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# Chemodivergent Hydrogenolysis of Eucalyptus Lignin with Ni@ZIF-8 Catalyst

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Reductive catalytic fractionation (RCF) of lignocellulosic biomass, that is, depolymerization of native lignin component into well-defined monomeric phenols in the first step, offers an opportunity to utilize entire biomass components. Herein, we report that Ni@ZIF-8 can serve as a chemodivergent catalyst in RCF of eucalyptus sawdust, thus selectively producing phenolic compounds having either propyl or propanol end-chain under different reaction conditions. In both cases, high yields of lignin monomers and high degree of delignification were achieved, next to well-preserved carbohydrate pulp suitable for further processing. Mechanistic study by using model compounds indicated that the dehydroxylation at  $\gamma$ -position of  $\beta$ -O-4 structure may be involved in selectivity-controlling step.

#### Introduction

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Lignocellulosic biomass represents the most abundant renewable carbon sources and is recognized as the most sustainable alternative to fossil resources.<sup>1-2</sup> In particular, lignin is a major component in lignocellulosic biomass,<sup>3</sup> as its distinctive aromatic backbone makes this biopolymer become a unique feedstock for low-molecular-weight aromatic chemicals.<sup>4-10</sup> However, current pretreatment technologies for biorefineries (such as Kraft and soda processes) are geared towards optimal carbohydrates (cellulose and hemicellulose) valorization,<sup>11,12</sup> which evokes the irreversible condensation of native lignin to form refractory C–C bonds at expense of reactive  $\beta$ -O-4 linkages.<sup>13</sup> The formed biorefinery lignin is more difficult to be transformed compared to the native biopolymer, and it is always treated as either a wasted product or a cheap energy source for incineration.<sup>4</sup>

The lignin-first biomass fractionation, wherein the catalytic fragmentation of native lignin in lignocellulosic matrix occurred preferentially with preservation of solid carbohydrate pulp suitable for further processing, provided a straightforward and efficient paradigm for sequent utilization of total biomass components.<sup>7,8</sup> Such processes usually utilized a heterogeneous metal catalyst, *i.e.* Ru,<sup>14-16</sup> Pd,<sup>17-22</sup> Ni,<sup>23-31</sup> Cu<sup>32</sup> and Mo,<sup>33,34</sup> aiming to cleave the C–O bonds of  $\beta$ -O-4 units to produce monomeric phenols bearing an end-chain. Given that the phenolic monomers act as platform molecules for

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PdZn/C<sup>19</sup> gave 4-n-propyl guaiacol/syringol, in contrast to Pd/C<sup>15</sup> catalyst, by which 4-n-propanol guaiacol/syringol were obtained preferably under similar conditions. In the case of Nibased catalysts, the introduction of a Lewis acid center such as iron oxide could shift the selectivity from 4-n-propanol phenols to 4-n-propyl phenols.<sup>27,30</sup> Lignin-derived monomers having a propenyl substituent, were also realized by Pd/C-catalysed transfer hydrogenolysis of lignocelluloses.<sup>17</sup> An organocatalyst,  $B(C_6F_5)_3$  resulted in 4-propyl and 4-silyloxypropyl substituted aromatics using hydrosilanes as reductants.<sup>40</sup> Recently, a solar energy-driven lignin-first approach for the depolymerization of native lignin was reported, where cadmium sulfide quantum dots served as an efficient catalyst and syringyl- and guaiacylderived ketones were generated as the major monomers.<sup>41</sup> From a practical standpoint, a catalytic system which can diverges to different kind monomers, that is, the producing of responsive monomeric phenols with a different functionalized end-chain through varying conditions in a controllable and selective version, and allowing for the remaining carbohydrate

aromatics and other chemicals,<sup>9,34-39</sup> the generation

monomeric phenols from lignin depolymerization in a chemoselectivity-controllable manner, therefore, is great of

interest and importance. Generally, the depolymerization of

lignin is considered as a catalyst-dependent process. In

reductive catalytic fractionation (RCF) of woody sawdust

processes, late transition metal catalysts such as Ru/C<sup>14,15</sup> or

component would be ideal. A recent study by Sels and coworkers described that the chemoselectivity of Ru/C-catalysed RCF of eucalyptus can be modulated by hydrogen pressure when *n*-butanol/water was used as a medium.<sup>16</sup> Porous metal-organic frameworks (MOFs) have become a promising functional catalysts support due to their

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Figure 1. Schematic representation of lignin and typical monomeric phenols structures from lignin-first biomass fractionation.

high porosity, large surface area and synergistic catalysis effects.<sup>42,43</sup> Among which, the ZIF-8 framework (Zn(MeIM)<sub>2</sub>, MeIM = 2-methylimidazole) features an large surface area and high chemical and thermal resistance (over 500 °C),<sup>43</sup> and the transition metals immobilized on ZIF-8 (metals@ZIF-8) have showed excellent catalytic activity for hydrogenation,44,45 aminocarbonylation<sup>46</sup>, hydrolysis of ammonia borane<sup>47,48</sup> and hydrocracking of Jatropha oil.49 Since the introduction of second metal center (for an examples, see Pd/C<sup>15</sup> vs PdZn/C<sup>19</sup> and  $Ni/C^{30}$  vs NiFe/C<sup>27</sup>) can modulate the chemoselectivity in lignin hydrogenolysis evidently, we envision that ZIF-8 containing Zn atoms may regulate the selectivity. Herein, we report that a Ni nanoparticles (NPs) supported on ZIF-8 (Ni@ZIF-8), can serve as a chemodivergent catalyst for hydrogenolysis of the native lignin in eucalyptus tree via lignin first concept, thus resulting in 4-n-propyl phenols or 4-npropanol phenols in a selective manner, respectively, by switching the reaction conditions. Substantiated by experimental evidences from model compound reactions, the possible reaction pathways leading to 4-propyl- and 4propanol phenols are also rationalized.

#### **Results and discussion**

The Ni@ZIF-8 catalyst was prepared according to previous report by using  $(C_5H_5)_2$ Ni and ZIF-8 as precursors *via* chemical liquid deposition method and subsequent reduction process.<sup>47</sup> The specific surface area (BET, 579 m<sup>2</sup> g<sup>-1</sup>) and pore volume



Figure 2. TEM images of Ni@ZIF-8. Scale bars in panel b and c were redrawn according to the magnification.

(0.31 cm<sup>3</sup> g<sup>-1</sup>) of Ni@ZIF-8 were both decreased after the immobilization of nickel on ZIF-8 (1450 m<sup>2</sup> g<sup>-1</sup> and 0.67 cm<sup>3</sup>g<sup>-1</sup>). The weight percentage of nickel element was estimated about 14 wt % according to ICP-AES analysis (Table S1). Powder X-ray diffraction (XRD) patterns of Ni@ZIF-8 demonstrated that the main diffractions were well in line with those of pristine ZIF-8, suggesting that the framework of ZIF-8 was maintained well in catalyst preparation process. No visible diffraction of Ni was detected in XRD patterns, probably due to Ni NPs are distributed on ZIF-8 in a small size version (Figure S1). TEM images in Figure 1 show that Ni NPs are dispersed on ZIF-8 as either nanocrystallites with 0.22 nm lattice spacing or cluster-type composed by 0.2 nm small particles (see also Figure S2). The TEM results are in good agreement with XRD observations that ZIF-8 can control the Ni NPs into small sizes.

To identify the reactivity and selectivity of the  $\beta$ -O-4 linkage of lignin, we first performed the decomposition reactions of model compound 1 in the presence of Ni@ZIF-8 (20 wt%) (Scheme 1). At 200 °C and 220 °C, Ni@ZIF-8-catalysed decomposition of 1 within 8 h proceeded through C-O bond cleavage, resulting in 4-n-propylguaiacol (G3) as major product in 37% and 44% yields, respectively. 4-n-Propylsyringol (G2) was also generated. Raising the reaction temperature to 240 °C gave G2 (28%) and G3 (24%) with almost equal selectivity. We then performed this reaction under a higher reaction temperature (260 °C), from which G2 was obtained as the major product (38%) in 8 h, together with the observation of G3 (12%) and guaiacol (68%). Prolonging the reaction time to 12 h at 260 °C led to the improvement of G2 to 44% (Scheme 1, eq 1). Obviously, the chemoselectivity can be tuned by the reaction conditions over Ni@ZIF-8 catalyst, and harsh conditions are propitious to the formation of a propyl endchain via dehydroxylation at γ-position. Performing this reaction under N<sub>2</sub> atmosphere (1 atm) at 200 °C for 8 h also led to C-O bond cleavage of compound 1. In addition to G2 (4.5%) and G3 (7%), guaiacol derivatives bearing a unsaturated end-chain, such as 4-propenylguaiacol G4 (12%), coniferyl alcohol G5 (6%) and 4-(3-methoxypropenyl)guaiacol G6 (6%)

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Scheme 1. Chemodivergent decomposition of  $\beta$ -O-4 model compounds with Ni@ZIF-8.

were all generated (Scheme 1, eq 2). Independent testing of 1 with Ni@ZIF-8 at a low reaction temperature (160 °C) in 3 h resulted in the only observation of unsaturated phenols **G4**, **G5** and **G6**, albeit in low yield (Figure S6). Therefore, it was supposed that these unsaturated phenols are the possible intermediates, which would be hydrogenated into **G2** and **G3** over Ni@ZIF-8.

In the case of  $\alpha$ -methoxylated model compound **7**, a possible intermediate generated from the nucleophilic substitution of **1** with MeOH,<sup>26,30</sup> the reactions occurred in a fashion akin to those of compound **1**, that is, the principally formation of **G3** with a propanol end-chain under the milder conditions (220 °C, 3 h, 43%) and **G2** with a propyl end-chain under the harsher conditions (260 °C, 8 h, 23%) (Scheme 1, eq 3). These results implied that **7** may be involved in the decomposition reaction of **1**.<sup>26</sup>

An isotope-labeled  $\beta$ -O-4 mimic **1-D2** was also treated with Ni@ZIF-8 at 240 °C for 8 h, from which both propyl- and propanol-substituted phenols were generated (scheme 2). Evidences from <sup>1</sup>H NMR spectrum and mass analysis confirmed that deuterium is still retained well at  $\alpha$  and  $\beta$  positions in **G2-D2** and **G3-D2** (Figures S9-11). This result indicated that the reaction pathways, such as enol ether generated from  $\alpha$ , $\beta$ -dehydration reaction<sup>35,39</sup> or C<sub> $\alpha$ </sub> carbonyl compound generated *via* dehydrogenation<sup>32</sup> or hydrogenolysis of C<sub>B</sub>-O followed by



Scheme 2. Ni@ZIF-8-catalysed decomposition of deuterated  $\beta$ -O-4 mimic.



Scheme 3. The reactivity of mono and dimeric phenols over Ni@ZIF-8.

dehydration,<sup>23,50</sup> are not viable route to **G2-D2** and **G3-D2** under current catalytic system, because  $\alpha$ -D or  $\beta$ -D would be lost there. Generally, the monolignol such as coniferyl alcohol **G5** is expected to be formed initially in hydrogenolysis of  $\beta$ -O-4 motifs.<sup>21,26</sup> Thereby, homolytic pathway, which starts from the phenolic OH group on  $\beta$ -O-4 structure and undergoes a quinone radical specie,<sup>21</sup> accords with the deuterated experiment. Alternatively, **G5** could also be formed *via* a concerted hydrogenolysis of C<sub> $\alpha$ </sub>-OH (or C<sub> $\alpha$ </sub>-OMe) and C<sub> $\beta$ </sub>-O bonds, wherein the free phenolic group is not necessary.

To assess the process of dehydroxylation at y-position, a key step leading to the formation of 4-n-propylguaiacol G2, we examined the reactivity of monophenols by Ni@ZIF-8 (Scheme 3). On the treatment of Ni@ZIF-8 at 260 °C for 8 h, monolignols G5 and S5 primarily underwent hydrogenation of C=C bond to form G3 (58%) and S3 (65%), respectively, rather than dehydroxylation reaction (and subsequent hydrogenation reaction) to form compounds G2 (6%) and S2 (3%). Other phenolic compounds having ethyl and 3-methoxypropyl groups were also observed (Figure S12). In case of the treatment of G3 and S3 with Ni@ZIF-8, no detectable reactions were observed (Figure S12). These results encourage us to explore the possibility of that the dehydroxylation reaction could take place at the dimeric stage. We then examined the cleavage of a model compound 8 without y-OH group. As shown in Scheme 3, the fragmentation of 8 in the presence of Ni@ZIF-8 furnished G2 and guaiacol in 66% and 72% yields, respectively. Observation of  $\alpha$ -methoxylated-8 (mass: 318 g mol<sup>-1</sup>) by GC-MS in decomposition of 1 as well as RCF of eucalyptus sawdust (vide infra) suggested that the dehydroxylation at y-position of  $\beta$ -O-4 structure may also be involved in the generation of compound G2 (Figures S16 and S17). It has been reported that the Lewis acid center, e.g., Zn<sup>19</sup> and Fe,<sup>27</sup> can promote the dehydroxylation at y-position in depolymerization of lignin and model compounds. Thereby, it was conceived that the Zn atoms in ZIF-8 may assist the hydrogenolysis of primary alcohol, especially at high reaction temperature.

Given the success of the Ni@ZIF-8 catalyst, it was examined on a synthetic lignin polymer with  $M_w$  as 3200 g mol<sup>-1</sup>, which was composed exclusively of guaiacyl unit linked by the  $\beta$ -O-4 substructures.<sup>51</sup> On the treatment of Ni@ZIF-8 under H<sub>2</sub> in MeOH, this polymer was cleaved and hydrogenolyzed into phenolic monomers. As the aforementioned dimer, the

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Figure 3. Ni@ZIF-8-catalysed chemodivergent hydrogenolysis of polymeric lignin model.

chemoselectivity can be controlled by the reaction temperature and time. The mild conditions (220 °C, 8 h) afforded total 44 % monomers with 71% selectivity toward **G3**; the harsh conditions (260 °C, 12 h) gave **G2** as the major product (23% yield, 63% selectivity) (Figure 3, see also Figure S13).

Having established conditions for the cleavage of dimeric and polymeric compounds that model the  $\beta$ -O-4 linkages of lignin, we investigated the direct hydrogenolysis of lignocellulosic biomass with Ni@ZIF-8 (20 wt%) in MeOH. Eucalyptus, a representational fast growing forest tree species, which consists of 24 wt% of Klason lignin, 42 wt% cellulose and 17 wt% hemicellulose (Table S3), was chosen as a substrate. The yield and chemoselectivity of phenolic monomers as well as the degree of delignification were all influenced by reaction conditions (Figure 4). At 220 °C and 3 MPa H<sub>2</sub> within 4 h, the treatment of eucalyptus sawdust (particle size ca. 0.5-1 mm) afforded a soluble fraction containing the majority of the lignin derived mass and an insoluble fraction containing the carbohydrate pulp and Ni@ZIF-8 catalyst. Evaporation of the MeOH and extraction with CH<sub>2</sub>Cl<sub>2</sub> of the soluble fraction afforded an oily product, from which the degree of delignification was estimated as 66% based on the Klason lignin weight.<sup>14</sup> The identification and quantification of lignin monomers in the soluble fraction were assessed on GC and GC-MS by comparison with authentic samples. The detailed distribution of phenolic monomers is depicted in Table S6 and Figure S15. Overall, more than 32 wt% of klason lignin was converted into well-defined monomeric phenols. Propanolsubstituted phenols, such as G3 (5.2 wt%) and S3 (10.4 wt%), were identified as the major depolymerized products compared with the monomers having a propyl end-chain G2 (2.3 wt%) and S2 (5.2 wt%). The S:G monomers ratio (2.2:1) is very similar to the syringyl/guaiacyl ratio of eucalyptus wood lignin.<sup>52</sup> Performing the reaction under N<sub>2</sub> atmosphere (1 atm) led to the decreasing of both total monomers yield (20.8 wt%) and the degree of delignification (46%), indicating the critical role of H<sub>2</sub> under Ni@ZIF-8 catalytic system. Further investigations by employing a range of H<sub>2</sub> pressures implied that 3 MPa is sufficient to reach the yield plateau, and to avoid shortness of H<sub>2</sub>.



Figure 4. Reductive catalytic fractionation of eucalyptus sawdust with Ni@ZIF-8.

The hydrogenolysis of eucalyptus sawdust was carried out under a series of reaction temperature with Ni@ZIF-8 (Figure 4). Decreasing the temperature to 160 °C led to significant drops of the delignification degree (15%) and the monomers yield (6.6 wt%). The observation of few compounds 2 is in consistent with the conclusion drawn from the model compounds, that is, the formation of 4-propyl phenols is a thermo-favored process. Thereby, we examined the experiments by raising the reaction temperature and prolonging time. As a result, the amount of total monomers, the selectivity to compounds 2, and the delignification degree were all improved. For example, the hydrogenolysis reaction carried out at 260 °C within 8 h gave 95% degree of delignification, 44.3 wt% yield of combined monomers and 55% selectivity to compounds G2 and S2. Other phenolic products, such as 4-ethyl-(1.2 wt%) and 4-(3-methoxypropyl)-substituted phenols (3.5 wt%), which were probably produced from Ni@ZIF-catalysed dehydroxymethylation and esterification of monolignols 6, respectively, were also detected. Prolonging the reaction time to 12 h at 260 °C led to slight decreasing of monomers yield (36.3 wt%), probably because of the recondensation of resulted products.<sup>33</sup>

To improve the selectivity towards **3** together with high total monomers yield, monitoring the resulting monomeric phenols as a

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Figure 5. Time profile of Reductive catalytic fractionation of eucalyptus sawdust with Ni@ZIF-8 at 220  $^{\circ}$ C.



**Figure 6**. Comparing of lignin oils generated from Ni@ZIF-8-catalysed hydrogenolysis of eucalyptus sawdust at 220 °C, 12 h (red line) and 260 °C, 8 h (blue line). (a) Gas chromatogram. (b) Molecular weight distribution.

function of time was obtained at 220 °C and 3 MPa H<sub>2</sub> (Figure 5). Within 12 h, the phenolic monomers were generated steadily over time to reach a 42 wt% combined yield, which is close to the expected theoretical maximum monomer yield of native eucalyptus lignin. The formation of propanol-substituted phenols **3** is correlated with reaction time in a linear fashion, finally to afford **G3** and **S3** in 29.6 wt% yield with a high selectivity of 80%. The stable state concentration of propyl-substituted phenols **2** in the course implied that the generation of **2** is suppressed under such reaction temperature. This scenario is in line with the observation in experiments of dimeric and polymeric model compounds. Under such conditions, the 89% degree of delignification suggested most lignin component in eucalyptus sawdust has been solubilized into MeOH *via* depolymerization.

Other alcoholic solvents, *e.g.*, EtOH and <sup>*i*</sup>PrOH, were also examined at 220 °C and 12 h (Table S5 and Figure S14). The total yield of monomers (32.7 wt% and 30.4 wt%, respectively) and the degree of delignification (80% and 78%, respectively) from EtOH and <sup>*i*</sup>PrOH were both declined by comparison with those from MeOH (42 wt% and 86%), while the selectivity towards **G3** and **S3** still remained high. Obviously, the more polar solvent (such as MeOH)<sup>53</sup> can not only enhance the delignification through penetrating lignocellulosic matrix and extraction the lignin, but also promote the fragmentation of the lignin oligomers to monomeric phenols.<sup>54</sup>

In sum, the optimized conditions for Ni@ZIF-8-catalysed direct hydrogenolysis of eucalyptus sawdust in MeOH, which can convert lignin component into 4-propylphenols **2** and 4-propanolphenols **3**, were established as 220 °C, 12 h and 260 °C, 8 h, respectively. Besides GC (Figure 6a), the evidence from gel permeation chromatography (GPC) analysis also substantiated the difference in selectivity (Figure 6b). The largest peak for compounds **2** (blue line)



Figure 7. 2D HSQC NMR spectra of lignin oils obtained from (a) 220 °C, 12 h and (b) 260 °C, 8 h.

showed a longer retention time compared to **3** (red line), in accord with their smaller molecular structure.<sup>15</sup>

A detailed analysis of the cleavage of lignin linkages and product distribution was gained by two-dimensional HSQC NMR spectroscopy (Figure 7). All signals of monomeric phenols were assigned based on the comparison with authentic samples. In both cases, the cross signals for lignin linkages, such as  $\beta$ -aryl ether ( $\beta$ -O-4, A), phenylcoumaran ( $\beta$ -5, B) and resinol ( $\beta$ - $\beta$ , C), almost completely disappeared. At the side chain region, the signals of  $\delta_{\rm C}/\delta_{\rm H}$  = 31.7/2.50, 34.8/1.70 and 61.0/3.43 ppm were ascribed to propanol chain in 3 (labeled in red), and the cross peaks corresponded to 4-propylphenols **2** were found at  $\delta_{\rm C}/\delta_{\rm H} = 37.9/2.44$ , 24.8/1.55 and 14.1/0.87 ppm (labeled in blue). The cross signals of propanol from 3 dominate in the HSQC spectrum from 220 °C and 8 h (Figure 7a), while the corresponding propyl signals from 2 show stronger intensity than propanol at 260 °C and 12 h (Figure 7b). The difference of product distribution was also illustrated by the comparison of their <sup>13</sup>C NMR spectra (Figure S18), being in line with the HSQC and chromatographic analysis.

The recycling ability of the catalysts is important for their potential applications in industry. In the solid fraction after hydrogenlysis of eucalyptus sawdust, Ni@ZIF-8 can be isolated from carbohydrate pulp by magnetic force. TEM imaging of the spent catalyst revealed that the Ni NPs are still well distributed on ZIF-8 with similar morphology to fresh catalyst (Figure S2c). ICP-AES analysis of spent catalyst implied a 13.5 wt% content of Ni, being slight lower than that of fresh catalyst (14 wt%). The spent catalyst was used directly in the following cycle at 260 °C and 8 h conditions.

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In the 3<sup>st</sup> run, the degree of delignification still remained 90%, and the total lignin monomers yield was determined as 30 wt% with good selectivity to 4-propanolphenols **3** (Table S8).

In the context of a sustainable and economically viable biorefinery, the survivability of (hemi)cellulose components in the solid pulp is important, as they can be valorized *via* downstream processing. We measured the compositions of solid pulp after the after the removal of catalyst (Table S9). Under 220 °C and 12 h conditions, the retentions of cellulose and hemicellulose were determined as 90% and 78%, respectively. In the case of high temperature (260 °C and 8 h), high preservation of cellulose (90%) was obtained, with observation of slight decrease of hemicellulose retention (67%). Obviously, hemicellulose easily undergoes degradation under high-temperature conditions.

#### Conclusions

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In summary, chemodivergent reductive catalytic fractionation of eucalyptus sawdust is demonstrated by using Ni@ZIF-8 catalyst in MeOH. High phenolic monomer yields close to the theoretical maximum were obtained, next to high retentions of cellulose and hemicellulose components. The chemoselectivity of hydrogenolysis of lignin can be tuned by the choice of reaction temperature and time, thus affording 4propanol- and 4-propyl-substituted phenols as major product, respectively. The reactivity study of  $\beta$ -O-4 mimics and corresponding monomeric phenols provided important information for understanding the mechanistic details.

#### **Conflicts of interest**

There are no conflicts to declare.

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Chemodivergent hydrogenolysis of eucalyptus biomass leading to 4-propanol- or 4-propyl-substituted phenols, together with well-preserved carbohydrate component, was achieved by using Ni@ZIF-8 catalyst.

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