Catalytic Effects of Various Acids on Microwave-assisted Depolymerization of Organosolv Lignin

Maimaitiaili Tayier,[a,b] Dengle Duan,[a,b] Yunfeng Zhao,[a,b] Rongsheng Ruan,[a,b,c] Yunpu Wang,[a,b,*] and Yuhuan Liu [a,b,*]

The catalytic effects of various acids (sulfuric acid, hydrochloric acid, phosphoric acid, and formic acid) on the depolymerization of organosolv lignin under mild microwave heating (approximately 100 W, 160 °C for 30 min) were investigated. The liquid product was separated from the solid residue and analyzed by gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR). The solid residue was analyzed with thermogravimetric analysis (TG-DTG) and observed by scanning electron microscopy (SEM). The experimental results showed that sulfuric acid exhibited a better catalytic effect than the other acids. The SEM and TG-DTG results showed that the solid residue from sulfuric acid-catalyzed depolymerization was not only remarkably smaller than that of the other groups, but also presented a faster thermal decomposition rate. The molecular weight (M_w, weight-average) of the liquid product (M_w = 1020) from sulfuric acid-catalyzed depolymerization was also lower than that of the other groups.

INTRODUCTION

Exploiting new energy sources and replacing depleted fossil fuels are currently some of the most concerning global issues. Lignocellulosic biomass (made up of cellulose, hemicellulose, and lignin) has been considered an alternative organic renewable resource for the production of biofuels and aromatic chemicals (Li *et al*. 2015). Lignin, a common primary ingredient in biomass, is a polymer consisting of three types of 4-propenyl-phenols units (p-hydroxyl-phenyl propanol, guaiacyl-propanol, and syringyl-propanol) interlinked *via* C-C bonds (5-5, β-β, β-5, and β-1 linkages) and C-O-C bonds (α-O-4, 5-O-4, and β-O-4) (Calvo-Flores and Dobado 2010). Based on its unique chemical structure, a wide variety of high value products, particularly aromatics, have the potential to be obtained from lignin. However, its complex three-dimensional (3D) structure and intensive hydrogen bonds also limit the direct use of lignin (Kubo and Kadla 2005).

Therefore, it is essential to develop a new, efficient, and green process for converting lignin into fuels and value-added chemicals. Over the past few decades, a wide variety of conversion methods have been explored, including hydrolysis (Mahmood *et al*. 2015), pyrolysis (Fan *et al*. 2017), liquefaction (Lin *et al*. 2001; Wang *et al*. 2017), gasification (Madenoğlu *et al*. 2016), biodegradation (Bugg *et al*. 2011), hydrogenolysis

(Ye *et al*. 2012), *etc*. Even though scientists have been making considerable progress, more extensive and comprehensive exploration is needed to convert lignin into desirable products.

Recently, microwave-assisted lignin depolymerization under mild reaction conditions has attracted more attention, due to its fast heating rate and high heating efficiency (Wang *et al*. 2016; Liu *et al*. 2017). Microwave technology can be used to directly heat internal molecules using an electromagnetic field, improving the depolymerization reaction rate and the desired product selectivity (Xiao *et al*. 2011; Zhu *et al*. 2016, 2017). Dong *et al*. (2014) studied microwave-assisted degradation of black-liquor lignin with formic acid, presenting that the liquid product consisted of bio-oil 1 (phenolic monomeric compounds) and bio-oil 2 (oligomers), 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). Shen *et al*. (2015) studied lignin solvolysis in formic acid under microwave heating with solid acid catalyst HUSY modified by oxalic acid as the catalysts, presenting that the highest yield of liquid product achieved was 88.3 wt.% (the aromatic monomer fraction as bio-oil 1 was 15.4% and the oligomer fraction as bio-oil 2 was 67.5%) with the addition of HUSY modified by 0.2 M oxalic acid (HUSY-0.2 M). 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.

Besides, recently scientists have focused on mechanistic investigation of acid-catalyzed cleavage of major bonds of the lignin, such as the β-O-4 and α-O-4 bonds, using lignin model compounds. Sturgeon *et al*. (2014) explored the mechanisms of acid cleavage of aryl-ether linkages using four lignin model compounds that exhibit the β-O-4 linkage with or without a neighboring phenolic hydroxyl group in the presence of aqueous H_2SO_4 at 150 °C, showing that the presence of a phenolic hydroxyl group dramatically increases the rate of acid-catalyzed β-O-4 bond cleavage and that the presence of a methoxy group on the phenyl ring alters the product distribution. However, there has not been a more comprehensive and comparative study of catalytic effects of three common inorganic acid and organic acid (formic acid) on lignin degradation under low power microwave heating.

Duan *et al*. (2017) studied low-power microwave-assisted depolymerization of organosolv lignin using ethanol/formic acid mixtures, showing that the total amount of phenolic compounds dramatically increased from 8.1% to 40.8% with a temperature increase from 100 °C to 200 °C. Based on this previous study, the objective of this paper is to explore the individual catalytic effects of three common inorganic acids (sulfuric acid, hydrochloric acid, and phosphoric acid) and formic acid on lignin degradation under low-power (below 80 W) microwave heating. The significance of this work is that it provides a theoretical basis for studying the mechanism of microwave-assisted acid-catalyzed lignin depolymerization. This study was conducted using a green, environmentally friendly, non-polluting chemical reaction system, with a microwave temperature and reaction time of 160 °C and 30 min, respectively. The resulting products were separated into liquid product and solid residue and analyzed using various techniques [high-performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and thermogravimetric analysis (TG-DTG)]. In the end, the catalytic effects of these acids were discussed.

EXPERIMENTAL

Materials

The raw materials used were bamboo culms that were obtained from Nanchang, Jiangxi Province, China. Ethanol organosolv lignin from bamboo was extracted in a laboratory based on the method presented in Fan *et al.* (2015). The extraction process for organosolv lignin in bamboo was mentioned in Deng *et al.* (2017). Elemental analysis (Vario EL III, Elementar, Germany) showed that the lignin was composed of 60.1% C, 5.9% H, 32.8% O, 0.5% N, and 0.3% ash. Ethanol (analytical grade) was purchased from Xi Long Scientific Co. (Guangdong, China), sulfuric acid, hydrochloric acid, phosphoric acid, and formic acid (analytical grade) were purchased from Da Mao Reagent Co. (Tianjin, China), and tetrahydrofuran (THF, HPLC grade) was purchased from Solario (Beijing, China).

Methods

Microwave depolymerization and products separation

The catalytic depolymerization of lignin was performed in a microwave reaction system (CEM Corporation, Matthews, NC, USA). The experimental process is illustrated in Fig. 1, and the experimental runs are listed in Table 1.

Table 1. List of Experimental Runs

Experiment Number	H_2SO_4 (mL)	HCl (mL)	H_3PO_4 (mL)	HCOOH (mL)	CH_3CH_2OH (mL)
1	0.3	-	-	-	11.7
2	-	0.3	-	-	11.7
3	-	-	0.3	-	11.7
4	-	-	-	0.3	11.7
5	-	-	-	-	12

First, 0.5 g of organosolv lignin were mixed with 11.7 mL of ethanol in a reactor, and then various acids (0.3 mL accounting for 2.5% of the total volume) were added. The concentrations of sulfuric acid (H_2SO_4), hydrochloric acid (HCL), phosphoric acid (H_3PO_4), and formic acid (HCOOH) were 3 mol/L, 6 mol/L, 2 mol/L, and 6 mol/L, respectively. Next, the mixture was placed in the microwave digestion instrument (CEM Corporation, Matthews, NC, USA) and stirred with a magnetic rotor for 2 min. The microwave reactor reaction temperature and reaction time were set at 160 °C and 30 min, respectively, and the microwave power was below 80 W. The temperature was raised to the designated temperature (160 °C) at a constant rate using a high power (80 W, approximately 2 min) setting. The temperature in the microwave reactor system was read through infrared sensing and maintained at the target value (160 °C) by an automatic power adjustment. After the reaction, the samples were cooled to room temperature, and then the liquid-solid mixture was filtered. The wet solid fraction was washed three times with ethanol. It was then dried at 100 °C in a vacuum environment until it had a constant weight. The filtrate was collected together with the ethanol, which was used for the solid fraction washing.

Afterwards, by adding 255 mL of water into the filtrate, the target compounds were precipitated from the aqueous solution. After centrifugation (5000 r/min) for 10 min and

dried at 30 °C in a vacuum environment for 12 h, the final product was obtained. Each experiment was conducted in triplicate and cited as the mean ± standard deviation.
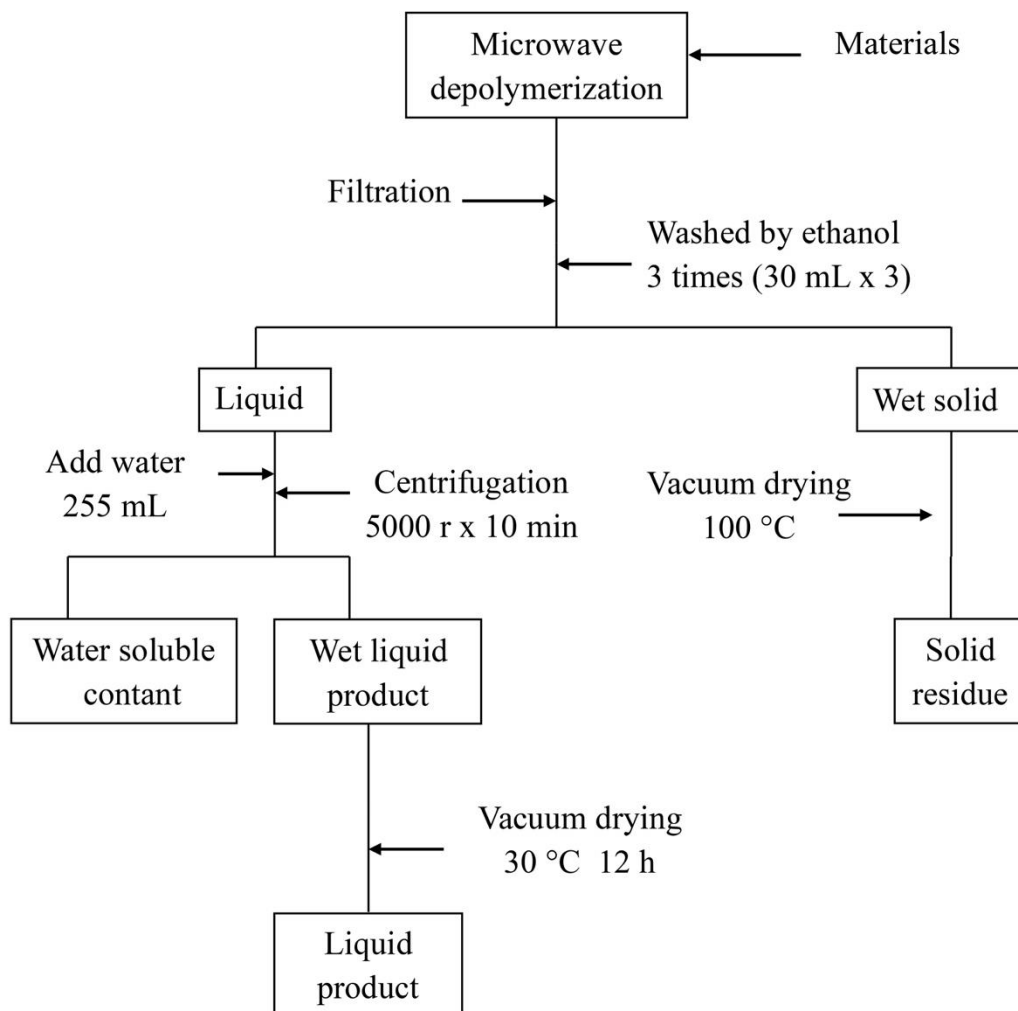

Fig. 1. The experimental process and separation of liquid product and solid residue

Degree of lignin liquefaction (DL, %)

　　　The liquid product was separated from the solid residue. The degree of lignin liquefaction (DL) was calculated by the lignin weight loss ratio (Eq. 1) from Shu *et al*. (2015), representing the yield of liquid product,

$$DL\ (\%) = (W_F - W_R)\ /\ W_F \times 100 \tag{1}$$

where W_F is the weight of lignin (g) and W_R is the weight of the solid residue (g).

Molecular weight determination

　　　The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (M_w/M_n) of the solid residue was determined by gel permeation chromatography analysis (GPC). The GPC analysis was performed using an Agilent G1312B HPLC device (G1312B binary pump; Agilent Technologies, Santa Clara, CA, USA), with the ultraviolet detector set at 280 nm. Next, 1 mg of liquid product was

dissolved in 1 mL of THF, and then the product (10 µL) was filtered through a 0.45-µm syringe filter. After filtration, the product was injected into a system of columns using THF as the eluent at a flow rate of 0.5 mL/min. Finally, polystyrene was used as the standard for calibration.

FT-IR spectroscopy

The FT-IR spectra of liquid products was recorded on a FT-IR spectroscope (NicoletiS5; Thermo Fisher, Waltham, MA, USA) using a KBr disc containing 1% samples. The scan was performed in the range from 4000 cm^{-1} to 400 cm^{-1} with 32 scans.

TG-DTG analysis

The thermogravimetric (TG) and the derivative thermogravimetric (DTG) analyses were run in a thermal analyzer (TGA 4000, PerkinElmer, Waltham, MA, USA). A 5 mg sample was heated from 30°C to 820 °C at a constant heating rate of 10 °C per min, and a high-purity nitrogen gas flow of 100 mL/min was used as the purge gas prior to experiment.

SEM analysis

A JEOL JSM-6701F SEM (JEOL, Tokyo, Japan) instrument was used to examine the morphology of solid residues to compare the effect of different acid treatments. Specimens were prepared for SEM inspection by sticking a sample on carbon glue and allowing it to be gold-plated with a JEOL JEC-560 instrument (JEOL, Tokyo City, Japan).

RESULTS AND DISCUSSION

Degree of Lignin Liquefaction

As shown in Fig. 2, the addition of acid clearly increased the DL. Acidic conditions contributed to the breakage of the ether bonds in the lignin molecules (Zakzeski and Weckhuysen 2011), such as β-O-4 and 4-O-5; therefore, higher liquefaction degrees were obtained in comparison with the non-acid-catalyzed reaction (bar 5 in Fig. 2).
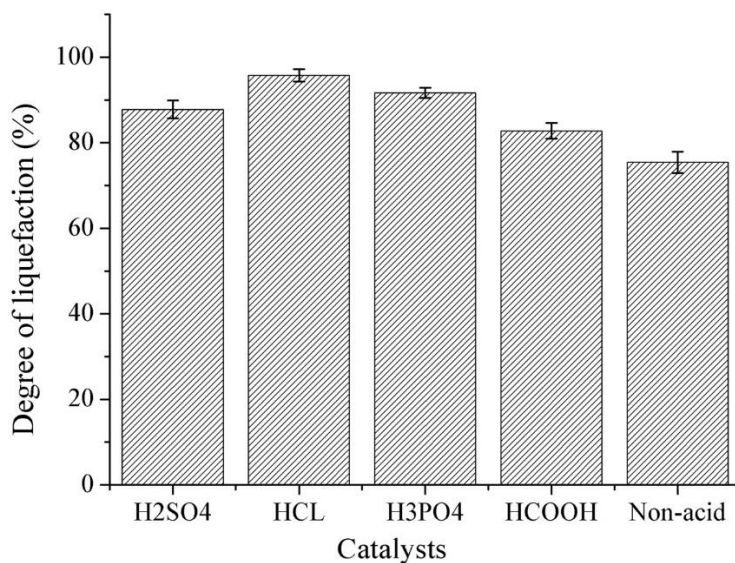

Fig. 2. Effect of various acids on DL

However, hydrochloric acid (HCl) showed a better catalytic efficiency than other acids on the DL, due to the Cl$^-$ ion playing a critical role in lignin degradation. The intensive hydrogen bond in lignin increases its recalcitrancy, but using an excellent hydrogen-bond acceptor such as Cl-, which has a high electronegativity and can be used extensively in biomass dissolution, greatly improved its conversion and liquefaction (Long *et al*. 2011). Shu *et al*. (2015) reported on the lignin depolymerization of various Lewis acids and mineral acids including HCl and sulfuric acid (H_2SO_4) cooperated with Pd/C, showing that the DL of HCl and H_2SO_4 was up to 90.8% and 88.6%, respectively, at 280 °C for 5 h.

Molecular Weight Determination

The molecular weight of liquid products, including the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (M_w/M_n), were analyzed by GPC and are shown in Table 2. It can be noticed that the M_n and M_w values of the first four groups (from 1 to 4 in Table 2 respectively used H_2SO_4, HCL, H_3PO_4, and COOCH as catalyst) were lower than the M_n and M_w values (1298 and 375, respectively) of the non-acid-catalyzed reaction (5 in Table 2). Moreover, the M_w values (1020) of H_2SO_4-catalyzed reaction (1 in Table 2) were lower than the others. This indicated that all of these acids were conducive to lignin depolymerization in varying degrees and H_2SO_4 exhibited better catalytic performance. The H_2SO_4 also showed better catalytic action in the other reaction systems. Deepa and Dhepe (2014) studied the solid acid-catalyzed depolymerization of lignin into value-added aromatic monomers, and also used H_2SO_4 and HCl under similar reaction conditions for comparison with solid acid. They found that the H_2SO_4-catalyzed reaction showed a higher yield (39%) for THF-soluble products than for the HCl-catalyzed reaction (29%). Sui *et al*. (2012) used H_2SO_4 to hydrolyze bagasse and found that treatment with H_2SO4 allowed for a 21% higher yield of levoglucosenone than the treatment with H_3PO_4. However, it is noteworthy that the value of M_w/M_n for HCl-catalyzed reaction and H_3PO_4-catalyzed reaction were fairly large, which indicated that the depolymerization products consisted of many small molecules of different sizes.

Table 2. Number-average Molecular Weight (M_n), Weight-average Molecular Weight (M_w), and Polydispersity Index (M_w/M_n)

Experiment Number	M_n	M_w	M_w / M_n
1	310	1020	3.29
2	238	1198	5.04
3	166	1173	7.06
4	361	1203	3.33
5	375	1298	3.46

FT-IR Spectroscopy

The FT-IR spectra of liquid products were performed in the range from 4000 cm^{-1} to 700 cm^{-1}, and the results are shown in Fig. 4. Typical bands corresponding to the functional groups are listed in Table 3.

It can be noticed that the FT-IR spectra of the liquid products from HCOOH-catalyzed reaction and non-acid-catalyzed reaction were similar to the spectra of raw lignin, indicating that the addition of FA did not lead to changes of the functional groups and chemical structure of the treated lignin. From the FT-IR spectra and molecular weights, it was observed that FA exhibited a relatively poor catalytic effect compared to other acids.

In general, FA is widely used in lignin depolymerization as a hydrogen donor, due to its prominent function in increasing the degree of liquefaction yields and preventing the repolymerization of reaction intermediates (Zhang *et al*. 2014).
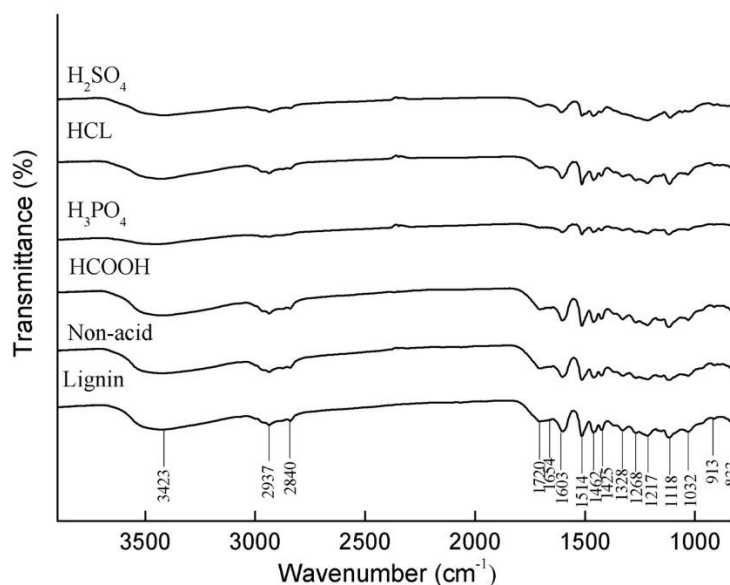

Fig. 3. FT-IR spectra of the lignin before and after depolymerization with various acids

Table 3. Typical Band Assignment of Infrared Absorption of Lignin Samples

Band Wavelength (cm^{-1})	Functional Group
3423	OH stretching
2937, 1462	CH stretching of methyl or methylene group
2840	C-H vibration in methyl
1720	C=O stretching
1654	Carbonyl stretching in lactone
1603, 1514, 1425	Aromatic skeletal vibrations
1492, 1396	C=C stretching vibration in the aromatic acid
1328, 1118	Syringyl units
1268	C-O groups in guaiacol rings
1217	C-O groups in syringol rings
1032	Aromaticin plane bending
913	C-H out-of-plane bending of guaiacyl units
833	C-H out-of-plane bending of syringyl units

Kristianto *et al*. (2017) studied acid hydrolysis lignin depolymerization using formic acid as an *in-situ* hydrogen source and Ru/C as a catalyst in supercritical ethanol (at 350 °C for 60 min, with a FA lignin mass ratio of 3), showing a bio-oil yield of up to 66.3 wt.% with an average molecular weight of 822 g/mol and an aromatic monomer content up to 6.1 wt.%. Huang *et al*. (2014) investigated kraft lignin depolymerization in a solvent combined system, which included water-ethanol and FA, and resulted in a high yield of bio-oil (> 90 wt.%) from kraft lignin without any catalysts. It is noteworthy that FA was sufficient in the above experiments as a hydrogen donor. Therefore, FA has a catalytic capacity that is clearly inferior to the other three inorganic strong acids tested in this study.

After catalysis with H_2SO_4, HCl, and H_3PO_4, the absorption intensities of the initial bands at 3423 cm^{-1} (O-H stretching), 2937 cm^{-1} (C-H stretching), 1720 cm^{-1} (C=O stretching), and 1268 cm^{-1} (C-O stretching) were weakened, indicating that these three inorganic strong acids were able to intrude into the lignin molecule and affect the structure of lignin. Moreover, it can be noticed that the FT-IR spectra of H_3PO_4-catalyzed reaction was different from others, not only in the amount of absorption peaks, which were fewer, but also in that the intensity of these peaks was weaker than those of the other two acids. Major absorption peaks included the peaks at 1603 cm^{-1} and at 1514 cm^{-1}, which are attributed to the aromatic skeletal vibrations.

TG-DTG Analysis

The TG and DTG plots of the resulting solid residues are shown in Figs. 4 and 5. As shown, the thermal decomposition of the solid residues could be divided into three stages according to different temperature ranges.
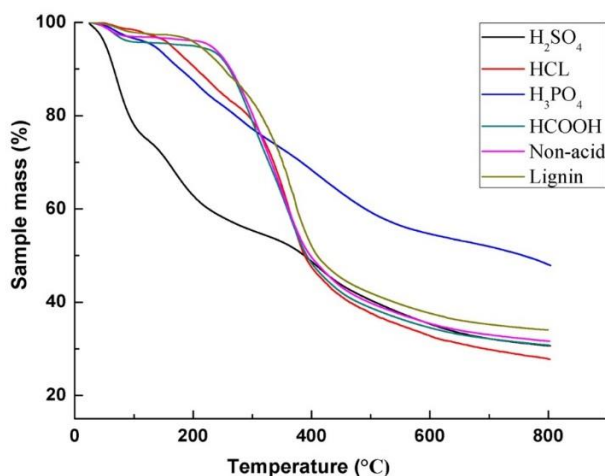

Fig. 4. TG profiles of solid residues from lignin depolymerization with various acids and raw lignin powder
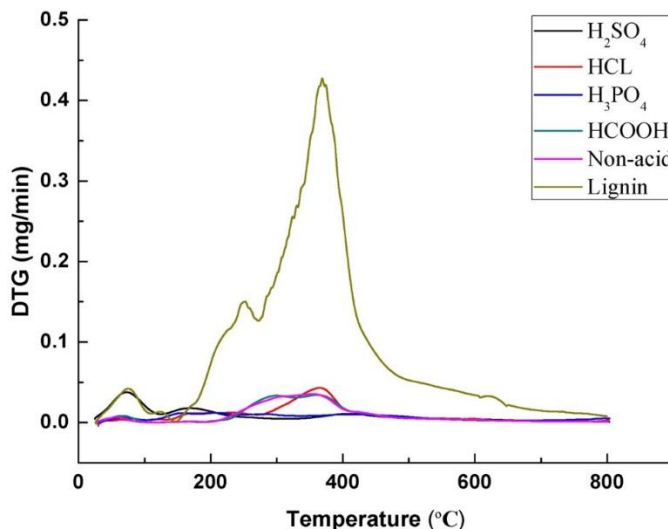

Fig. 5. DTG profiles of solid residues from lignin depolymerization with various acids and raw lignin powder

The main loss of the first stage (from 30 °C to 130 °C) was water- and light-volatile compounds. The second and third stages represented the decomposition processes of high-temperature degradable compounds and high-temperature non-degradable compounds, respectively.
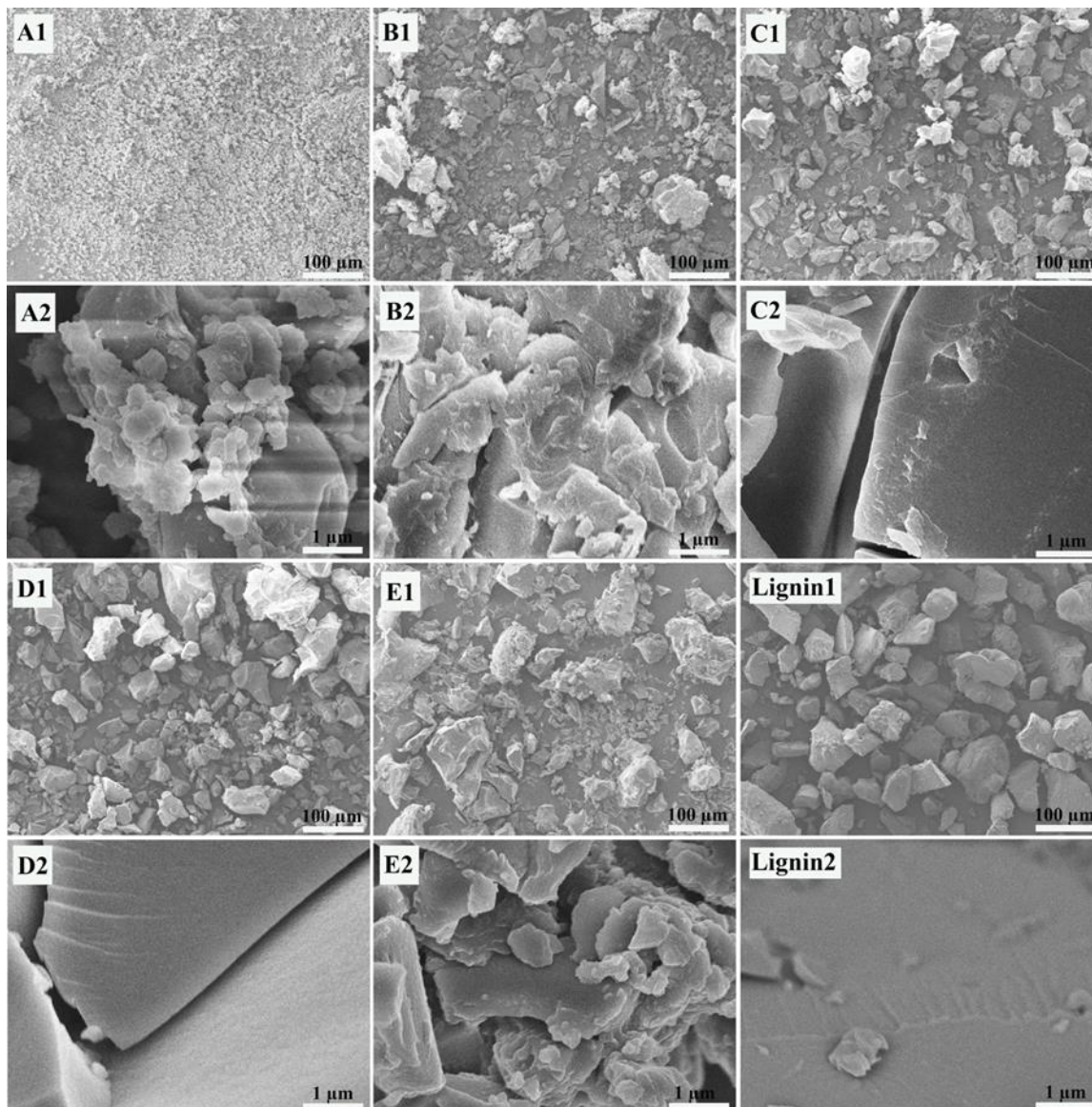

Fig. 6. SEM images of solid residues from lignin depolymerization with various acids and raw lignin powder; Note: A1 and A2, solid residue (200× and 20000×) from H_2SO_4-catalyzed reaction ; B1 and B2, solid residue (200× and 20000×) from HCL-catalyzed reaction; C1 and C2, solid residue (200× and 20000×) from H_3PO_4-catalyzed reaction; D1 and D2, solid residue (200× and 20000×) from HCOOH-catalyzed reaction; E1 and E2, solid residue (200× and 20000×) from non-acid-catalyzed reaction; Lignin1 and Lignin2, raw lignin material (200× and 20000×).

The thermal behaviors of the products from HCOOH-catalyzed reaction, non-acid-catalyzed reaction, and the raw lignin material were similar, and weight loss mainly occurred in the second stage, indicating that the main constituent of these residues was

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high-temperature degradable compounds. However, H_3PO_4-catalyzed reaction exhibited completely different behaviors and decomposed between 100 °C and 500 °C; its Y_{char} (Y_{char} = $TG_{ultimate}$ / raw sample weight) of 47.9% was much bigger than the other samples, indicative of a high content of high-temperature non-degradable compounds. Different from the other samples, H_2SO_4-catalyzed reaction thermally decomposed between 30 °C and 130 °C and presented a faster thermal decomposition rate, which indicated that the decomposition products mainly consisted of water- and light-volatile compounds.

Microstructure Morphology of Residues

The microstructure of the solid residues by different acids for depolymerization were imaged by SEM (Fig. 6). As shown, at the same magnification of 200×, the size and shape of the raw lignin particles were relatively uniform, but after degradation under microwave radiation with different acids, varying degrees of change were observed. Particularly, the residue size treated with microwave depolymerization with H_2SO_4 was considerably smaller compared to the raw lignin particles and other groups that were degraded. It indicated that H_2SO_4 has a stronger catalytic effect on lignin, corresponding to the results of TG-DTG and molecular weight analysis.

However, it can be noticed that only several cracks appeared on the surface of Residue 3 at the same magnification of 20,000×, and these cracks were considerably sharp and rigid. The aforementioned results of TG-DTG analysis also showed that Residue 3 mainly consisted of high-temperature non-degradable compounds, indicating that H_3PO_4 promoted the repolymerization of lignin.

CONCLUSIONS

1. The main functional groups, including -OH, C-H, C=O, and C-O, decreased after catalysis with H_3PO_4, HCl, and H_2SO_4. The addition of various acids increased the DL, but HCl showed better catalytic efficiency than the other acids on the DL, due to the excellent hydrogen-bond acceptor Cl- and its high electronegativity. Additionally, the M_n and M_w values resulting from the addition of various acid types (from 1 to 4 in Table 2) were lower than the M_n and M_w values (1298 and 375) of non-acid-catalyzed reaction. Among them the M_w value (1020) of H_2SO_4-catalyzed reaction was the lowest.

2. The solid residue from H_2SO_4-catalyzed reaction not only thermally decomposed in the first stage of the experimental process from 30 °C to 130 °C, which was due to water- and light-volatile compounds, but also showed the smallest fragments of the other groups. Therefore, H_2SO_4 was judged to show the best catalytic effects on lignin depolymerization. In addition, H_3PO_4 promoted lignin repolymerization.

ACKNOWLEDGMENTS

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