Microwave-assisted Depolymerization of Lignin with Metal Chloride in a Hydrochloric Acid and Formic Acid System

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A microwave-assisted depolymerization method of lignin with various metal chloride catalysts ($MgCl_2$, $AlCl_3$, $FeCl_3$, $ZnCl_2$, and $MnCl_2$) in a formic acid and hydrochloric acid system under mild conditions (160 °C for 30 min) was studied. The resulting bio-oil was identified by a gas chromatography-mass spectrometer, and the solid residue was analyzed by Fourier transform infrared spectroscopy (FT-IR). Furthermore, the molecular weight change of lignin after the reaction was measured by gel permeation chromatography. The $MnCl_2$ catalyzed lignin to produce most aromatic monomers, including approximately 23.0% G-type, 11.9% S-type, and 14.8% H-type monomer compounds. Different metal chloride catalysts had different effects on the depolymerization of lignin, which were embodied in the type and content of the products. It was also worth noting that the catalytic effects of transition metal chlorides on lignin may have been related to each chloride's cation radius.

Keywords: Organosolv lignin; Microwave-assisted; Metal chloride; Hydrochloric and formic acid system

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INTRODUCTION

With the rapid depletion of fossil resources, there is an urgency to find alternative renewable energy resources. Lignocellulosic biomass (made up of cellulose, hemicellulose, and lignin) is considered to be an alternative organic renewable resource for the production of biofuels and aromatic chemicals (Li *et al.* 2015). In theory, lignin, based on its chemical structure, is a feasible raw material for the production of phenols (Higuchi 1990). Also, the efficient degradation of paper in composting plants means that biodegradation of lignin is also needed (Tuomela *et al.* 2000). However, its complex three-dimensional (3D) structure and diverse chemical bonds limit the direct uses of lignin. Thus, the efficient depolymerization of lignin into more phenolic compounds has become a hot spot in research (Asina *et al.* 2017).

As an emerging thermochemical method, microwave heating has the advantages of fast speed and high efficiency (Liu *et al.* 2017). Its magnetic field is capable not only of producing thermal effects, but also generating non-thermal effects, causing the violent vibration of some chemical bonds and bond breaking (Toledano *et al.* 2013). Therefore, microwave heating can degrade lignin under mild conditions. Dhar and Vinu (2017) investigated the microwave-assisted degradation of alkali lignin in the presence of different organic solvents. They showed that a significant yield of phenolics (20 wt%) containing acetosyringone, guaiacol, syringaldehyde, anisole, and lignin dimers (m/z 306, 322 Da) were produced at 100 °C in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), while at 140 °C, 11 wt% phenolics were obtained in ethylene glycol (EG). Dong *et al.* (2014) studied the microwave-assisted degradation of black-liquor lignin with formic acid, showing that the liquid product consisted of bio-oil 1 (phenolic monomeric compounds) and bio-oil 2 (oligomers), and achieved a maximal yield of 64.1% at 160 °C after 30 min (the yield for bio-oil 1 was 9.7% and 54.4% for bio-oil 2). Toledano *et al.* (2014) studied lignin depolymerization into simple aromatics with different metal nanoparticles on mesoporous Al-SBA-15 using a mild microwave-assisted approach. The results showed that the catalyst containing 10 wt% nickel achieved the highest degree of lignin depolymerization, with a maximum yield of 30% bio-oil after a short reaction time (typically 30 min of microwave irradiation).

Formic acid used as a catalyst and hydrogen donor in the depolymerization of lignin has been shown to be effective by many experiments. Ouyang *et al.* (2015) established that formic acid, as a hydrogen donor, provides *in situ* hydrogen, and its hydrogen supply ability is better than that of an external hydrogen source. Formic acid is also a readily available green reagent in biorefineries (Xu *et al.* 2012). Furthermore, HCl as a typical protonic acid can effectively promote the fracture of the ether bond in lignin and promote depolymerization (Zhang *et al.* 2014).

Moreover, recently scientists have found that Lewis acids, such as aluminum chloride ($AlCl_3$) and manganese chloride ($MnCl_2$), *etc.*, are excellent hydrogen bonding acceptors and nucleophilic reagents (Güvenatam *et al.* 2015). Many experiments have studied the depolymerization of lignin catalyzed by different chlorides. Maldhure and Ekhe (2013) have studied the pyrolysis of purified kraft lignin in the presence of $AlCl_3$ and $ZnCl_2$ at 300 °C to 400 °C, and found that the presence of $ZnCl_2$ yielded comparatively more liquid products, whereas the presence of $AlCl_3$ yielded comparatively more gaseous products. Pan *et al.* (2015) investigated the degradation of lignin model compounds with metal salts assisted by microwave. The results showed that chromium chloride ($CrCl_3$) and $MnCl_2$ were the most effective in the degradation of the lignin model compounds. Du *et al.* (2017) concluded that either polyoxometalate (POM) or ferric chloride ($FeCl_3$) was used as the catalyst and charge transfer agent in anode. However, the study by Jia *et al.* (2016) proved that $FeCl_3$, copper chloride ($CuCl_2$), and $AlCl_3$ were effective for the β-O-4 bond cleavage of the phenolic lignin model compound guaiacyl glycerol-β-guaiacyl ether (GG). Furthermore, the HCl formed *in situ* by the hydrolysis of metal chlorides catalyzed the β-O-4 bond cleavage. According to Kinrade *et al.* (1999), the addition of KCl, $CaCl_2$, and magnesium chloride ($MgCl_2$) promoted the decomposition of the experimental sample and reduced the coke yield of lignin.

This paper is based on related previous research conducted in the authors' laboratory. According to Duan *et al*. (2017), the best conditions for the low-power microwave-assisted depolymerization of organosolv lignin is a temperature of 160 °C and a duration of 30 min. Compared with a water, methanol, and isopropanol system, ethanol was the only effective solvent for the depolymerization process (Jing *et al.* 2016). According to the previous work by the author and colleagues of the same laboratory, the effects of different mixed acid systems (HCl-HCOOH system, H_3PO_4-HCOOH system, and H_2SO_4-HCOOH system) were studied. The weight-average molecular mass (M_w) and number-average molecular mass (M_n) of lignin depolymerization products reached the minimum when the hydrochloric acid and formic acid system was present. The optimal ratio for ethanol, formic acid, and hydrochloric acid is 2:1:1. This study used ethanol as a swelling agent, a formic acid and hydrochloric acid system as hydrogen donors, metal chloride as a catalyst, and was conducted using a microwave at 160 °C for 30 min. The resulting products were separated into oil product and solid residue and analyzed using the following techniques: high-performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FT-IR), and gas chromatography-mass spectrometer (GC-MS). The catalytic abilities of different metal chlorides are discussed under these circumstances. In this paper, the authors explored the catalytic ability of metal chlorides in the depolymerization of lignin into aromatic monomers under mild reaction conditions, aiming to provide a theoretical basis for lignin depolymerization.

EXPERIMENTAL

Materials

Ethanol (99%), formic acid (analytical grade), ethyl acetate, and tetrahydrofuran (HPLC grade) were purchased from Da Mao Reagent Co. (Tianjin, China). The $AlCl_3$, $FeCl_3$, $MnCl_2$, $ZnCl_2$, and $MgCl_2$ were provided by Xi Long Scientific Co. (Guangdong, China). Hydrochloric acid was obtained from Solarbio (Beijing, China).

Methods

Alcohol-soluble lignin extraction

Lignin was extracted using an adaptation of the method of Fan *et al.* (2016). Dried bamboo was first cut into pieces, sieved, extracted with methylbenzene/ethanol (2:1, v/v), and then air-dried to acquire dewaxed bamboo powder. The bamboo powder (150 g) was dissolved in 50% ethanol aqueous solution (8:1, v/v) and then loaded into the autoclave set at 180 °C for 3h. After the reaction, the mixture was vacuum-filtered and dried to obtain the lignin powder.

Low-power microwave depolymerization

The experimental materials were mixed according to Table A1. Briefly, 1 g lignin, 0.005 mol metal chloride, 10 mL hydrochloric acid, and 10 mL formic acid (1:1, v/v) system was dissolved into 20 mL ethanol.

Lignin depolymerization was performed in the MDS-6G microwave digestion system (Sineo, Shanghai, China). The reaction temperature was set at 160 °C, after which, according to the previous study of Duan *et al.* (2017), the depolymerization reaction played the dominant role in the lignin degradation process, with a reaction time of 30 min.

Product separation and analysis method

After reaction, the reactants were cooled to room temperature prior to filtration. Then the mixture was filtered to separate the liquid part from the solid part. The pH of the liquid part was regulated to 6 using 2 mol/L sodium hydroxide solution (NaOH). It was then extracted with ethyl acetate to obtain the aqueous and organic phases. The organic phase was evaporated and the bio-oil was obtained.

The bio-oil was detected by GC-MS. The solid part was cleaned with deionized water three times and dried at 60 °C in the vacuum-drying box for 1 h. A portion taken from the dry solid was dissolved with tetrahydrofuran, and analyzed by GPC-HPLC. Another portion taken from the dry solid was analyzed by FT-IR. The specific experimental treatment process is shown in Fig. 1.

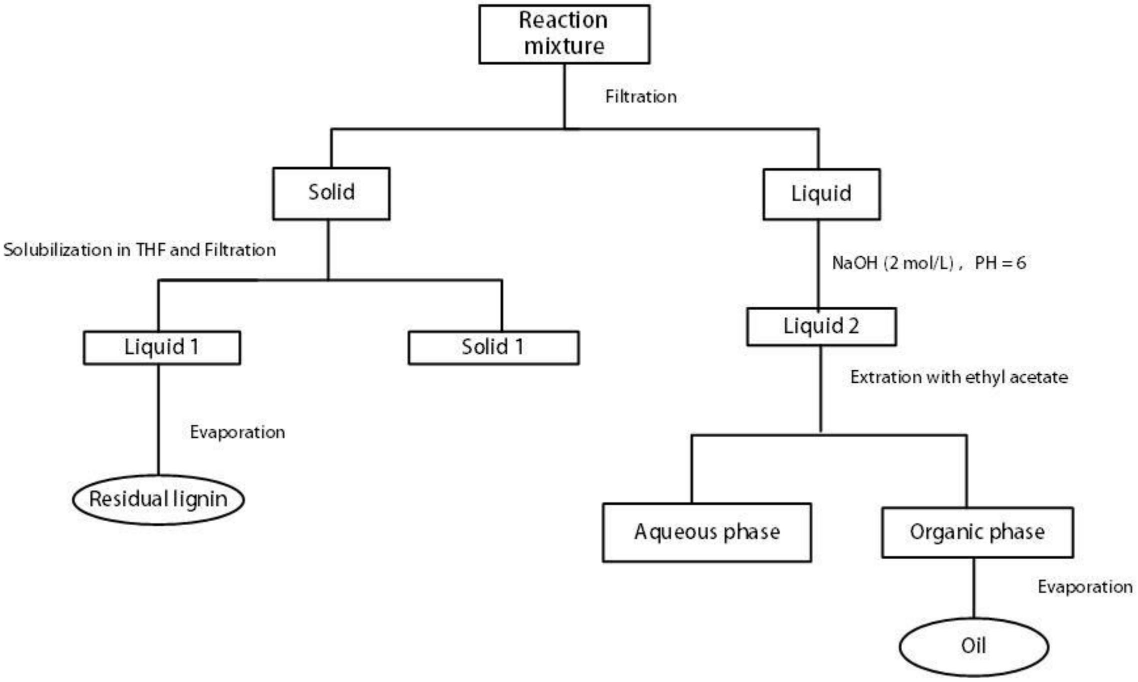


Fig. 1. Schematic process of lignin depolymerization and separation of the reaction products

The selectivity of monophenolic compounds (Y_{MC})

The method for calculating the selectivity of monophenolic compounds is as follows, with Eqs. 1 and 2,

$$W_O = W_L - W_R \quad (1)$$

$$Y_{MC} = \sum W_P / W_O \quad (2)$$

where W_O is the mass of the bio-oil (g), W_L is the mass of lignin (g), W_R is the mass of residual lignin (g), Y_{MC} is the selectivity of monophenolic compounds (%), and $\sum W_p$ is the weight (g) of the sum of identified monophenolic compounds *via* GC-MS.

Analysis method of bio-oil

The oil samples obtained in Fig. 1 were first dissolved in methyl alcohol for detection. In this experiment, the authors used a gas chromatograph-mass spectrometer (GC-MS). The GC-MS analysis was performed using a GC-7890B, MS-7000D from Agilent Technologies (Santa Clara, CA, USA) equipped with a thermal conductivity detector (TCD) and an Agilent capillary column (HP-PONA, 50 m × 200 μm × 0.5 μm). The column temperature program started at 50 °C for 2 min and then was raised to 120 °C at a rate of 10 °C/min (held for 5 min at this temperature), increased to 280 °C at a rate of 10 °C/min (held for 8 min at this temperature), and then increased to 300 °C at a rate of 10 °C/min (held for 10 min at this temperature). The injection sample volume was 2 μL, with a split ratio of 50:1. The ion source temperature was 230 °C for the mass selective detector. Helium was employed 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 NIST14 data library. The relative content of each compound in the products was determined by semi-quantitative methods according to the chromatographic percentage.

Analysis method of lignin structure

For residual lignin, FT-IR spectroscopy (Nicolet iS5, Thermo Fisher, Waltham, MA, USA) was used to characterize the functional groups of the raw material and depolymerization products. The samples were ground and mixed with KBr and the spectra were scanned in the range of 4000 cm^{-1} to 700 cm^{-1} with 32 scans at a 4-cm^{-1} spectral resolution per sample. Each sample was scanned three times to eliminate operation error.

Analytical method for the molecular weight of residual lignin

The changes in the molecular weight of residual lignin were studied by GPC (Mono GPC-100, 7.8 mm × 300 mm, Sepax Technologies, Suzhou, China). The HPLC can detect changes in compounds' composition in a rapid, efficient, and simple way. Therefore, in addition to identification by GC-MS, the authors also conducted a HPLC analysis for quantitative analysis of the compounds. All of the samples were first dissolved in tetrahydrofuran (THF) for analysis. Then, they were filtered by a 0.45-μm membrane with a syringe filter.

The gel permeation chromatography-high-performance liquid chromatography (GPC-HPLC) instrument (G1312B binary pump; Agilent Technologies, Santa Clara, USA; UV detector at 254 nm; GPC column at a column temperature of 30 °C) was used to determine the molecular weight of the product. The mobile phase was THF at a flow rate of 0.5 mL/min. A polystyrene standard calibration curve was adopted to calibrate the number average molecular weight (M_n) and weight average molecular weight (M_w) of the samples. The authors applied this method to estimate the degree of lignin depolymerization as well.

RESULTS AND DISCUSSION

Yield of Depolymerization Products Bio-oil

Wan *et al*. (2009) found that $MgCl_2$ could increase the bio-oil yield by either suppressing charcoal yield or gas yield or both during microwave-assisted pyrolysis of corn stover and aspen wood. Its catalysts may function as a microwave absorbent to speed up heating. Toledano *et al*. (2016) adopted base catalysts to depolymerize organosolv lignin of olive tree pruning in a batch reactor and found that the yield of oil reached 20% at 300 °C for 40 min. Liu *et al*. (2017) investigated lignin degradation in isopropanol under mild microwave-assisted heating, showing that the highest yield of liquid product obtained was 45.4% using a temperature of 120 °C with a reaction time of 30 min, together with a char yield of 38.6% and 14.7% residual lignin. Also, Wang *et al*. (2017) studied microwave-assisted depolymerization of black-liquor lignin in formic acid, concentrating on the yield of liquid fractions as bio-oil 1 (mainly aromatic monomers) and bio-oil 2 (mainly aromatic oligomers) and the distribution of the specific compositions. Bio-oil 1 (9.69%) and bio-oil 2 (54.39%) achieved their maximum yields under 160 °C with the reaction time of 30 min.

According to Table 1, it was apparent that the metal chloride improved the yield of bio-oil compared with no catalyst. Among all the catalysts, $MnCl_2$ showed the best catalytic effect. Compared with the results by Wang *et al*. (2017), the yield of oil improved. Moreover, it was found that the yield of oil catalyzed by $ZnCl_2$ and $MnCl_2$ reached more than 70%.

Table 1. Yield of Bio-oil (W_o)

	No Catalyst	$MgCl_2$	$AlCl_3$	$FeCl_3$	$ZnCl_2$	$MnCl_2$
W_L(g)	1	1	1	1	1	1
W_R(g)	0.3847	0.3296	0.6677	0.6719	0.7101	0.7365
W_O(g)	0.6153	0.6704	0.6677	0.6719	0.7101	0.7365

Compounds of Depolymerization Products Identified by GC-MS

Lignin depolymerization products are diverse, including mainly guaiacyl (G-type, 2-methoxy-4-propylphenol), syringyl (S-type, 1,3-dimethoxy-2,5-dimethylbenzene), and p-hydroxy phenyl (H-type, 4-propylphenol) species (Grabber *et al.* 1997).

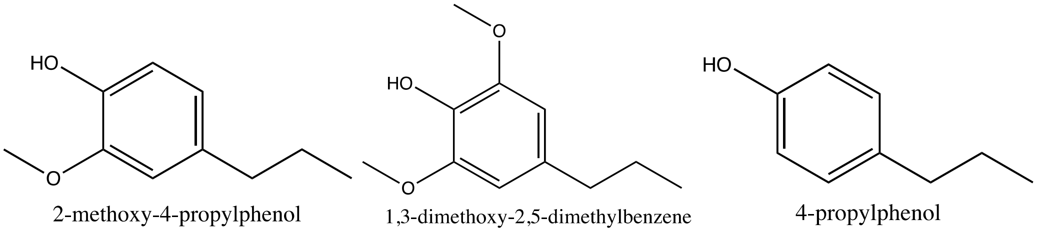


Fig. 2. Three basic phenyl propane structure units of lignin

From Figs. 2 and 3, it was evident that catalysts improved the total yield of monophenols compared to that without catalysts. This may be because metal chlorides used in this catalytic system are hydrolyzed, causing the production of Brønsted acid and the HCl formed *in situ* by the hydrolysis of metal chlorides catalysts (Davoudzadeh *et al.* 1985).

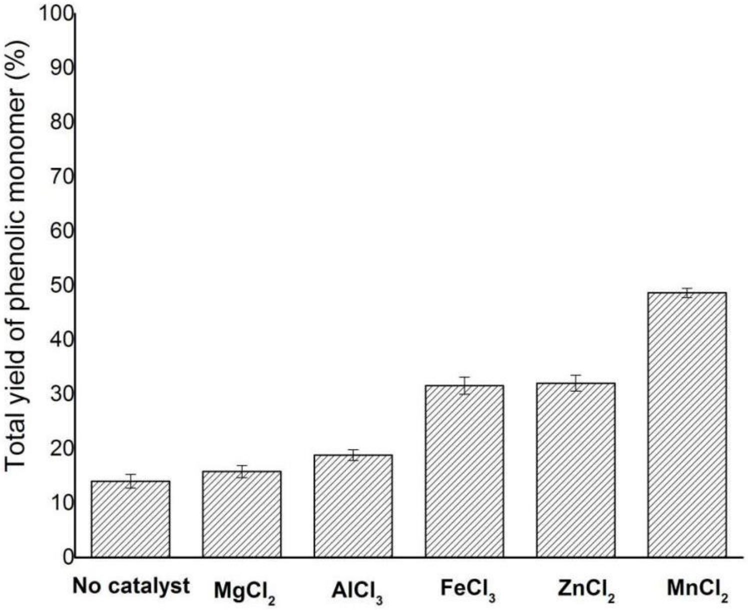


Fig. 3. The percentages of total monomer content of lignin depolymerization generated by different catalysts

Therefore, oxonium salt can be formed when H^+ attacks the etheric O atom, which activates the C-O bond, favoring the cleavage of the β-O-4 bond (Zhang *et al.* 2014). For example, $ZnCl_2$, during the cleavage of β-O-4, Zn^{2+} coordinated with the O atom positioned in the β-O-4, which could have weakened the bond of C_α- C_β. The weakened C_α- C_β bond was then cleaved, resulting in the formation of vanillin (Fig. 4) (Lim *et al.* 2013).

The total amount of the phenolic monomer gradually increased in the following order: No catalyst < $MgCl_2$ < $AlCl_3$ < $FeCl_3$ < $ZnCl_2$ < $MnCl_2$. Among all of the catalysts, $MnCl_2$ showed the highest catalytic effect, with the highest total yield of mono-phenols. With $MgCl_2$, the lignin produced the least mono-phenol compounds. For $MgCl_2$ and $AlCl_3$, this may have been caused by the effect of Lewis acid. A stronger acidity of the metal chloride resulted in a potentially stronger catalytic effect. However, this trend may not be suitable for $FeCl_3$, $ZnCl_2$, and $MnCl_2$. It is known that magnesium is an alkali-earth metal, but zinc, iron, and manganese are transitional metals. This different characteristic also causes them to produce different effects on the reaction mixture, thus producing different products. According to Xianwu *et al.* (2007), the catalytic mechanism of alkali/alkaline earth metal chlorides is distinct from that of transition metal chlorides. All transition metal chlorides had stronger catalytic effects than alkaline earth metal chlorides in this experiment. As opposed to alkaline earth metal chlorides, the accurate catalytic mechanism of transition metal chlorides has not been reported. One possible explanation is that transition metal chlorides always have a larger cation radius, which may influence their catalytic effect (Zhdanov and Brown 1965). These results were also in agreement with the study of Shu *et al.* (2015). For transition metal chlorides, a larger cation radius resulted in a stronger catalytic effect.

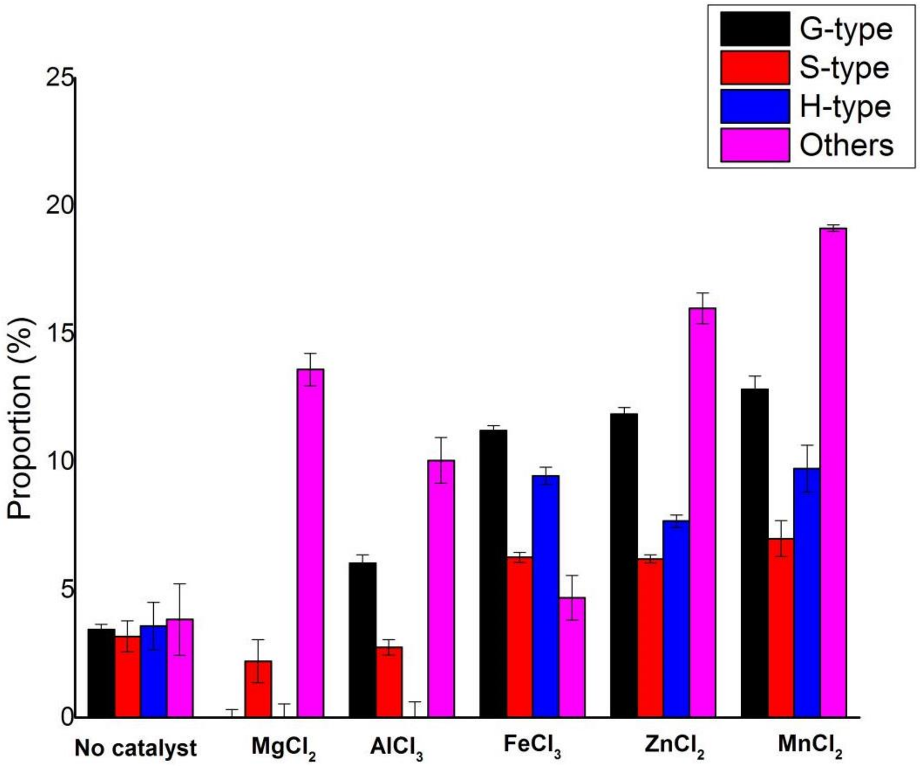
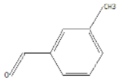
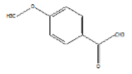
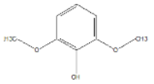
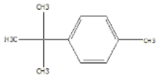
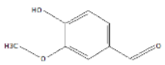
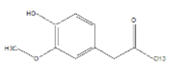
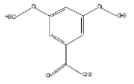
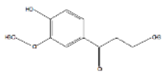


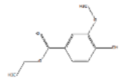
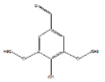
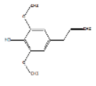
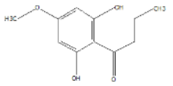
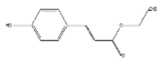
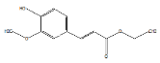
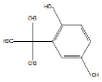
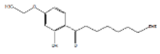
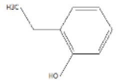
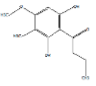
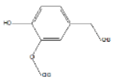
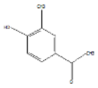
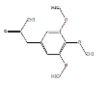
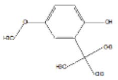
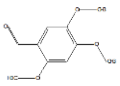
Fig. 4. The proportion of different types of phenolic monomer in all monomers of the lignin depolymerization products

Specific types of phenolic monomers are shown in Fig. 4. In the presence of no catalyst, the yield of each species of monomers was similar. However, in the presence of catalyst, the production of each monomer was different, which fully reflects the different effects of each catalyst.

It was shown that transition metal chlorides $MnCl_2$, $ZnCl_2$, and $FeCl_3$ catalyzed the depolymerization of lignin to produce a variety of products. However, alkaline earth metal chlorides $MgCl_2$ and $AlCl_3$ were more effective at producing certain products. Both $MgCl_2$ and $AlCl_3$ had a weak effect on producing H-type phenolic compounds. It was also noteworthy that when $MgCl_2$ was used as a catalyst, G-type monomer compounds were hardly produced either. This may be because under low temperatures, the depolymerization of lignin is considerable through the cleavage of inter-unit linkages (such as α-O-4 and β-O-4 bonds) on account of their relatively low bond dissociation energy (Hu *et al.* 2013), and the cleavage of bond that helps to produce H-type compounds requires more energy. Compared with $MnCl_2$ or $ZnCl_2$, the existence of $FeCl_3$ produced a lower proportion of other species of monophenols. This indicated that $FeCl_3$ was more effective at producing G-type, H-type, and S-type monomer compounds.

Table 2. Main Monomers in the Products of Lignin Depolymerization Under the Catalysis of Different Catalysts

No.	Compound	Structure	No Catalyst	$MgCl_2$	$AlCl_3$	$FeCl_3$	$ZnCl_2$	$MnCl_2$
1	Benzaldehyde, 3-methyl-		5.40%	—	—	—	—	2.21%
2	4-Acetylanisole		0.46%	—	—	—	—	—
3	Phenol, 2,6-dimethoxy-		3.47%	4.91%	3.94%	1.95%	6.16%	1.91%
4	Phenol, 4-(1,1-dimethylethyl)-		1.02%	—	—	—	—	—
5	Vanillin		1.41%	—	—	1.13%	1.73%	2.78%
6	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-		0.57%	—	—	—	4.35%	2.31%
7	3',5'-Dimethoxyacetophenone		1.86%	—	—	—	—	—
8	Butyrovanillone		1.69%	—	—	4.40%	4.90%	3.76%

9	Benzoic acid, 4-hydroxy-3-methoxy-, ethyl ester		1.30%	—	—	—	3.32%	2.16%
10	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-		4.64%	—	—	3.73%	5.84%	6.87%
11	Phenol, 2,6-dimethoxy-4-(2-propenyl)-		1.32%	—	—	—	—	1.62%
12	Desaspidinol		3.68%	10.33%	9.64%	—	22.96%	10.98%
13	p-Hydroxycinnamic acid, ethyl ester		9.64%	—	—	8.57%	14.86%	14.46%
14	Ethyl (2E)-3-(4-hydroxy-3-methoxyphenyl)-2-propenoate		5.28%	—	8.68%	4.66%	8.66%	7.74%
15	t-Butylhydroquinone		—	—	2.55%	—	1.47%	2.20%
16	4'-Ethoxy-2'-hydroxyoctanophenone		—	—	2.28%	—	—	—
17	Phenol, 2-ethyl-		—	—	—	1.10%	1.86%	1.03%
18	Aspidinol		—	—	—	3.15%	—	—
19	Phenol, 4-ethyl-2-methoxy-		—	—	—	—	—	0.31%
20	4-Hydroxy-3-methylacetophenone		—	—	—	—	—	0.79%
21	3,4,5-trimethoxyphenyl-2-propanone		—	20.02%	—	—	—	—
22	3-tert-Butyl-4-hydroxyanisole		—	—	—	—	—	1.09%
23	Benzaldehyde, 2,4,5-trimethoxy-		—	—	—	—	—	5.90%

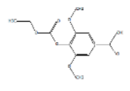
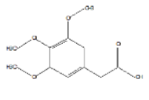
24	4-Ethoxycarbonyloxy-3,5-dimethoxybenzoic acid		—	—	—	—	4.68%	—
25	3,4,5-Trimethoxyphenylacetic acid		—	—	—	—	—	4.22%

Table 2 shows the different monomers in the products of lignin depolymerization. As shown, some of the products yielded only with the presence of a specific catalyst. For example, vanillin (4-hydroxy-3-methoxybenzaldehyde), as the major flavor constituent of vanilla, has a wide range of applications in the food industry and in perfumery (Araújo *et al*. 2010). Vanillin is also very useful in the synthesis of several pharmaceutical chemicals (Bjoersvik and Liguori 2002). Vanillin almost did not appear with $MgCl_2$ or $AlCl_3$, but it reached the highest yield when there was 2.78% $MnCl_2$ present. Vanillin production could be associated with the release of guaiacyl intermediates (Guerra *et al*. 2006). The important precursor to producing vanillin is 4-(1,3-dihydroxypropyl)-2-methoxyphenol through H abstraction. This is a result of β-O-4cleavage (Lin *et al.* 1997). The authors speculate that transition metal chlorides are more likely to induce the precursor to producing vanillin.

Aspidinol [1-(2,6-dihydroxy-4-methoxy-3-methylphenyl)butan-1-one], which is a compound comprising a C_4 chain, is considered to be among the intermediates leading to the production of phthalates (Pineda *et al*. 2011). It only appeared in the presence of $FeCl_3$. In contrast, desaspidinol (Thring and Breau 1996) appeared when lignin was catalyzed by catalysts other than $FeCl_3$. The difference between aspidinol and desaspidinol is that the former has one more methyl group than the latter, which demonstrates that the catalyst $FeCl_3$ helps to maintain the presence of methyl.

According to the study made by Shu *et al.* (2018), a metal chloride catalyst such as $ZnCl_2$ could promote the occurrence of etherification remarkably. The Lewis acid sites in metalchloride were also conducive to reduce the dissociation energy of β-O-4 bond. Transition metal chlorides catalysts such as $CrCl_3$ could interact with the oxygen electron pair and promote the cleavage of the methoxyl group, which resulted in the rapid conversion of guaiacols to phenols. The occurrence of alkylation was also promoted, which improved the stability of the products. High reaction temperature and long reaction time both could promote the occurrence of demethoxylation and alkylation, producing a lot of alkylphenols.

FT-IR Spectra of the Original and Regenerated Lignin

The FT-IR spectra of liquid products were recorded in the range of 4000 cm^{-1} to 700 cm^{-1}, and the results are shown in Fig. 5.

The main peaks of the chemical functional groups present in lignin before and after depolymerization were found at 3430 cm^{-1}, 2985 cm^{-1}, 2829 cm^{-1}, 1610 cm^{-1}, 1514 cm^{-1}, 1491 cm^{-1}, 1369 cm^{-1}, 1261 cm^{-1}, 1216 cm^{-1}, 1172 cm^{-1}, 1117 cm^{-1}, 1008 cm^{-1}, 832 cm^{-1}, 798 cm^{-1}, and 773 cm^{-1}. The infrared spectra of lignin before and after depolymerization were different, which demonstrated that the lignin components changed during the depolymerization process. The infrared spectra of lignin with or without catalysts were different, which meant that the catalyst played an important role in lignin depolymerization. The infrared spectra of lignin with different catalysts were various, which indicated that different catalysts or, precisely, different metal cations played different catalytic roles in lignin depolymerization.

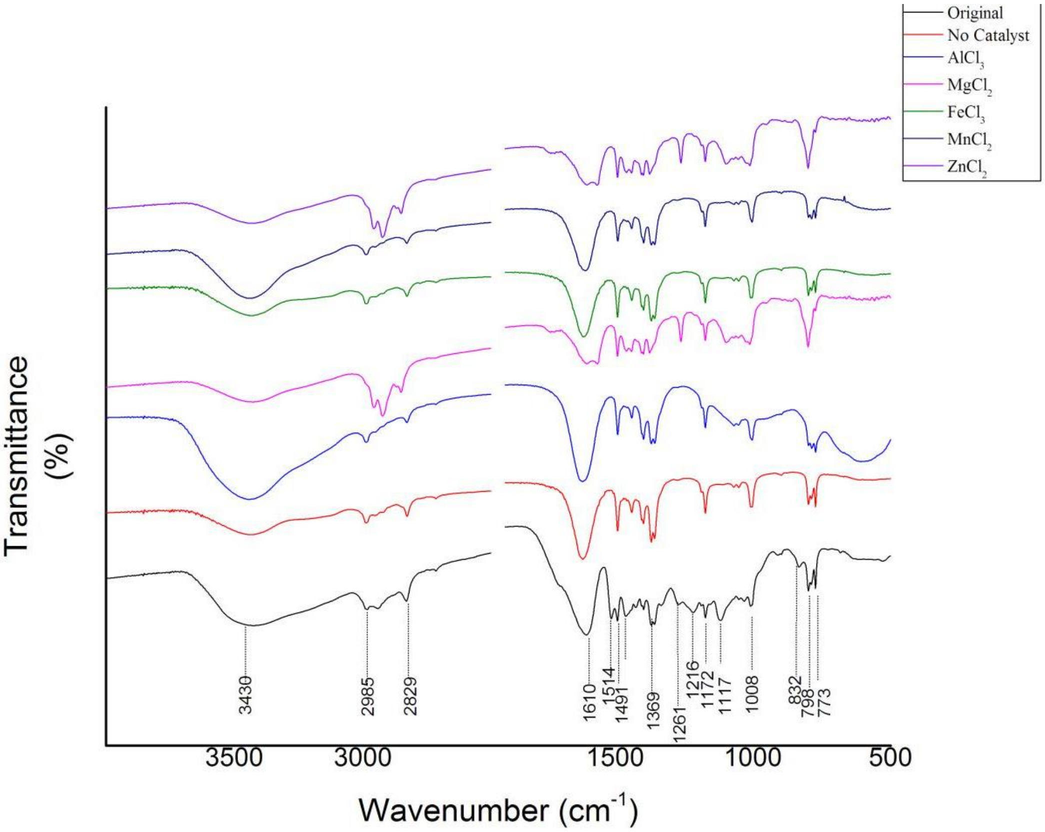


Fig. 5. FT-IR spectra of the lignin before and after depolymerization with various metal chloride catalysts

Among these peaks, the broad peak at approximately 3430 cm^{-1} was related to the –OH stretching absorption of the aliphatic hydroxyl and phenolic hydroxyl groups. Figure 5 shows that in addition to being catalyzed by $AlCl_3$ or $MnCl_2$, the hydroxyl content of lignin depolymerization products was reduced. Combined with GC-MS, the authors inferred that lignin depolymerization catalyzed by $AlCl_3$ and $MnCl_2$ may have produced more products that contained phenolic hydroxyl groups.

The wavenumbers at approximately 2985 cm^{-1} and 2829 cm^{-1}, assigned to the C-H vibration in methyl, were weaker in the lignin depolymerization products compared with the raw lignin. Therefore, a decrease in the methyl groups was indicated. It is worth mentioning that when $MnCl_2$ or $ZnCl_2$ was present, the C-H group may have had a certain displacement and both 2985 cm^{-1} peaks and 2829 cm^{-1} peaks shifted to the middle. This may have been caused by changes in the C-H group during the process of depolymerization, such as hydrogenation or hydrogen reduction.

There are four main vibrations of C=C double bonds in mononuclear aromatic hydrocarbons, which appear in the range of 1620 cm^{-1} to 1450 cm^{-1} (Xie *et al.* 2015). As shown in Fig. 5, the peaks appeared around 1610 cm^{-1} and 1491 cm^{-1}, regardless of which catalyst was used. However, the peaks at 1514 cm^{-1} disappeared in the catalytic products after depolymerization. This may have been caused by a series of substitutions of the groups on the aromatic ring during depolymerization. Additionally, the absorption peak at 1514 cm^{-1} was weakened after depolymerization, which may indicate that the aromatic rings were partially opened.

In addition, the peaks near 1032 cm^{-1}, which are associated with the stretching vibration of the C–O single bond in the esters, aldehydes, and ketones, disappeared in all the depolymerization products. It was speculated that esters, aldehydes, and ketones decreased in all products.

GPC-HPLC Analysis of Residual Lignin Degradation Products

Table 2 shows that the M_w and M_n of processed lignin decreased compared with the original lignin. This meant that through the reaction with the catalysts, lignin was degraded into smaller molecules. It was evident that the M_w or M_n of lignin depolymerization products with different catalysts had nothing in common. This also demonstrated that the effect of each metal cation on lignin depolymerization was distinct.

For the M_w of lignin depolymerization products, the number ranged from 1389 (when it was catalyzed by $FeCl_3$) to 1270 (when it was catalyzed by $AlCl_3$). This data roughly reflected the average molecular weight of depolymerization products. It was concluded that $AlCl_3$ showed favorable catalytic activity in the experiment. As for M_n, the number ranged from 822 (when it was catalyzed by $MgCl_2$) to 610 (when it was catalyzed by $MnCl_2$). This may have been because depolymerization products include more high molecular weight products in the presence of $MgCl_2$. However, when $MnCl_2$ was used as a catalyst, lignin depolymerization products included more low molecular weight molecules. In the authors' statistical data, M_w/M_n was used to measure the range of molecular weight. Table 3 shows that the molecular weight distribution of depolymerization products was the most extensive when $AlCl_3$ was used to catalyze depolymerization.

Table 3. Weight-average Molecular Mass (M_w), Number-average Molecular Mass (M_n), and Distributions (M_w/M_n) of Depolymerization Products

Name	M_w	M_n	M_w/M_n
Raw lignin	1597	1461	1.0930
No catalyst	1332	672	1.9821
$MgCl_2$	1311	822	1.5949
$FeCl_3$	1389	788	1.7627
$ZnCl_2$	1289	757	1.7028
$MnCl_2$	1307	610	2.1426

CONCLUSIONS

1. The Formic acid and Lewis acid system effectively catalyzed the depolymerization of lignin. In this experiment, the total amount of the phenolic monomer catalyzed by different metal chlorides gradually increased in the following order: No catalyst < $MgCl_2$ < $AlCl_3$ < $FeCl_3$ < $ZnCl_2$ < $MnCl_2$. The $MnCl_2$ had the best catalytic effect. The highest total monomer yield was 48.7%, including approximately 23.0% G-type, 11.9% S-type, and 14.8% H-type monomer compounds.
2. Different catalysts had different effects on the depolymerization of lignin, which were embodied not only in the type but also in content of the products. Transition metal chlorides $MnCl_2$, $ZnCl_2$, and $FeCl_3$ catalyzed the depolymerization of lignin to produce

a variety of products. However, alkaline earth metal chlorides, $MgCl_2$ and $AlCl_3$, were more effective at producing certain products.

3. Under the conditions of this experiment, lignin produced the most vanillin (2.78%) in $MnCl_2$ depolymerization.

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APPENDIX

Table A1. List of Reactants

No.	Lignin (g)	Ethanol (mL)	HCl (mL)	HCOOH (mL)	$AlCl_3$ (mol)	$FeCl_3$ (mol)	$MnCl_2$ (mol)	$ZnCl_2$ (mol)	$MgCl_2$ (mol)
1	1	20	10	10					
2	1	20	10	10	0.005				
3	1	20	10	10		0.005			
4	1	20	10	10			0.005		
5	1	20	10	10				0.005	
6	1	20	10	10					0.005