

## Phenolics Production through Catalytic Depolymerization of Alkali Lignin with Metal Chlorides

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Lignin is an important renewable source of phenolic products. In this study, alkali lignin was depolymerized to produce phenolic compounds. The effects of catalyst, solvent, reaction time, and reaction temperature on the yields of liquid products and volatile fractions were investigated in detail. Compared with the solvents water and octane, alcohols can significantly promote depolymerization of lignin due to the excellent solubility of the degradation products and intermediates. Under the conditions of 300 °C for 2 h in the solvent ethanol, the highest yields of liquid products (75.8 wt%) and volatile fraction (38.1 wt%) were obtained over a ZnCl<sub>2</sub> catalyst. Gas chromatograph-mass spectroscopy analysis demonstrated that the volatile fraction was composed of guaiacols (15.09 wt%), phenols (15.79 wt%), and syringols (2.28 wt%). Furthermore, the mechanism for lignin depolymerization is discussed.

*Keywords:* Alkali lignin; Catalytic depolymerization; Metal chlorides; Phenolic compounds

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### INTRODUCTION

Biomass is mainly composed of cellulose, hemicellulose, and lignin. Typically, carbohydrate components can be converted into ethanol fuels (Audu *et al.* 2012; Kang *et al.* 2012), alkane fuels (Fischer *et al.* 2011), and chemical intermediates via diverse processes (Sahu and Dhepe 2012; Zhang and Yu 2013). In these processes, lignin, which ranges between 15 to 30% by mass and approximately 40% by energy in woody biomass, is removed as residue. Moreover, large amounts of lignin and lignin-containing residues are discharged as a by-product of the paper pulp process every year. Lignin is a three-dimensional amorphous polymer consisting of methoxylated phenylpropane structures (Zakzeski *et al.* 2010). Lignin can be used as an alternative raw material for the production of phenolic compounds due to its unique structure and chemical properties. Therefore, in the past, various methods were explored for the production of value chemicals and phenolics.

Pyrolysis is a straightforward approach to breaking down lignin into smaller fragments and obtaining a liquid product (bio-oil) (Ben and Ragauskas 2011; Mukkamala *et al.* 2012; Wang *et al.* 2013). However, poor liquid yields, complex components, and large amounts of solid residues are the main barriers for this technology (Jiang *et al.* 2010). To circumvent the flaws of pyrolysis and obtain value-added phenolic chemicals, various solvents have been used for lignin depolymerization. These include water (Fang *et al.* 2008; Tymchyshyn and Xu 2010), ethanol (Ye *et al.* 2012a), and butanol, phenol, water-alcohol mixtures, water-phenol mixtures, and ionic liquids (Cox and Ekerdt 2012;

Okuda *et al.* 2004; Saitu *et al.* 2003). It has been suggested that alcohols exhibit higher activity in the production of liquid product than water because they are miscible with the depolymerized aromatic compounds and thereby can help prevent recombination. Nevertheless, water-alcohol and water-phenol mixtures show high activity in the production of phenolics.

In addition to the solvent, the catalyst also plays a key role in determining components of phenolics. Xu *et al.* (2012) reported the depolymerization of switchgrass lignin with formic acid over a Pt/C catalyst, in which the largest yield of the identified phenolics was 21% by weight. Similarly, the hydrogenolysis of lignin over a Pt/C catalyst was also carried out by Torr *et al.* (2011). The main monomeric products (total yields of dihydroconiferyl alcohol and 4-n-propyl guaiacol) were produced with maximum yields of 22%. The catalytic degradation of lignin was also explored over sulfide catalysts (Horáček *et al.* 2012), Raney Ni (Wang and Rinaldi 2012), and Ru-based catalysts supported on mesoporous  $\text{SO}_4^{2-}/\text{ZrO}_2/\text{SBA-15}$  (Tang *et al.* 2010). Compared with the approach of thermal pyrolysis, the yields of monomer products are frequently high, and the product mixtures are generally simple.

Recent investigations regarding the degradation of lignin using metal chlorides as catalysts are relatively rare, although the studies were carried out decades ago. This may be attributed to the lower yield of liquid products and the high yield of solid residues. For example, Hepditch and Thring (2000) reported that most of the solvolysis lignin was recovered as solid residues when depolymerization was employed in a batch reactor using the  $\text{NiCl}_2$  and  $\text{FeCl}_3$  as catalysts, and the yields of liquid product only ranged from 5.4 to 17.5% by weight. However, Sugita *et al.* (1988) reported that the liquid product with the highest yields of 24% was obtained from the hydrogenolysis of kraft lignin with the catalyst  $\text{FeCl}_3$  and solvent tetralin at 400 to 420 °C. In the identifiable products obtained from this method, the phenols and cresols accounted for 70 to 80%.

Compared with heterogeneous catalysts, these metal chloride catalysts should in theory allow for better reactivity, affording higher conversion and product yields due to the intimate mixing of reactants and short contact times. Moreover, the metal chlorides can also be recovered and reused (Deng *et al.* 2012). To obtain higher yield of liquid product with high selectivity for phenolic compounds, a number of commercial metal chlorides combined with alcohol solution were used for the depolymerization of lignin in this study. The effects of the reaction temperature, reaction time, types of metal chloride, and types of solvent, as well as the yield of phenolic compounds, their composition, and the depolymerization mechanisms were investigated. Because lignin was effectively depolymerized over metal chlorides in different solvents, the metal chlorides that developed may be useful in the study of depolymerization of other lignin-containing (*e.g.*, black liquor, hydrolytic residues) biomass. In addition, the recovery and reutilization of metal chlorides are other areas for future study.

## EXPERIMENTAL

### Materials

Alkali lignin was purchased from Sigma Aldrich Co. Ltd (St Louis MO, USA). Its proximate analysis and elemental composition were analyzed, and the results are provided in Table 1.

The analytical-grade reagents aluminum chloride ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ), zinc chloride ( $\text{ZnCl}_2$ ), copper chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ), methanol, ethanol, butanol, diphenyl ether, and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) were purchased from Tianjing Kemiou Chemical Reagent Co. Ltd (Tianjing, China). All materials and chemical reagents were used without further purification.

**Table 1.** Ultimate and Proximate Analysis of Lignin (Air Dry Basis)

	Ultimate analysis (wt%)				Proximate analysis (wt%)			
	C	H	N	S	V	FC	M	A
Alkali lignin	61.05	7.08	0.95	2.18	63.68	29.28	3.14	3.9
V-Volatiles; FC-Fixed Carbon; M-Moisture; A-Ash								

## Methods

The depolymerization reactions of lignin were performed in a 100-mL stainless autoclave equipped with an electromagnetic stirrer. For each run, lignin (1.0 g), catalyst (0.001 mol), and solvent (40.0 mL) were loaded into the autoclave, the  $\text{H}_2$  pressure was raised to 1.0 MPa after displacing air, and the autoclave was sealed. The reactor was heated to the desired temperature while the reagents were stirred at 400 rpm. The reactor was cooled to room temperature and opened when the reaction was complete. The obtained liquid product was filtered through filter paper with a mesh size of 45  $\mu\text{m}$ , weighed, and analyzed by gas chromatograph-flame ionization detector (GC-FID) and gas chromatograph-mass spectroscopy (GC-MS). The solid residues were dried at 85 °C for 12 h and then weighed. In addition, with regard to depolymerization of lignin performed in the water solvent, the liquid products were obtained by extraction with  $\text{CH}_2\text{Cl}_2$ .

To explore the effect of temperature on the ether bond depolymerization in isolation, the depolymerization of diphenyl ether, which was chosen as a model compound for the 4-O-5 bond, was also carried out in ethanol at different temperature.

### Product analysis

Lignin-derived products were recovered from the system as liquid products (LP) and solid residues (SR). The yield of gas products were negligible. Thus, the yields of liquid product were defined in the following formula,

$$X = \frac{m_{\text{lignin}} - m_{\text{SR}}}{m_{\text{lignin}}} \times 100\% \quad (1)$$

where  $m_{\text{lignin}}$  is the mass of lignin loaded in the reactor and  $m_{\text{SR}}$  is the mass of the solid residue after the depolymerization reaction.

The qualitative analysis of the volatile components of the liquid product was carried out by a GC-MS (Agilent 7890A/5975C, USA) equipped with a HP-5 column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$ ) and determined by National Institute of Standards and Technology (NIST) 08 MS library. The carrier gas was He with 99.995% purity, and the oven temperature program ranged from 40 °C (holding for 5 min) to 250 °C (holding for 10 min) at a rate of 10 °C  $\text{min}^{-1}$ . The ion trap detector had a mass range of 50 to 500 m/z

with scan times of 1 s. The mass spectrometer ion source operated at 250 °C with a 70-eV ionization potential.

The quantitative analysis was carried out by a GC-FID (Agilent 7890A, USA) equipped with a HP-5 column (30 m × 0.32 mm × 0.25 μm), wherein benzyl alcohol was used as the internal standard compound.

The compounds identified by GC-FID were defined as the volatile fraction (VF). The mass of volatile fractions was calculated based on the internal standard, and the yields of volatile fraction were defined in the following formula,

$$Y_{VF} = \frac{m_{VF}}{m_{lignin}} \times 100\% \quad (2)$$

where  $m_{VF}$  is the volatile fraction contained in the liquid product.

The yields of main components were also obtained based on the following formula,

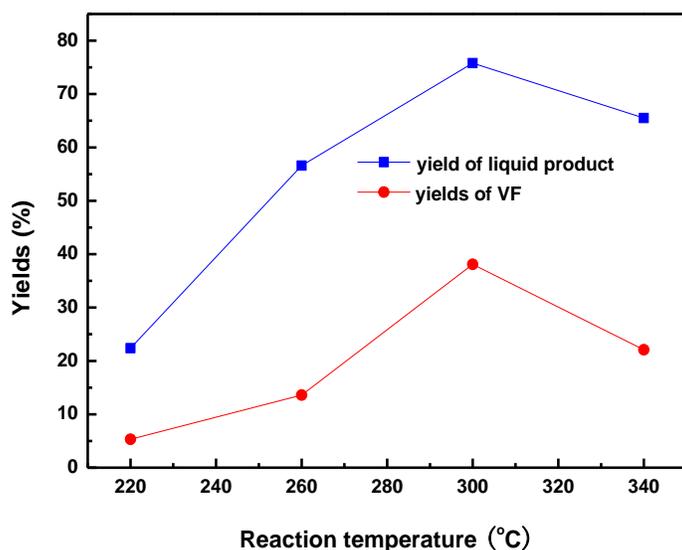
$$Y_i = \frac{m_i}{m_{lignin}} \times 100\% \quad (3)$$

where  $m_i$  represents the mass of component  $i$ , as determined by GC-FID.

## RESULTS AND DISCUSSION

### Effects of Reaction Temperature on Lignin Depolymerization

Figure 1 shows the progress of lignin depolymerization at different reaction temperatures with ZnCl<sub>2</sub> catalyst in ethanol. When the reaction temperature increased from 220 to 300 °C, the yields of liquid product and volatile fraction increased from 32.4% to 75.8% and from 5.3% to 38.1%, respectively, which means that the elevated temperature significantly facilitated the depolymerization of lignin.



**Fig. 1.** Effect of reaction temperature on the yields of liquid product and volatile fraction (solvent: ethanol;  $t = 2$  h; catalyst: ZnCl<sub>2</sub>)

The bond dissociation enthalpies for main linkages of lignin are listed in Table 2. Generally, the C-C linkages are stable and difficult to break under mild conditions. The weak ether linkages, such as  $\alpha$ -O-4, 4-O-5, and  $\beta$ -O-4 are cleaved prior to the C-C linkages. Of the major ether bonds contained in lignin, the 4-O-5 bond is the strongest. Therefore, diphenyl ether was chosen as a model compound for 4-O-5 bond to explore the effects of temperature on the cleavage of the ether bond.

**Table 2.** Bond Dissociation Enthalpies for Main Linkages of Lignin \*

Type of bond contained in lignin	Bond dissociation enthalpies (kJ mol <sup>-1</sup> )
$\beta$ -O-4	290-305
4-O-5	330
$\alpha$ -O-4	215
$\beta$ -1	280
$\alpha$ -1	360-390
5'-5	490

\* adapted from Parthasarathi *et al.* 2011.

As shown in Table 3, cleavage of the aryl ether bond was not observed at 220 °C, while about 5.3% of the ether bond was dissociated at 260 °C. Obviously, the cleavage of the ether bond increased as temperature increased. This result confirms that higher temperature can facilitate the cleavage of ether bonds and depolymerization of lignin towards simpler molecules, resulting in higher yields of liquid products and volatile fraction. However, both decreased markedly when the temperature further increased to 340 °C, which can be attributed to the repolymerization of the reaction intermediates/oligomer products. This result is consistent with previous studies (Ye *et al.* 2012a; Yuan *et al.* 2010), in which the yield of solid residues increased with increasing temperature. Therefore, 300 °C is a desirable reaction temperature for lignin depolymerization. Nevertheless, the high conversion of lignin made it difficult to investigate the effects of parameters such as catalysts, solvent, and reaction time. Instead, in our studies, the experiments of lignin depolymerization were performed at 260 °C, where the depolymerization of lignin was incomplete.

**Table 3.** Depolymerization of Diphenyl Ether at Different Temperature

Temperature (°C)	Conversion (%)
220	-
260	5.3
300	17.7
340	33.6

Solvent: ethanol; no catalyst.

### Catalyst Testing in Depolymerization of Lignin

The influence of catalyst on lignin depolymerization in water or ethanol was investigated at 260 °C, and the results presented in Fig. 2. In the water solvent, the metal chloride catalysts yielded higher liquid products and volatile fractions relative to the absence of catalyst. The reason is that metal chlorides used in this catalytic system are hydrolyzed, causing the production of Brønsted acid. Therefore, oxonium salt can be formed when H<sup>+</sup> attacks the etheric O atom, which activates the C-O bond, favoring the cleavage of the ether bond. Obviously, the acidity of the catalyst plays a crucial role in

the depolymerization of lignin. Thus, it is reasonable that additional  $\text{H}_3\text{PO}_4$  yielded the highest liquid product and volatile fraction.

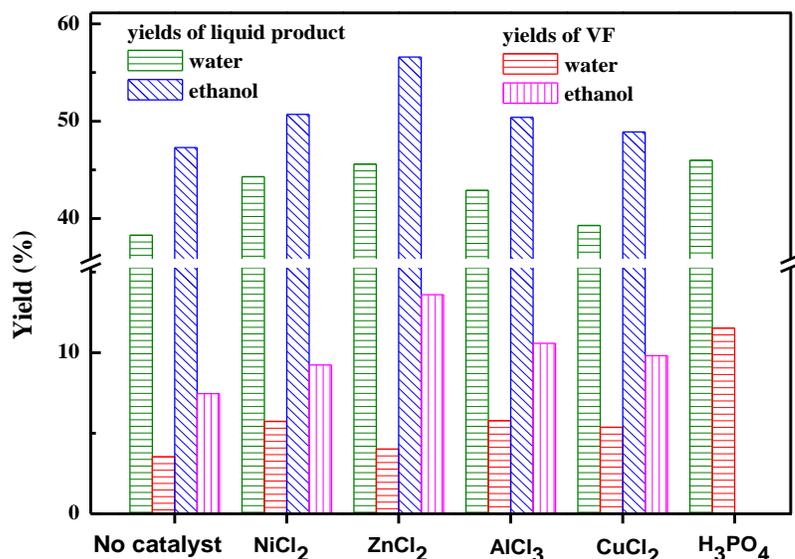


Fig. 2. Effect of catalysts on the yields of liquid product and volatile fraction ( $T = 260\text{ }^{\circ}\text{C}$ ;  $t = 2\text{ h}$ )

Though the yields of volatile fraction were relatively low, the major components were phenolic compounds as listed in Table 4.

**Table 4.** Main Components of the Volatile Fraction Obtained from Lignin Depolymerization\*

Components	Yields <sup>†</sup> / %					
	No Catalyst	CuCl <sub>2</sub>	AlCl <sub>3</sub>	ZnCl <sub>2</sub>	NiCl <sub>2</sub>	H <sub>3</sub> PO <sub>4</sub>
Phenol	0.6	0.18	0.17	0.15	1.74	0.51
Phenol, 2-methoxy-3-methyl-	-	0.15	0.42	0.21	0.1	0.14
Phenol, 2-methoxy-	1.66	3.35	3.41	2.14	2.21	8.6
Phenol, 4-ethyl-2-methoxy-	-	0.19	0.25	0.29	0.08	0.1
Phenol, 4-methyl-	-	-	-	-	0.65	-
Phenol,3-methyl-	-	-	-	-	0.16	-
Phenol, 2-methy-4-propyl-	-	-	-	0.11	-	-
Phenol, 2-methoxy-4-propyl-	-	-	-	0.16	-	0.1
Ethanone,1-(4-hydroxy-3-methoxyphenyl)-	0.16	0.18	0.19	0.18	0.03	0.14
Propan-2-one, 1-(4-isopropoxy-3-methoxyphenyl)-	0.44	-	-	-	-	-
Vanillin	0.2	0.27	0.23	0.23	0.06	0.18
Benzeneacetic acid, 4-hydroxy-3-methoxy-	-	0.76	0.40	0.31	0.09	0.97
Total	3.06	5.08	5.07	3.78	5.12	10.74

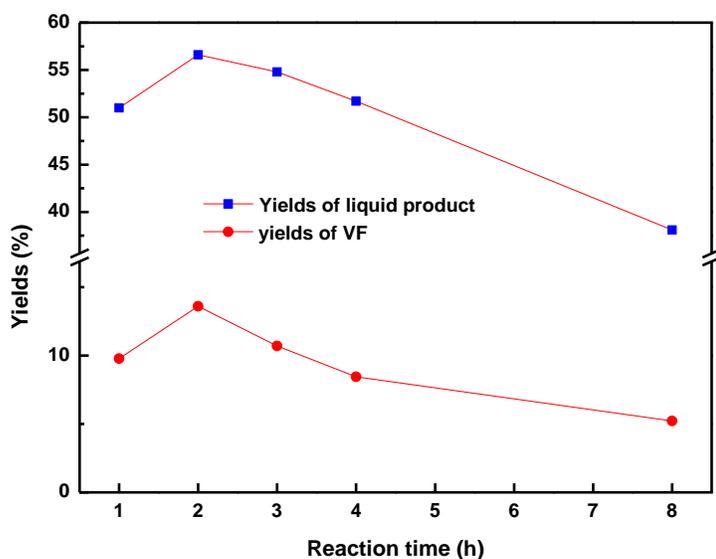
Reaction conditions: solvent: water;  $T = 260\text{ }^{\circ}\text{C}$ ;  $t = 2\text{ h}$ .  
<sup>†</sup> Components listed are those represented by more than 0.1% of the yields determined by GC-FID.  
 - The component was not detected or its relative content was lower than 0.1%.

The content of the guaiacol 2-methoxy-phenol was the highest, and interestingly, the yield was as high as 8.6% when  $\text{H}_3\text{PO}_4$  was used as the catalyst. The reason is that  $\text{H}_3\text{PO}_4$  is a type of proton acid with medium strength acidity, which can improve the efficiency of the lignin degradation process and obtain a higher yield for monomers (Yan *et al.* 2008).

In the solvent ethanol, the catalytic performance of metal chlorides for lignin depolymerization was improved significantly, as shown in Fig. 2. In particular,  $\text{ZnCl}_2$  was found to be the most efficient where the yields of liquid product and identified volatile fraction were 56.6 wt% and 13.6 wt%, respectively.

### Effects of Reaction Time on Lignin Depolymerization

The effect of reaction time on the yields of liquid product and volatile fraction was further investigated at 260 °C with  $\text{ZnCl}_2$  in ethanol (Fig. 3). At the reaction time of 1 h, the yield of liquid product was more than 50 wt%, with the maximum for yields of liquid product and volatile fraction obtained at the reaction time of 2 h. It may be deduced that most lignin-containing ether bonds and easily cleaved C-C bonds are broken, and the lignin degradation reaction is essentially completed after 2 h of reaction time (Wahyudiono *et al.* 2008). However, with the reaction time lengthened further, the yields of liquid product and volatile fraction decreased gradually. The reason is that the obtained liquid product (including phenolic compounds and depolymerized lignin intermediates/oligomer products) is unstable under the catalytic system, causing a tendency for repolymerization (Ye *et al.* 2012a) and resulting in decreases of both liquid product and volatile fraction.



**Fig. 3.** Effect of reaction time on the yields of liquid product and volatile fraction (solvent: ethanol;  $T = 260$  °C; catalyst:  $\text{ZnCl}_2$ ).

### Effects of Solvent on Lignin Depolymerization

Figure 4 shows the effect of solvent on the yields of liquid products and volatile fraction produced with or without  $\text{ZnCl}_2$  at 260 °C. Depolymerization of lignin using nonpolar octane as the solvent was also carried out for comparison with the reactions performed in polar solvent. As shown in Fig. 4, octane was less effective than polar solvent in the absence of catalyst. Yields of the liquid product and volatile fraction in

octane were only 22.6% and 4.6%, respectively, and they increased in polar solvent of water and alcohols.

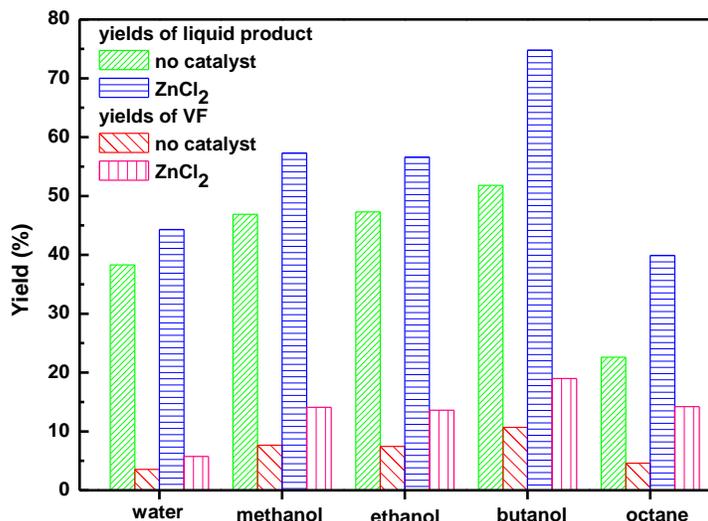


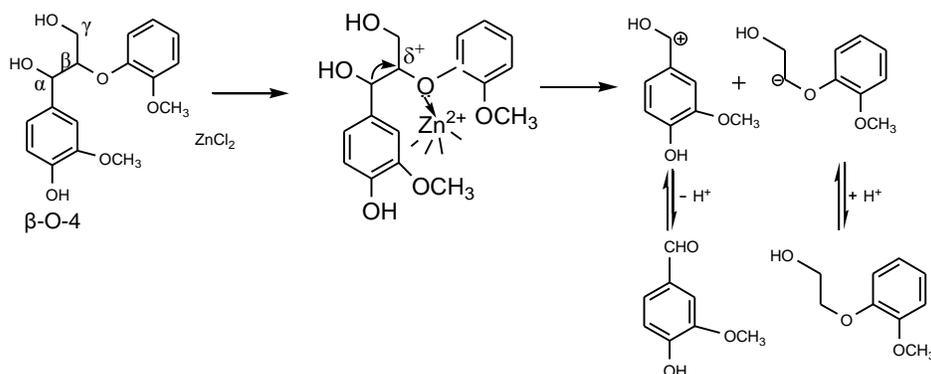
Fig. 4. Effect of solvent on the yields of liquid product and volatile fraction ( $T = 260\text{ }^{\circ}\text{C}$ ;  $t = 2\text{ h}$ )

It is noteworthy that the yields of liquid product and volatile fraction obtained in the alcohol solvents were higher than those of water. There are two reasons which may account for this. First, the interaction between alcohol solvent molecules and polar groups of lignin can produce a solvent effect of lignin depolymerization. Moreover, the depolymerized products can also be dissolved in the alcohol solvent, which can promote the depolymerization reaction and lead to the improvement in the yields of liquid product and volatile fraction. Second, carboxylic acids produced during the process of lignin hydrolysis tend to recombine with other products, resulting in the formation of carbonaceous residue. However, these carboxylic acids were esterified with alcohol in this system, suppressing the recombination reactions between the carboxylic acids and the depolymerized lignin intermediates/products (Yoshikawa *et al.* 2013). This was further confirmed by the fact that esters were detected in the volatile fraction (Table 5).

For the depolymerization of lignin with  $\text{ZnCl}_2$ , the yields of liquid product and volatile fraction obtained in octane significantly increased to 39.9% and 15.2%, respectively. The reason is that  $\text{ZnCl}_2$  acts as a Lewis acid catalyst for the lignin depolymerization in octane. For example, during the cleavage of  $\beta\text{-O-4}$ ,  $\text{Zn}^{2+}$  coordinated with O atom positioned in the  $\beta\text{-O-4}$ , which could weaken the bond of  $\text{C}_\alpha\text{-C}_\beta$ . The weakened  $\text{C}_\alpha\text{-C}_\beta$  bond was then cleaved, resulting in the formation of vanillin (Scheme 1). A similar cleavage mechanism for the  $\text{C}_\alpha\text{-C}_\beta$  had been found in the literature (Lim *et al.* 2013).

Figure 4 illustrates that the yields of liquid product and volatile fraction obtained in methanol approximated those of ethanol. However, the experiments using butanol as solvent showed an obvious increase in the yields of liquid product and volatile fraction. For example, in the presence of  $\text{ZnCl}_2$ , the yields of liquid product and volatile fraction were 57.23% and 14.1% in methanol, and increased to 74.8% and 18.99%, respectively when butanol was used as solvent. Methanol, ethanol, and butanol are Lewis basic solvents (Wang and Rinaldi 2012). To a certain extent, there can also be coordination of some groups with the  $\text{ZnCl}_2$  catalyst; such behavior is expected for ether bonds and

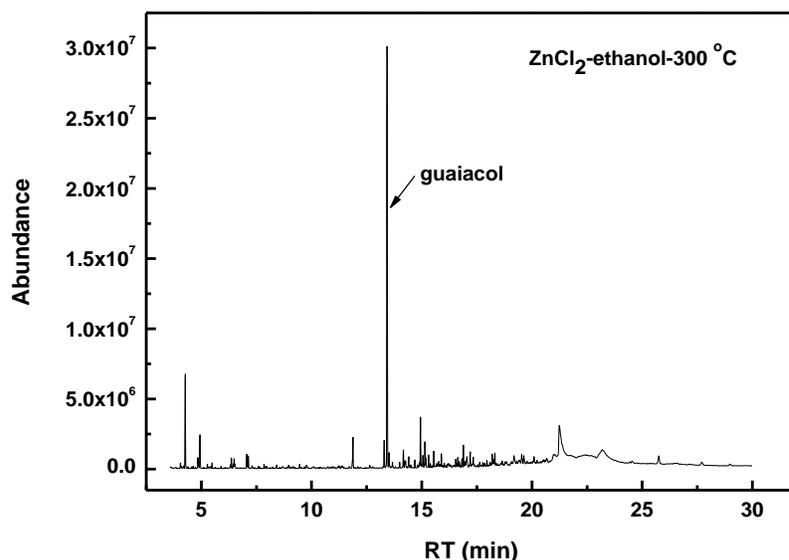
hydroxyl groups contained in lignin. The alcohol solvent can compete with ether bonds and hydroxyl groups, suppressing the catalytic performance of  $\text{ZnCl}_2$  during the process of lignin depolymerization. For the long-chain linear alcohols, the Lewis basicity decreases with the chain length (Wang and Rinaldi 2012). Hence, the effect of butanol on the catalytic depolymerization of lignin is lowest due to the weakest Lewis basicity.



**Scheme 1.** Cleavage of the  $\beta$ -O-4 bond catalyzed by Lewis acid

### Main Components of the Volatile Fraction

Figure 5 showed a typical GC-MS profile of the volatile fraction obtained from lignin depolymerization with  $\text{ZnCl}_2$  in ethanol at 300 °C. More than 100 peaks were observed on the ion chromatograms, implying that the components of the volatile fraction are rather complex. Quantitative analysis of the major components contained in the volatile fraction was carried out by GC-FID according to the added internal standard, and the results are displayed in detail in Table 5.



**Fig. 5.** Ion Chromatogram for the volatile fraction obtained from lignin depolymerization (catalyst:  $\text{ZnCl}_2$ ; solvent: ethanol;  $T = 300$  °C;  $t = 2$  h)

With an overview of Table 5, it is not surprising to find that the identified volatile fraction was a complex mixture of phenolic compounds, which is expected because the major structure of lignin is composed of these phenolic derivatives.

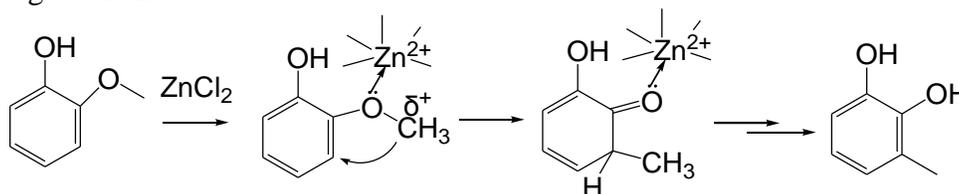
**Table 5.** Main Components of the Lignin-derived Volatile Fraction\*

Component	Yields <sup>‡</sup> (%)	Component	Yields <sup>‡</sup> (%)
<b>Phenols</b>	<b>15.79</b>	<b>Guaiacols</b>	<b>15.09</b>
Phenol, methyl-	0.36	Phenol, 2-ethoxy-	0.80
Phenol	1.49	Phenol, 2-methoxy-	11.93
Phenol, ethyl-	0.80	Phenol, 2-Methoxy-6-methyl-	0.48
Phenol, 2,4-bis(1-methylethyl)-	0.39	Phenol, 2-methoxy-3-methyl-	0.23
Phenol, trimethyl-	0.12	Phenol, 2-Methoxy-5-methyl-	0.21
Phenol, 3,5-diethyl-	0.25	Phenol, 2-methoxy-4-methyl-	0.37
Phenol, 2,3,5,6-tetramethyl-	0.13	Phenol, 4-ethyl-2-methoxy-	1.06
Phenol, 2,4-bis(1,1-dimethylethyl)-	0.48	<b>Syringols</b>	<b>2.28</b>
1,3-Benzenediol, 4-ethyl-	0.16	Benzene, 1,2-dimethoxy-	1.05
1,4-Benzenediol, 2,3,5-trimethyl-	0.93	Benzene, 1,4-dimethoxy-2-methyl-	0.12
Phenol, 2-(1,1-dimethylethyl)-5-methyl-	0.11	Benzene, 4-butyl-1,2-dimethoxy-	0.37
Propofol	0.86	Benzene, 1-butyl-4-methoxy-	0.17
Phenol, 6-tert-Butyl-2,4-dimethyl-	0.18	Benzaldehyde, 2-ethoxy-5-methoxy-	0.11
Butylated Hydroxytoluene	0.20	3,4-Dimethoxybenzylideneacetone	0.46
1,2-Benzenediol, 3-methyl-	1.23	<b>Others</b>	<b>1.31</b>
1,2-Benzenediol	5.39	Quinoline, 2-(3-tolyl)-	0.15
1,4-Benzenediol, 2-(1,1-dimethylethyl)-	1.89	Benzene, hexaethyl-	0.30
Phenol, 3-Methyl-4-isopropyl-	0.53	Benzene, 1,2,4,5-tetraethyl-	0.3
Benzenemethanol, 4-(1,1-dimethylethyl)-	0.27	Benzoic acid, 4-(1-methylethyl)-	0.12
		Ethanol, 2-[4-(1-methylethyl)phenoxy]-	0.10
		Benzenethiol, 4-(1,1-dimethylethyl)-	0.12
		1H-Indene, 3-ethenyl-2,3-dihydro-1,1-dimethyl-ethyl ester	0.10
		2-hexenoic acid ethyl ester	0.12
* Conditions: catalyst: ZnCl <sub>2</sub> ; t = 2 h; solvent: ethanol; T = 300 °C.			
‡ Components listed are those represented by more than 0.1% of the yields determined by GC-FID.			

According to reports on the decomposition of lignin model compounds and cornstalk lignin (Liu *et al.* 2011; Ye *et al.* 2012b), the main phenolic products can be classified as three types: H-type (phenols, derived from P-hydroxyphenyl subunits), G-type (guaiacols, derived from guaiacyl subunits), and S-type (syringols, derived from syringyl subunits). Of these phenolic compounds, guaiacol was the most abundant component, with a yield of 11.93%. All the phenols, such as dimethylphenol, trimethylphenol, and 2-methyl-5-propenylphenol, accounted for yields of 15.79%. In addition, most of the detected phenolic compounds with a carbon atom number of C<sub>6</sub> to C<sub>10</sub> are the most desirable components for a fungible liquid transportation fuel via hydrodeoxygenation (Zhang *et al.* 2013a, b). Hence, it is important to obtain higher yields of phenolic compounds to enable the industrial use of lignin. To achieve this purpose, researchers have explored the depolymerization of lignin over noble metal catalysts, obtaining identifiable phenolic yield above 21% (Torr *et al.* 2011; Xu *et al.* 2012). Further research on the improvement of the yields of phenolics is ongoing.

In addition, it is noteworthy that a large amount of phenol (benzenediol and alkyl substituted phenols) were obtained over ZnCl<sub>2</sub> and ethanol solvent (Table 5). It can be

inferred that the side-chain cleavage, methyl transfer, and demethylation reaction of phenolic compounds occurred in the process of lignin depolymerization. Taking guaiacol as an example, the mechanism of the methyl transfer can be elucidated as follows: the lone pair electrons of the oxygen atom contained in the methoxyl group coordinate with the vacant orbital of  $Zn^{2+}$ , causing the bond of  $ArO-CH_3$  to weaken. The weakened O-C bond cleaves heterolytically, and the positively charged methyl group can be transferred to the aromatic ring, followed by the formation of the methyl-catechol. The *o*-methylcatechol (3-methyl-1,2-benzenediol) detected in the products of the volatile fraction validates the proposed mechanism (Scheme 2). More significantly, the number of carbon atoms in the skeleton of degradation products increased due to the transfer of methyl to the aromatic ring, suggesting a decrease of carbon loss during the process of lignin degradation.



**Scheme 2.** Schematic diagram of the methyl transfer

## CONCLUSIONS

1. The depolymerization of alkali lignin was performed over different metal chlorides. Of the tested metal chlorides,  $ZnCl_2$  exhibited the greatest efficiency in ethanol, where the yields of the liquid product and volatile fraction were 56.6 wt% and 13.6 wt%, respectively.
2. Reaction temperature had a remarkable effect on the yield of the liquid products and volatiles. Under the conditions of 2 h and 300 °C, the liquid product yield of 75.8% and volatile fraction yield of 38.1% were obtained over the  $ZnCl_2$  catalyst in ethanol. The main components of the obtained volatile fraction were phenolic compounds, such as guaiacol (yield of 11.93 wt%), phenol (1.49 wt%), benzenediol (5.39 wt%), 4-ethyl-2-methoxy-phenol (1.06 wt%), and 1,2-dimethoxy-benzene (1.05 wt%). With an increase in temperature and reaction time, the yield of the liquid product and volatile fraction decreased.
3. The solvent alcohol can promote the depolymerization of lignin. This is especially true for butanol, which significantly promoted depolymerization of lignin due to its lower interaction with the Lewis acid and higher solubility for the degradation products and intermediates. The yields of the liquid product and volatile fraction reached 74.8% and 18.99%, respectively.
4. In aqueous metal chloride solutions, the depolymerization of lignin was catalyzed by a Brønsted acid, while the metal chlorides act as a Lewis acid in the alcohol solvent and octane solvent.
5. The highlight of this work is that high yield of liquid product and volatile fraction (phenolics) can be obtained from depolymerization of lignin over metal chloride and solvent alcohol. This is attractive for the use of lignin as high-grade chemicals.

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