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# Depolymerization of Cellulolytic Enzyme Lignin for the Production of Monomeric Phenols over Raney Ni and Acidic Zeolite Catalysts

Yetao Jiang,<sup>†</sup> Zheng Li,<sup>†</sup> Xing Tang,<sup>†</sup> Yong Sun,<sup>†</sup> Xianhai Zeng,<sup>\*,†</sup> Shijie Liu,<sup>‡</sup> and Lu Lin<sup>\*,†</sup>

<sup>†</sup>College of Energy, Xiamen University, Xiamen, Fujian 361102, People's Republic of China

<sup>‡</sup>Department of Paper and Bioprocess Engineering, State University of New York College of Environmental Science and Forestry, Syracuse, New York 13210, United States

## S Supporting Information

**ABSTRACT:** In the present study, cellulolytic enzyme lignin, which was isolated from enzymatic hydrolysis residues of bamboo, could be efficiently depolymerized into oily products with a yield of over 60 wt % using a range of acidic zeolites and/or Raney Ni catalysts. The degraded products are mainly composed of phenolic monomers, which can be used as versatile chemicals or the precursor for biofuel production. The yields of monophenols were 12.9 wt % and no more than 5.0 wt % when catalyzed by Raney Ni or acidic zeolites, respectively. However, a yield of monophenols as high as 21.0–27.9% was obtained using a Raney Ni combination with acidic zeolite catalysts. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry analysis revealed that the depolymerization level of the oily fraction catalyzed by a combination of catalysts was more complete in comparison to those catalyzed by an independent catalyst. The results indicated that the catalytic activity of a fully heterogeneous catalyst combination for the depolymerization of cellulolytic enzyme lignin was proven to be superior to that of either component alone.

## 1. INTRODUCTION

With the depletion of fossil resources, extensive studies have recently been focused on the sustainable supply of energy and chemicals from renewable resources. Biomass, as a practical, alternative source of renewable liquid fuel, have attracted great attention in recent years.<sup>1–4</sup> Multiple catalytic strategies have been successfully established and applied in the conversion of lignocellulose, the most abundant biomass resource, to monosaccharides and subsequent fuels or chemicals.<sup>4–7</sup>

Lignin is the second largest constituent of lignocellulosic biomass, which takes up 15–30% of the weight and 40% of the energy of lignocellulose.<sup>8</sup> However, up to date, it is still a grand challenge for efficient utilization of lignin because of the diverse functional groups of basic units and complex covalent bonds in its structure.<sup>9</sup> As a versatile feedstock, lignin can be converted to a variety of useful chemicals.<sup>10</sup> In view of its abundant polyphenolic structure, lignin is an ideal feedstock to be subjected to catalytic depolymerization for production of low-molecular-weight species, such as substituted phenolic and aromatic monomers, which can be refined to versatile chemical reagents or hydrocarbon biofuels via the hydrodeoxygenation process.<sup>11–13</sup> The yield and composition of the monomeric products were strongly associated with the nature of the lignin macromolecule and the processes applied for lignin production from lignocellulosic feedstock.<sup>14,15</sup> Studies were focused on the depolymerization of alkali lignin from the pulp and paper industry or organosolv lignin,<sup>15–20</sup> whereas few studies were aimed at the depolymerization of cellulolytic enzyme lignin, which could be the major feedstock of lignin with the boom of the biorefinery industry in the near future.

Nickel-based catalysts were known for the depolymerization of lignin to aromatic monomers. Sulfided NiMo<sup>21</sup> and Ni-based bimetallic catalysts, such as NiAu,<sup>22</sup> were found with high

activity in organosolv lignin depolymerization. A two-step mechanism involved in the process of lignin depolymerization was proposed by Song and co-workers.<sup>23</sup> The Ni content in nickel–tungsten heterogeneous catalysts had little effect on the yields of monomeric phenolic compounds; however, gas products were favored with a higher Ni content catalyst.<sup>24</sup> Solubility of cellulolytic enzyme lignin in organic solvents was enhanced after Raney-Ni-catalyzed hydrogenolysis.<sup>25</sup> Besides this, solid acids, such as acidic zeolites, were also usually used for catalyzed lignin valorization.<sup>26,27</sup> Deactivation and regeneration of the H-USY zeolite in the lignin depolymerization process was also studied, and coke deposition on the catalyst proved the main reason for deactivation.<sup>28</sup> Recently, Deepaa and Dhepe demonstrated that Kraft lignin could be efficiently converted into aromatic monomers over solid acid.<sup>15</sup>

In our study of cellulolytic enzyme lignin from bamboo residues used as the feedstock for catalytic degradation using kinds of acidic zeolites as catalysts, only negligible monomer yields less than 5% were achieved, whereas in the present fully heterogeneous catalyst combination of Raney Ni and acidic zeolites, we found that cellulolytic enzyme lignin could be converted to monomeric phenols with a yield higher than catalyzed by either component alone. Here, we investigated the role of zeolites in promoting Raney-Ni-catalyzed lignin depolymerization and optimized the combined catalysts of Raney Ni zeolites.

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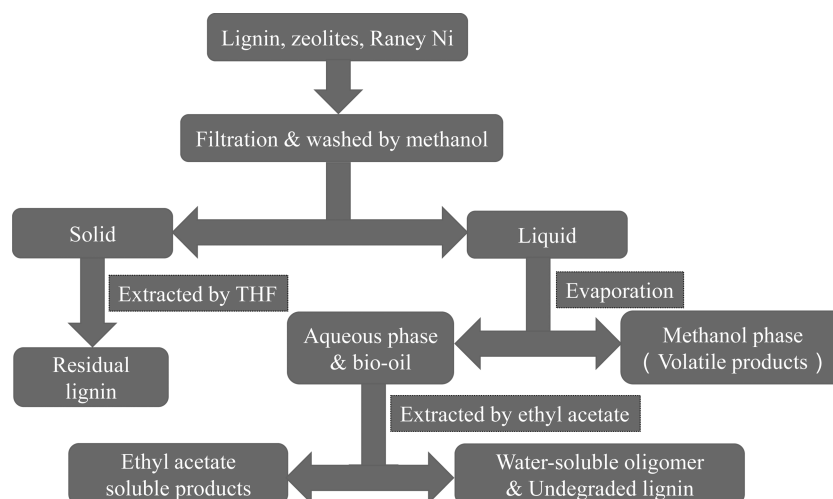


Figure 1. Process of lignin degradation and product separation.

## 2. MATERIALS AND METHODS

**2.1. Materials.** The crude cellulolytic enzyme lignin was kindly supplied by Broany Bioenergy Co., Ltd. (Xiamen, China) (more information available in the Supporting Information). All other chemicals were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification.

**2.2. Catalyst Preparation and Characterization.** H-form USY zeolites were prepared from ultrastable Y by ammonium ion ( $\text{NH}_4^+$ ) exchanging in aqueous  $\text{NH}_4\text{NO}_3$  solution (1 mol/L) at 353 K for 8 h, followed by drying at 393 K for 4 h and calcinating at 783 K for 4 h.  $\text{SO}_4^{2-}$ /USY catalyst (5 wt %) was prepared by pore volume co-impregnation of the USY carrier in an aqueous sulfuric acid solution, followed by drying at 393 K for 4 h and calcinating at 783 K for 4 h. Other molecular sieves were purchased from Nankai University Catalyst Co., Ltd. (Tianjing, China) and calcined at 783 K for 4 h before use. Raney Ni was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). The surface area of the fresh and recovered catalysts was calculated by nitrogen adsorption–desorption isotherms, which was measured by static  $\text{N}_2$  physisorption at 77.3 K with a Micrometrics TriStar II 3020 (Micrometrics Instrument, Norcross, GA). Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet 370 spectrometer conducting from 4000 to 500  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

**2.3. Lignin Depolymerization and Product Separation.** The depolymerization reactions were carried out in a 100 mL cylindrical stainless-steel high-pressure reactor (PARR Instrument Company, Moline, IL). The scheme for lignin degradation and product separation process is shown in Figure 1. In a typical run for lignin depolymerization, lignin (0.5 g), zeolites (0.5 g), Raney Ni (0.5 mL, ca. 50% by weight of water/50% by weight of catalyst), and methanol/water (5:2, v/v, 50 mL) were introduced into the autoclave, sealed, and purged 3 times with  $\text{N}_2$ . Subsequently, the reaction mixture was heated to the designed temperature and maintained for a given time. After the reaction, the reactor was cooled to room temperature quickly to terminate the reaction and the gaseous product was collected for further analysis. The liquid product stream was filtered, and the solid fraction, including catalysts and residues, was extracted with tetrahydrofuran. Methanol in the filtrate was removed by vacuum distillation at 308 K. The remaining aqueous phase containing oily droplets was extracted with ethyl acetate (15 mL) 3 times. The ethyl acetate soluble phase was dried with anhydrous magnesium sulfate and vacuum distillation at 313 K to obtain lignin-derived oily products.

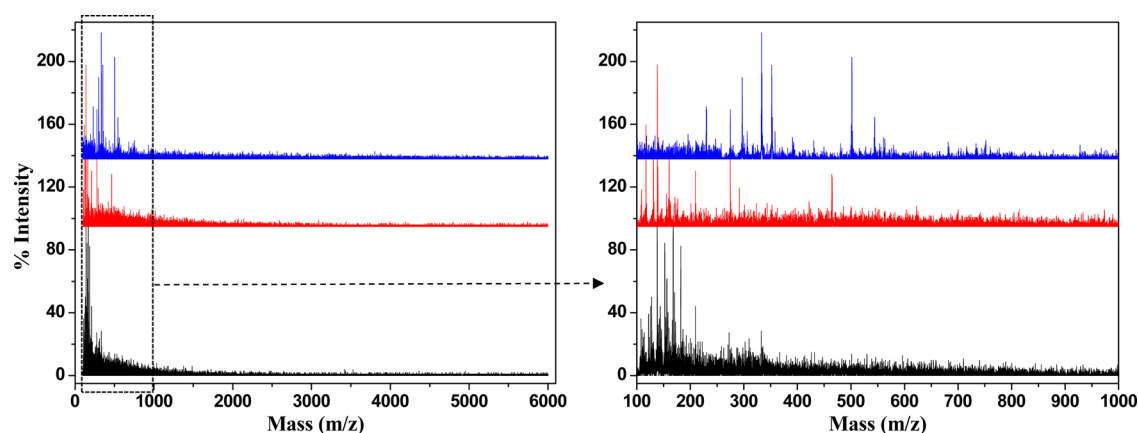
**2.4. Product Analysis.** The gas fraction from the depolymerization process was analyzed with gas chromatography (GC, Shimadzu GC-2010 Plus) equipped with a thermal conductivity detector (TCD) and a Varian CP7429 column (length, 60 m; inner diameter, 0.53 mm; and film thickness, 10  $\mu\text{m}$ ). The oven, injector, and detector temperatures were kept at 308, 373, and 423 K, respectively.

The monomeric reaction products were identified by a Shimadzu GCMS-QP2010SE instrument with a Rtx-5MS column (length, 30 m; inner diameter, 0.20 mm; and film thickness, 0.33  $\mu\text{m}$ ) and electron impact ionization (EI). Carrier gas was He with an elution rate of 1.85 mL/min (50 cm/s) and a split ratio of 5:1. The sample was injected (1  $\mu\text{L}$ ) from the autosampler, and the temperature program was as follows: initial oven temperature was set to 343 K for 2 min, then was heated to 553 K at 7 K/min, and was held at 553 K for 8 min. The inlet and gas chromatography–mass spectrometry (GC–MS) detector temperatures were kept at 543 and 473 K, respectively. Mass spectrometry (MS) spectra were compared to the spectra gathered at the National Institute of Standards and Technology (NIST).<sup>20</sup> Semi-quantitation by GC–MS was carried out using acetophenone as the internal standard.<sup>12,29</sup> Determinations were performed using full-scan mode; characteristic ions with highest abundance were selected as the quantitative ion peak; and nine major compounds were identified and semi-quantified (see page 5 of the Supporting Information for details of the semi-quantitative method by GC–MS). The yield in weight percent is given as the weight of each product per weight of initial lignin multiplied by 100%. The mass balance was calculated, and the result was  $91 \pm 4\%$  in this work (see Figure S4 of the Supporting Information).

Identification of the molecular mass was performed on AB SCIEX matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI–TOF–MS, TM 5800, Applied Biosystems, Framingham, MA). Saturated 2,5-dihydroxybenzoic acid (DHB, Bruker) solution [in acetonitrile/distilled water containing 0.1% trifluoroacetic acid (TFA), 4:6] was used as the matrix. DHB (1  $\mu\text{L}$ ) and the analyte solution (1  $\mu\text{L}$ ) were mixed completely; then 1  $\mu\text{L}$  of the mixture was loaded on the target; and the solvent was removed by air drying. The instrument conditions are referenced in a previous report.<sup>23</sup>

## 3. RESULTS AND DISCUSSION

**3.1. Determination of the Molecular Mass of Degradation Products.** Different zeolites and/or Raney Ni catalysts gave a similar oily product yield of ca. 60 wt % for the ethyl acetate extract, whereas yields of monomeric phenols were significantly different, ranging from 2.9 to 27.9 wt % (see Table 3). Subjected to detection limits of GC–MS, only monomeric and a few dimeric degradation products could be identified and the other oligomers with higher molecular weight could not be detected. The existence of oligomers could be confirmed by electrospray ionization (ESI) (see Figure S6 of the Supporting Information), because fragment ions with a larger charge-to-mass ratio ( $m/z$ ) than monomers were



**Figure 2.** MALDI-TOF-MS for molecular weight determination of the reaction mixture catalyzed by Raney Ni (blue) or H-USY and Ni (red) and ethyl acetate extracts from degradation products catalyzed by H-USY and Ni (black).

**Table 1.** Compare *in-Situ*-Generated Hydrogen to Extra Hydrogen on Lignin Depolymerization

entry	atmosphere <sup>a</sup>	solvent	substrate	final pressure (bar)	bio-oil (wt %)	monophenols (wt %)
1	N <sub>2</sub>	methanol	blank	27		
2	N <sub>2</sub>	methanol	lignin	23	64.2	25.4
3	H <sub>2</sub>	methanol	lignin	21	69.7	26.1
4	N <sub>2</sub>	ethanol	blank	15		
5	N <sub>2</sub>	ethanol	lignin	12	48.7	13.5
6	H <sub>2</sub>	ethanol	lignin	9	51.2	14.4

<sup>a</sup>Initial pressure = 10 bar.

**Table 2.** Effect of Different Zeolites and/or Raney Ni Catalysts on the Depolymerization of Lignin to Phenolic Products<sup>a</sup>

compound	yield (wt %)								total
	1	2	3	4	5	6	7	8	
H-USY and Ni	0.4	2.4	1.9	1.5	8.7	1.6	1.6	9.8	27.9
H-Y and Ni	0.6	3.4	1.2	0.5	10.0	1.8	0.8	5.9	24.2
USY and Ni	0.5	3.2	1.5	0.6	11.7	2.4	0.9	6.8	27.6
H-ZSM-5 and Ni	0.2	2.7	1.6	0.6	10.6	1.3		8.9	25.9
SO <sub>4</sub> <sup>2-</sup> /USY and Ni	0.3	1.7	1.0	0.6	9.4	1.8	1.5	4.6	21.0
Hβ and Ni	0.2	1.7	2.3	0.4	12.4	1.3	0.7	8.3	27.3
MOR and Ni	0.2	3.3	1.4	0.5	11.0	0.9	0.5	7.2	25.0
Raney Ni	0.5	0.9	0.9	0.7	3.7	0.8	1.8	3.6	12.9
Hβ					0.6		2.0	2.0	4.5
H-USY	0.2	0.3	0.3	0.2	0.3		0.6	1.1	3.0
blank									

<sup>a</sup>Reaction conditions: 0.5 g of lignin, 0.5 g of zeolites, 0.5 mL of Raney Ni catalyst (ca. 50% by weight of water/50% by weight of catalyst), H<sub>2</sub>O/CH<sub>3</sub>OH (2:5, v/v), 1 atm N<sub>2</sub>, 543 K, 500 rpm, and 30 min.

detected. To reveal the molecular weight distribution of the depolymerized products, it was requisite to obtain more insight into the depolymerization degree of lignin molecules. MALDI-TOF-MS has been demonstrated to be an advanced spectroscopic technique, which could be used for the molecular mass determination of large molecules and complex mixtures with a wide molecular weight distribution in synthetic and natural macromolecules.<sup>30</sup> The *m/z* in the MS spectrogram could be recognized corresponding to the absolute molecular mass of the analyte.

In this work, the molecular weight determination of products in the reaction mixture were carried out and mass spectra are represented. As seen from Figure 2, the molecular mass distribution in the reaction mixture catalyzed by Raney Ni covers a molecular weight range from *m/z* of approximately 200 to 600, which was larger than that catalyzed by H-USY and

Ni. The molecular weight distribution of products in the ethyl acetate extracts derived from degradation products catalyzed by H-USY and Ni was mainly concentrated in *m/z* ca. 100–200, which corresponds to the molecular mass of substituted monomeric phenols. This indicates that the depolymerization degree of the oily fraction catalyzed by mixed catalysts was more complete compared to those catalyzed by a single catalyst.

Song et al. concluded that lignin was first fragmented into smaller lignin species in the alcohol medium over a nickel-based catalyst, and the presence of gaseous H<sub>2</sub> had no effect on the lignin conversion.<sup>23</sup> This could also be approved by our experimental results; that is, a hydrogen atmosphere was found to have negligible-impact monophenol production during lignin depolymerization (entries 2 and 3 in Table 1). However, a certain proportion of *in-situ*-produced hydrogen was detected by GC analysis (Table 3), which was probably formed via

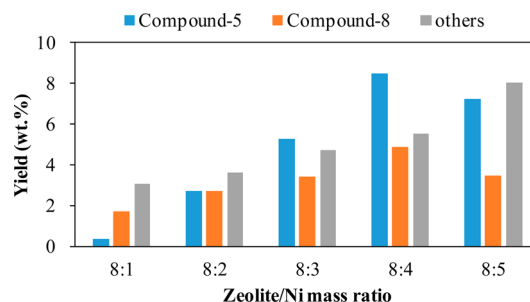
methanol reforming because the reaction was conducted under a nitrogen atmosphere initially. When the reaction was performed with ethanol as the solvent, which was hard to generate hydrogen, the yield of monophenols decreased from 25.4 to 13.5 wt % and the improvement of adding extra hydrogen is not obvious, suggesting the better activity of *in-situ*-generated hydrogen species in the case of lignin depolymerization without regard to differences of solvent effects. Recently, Ford and co-workers reported that lignin and even lignocellulose could be disassembled into organic liquids by a single step in methanol medium. The reducing equivalents for these transformations are derived by the reforming of MeOH to *in-situ*-producing hydrogen.<sup>18,31,32</sup>

**3.2. Effect of Zeolites and/or Raney Ni Catalysts.** Inspired by previous studies,<sup>15</sup> H-USY was prepared to catalyze the depolymerization of cellulosytic enzyme lignin. However, a low catalyst activity was found for the depolymerization of this type of lignin into monomers with a total yield of 2.9 wt %. While Raney Ni was added to the above-mentioned reaction system, the yield of phenolic products was markedly increased. In this paper, Raney Ni and/or various zeolite catalysts were screened for their performances (Table 2). The main products obtained in the presence of zeolites and Ni catalysts were verified to be compounds 1–8. It can be seen that the yield of monophenols was increased from 12.9 wt % (catalyzed by Ni only) to 21.0–27.9 wt % (catalyzed by Ni and zeolites); in contrast, the monophenol yield was less than 5 wt % when representative zeolite catalysts were used alone (Table 2). One can thus infer that Raney Ni and acidic zeolite bicomponent catalysts had distinctly synergetically catalytic effects for the degradation of cellulosytic enzyme lignin. During the reaction catalyzed by these bicomponent catalysts, it is assumed that Raney Ni acted as the lignin-cracking and methanol-reforming catalyst and zeolite acted as the Brønsted and/or Lewis solid acid for acidic ether solvolysis and dehydration.

In contrast to the USY zeolite, the catalytic performance of H-form USY was slightly different. The lower activity of supported  $\text{SO}_4^{2-}$ /USY may be attributed to its excessive acid sites that led to the yield of phenolic products dropping to 21.0 wt %, the lowest of bicomponent catalysts. The work by Toledano et al. has also shown that acid could be applied as a capping agent to avoid repolymerization of some active fragments, which seemed prone to form char at the expense of the yields of oil monomeric compounds.<sup>33</sup>

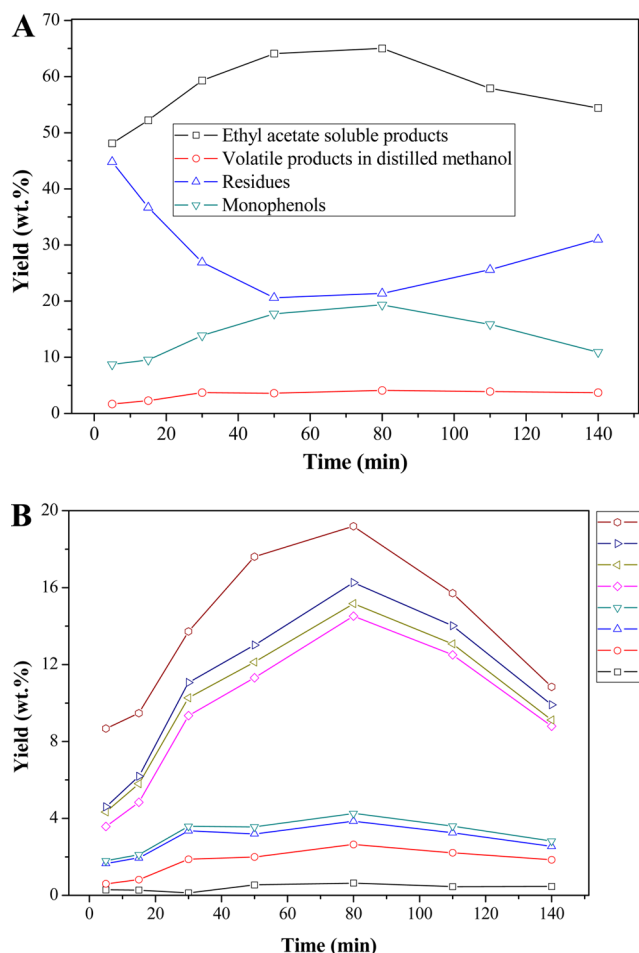
**3.3. Effect of the Zeolite/Ni Ratio.** As seen from Table 2, both zeolites and Raney Ni were found to be active for the depolymerization of lignin. Still, a suitable proportion of acid strength or acid amount to metal Ni was required for better catalytic performances. Figure 3 showed the effect of the zeolite (H-USY)/Ni ratio on the yield of phenolic monomers and the distributions of main products at 523 K. With the ratio H-USY/Raney Ni decreased from 8:1 to 8:4 by weight, the yield of total monophenolic products increased from 5.1 to 18.9 wt %. Nevertheless, when the ratio was decreased to 8:5, yields of total phenolic monomers did not rise and main compounds, such as 5 and 8, even declined to some extent. The cracking reaction was enhanced with increasing the proportion of Ni, thus forming more radical fragments without enough acid sites to block further side reactions, which can degrade further into gaseous products or polymerize to form larger oligomers; in return, the monomer fraction of the oil was decreased.

**3.4. Effect of the Reaction Parameters on the Composition of the Products.** When zeolite H $\beta$  and



**Figure 3.** Effect of the zeolite/Ni ratio on the yield of phenolic monomers and the distributions of main products. Reaction conditions: 0.5 g of lignin, 0.5 g of H-USY,  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  (1:5, v/v), 1 atm  $\text{N}_2$ , 523 K, 500 rpm, and 30 min.

Raney Ni bicomponent catalysts were employed in the study, the influence of the reaction time on the yield of phenolic monomers and the distribution of main products was investigated at 523 K (Figure 4), and the results showed that the reaction time had significant effects on the yields of monophenolic products. The yields of phenolic monomers increased from 8.7 to 19.2 wt % when the reaction time was extended from 5 to 80 min. A longer reaction time was also expected to enhance selectivity toward monomeric phenols.<sup>20</sup>

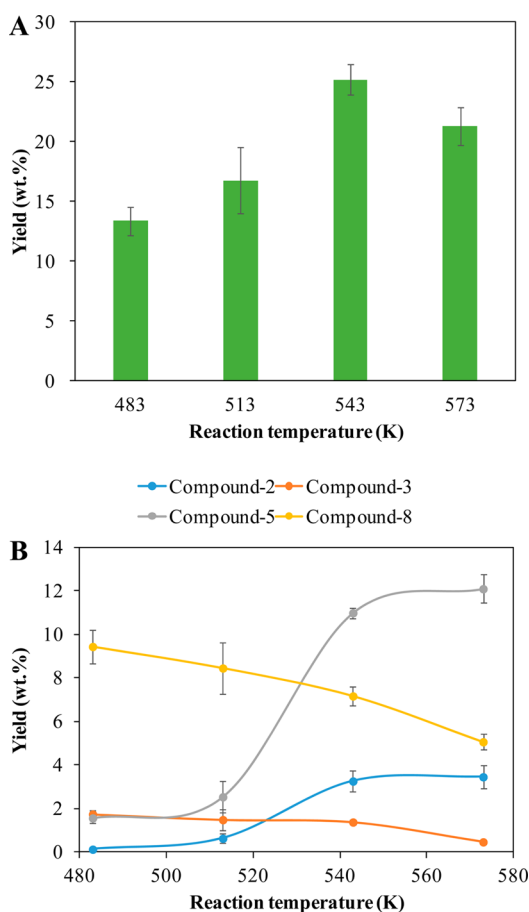


**Figure 4.** Effects of the reaction time on the yield of bio-oil and monophenolic product distribution. Reaction conditions: 0.5 g of lignin, 0.5 g of H $\beta$ , 0.5 mL of Raney Ni,  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  (1:5, v/v), 1 atm  $\text{N}_2$ , 523 K, and 500 rpm.



However, increasing the reaction time from 80 to 140 min resulted in a decline of the yields of monomeric phenols from 19.2 to 10.8 wt %. When the blank experiment was performed without lignin, the growth curve of the system pressure over time was similar to the experiment with lignin depolymerization. The increase of the reaction system pressure could be due to generated gas derived from decomposition of methanol. As shown in Figure 4A with increasing the reaction time, yields of ethyl-acetate-soluble products present first an increasing trend and then a decreasing trend, which is in line with the trend of the monomer yield yet opposed to the yield of residues. It can be inferred that lignin undergoes repolymerization after a long time reaction, leading to more hardly extractable lignin of high molecular weight, and therefore, the yield of monophenols was reduced.

To evaluate the effect of the temperature on the catalytic activity, reactions were performed from 483 to 573 K with MOR zeolite as the catalyst. As seen from Figure 5A, the yields



**Figure 5.** Effects of the reaction temperature on the yield of phenolic monomers (above) and the distributions of main products (below). Reaction conditions: 0.5 g of lignin, 0.5 g of MOR, 0.5 mL of Raney Ni,  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  (2:5, v/v), 1 atm  $\text{N}_2$ , 500 rpm, and 30 min.

of phenolic monomers were enhanced from 13.6 wt % at 483 K until an optimum temperature of 543 K, wherein a yield of 25.2 wt % was obtained. Nevertheless, a further increase of the temperature to 573 K rendered a yield of 21.3 wt %.

Effect of the reaction temperature on the distribution of main products was also investigated, and the result is shown in Figure 5B. The concentration of compound 2 increased from 0.1 wt % at 482 K to 3.5 wt % at 573 K, while compound 3 decreased

from 1.7 to 0.5 wt % under the same conditions. This result might ascribe that a higher temperature is favorable to catalytic hydrogenation of the double bond of compound 3, corresponding to the phenomenon that a volume of hydrogen was detected in the gaseous phase. In comparison to the variation of the hydrogen concentration catalyzed by Ni only in the experiment, a higher hydrogen consumption was found when MOR zeolite was added or when the reaction temperature was increased (Table 3).

A similar trend could also be observed in Figure 5B for the concentration of compounds 5 and 8 when a varied temperature was exerted. A relatively low temperature is favorable to produce compound 8. However, when the reaction temperature was higher, the yield of compound 5 increased noticeably, while the yield of compound 8 declined. In light of the structure of compounds 5 and 8, it was inferred that compound 8 might be the precursor of compound 5. However, it was more likely that compound 8 was subjected to oxidized cracking of the terminal double bond to carboxyl rather than via the hydrogenation process, as in compound 3. Additionally, Table 3 shows that a certain amount of oxygen was produced during the reaction, and it is determined unlikely to be impurity based on repeated experiments, although figuring out the sources of oxygen is difficult.

**3.5. Recycling Test of Catalysts.** In view of the evaluation of the lifetime of zeolites and Ni bicomponent catalysts, USY zeolite combined with Raney Ni catalysts were subjected to repeated use. In a typical procedure, the solid catalysts were centrifuged and separated from the mixture of the reaction products, and the recycled catalysts were then reused without any additional treatment. As seen from Figure 6, the activity of the catalyst was decreased drastically with increasing cycles of reuse. After the fifth run, the yields of phenolic monomers were almost equal to that catalyzed by Ni alone under the identical reaction conditions. Activity of the reused USY combined Raney Ni catalysts were found to drop by ca. 66 wt % of the initial activity after 7 recycles, indicating that the catalysts were unstable in subsequent reactions. Even if these catalysts were regenerated by refluxing with tetrahydrofuran (THF) several times, the activity of catalysts did not recovered distinctly.

To gain more insight into the catalyst deactivation, the surface area of the catalysts was measured (see Table S6 of the Supporting Information) and FTIR spectra of the catalysts were also recorded (see Figure S7 of the Supporting Information). It can be seen from Figure S7 of the Supporting Information, absorption peaks around 1600 and 1450  $\text{cm}^{-1}$ , the characteristic peaks of lignin and lignin-derived fractions, were both observed in the spent and regenerated catalysts. The peak at about 2920  $\text{cm}^{-1}$ , representative of the stretching vibration of C–H, was also observed in the spectra. Thus, the deactivation should mainly be attributed to the fouling of the active component by lignin-derived oligomers or carbon residues, which, in turn, resulted in noticeable declination of the specific active surface area of the catalysts (see Table S6 of the Supporting Information). Mikkola and Salmi<sup>34</sup> also proposed that one of the reasons of deactivation for the Raney Ni catalyst might be attributed to adsorbed organic residues during the hydrogenation process of xylose to xylitol. Because there was little oxygen existing in the gaseous mixture of the products, the surface oxidation of elemental Ni might happen, which could also lead to the deactivation of the catalytic activity.

Table 3. Concentrations (% v/v) of Components in Gaseous Products<sup>a</sup>

	MOR and Ni (%)	MOR and Ni (%) <sup>b</sup>	Ni only (%)	MOR only (%) <sup>c</sup>	blank (%) <sup>c</sup>
H <sub>2</sub>	29.7	15.1	33.1		
O <sub>2</sub>	1.0	7.8	2.0	0.2	0.1
N <sub>2</sub>	28.6	30.6	25.0	94.7	95.9
CO	1.0	1.4	9.1		
CH <sub>4</sub>	26.3	27.9	15.0		
CO <sub>2</sub>	6.0	7.5	5.0	0.7	0.2
unidentified	7.3	9.7	10.8	4.4	3.8

<sup>a</sup>Reaction conditions: 0.5 g of lignin, H<sub>2</sub>O/CH<sub>3</sub>OH (2:5, v/v), 1 atm N<sub>2</sub>, 513 K, 500 rpm, and 30 min. <sup>b</sup>Reaction was performed at 543 K, and other conditions were equal. <sup>c</sup>Reaction was performed with 1 MPa N<sub>2</sub>, and other conditions were equal.

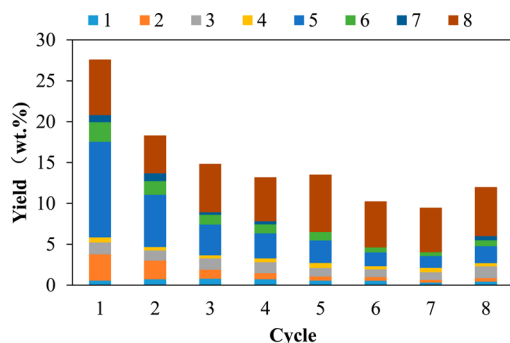


Figure 6. Recycling of the catalysts in the degradation of lignin to phenolic monomers. Reaction conditions: 0.5 g of lignin, 0.5 g of USY, 0.5 mL of Raney Ni, H<sub>2</sub>O/CH<sub>3</sub>OH (2:5, v/v), 1 atm N<sub>2</sub>, 500 rpm, 543 K, and 30 min. The catalysts used in the eighth cycle were regenerated by refluxing with THF.

#### 4. CONCLUSION

It was demonstrated that cellulolytic enzyme lignin could be efficiently converted to value-added monomeric phenols over Raney Ni and zeolite bicomponent catalysts. The yield of monophenols was increased from 12.9 wt % when catalyzed by Raney Ni only to 21.0–27.9 wt % when catalyzed by Ni and acidic zeolite bicomponent catalysts. In contrast, the monophenol yield was less than 5% when zeolite catalysts were exerted alone in the experiment. The MALDI–TOF spectrum indicated that the macromolecule of lignin was well-depolymerized into small fragments. It is proven that zeolites play an important role in promoting Raney-Ni-catalyzed lignin depolymerization. On the basis of our experiments and other research results, we concluded that (i) the catalytic activity of a fully heterogeneous catalyst combination for the depolymerization of cellulolytic enzyme lignin was proven to be superior to that of either component alone, which was attributed to the synergetic effect of acidic zeolites and Raney Ni catalyst; (ii) the acidic zeolite could contribute to the formation of carbonium ions, and a mechanism of depolymerization/repolymerization of the lignin via carbonium ions catalyzed by acids has been reported; (iii) the proper proportion and acid strength of zeolite was necessary for better synergetic effects combined with Raney Ni; and (iv) the zeolite could possibly act as a blocking agent to prevent reaction between unstable lignin fragments and original lignin to produce undesired polymers with higher molecular weight. However, in view of the severe deactivation of the catalysts observed in the present experiment, further studies should be focused on the exploration of deactivation mechanisms of the recycled catalysts and development of novel catalysts with higher stability.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Origin of the lignin used in this study and its differences and additional graphs illustrating the described results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### ■ AUTHOR INFORMATION

##### Corresponding Authors

\*Telephone/Fax: +86-592-2880701. E-mail: [xianhai.zeng@xmu.edu.cn](mailto:xianhai.zeng@xmu.edu.cn).

\*Telephone/Fax: +86-592-2880702. E-mail: [lulin@xmu.edu.cn](mailto:lulin@xmu.edu.cn).

##### Notes

The authors declare no competing financial interest.

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