# Low-Power Microwave Radiation-assisted Depolymerization of Ethanol Organosolv Lignin in Ethanol/Formic Acid Mixtures

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Ethanol organosolv lignin separated from bamboo was depolymerized by low-power microwave radiation (~80 W) using ethanol as a swelling agent and formic acid as a hydrogen donor solvent. After increasing the temperature from 100 to 200 °C, the total amount of phenolic compounds in the products increased from 8.1% to 40.8%, and both the weight average molecular weight ($M_w$) and number average molecular weight ($M_n$) of the products from the lignin depolymerization decreased. With extended reaction time from 20 to 60 min, the total amount of phenolic compounds and molecular weight did not remarkably change. In addition, Fourier transform infrared (FT-IR) spectroscopy showed that oxidative fracture was the primary way that lignin depolymerized. The severity factor played an important role in converting lignin into small molecular substances, and the evaluation showed that the microwave temperature was more influential on the lignin depolymerization than the reaction time. Because depolymerization and repolymerization of fragments both occurred during the microwave radiation process, it is critical to inhibit repolymerization of degraded fragments for the efficient degradation of lignin. This study not only provides a theoretical basis for studying the mechanism of microwave-assisted lignin degradation but is also important for the determination of a cost-effective lignin depolymerization method.

*Keywords: Lignin; Low microwave radiation; Depolymerization; Ethanol; Formic acid*

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## INTRODUCTION

After cellulose, lignin is the second most abundant natural polymer on earth (Li *et al*. 2012). Lignin is widely distributed in plant cell walls and possesses a complex structure, which consists of coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol polymers. Lignin functions as a biological barrier against pathogens (Toledano *et al*. 2014b). At present, valuable applications for this underutilized resource have attracted considerable attention. With the development of ethanol biorefineries, lignin has become a noteworthy potential feedstock for biofuels and aromatic chemicals (Jiang *et al*. 2010). For example, as the primary plant biomass component, lignin contains numerous oxygen functional groups, such as hydroxyl, carbonyl, and carboxyl groups. Therefore, phenolic chemicals can be obtained from lignin by chemical degradation processes (Wahyudiono *et al*. 2008). In addition, by breaking down the lignin into small molecules, several compounds, such as vanillin, can be commercially produced (Hocking 1997). However, lignin degradation remains a challenge because of the highly complex structure of lignin, technological barriers, and adverse economic considerations (Badamali *et al*. 2008; Jiang *et al*. 2010).

Several studies have investigated the mechanism of lignin degradation, including fast pyrolysis, hydrogenolysis, oxidation, lignin depolymerization in supercritical solvents, ionic liquid pretreatment, and catalysts in lignin conversion (Pandey and Kim 2011). Under rapid pyrolysis conditions, lignin is converted directly into a liquid product, which is referred to as “bio-crude” or “bio-oil.” The resulting “bio-crude” or “bio-oil” can be upgraded through various processes, such as those used in traditional petroleum refineries (Patwardhan *et al*. 2011). Wang *et al*. (2014) reported that after catalytic pyrolysis by the Zn/ZSM-5 catalyst coupled with a microwave pyrolysis reactor, lignin was primarily degraded and dehydrated to produce propenyl–guaiacols. Badamali *et al*. (2009) reported the complete degradation of the lignin model phenolic monomer, which was catalyzed by Co(salen)/SBA-15 under microwave radiation for 40 min. Wen *et al*. (2014) pretreated poplar alkaline lignin with ionic liquids and found that after pretreatment, the β-O-4′ bond of lignin was cleaved, resulting in an increase in phenolic –OH. However, a dehydration reaction occurred that resulted in a decrease in aliphatic –OH. In addition, the β-β′ and β-5′ linkages were depolymerized, resulting in a decrease in the molecular weights (Wen *et al*. 2014). One of the disadvantages of these methods is the requirement for extreme reaction conditions, such as high pressure or temperature, to accomplish the depolymerization of lignin (Nanayakkara *et al*. 2014).

At present, environmental interest is the key to lignin degradation. Environmentally friendly processes have attracted increasing attention (Gu *et al*. 2012). Liquefaction is a good method to degrade lignin, and solvent selection is crucial to improve the economics of the process (Xiao *et al*. 2011; Xie *et al*. 2015). Ethanol as a swelling agent and formic acid as a hydrogen donor solvent have been used to establish a mild and environmentally friendly system to convert lignin to small molecular products (Pandey and Kim 2011; Gasson *et al*. 2012). Ethanol is attractive for lignin degradation because of its high solvency for biomass and low critical temperature (Gasson *et al.* 2012). In addition, using ethanol as a solvent results in a less oxygenated oil fraction and virtually no solid residue (Gellerstedt *et al*. 2008; Gasson *et al*. 2012). Formic acid decomposes into $CO_2$ and active hydrogen under heating conditions, which results in lignin hydrogenation (Pandey and Kim 2011).

Bamboo is a highly abundant resource in China with a large plantation area and annual yield. Bamboo is composed of hemicellulose, cellulose, and lignin (Dong and Xiong 2014). Bamboo lignin depolymerization leads to the industrial production of valuable industrial and food products, such as vanillin, vinylguaiacol, optically active lignans, ferulic acid, and monolignol dimers (Lou *et al*. 2010).

Compared with traditional heating, microwave radiation has many advantages, including low reaction temperatures, short reaction times, and high yields of the target products (Ouyang *et al*. 2015). However, the majority of studies concerning microwave radiation have focused on depolymerizing lignin by high microwave power, *i.e.*, in general, greater than 400 W (Dong *et al*. 2014; Toledano *et al*. 2014b). Studies on low microwave power-assisted depolymerization of bamboo lignin are few, and this lack of research on this topic is not beneficial to the study of the lignin depolymerization mechanism under microwave heating. Research on low microwave radiation assistance in lignin depolymerization not only provides a theoretical basis for studying the mechanism of microwave-assisted lignin degradation, but is also important for determining a cost-effective method for the depolymerization of lignin.

In the present study, low microwave radiation (~ 80 W) was applied in ethanol organosolv lignin depolymerization when using ethanol as a swelling agent and formic acid as a hydrogen donor solvent. Ethanol organosolv lignin was isolated from bamboo and subjected to mild microwave radiation at temperatures ranging from 100 to 200 °C and reaction times of 20 to 60 min. The product characteristics from the lignin depolymerization were evaluated.

## EXPERIMENTAL

### Materials and Reagents

Bamboo culms (natural material) were obtained from Nanchang, Jiangxi Province, China. Ethanol (analytical grade) was from Xi Long Scientific Co. (Guangdong, China), formic acid (analytical grade) was obtained from Da Mao Reagent Co. (Tianjin, China), and tetrahydrofuran (THF, HPLC grade) was purchased from Solarbio (Beijing, China).

### Methods

*Extraction of ethanol organosolv lignin from bamboo*

The bamboo lignin was extracted using the method of Fan *et al*. (2015). In brief, dried bamboo culms were cut into small pieces, sieved, extracted with methylbenzene/ethanol (2:1, v/v), and finally air-dried to obtain a dewaxed bamboo powder. The resulting dried bamboo powder (150 g) and 50% ethanol aqueous solution (8:1, v/v) were cultivated in an autoclave at 180 °C for 3 h with a 10 °C/min heating rate, kept within a ± 2 °C range. After cultivation, the mixture was vacuum-filtered and dried as described by Fan *et al*. (2015) to obtain the bamboo lignin powder.

*Microwave depolymerization*

Lignin was depolymerized by ethanol and formic acid with microwave heating. All experiments were conducted using a microwave reaction system (CEM Corporation, USA), and the conditions of each experiment are shown in Table 1. Lignin (0.5 g) was mixed with 8 mL of formic acid and 4 mL of ethanol in each tube, and the tube was covered with a rubber cap with a small hole. The experiments were conducted at various times (20 to 60 min) and temperatures (100 to 200 °C). The power of the microwave used in this work was less than 80 W. Before the experiment, the sample was placed in a microwave digestion instrument and stirred with a magnetic rotor for 2 min. The temperature was raised to the designated temperature at low power (80 W, ~2 min), followed by a steady step, during which the power varied to maintain the temperature at the target value. The temperature in the microwave reactor system was monitored by infrared sensing. To prevent hotspot problems, a magnetic rotor was added in the tube before the reaction was initiated. After the reaction, the samples were cooled to room temperature (~20 min). Then, the formic acid and ethanol were evaporated under vacuum, and the resulting mixture was stored in darkness for subsequent experiments. Each experiment was conducted in duplicate to ensure consistent results.

The severity factor, $R_0$, combines the temperature and time into a single factor, the effective reaction conditions, and is defined as follows (Kim *et al*. 2014),

$$R_0 = \int_0^t exp\left(\frac{T_i - T_b}{\bar{w}}\right)\mathrm{dt} \tag{1}$$

$$\log R_0 = \log\left[t\left(\frac{T_i - T_b}{\bar{w}}\right)\right] \tag{2}$$

where $T_i$ is the reaction temperature (°C), $T_b$ is the base temperature (100 °C), $w$ is the fitting parameter (14.75), and $t$ is the reaction time (min).

**Table 1.** List of Reaction Conditions and Severity Factors

| Exp. No. | Reaction Temperature (°C) | Reaction Time (min) | Log $R_0$ |
|---|---|---|---|
| 1-1 | 100 | 30 | 1.48 |
| 1-2 | 120 | 30 | 2.08 |
| 1-3 | 140 | 30 | 2.68 |
| 1-4 | 160 | 30 | 3.27 |
| 1-5 | 180 | 30 | 3.87 |
| 1-6 | 200 | 30 | 4.47 |
| 2-1 | 160 | 20 | 3.10 |
| 2-2 | 160 | 30 | 3.27 |
| 2-3 | 160 | 40 | 3.40 |
| 2-4 | 160 | 50 | 3.50 |
| 2-5 | 160 | 60 | 3.58 |

### *Product characterization*

The samples were dissolved in methyl alcohol prior to analysis. The composition of the phenolic compounds of the samples was identified using a gas chromatograph–mass spectrometer (GC–MS) (Agilent Technologies, California, USA) coupled with a thermal conductivity detector (TCD) and an Agilent capillary column (DB-35 ms, California, USA; 0.25 mm × 30 m × 0.25 μm). The column temperature was kept at 60 °C for 2 min and then raised to 300 °C at a rate of 10 °C/min. The injection sample size was 2 μL, with a split ratio of 20:1. The ion source temperature was 230 °C for the mass selective detector. Helium was selected as the carrier gas, and the flow rate was 1.0 mL/min. The compounds were identified by comparing the spectrograms with those in the NIST data library. The relative content of each compound in the products was determined by semi-quantitative methods according to the chromatographic percentage.

### *Molecular weight determination*

The molecular weight of the product was determined by a gel permeation chromatography–high-performance liquid chromatography (GPC–HPLC) instrument (G1312B binary pump, Agilent Technologies, State of California, USA, UV detector at 280 nm; GPC column at a column temperature of 30 °C). The samples were dissolved in THF prior to analysis. The samples were then filtered through a 0.45-μm syringe filter. THF, at a flow rate of 0.50 mL/min, was used as the mobile phase. A polystyrene standard calibration curve was used to calibrate the number average molecular weight ($M_n$) and weight average molecular weight ($M_w$) of the samples. This method is also useful for evaluating the degree of lignin depolymerization.

*Characterization of functional groups*

Characterization of the functional groups of the raw material and depolymerization products was accomplished by Fourier transform infrared (FT–IR) spectroscopy (Nicolet iS5, Thermo, USA). The samples were ground with KBr, and the spectra were recorded in the range of 4000 to 700 $cm^{-1}$ with 16 scans and at a 4 $cm^{-1}$ spectral resolution per sample.

## RESULTS AND DISCUSSION

### Compounds of Depolymerization Products Identified by GC–MS

The experiments were conducted to study the influence of microwave temperature and reaction time on the products obtained under mild conditions. After treatment under various microwave conditions, the lignin was converted into small molecular chemical compounds. This research primarily exhibited the value-added phenolic compounds obtained from lignin depolymerization. Figures 1 and 2 show that seven compounds were obtained. Among these compounds, the G-type ones included guaiacol, vanillin, and homovanillyl alcohol, and the S-type ones included syringol, syringaldehyde, acetosyringone, and desaspidinol.

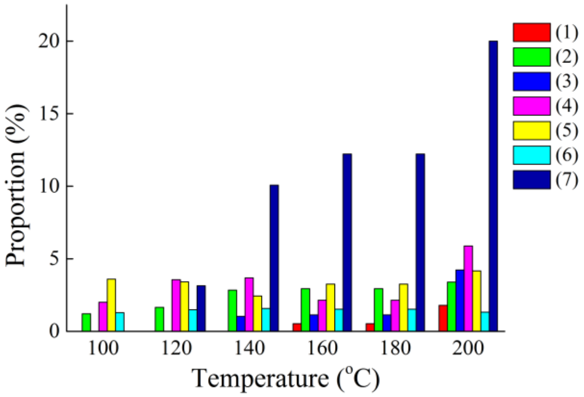

**Fig. 1.** The components and their relative area percentage of phenolic compounds in the products identified by GC-MS at different microwave temperatures (30 min), where (1) is guaiacol, (2) is vanillin, (3) is homovanillyl alcohol, (4) is syringol, (5) is syringaldehyde, (6) is acetosyringone, and (7) is desaspidinol

Figure 1 shows that changing the microwave temperature exerted a considerable influence on the product distribution of the phenolic compounds. Guaiacol was not detected by GC–MS when the microwave temperature was lower than 160 °C. Homovanillyl alcohol was not detected by GC–MS when the microwave temperature was lower than 140 °C. At a temperature of 100 °C, no desaspidinol was observed in the products from lignin depolymerization, possibly because of several relatively stable chemical bonds (Hu *et al*. 2013). In general, as the microwave temperature increased, the yield of vanillin gradually increased, which indicated that the rate of vanillin formation reaction was higher than that of the polycondensation reaction, except at 180 °C (Dong *et al*. 2014). The syringol yield exhibited the same tendency as that of vanillin; therefore, it is suggested that the rate of the syringol formation reaction was higher than that of the polycondensation reaction, except at 160 °C. The desaspidinol yield gradually increased as the microwave temperature increased from 100 to 180 °C and then remained constant until 200 °C. The change in yield of syringaldehyde and acetosyringone as the microwave temperature increased from 100 to 200 °C may have been due to the bond dissociation energy from the C-C and C-O bonds, which indicates a competitive kinetic relationship (Hu *et al*. 2013; Dong *et al*. 2014). In general, acetosyringone was not remarkably changed by the microwave temperature, *i.e.*, it changed from 1.28% to 1.32% as the microwave temperature increased from 100 to 200 °C; therefore, there was a possible dynamic balancing state between the rate of the acetosyringone formation and polycondensation reactions.

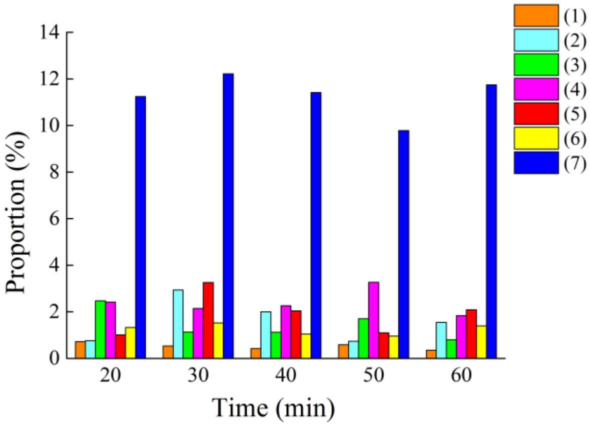

**Fig. 2.** The components and their relative area percentage of phenolic compounds in the products identified by GC-MS at different microwave times (160 °C), where (1) is guaiacol, (2) is vanillin, (3) is homovanillyl alcohol, (4) is syringol, (5) is syringaldehyde, (6) is acetosyringone, and (7) is desaspidinol

As can be seen in Fig. 2, the guaiacol yield at 160 °C was not noticeably influenced by the microwave time. When the microwave time was increased from 20 to 60 min, the guaiacol yield changed from 0.72% to 0.35%. For homovanillyl alcohol, the yield generally decreased from 2.47% to 0.80% as the reaction time increased from 20 to 60 min. The yields of acetosyringone and desaspidinol were not remarkably changed by the reaction time, which suggests there was a possible dynamic balancing state between the rate of the formation reaction and polycondensation reaction at 160 °C, regardless of the reaction time. With an increase in the reaction time from 20 to 60 min, the vanillin and syringaldehyde yields increased from 0.76% to 1.55% and 1.01% to 2.09%, respectively. During the reaction at 160 °C and 50 min, the syringol yield reached its highest value (3.27%). The phenolic compounds from the lignin depolymerization reaction are mostly derived from the cleavage of bonds among three phenylpropane units, namely, syringylpropane (3,5-diamethoxy-4-hydroxyphenylpropane) (S), guaiacylpropane (4-hydroxy-3-methoxy-phenylpropane) (G), and 4-hydroxyphenylpropane (H) groups (Monteil-Rivera *et al*. 2013; Toledano *et al*. 2014b). Figures 1 and 2 show that the total amount of S-type compounds was higher than that of the G-type compounds. In addition, the total amount of phenolic compounds increased from 8.1% to 40.8% with increasing microwave temperature. However, no major change was observed for the total amount of phenolic compounds with the extension of the reaction time from 20 to 60 min. The variation in the quantities of phenolic compounds from the lignin depolymerization reaction may have been due to the hydrogenolyzation of the three phenylpropane units under the selected conditions, which may have been remarkably affected by the use of the severity factors (Table 1) (Kim and Park 2013; Toledano *et al*. 2014b). When the reaction time was set at 30 min, the value of $R_0$ noticeably increased, from 1.48 to 4.47, with an increase in the microwave temperature. However, when the microwave temperature was set to 160 °C and the reaction time increased, no evident change was observed in the $R_0$ value. Therefore, the influence of the microwave temperature on lignin depolymerization at a set time was larger than that of the reaction time at a set microwave temperature.

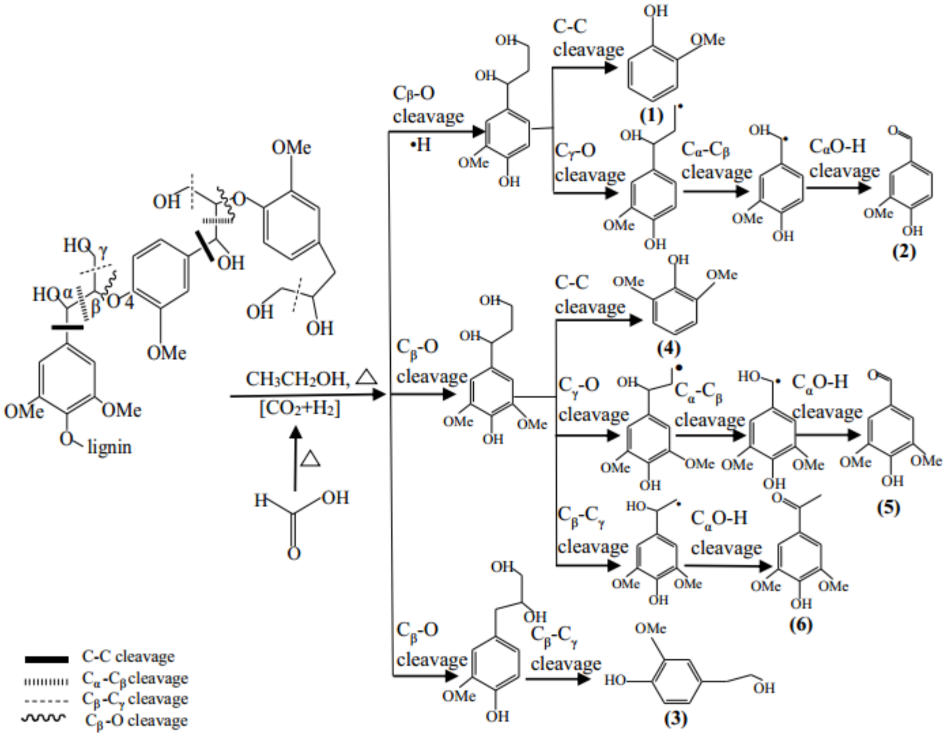

**Fig. 3.** The possible mechanism of phenolic compound generation from lignin depolymerization (Shen *et al*. 2015)

The possible generation mechanism of phenolic compounds from the lignin depolymerization reaction is shown in Fig. 3. The presence of desaspidinol is not clearly understood. Toledano *et al*. (2014b) reported that for lignin depolymerization to aromatics *via* mild microwave-assisted hydrogen-free hydrogenolysis and when tetralin was used as a solvent, no desaspidinol was found in the products. In contrast, when formic acid was used as a solvent, desaspidinol was found in the products from the lignin depolymerization. Toledano *et al*. (2014b) concluded that the formation of desaspidinol depends on the solvent utilized in the system. Jiang *et al*. (2010) studied the composition of the lignin pyrolysis products at various temperatures (from 400 to 800 °C). Desaspidinol was detected in both Alcell lignin and Asian lignin pyrolysis products by pyrolysis GC–MS. As the temperature increased from 400 to 800 °C, the proportion of desaspidinol decreased from 0.555 wt.% to 0.275 wt.% in the Alcell lignin pyrolysis vapor, and from 0.134 wt.% to 0.038 wt.% in the Asian lignin pyrolysis vapor (Jiang *et al*. 2010).

## Molecular Weight Determination

Table 2 presents the $M_w$ and $M_n$ values, as well as the molecular weight distribution ($M_w/M_n$), of the depolymerization products. For a reaction time of 30 min, $M_w$ and $M_n$ underwent a dynamic change process with increasing microwave temperature. The $M_w$ and $M_n$ values at 120 °C (1121 and 660, respectively) were lower than those values at 100 °C (1335 and 754, respectively), which suggests there was a depolymerization phenomenon for lignin under low-power microwave heating as the temperature increased from 100 to 120 °C. However, as the temperature further increased to 140 °C, the values of $M_w$ and $M_n$ were 1304 and 801, respectively, which were higher than at 120 °C. This suggested that there was a repolymerization phenomenon for the molecules produced under low-power microwave heating as the temperature increased from 120 to 140 °C. The repolymerization reaction is primarily caused by the reaction between the unstable oligomer or intermediate products and original lignin, which results in unconverted lignin with a higher molecular weight than the initial lignin (Li *et al*. 2007; Toledano *et al*. 2014a). As the microwave temperature increased from 140 to 180 °C, the values of $M_w$ and $M_n$ decreased from 1304 and 801 to 1026 and 348, respectively. This finding suggested that lignin was depolymerized into several small molecules. In addition, as the temperature further increased to 200 °C, the values of $M_w$ and $M_n$ slightly increased to 1055 and 358, respectively; therefore, the lignin molecule may have repeated the depolymerization and repolymerization reactions as the temperature increased from 100 to 200 °C under low-power microwave conditions. However, the $M_w$ and $M_n$ values decreased in general, which indicated that the rate of the repolymerization reaction was lower than that of the depolymerization reaction (Roberts *et al*. 2011; Toledano *et al*. 2014a). When the temperature was 180 °C, the lowest values were obtained for the $M_w$ and $M_n$, which were 1026 and 348, respectively. It was concluded that microwaves can assist the lignin depolymerization reaction within a certain temperature range. This outcome was slightly different from that reported by Dong *et al*. (2014), who studied lignin depolymerized by formic acid with a fixed microwave power mode (600 W) and found that by increasing the microwave temperature, both $M_n$ and $M_w$ decreased at first, and then increased, with their lowest values obtained at 160 °C (4529 and 1886, respectively). When the microwave temperature exceeded 160 °C, the repolymerization reaction played the dominant role in the lignin degradation process, which improved the $M_w$ and $M_n$ to a certain extent (Dong *et al*. 2014).

**Table 2.** Molecular Weight-Average ($M_w$), Number-Average ($M_n$), and Distributions ($M_w/M_n$) of the Depolymerization Products

| Run | $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|
| 1-1 | 754 | 1335 | 1.77 |
| 1-2 | 660 | 1121 | 1.70 |
| 1-3 | 801 | 1304 | 1.63 |
| 1-4 | 532 | 1173 | 2.20 |
| 1-5 | 348 | 1026 | 2.95 |
| 1-6 | 358 | 1055 | 2.95 |
| 2-1 | 551 | 1284 | 2.33 |
| 2-2 | 532 | 1173 | 2.20 |
| 2-3 | 663 | 1361 | 2.05 |
| 2-4 | 507 | 1187 | 2.34 |
| 2-5 | 544 | 1256 | 2.31 |

The effect of the microwave time on the molecular weight of the depolymerization products was similar to the effect of the microwave temperature. At 160 °C, $M_w$ and $M_n$ also showed a dynamic change process. After microwave heating for 30 min at 160 °C, the $M_w$ and $M_n$ values (1173 and 532, respectively) were lower than those obtained at 20 (1284 and 551, respectively) and 40 min (1361 and 663, respectively). Further increasing the microwave heating time to 50 min resulted in the $M_w$ and $M_n$ decreasing to 1187 and 507, respectively. Then, at a reaction time of 60 min, the $M_w$ and $M_n$ increased to 1256 and 544, respectively. With the extension of the microwave time from 20 to 60 min at 160 °C, the lignin molecule repeatedly underwent the depolymerization and repolymerization reactions. However, no remarkable differences in the values of $M_w$ and $M_n$ were observed when the microwave time increased from 20 to 60 min at 160 °C, as there was only a slight decrease for $M_w$ and $M_n$ between 20 (1284 and 551, respectively) and 60 min (1256 and 544, respectively). Dong *et al*. (2014) reported that longer microwave heating times inhibited the apparent depolymerization of lignin. Ouyang *et al*. (2015) showed that, compared with traditional heating, microwave heating promoted the alkali lignin depolymerization of wheat straw and prolonged microwave heating times accelerated the recondensation of depolymerized lignin fragments.

## FT-IR Spectra

The FT-IR spectra can be used to determine the physicochemical properties and chemical functional groups of lignin (Wen *et al*. 2013). The FT-IR spectra of the lignin before and after depolymerization under various microwave conditions were characterized in the 700 to 4000 cm$^{-1}$ range, and the results are shown in Figs. 4 and 5.

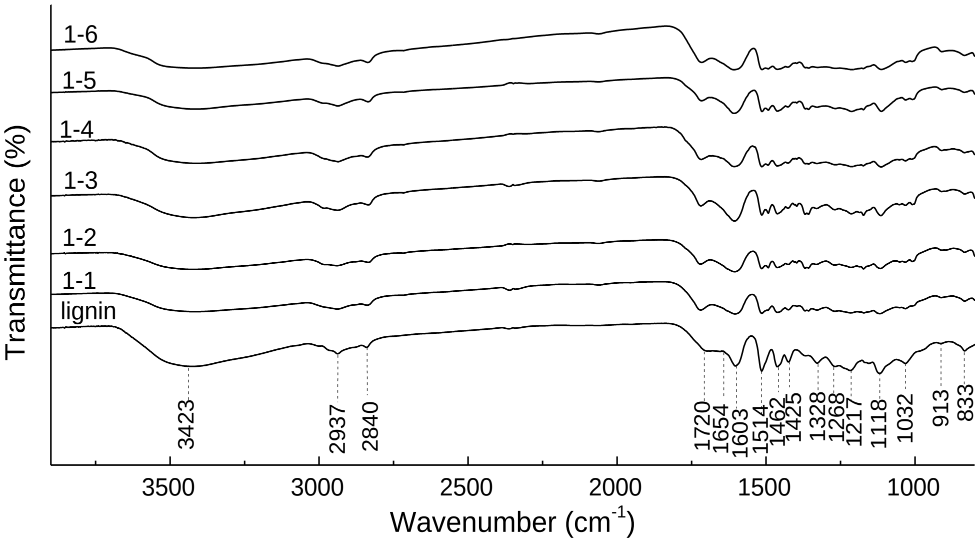

**Fig. 4.** FT-IR spectra of the lignin before and after depolymerization at various microwave temperatures and 30 min

The main peaks of the chemical functional groups present in the lignin before and after depolymerization were observed at 3423, 2937, 2840, 1720, 1654, 1603, 1514, 1462, 1425, 1328, 1268, 1217, 1118, 1032, 913, and 833 cm$^{-1}$. Among these peaks, the broad peak at approximately 3423 cm$^{-1}$ was related to the –OH stretching absorption of the aliphatic hydroxyl and phenolic hydroxyl groups.

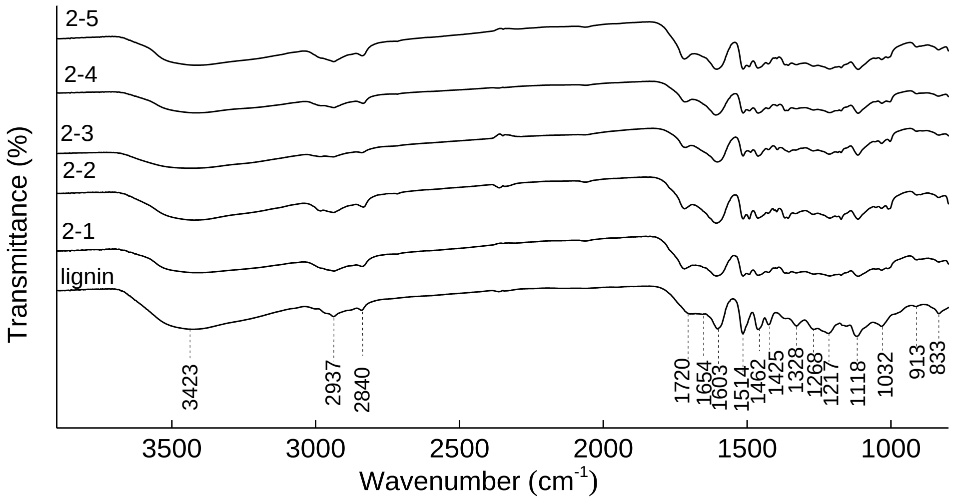

**Fig. 5.** FT-IR spectra of the lignin before and after depolymerization at 160 °C and various microwave times

Figures 4 and 5 show that the peak around 3423 cm$^{-1}$ of the degradation products was evidently weakened by the microwave radiation, which suggests that the amount of –OH groups in the lignin depolymerization products decreased after the microwave treatment. The signal of the peak at 1720 cm$^{-1}$ assigned to the stretching C=O groups was sharper and clearer in the degraded products than in the raw lignin, which indicates a higher carbonyl content in the depolymerization products. This was explained by the fact that the oxidation of hydroxyl groups into carbonyl groups was promoted by the microwave radiation (Xiao *et al*. 2011).

The band at 2937 cm$^{-1}$, which was assigned to the C-H vibration in methyl, was weaker in the lignin depolymerization products compared with the raw lignin; therefore, a decrease in the methyl groups is indicated. The decrease in methyl meant the abscission of the C3 structure and stood for the cleavage of the β-O-4 bond, which suggests the generation of monophenolic compounds and the breakage of long carbon chains (Xiao *et al*. 2011; Ouyang *et al*. 2014). This was in accordance with the aforementioned results of the GC-MS and molecular weight analyses. In addition, the signals at 1268 and 1217 cm$^{-1}$ originated from C-O groups in the guaiacol and syringol rings, respectively, and were weakened after the lignin depolymerization, which indicates the cleavage of C-O bonds and a decrease of methoxyl groups in the lignin structure after treatment by microwave radiation.

The signal at 1514 cm$^{-1}$ was assigned to the aromatic skeletal vibrations and was present in all of the spectra of the lignin before and after depolymerization, which demonstrates that the aromatic rings still existed after depolymerization. However, the absorption peak at 1514 cm$^{-1}$ was weakened in the lignin depolymerization products compared with the raw lignin, which suggests that the aromatic rings were partially opened. Figures 4 and 5 show that the spectra patterns of the lignin before and after depolymerization had a slight difference, which demonstrates that the main chemical functional groups of the lignin before and after degradation under microwave radiation were slightly different. In addition, the depolymerization products contained incompletely degraded lignin.

## CONCLUSIONS

1. As the temperature increased from 100 to 200 °C, the total amount of phenolic compounds in the products increased. Among the products, the total amount of S-type compounds in the products was higher than that of the G-type compounds. Additionally, the $M_w$ and $M_n$ of the products from lignin depolymerization decreased. However, when the reaction time was increased from 20 to 60 min at 160 °C, both the total amount of phenolic compounds and molecular weight did not remarkably change.
2. Increasing the microwave temperature within a certain range effectively promoted lignin degradation, whereas lengthening the reaction time of microwave radiation at a certain microwave temperature had a minimal effect on the lignin depolymerization.
3. After lignin depolymerization, the products contained relatively smaller fragments and a portion of incompletely degraded lignin, and the aromatic rings were still present in the products and partially opened. Under low microwave radiation, lignin depolymerization occurred mainly through oxidation cleavage. During microwave treatment, the lignin primarily underwent depolymerization and repolymerization reactions. Our future work will be focused on the separation and extraction of aromatic compounds from lignin depolymerization product, and then further apply to manufacture high-value bulk and fine chemicals.

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