-heater (mesh reactor) studies proved that lignin oligomers (PL) are the main products of lignin primary pyrolysis reactions and that the monolignols typically observed in Py-GC/MS studies are in fact a product of secondary reactions. Oil yields obtained from the pyrolysis of organosolv lignin in a vacuum screen heater reached a maximum (90%) at around 450 °C. The oil yield obtained in the vacuum screen heater was much higher and the gas (<6%) and char (10%) yields were much lower than those reported for fluidized-bed, Py-GC/MS, and micropyrolysis reactors, confirming that the secondary reactions in PL are important. GPC results also show that, when the reaction temperature of the screen heater rose, the molar mass of the lignin oil increased.

The effect of the pyrolysis temperature on the yield and composition of lignin oligomers in industrially relevant conditions was studied in a fluidized-bed reactor. The maximum yield of PL was reached at 530 °C. It is concluded that decarboxylation and demethoxylation reactions are promoted at higher temperatures. The methoxylated phenols were dramatically decreased during pyrolysis at higher temperatures, indicating that the methoxyl functional groups are reactive and temperature-sensitive. The formation of carbonyl groups at higher temperatures could be derived from the conversion of hydroxyl groups or the cleavage of the ether bonds. The molar mass of PL was unchanged as the pyrolysis temperature increased because of the combined effect of primary and secondary reactions.

AUTHOR INFORMATION

Supporting Information

Chromatographic Figures of S1, S2, and S3. 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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