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Catalytic ethanolysis of enzymatic hydrolysis lignin over an unsupported nickel catalyst: the effect of reaction conditions

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Abstract: The effect of reaction conditions on ethanolysis of enzymatic hydrolysis lignin (EHL) with the unsupported nickel catalyst, *i.e.* Ni (220H), was investigated. The 2D-HSQC NMR analysis of liquid products revealed that both the ether and C-C linkages in EHL were cleaved during the reaction, and the ether linkages were completely cleaved at mild reaction conditions, while the cleavage of C-C linkages needed harsh reaction conditions. At 280 °C under 2 MPa H₂ within 6 h, the highest aromatic monomer yield of 28.5 wt% was achieved. Further increasing the reaction temperature to 300 °C or decreasing the initial hydrogen pressure to 0 MPa was conducive to the repolymerization reaction. The ortho-alkyl phenol monomers originated from the alkyl free radicals produced from ethanol. Under 0 MPa H₂, the hydrogenation of the -HC=CH- in side chains were inefficient, and hence the decarboxylation and alkenyl elimination reaction of side chains were favorable.

Keywords: Biomass, Enzymatic hydrolysis lignin, Ethanolysis, Unsupported nickel catalyst, Reaction pathway

1. Introduction

Lignocellulose, mainly composed of cellulose, hemicellulose and lignin, is the most abundant form of biomass ¹. Utilizing lignocellulose to produce chemicals and fuels is the second generation (2G) biomass refining technologies, which reduces the reliance on nonrenewable fossil resources, and has been an intensively explored topic in recent years ². Bioethanol is by far the most widely used biofuel for transportation worldwide ³. Production of 2G bioethanol via enzymatic hydrolysis and fermentation of cellulose

and hemicellulose in agricultural wastes, such as corn stalk/cob, has been a promising technology of 2G biofuel, but it leaves the enzymatic hydrolysis lignin (EHL), as a large volume solid waste ^{4,5}. Lignin is generally an amorphous tridimensional polymer which is mainly composed of three aromatic primary units, *i.e.*, sinapyl (S), coniferyl (G), and p-coumaryl (H) alcohols, connected by ether and C-C linkages ⁶. In particular, lignin in corn stalk/cob contains a high content of p-coumaric acid (pCA) and ferulic acid (FA), which are ester-linked and ether-linked to other units ⁶. Due to the aromatic feature, lignin has the great potential to replace fossil feedstocks for producing aromatic chemicals ².

One promising strategy of lignin utilization is the reductive catalytic solvolysis with the existence of hydrogen gas or a hydrogen donor ⁷. Compared with noble-metal catalysts, the catalysts based on earth abundant elements are more favorable due to their low cost. Cu ⁸⁻¹⁰, Mo ¹¹⁻¹⁶ and Ni-based ¹⁷ catalysts have been successfully employed to the depolymerization of lignin into monomers. Although alcohol solvents can serve as hydrogen donors for lignin solvolysis, ¹⁸ H₂, showing a significant role for hindering the repolymerization, is also added into the reaction, especially when using catalysts with high hydrogenation activity, such as Ni catalysts. ^{19,20} Traditional supported Ni catalysts, such as Ni/C ²¹ and Ni/Al₂O₃ ²², have been utilized on the reductive catalytic solvolysis of EHL with H₂, but low monomer yields were obtained. Previously, we prepared a number of unsupported Ni catalysts from nickel formate decomposition ²³. These catalysts showed high activities for the ethanolysis of EHL into aromatic monomers, and, among these catalysts, the Ni (220H) catalyst had the highest yield of aromatic

monomers²³. Nevertheless, the cleavage of various linkages of EHL and the conversion of primary monomers during EHL ethanolysis over Ni catalyst need to be further investigated.

Herein, the effect of reaction conditions on EHL ethanolysis over Ni (220H), including reaction temperature, reaction time and initial hydrogen pressure, were investigated. The liquid products obtained under different reaction conditions were analyzed by 2D-HSQC NMR and FT-IR analysis. Both the ether and C-C linkages in EHL were cleaved during the reaction, and the cleavage of different type linkages under different reaction conditions was discussed in detail. In addition, the pathways of EHL to stable monomers were proposed.

2. Experimental

2.1. Materials

The enzymatic hydrolysis lignin (EHL) was provided by Shandong Long Li biological technology Co., Ltd. It is obtained from the microbial enzymatic hydrolysis process of corncob conversion to ethanol. The EHL contains 91.2 wt% of lignin, 0.12 wt% of residual carbohydrate and 0.59 wt% of ash, determined by NREL method (NREL/TP-510-42618). The weight percentages of C, H, O, N, and S in EHL are 61.29, 6.69, 29.61, 0.98, and 0.01 wt %, respectively, determined by an Elementar system model Vario Micro cube (Elementar). The major inorganic elements of EHL are Cl (0.797 wt %), Na (0.089 wt %), P (0.089 wt %), Fe (0.050 wt %), and Si (0.045 wt %), determined by X-Ray fluorescence spectrometry (Bruker AXS, S4 Pioneer). Before

reaction, EHL was crushed into powders (60-80 meshes), and dried at 100 °C for 12 h.

Nickel formate ($\text{Ni}(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$) was provided by Alfa Aesar. The ethanol (analytical grade) was purchased from Guangfu Inc.

2.2. Catalyst preparation

The Ni (220H) catalyst was prepared from nickel formate decomposition in H_2 ²³. The detailed preparation method and characterization of the catalyst were shown in *Supporting information*. Ni (220H) only contains Ni particles with the average nickel particle size of 53.9 nm.

2.3. Reaction condition

The ethanolysis reaction was carried out in a 300 mL batch reactor (Parr 4566, made of Hastelloy) equipped with a temperature controller (Parr 4848) and a pressure sensor. In a typical run, the batch reactor was loaded with 1.0 g EHL, 0.3 g Ni (220H) catalyst and 60 mL ethanol. It was sealed and purged with N_2 for six times and then purged with H_2 for three times. Afterwards, the reactor was pressurized to the desired pressure with H_2 , and then heated to the prescribed temperature and kept for the prescribed reaction time with a fixed stirring rate of 600 rpm. The reaction time was denoted as 0 h when the prescribed reaction temperature was reached. After the reaction, the solid residue and liquid products was separated by filtration.

2.4. Product analysis

The monomers in liquid products were analyzed qualitatively and quantitatively with GC-MS (Agilent 6890-5973) and GC-FID (Agilent 6890), respectively. The HP-5 MS (30 m $\times$ 0.25 mm $\times$ 0.25 μm) capillary column was used, and the working

conditions for both GCs were exactly same. The GC parameters used for the analysis were: injector temperature 280 °C; detector temperature 300 °C; split ratio 1:50. The oven temperature program was set from an initial temperature of 45 °C to a final temperature of 250 °C at 5 °C/min, and then held at the final temperature for 7 min. For MS detector, 2 min of solvent delay was set, and the mass detector was set to scan from 10 to 500 m/z. The products were identified by comparing their mass spectra with standard mass spectra in the system's database (NIST02). The products were quantified with anisole as an internal standard. The total monomer yield was calculated with the following equation:

$$\text{Total monomer yield (wt\%)} = \frac{m_{\text{monomers}}}{m_{\text{EHL}}} \times 100\%$$

m_{monomers} : The mass of total monomers

m_{EHL} : The mass of EHL put into the reactor

The solvent in liquid products was removed through vacuum evaporation before analyzing with two-dimensional heteronuclear single quantum coherence-nuclear magnetic resonance (2D-HSQC NMR) and Fourier transform infrared spectroscopy (FT-IR). 2D-HSQC NMR spectra of EHL and liquid products were recorded on a Bruker AVANCE III HD 400 MHz. 40 mg EHL or liquid product was dissolved in 0.5 mL of DMSO- d_6 as the deuteration NMR solvent. FT-IR spectra of EHL and liquid products were collected in the transmission mode on a Nexus spectrometer (Thermo Nicolet Co.). The spectra were obtained after 32 scans, and recorded in the region 4000-400 cm^{-1} with a resolution of 4 cm^{-1} . The pellets were prepared by mixing 20 mg of sample in 200 mg KBr.

3. Results

3.1. Effects of reaction condition

3.1.1. The temperature

The effect of the reaction temperature on the total monomer yield and the yields of different sort of monomers was measured under 2 MPa H₂ with the reaction time of 6 h and is illustrated in Fig. 1(a). EHL was completely liquefied without the formation of char in the range of 220-300 °C. As the temperature increased, the total monomer yield increased from 19.8 at 220 °C to 28.5 wt % at 280 °C and then decreased to 26.3 wt% at 300 °C. Monomers containing -HC=CH- in their side chains, *i.e.* para-allyl syringol and un-hydrogenated ferulic/p-coumaric acid ethyl ester, were only detected at 220 °C with the total yield of 2.1 wt%. Both the yields of aromatic esters (Es in table 1) and para-propanol-substituted phenols (Pol) increased from 220 to 260 °C, and then decreased from 260 to 300 °C, reaching the maximum values of 11.3 and 3.3 wt% at 260 °C, respectively. The yield of phenols without side chains (Ph) increased gradually from 0.5 to 1.8 wt% as the temperature increased from 220 to 280 °C, and then decreased to 1.7 wt% as the temperature further increased to 300 °C. The yield of alkyl substituted phenols only containing para-alkyl substituents (PA) also increased and then decreased in the temperature range of 220 to 300 °C, reaching the maximum value of 11.4 wt% at 280 °C. Nevertheless, the yield of alkyl substituted phenols containing ortho-alkyl substituents (OA) increased with the increase of temperature, reaching the maximum value of 1.6 wt% at 300 °C. Especially, OA were not detected at 220 °C.

3.1.2. The reaction time

The effect of the reaction time was examined at 280 °C under 2 MPa H₂, and the result is illustrated in Fig. 1(b). The reaction time 0 h means that the reactor cooled down immediately when it was heated to 280 °C. EHL was already completely liquefied at 0 h, and char was not detected for all the tests. As the reaction time increased from 0 to 6 h, the total monomer yield increased gradually from 20.7 to 28.5 wt% and then remained constant with prolonging the reaction time to 8 h. Meanwhile, monomers containing -HC=CH- in their side chains were not detected during 0 to 8 h. The yields of PA increased as the reaction time increased from 0 to 8 h, reaching the maximal values of 11.6 wt%. The yield of Pol increased from 0 to 4 h, reaching 3.0 wt%, and then slowly decreased during 4 to 8 h. The yield of Es, Ph and OA all increased as the reaction time increased from 0 to 6 h, reaching 11.1 wt%, 1.8 wt% and 0.9 wt%, respectively, and then leveled off with further prolonging the reaction time to 8 h.

3.1.3. The initial hydrogen pressure

The effect of initial hydrogen pressure was monitored at 280 °C with the reaction time of 6 h and is illustrated in Fig. 1(c). Char was only observed at 0 MPa H₂. The Raman spectrum analysis (*Supplement file*, Fig. S2) also verifies that both amorphous and graphitic carbon were formed when the catalyst was used at 0 MPa H₂, and no carbon was formed at 2 MPa H₂. The total monomer yield gradually increased from 22.5 to 28.5 wt% with the increase of the initial hydrogen pressure from 0 to 2 MPa, and remained constant as the initial hydrogen pressure further increased to 3 MPa. Monomers containing -HC=CH- were not detected even at 0 MPa H₂. The yield of Es

increased dramatically from 2.9 to 11.1 wt% as the initial hydrogen pressure increased from 0 to 2 MPa, and then increased slightly to 11.3 wt% with further increase of the initial hydrogen pressure to 3 MPa. From 0 to 3 MPa H₂, the yield of Pol gradually increased from 1.5 to 2.9 wt%, but the yields of Ph and OA gradually decreased from 2.9 to 1.8 wt% and from 3.2 to 0.9 wt%, respectively. The yield of PA was not changed obviously with the change of initial hydrogen pressure, which slightly increased in the 0 to 1 MPa range and then slightly decreased in 1 to 3 MPa range with the maximum value of 11.5 wt%.

3.2. The structural characteristics of EHL and its conversion products

3.2.1. Nuclear magnetic resonance analysis

2D-HSQC NMR spectra of the EHL before reaction and the products after the reaction with Ni (220H) catalyst are illustrated in Fig. 2. The C-H cross signals of structures can be recognized according to published literatures^{8, 21, 24-27}. The spectra exhibit three regions: aliphatic C-H bonds correlation region in which C atoms are not directly connected to O atoms (H-C-C- correlation region, $\delta\text{C}/\delta\text{H}$ 5-50/0-3.5 ppm), aliphatic C-H bonds correlation region in which C atoms are directly connected to O atoms (H-C-O- correlation region, $\delta\text{C}/\delta\text{H}$ 45-95/3-6.0 ppm) and aromatic AC-H bonds correlation region ($\delta\text{C}/\delta\text{H}$ 95-150/6-8.0 ppm).

The spectra of EHL is shown in Fig. 2(a). In the H-C-C- region, only the signal of -CH₃ was recognized. In the H-C-O- region, the strong signals of methoxyls and the structure of β -O-4 aryl ether (A) were recognized²⁴. The signals of the resinol structure (B) which is formed by β - β and α -O- γ linkages and the phenylcoumarane structure (C)

which is formed by β -5 and α -O-4 linkages were also identified ²⁴. In the AC-H region, the signals of syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units were all recognized, and the signals of p-coumaric acid (pCA) and ferulic acid (FA) units were also detected ²⁴.

The spectra of the liquid products obtained after the reaction are shown in Fig. 2(b). In the H-C-C- region, the intensity of the signals of -CH₃ became much stronger than that in EHL. Meanwhile, the C-H cross signal of alkyl side chains, such as C $_{\alpha}$ -H $_{\alpha}$ cross signal of para-methyl (PM $_{\alpha}$), para-ethyl (PE $_{\alpha}$) and para-propyl (PP $_{\alpha}$) were detected ^{8, 21, 25}. The C $_{\alpha}$ -H $_{\alpha}$ and C $_{\beta}$ -H $_{\beta}$ cross signal of ester side chain (Es $_{\alpha}$ and Es $_{\beta}$) and para-propanol side chain (Pol $_{\alpha}$ and Pol $_{\beta}$) were also recognized ^{8, 21, 25}. In the H-C-O- region, the signals of original linkages in EHL all disappeared, and the C $_{\gamma}$ -H $_{\gamma}$ cross signals of Pol (Pol $_{\gamma}$) and Es (Es $_{\gamma}$) were detected ^{8, 25}. The signal of methoxyls was slightly weakened compared with that in EHL. In the AC-H region, Due to the hydrogenation of the -HC=CH- in pCA and FA units, the C-H cross signals of pCA and FA units disappeared, and the signals of hydrogenated p-coumaric/ferulic acid derivatives (H-pCA/H-FA) appeared ²¹. Meanwhile, the C-H cross signal of the depolymerized S unit (S') appeared, and the signal of original S unit in EHL disappeared ²⁶. The signals of depolymerized H and G units were not recognized due to the overlap with the signals of H-pCA and H-FA.

The 2D-HSQC NMR spectra of the liquid products obtained at different reaction temperature under 2 MPa H₂ with the reaction time of 6 h are shown in Fig. 3(a-e). At 220 °C, the C-H cross signals of ether linkages originally existing in EHL already

disappeared, but new C-H cross signals appeared at $\delta\text{C}/\delta\text{H}$ 63.0/3.7-3.3 ppm and $\delta\text{C}/\delta\text{H}$ 46.0/3.0 ppm, corresponding to the $\text{C}_\gamma\text{-H}_\gamma$ and $\text{C}_\beta\text{-H}_\beta$ in a new structure (C') which is formed from the cleavage of ether linkages in structure C and connected via C-C linkages²⁵. With the increase of the reaction temperature, the C-H cross signals of C' structures gradually diminished, and disappeared at 280 °C. The spectra of liquid products obtained after reaction with different time at 280 °C under 2 MPa H_2 are presented in Fig. 3(f-j). At 0 h, the C-H cross signals of ether linkages already disappeared, and the C-H cross signals of C' structures were also detected. A reduction in the intensity of signals of C' was also observed with prolonging the reaction time. Even though under 0 MPa H_2 , the signals of ether linkages already disappeared at 6 h, and the C-H cross signals of C' structures were detected (Fig. 3(k)). Even without catalyst, the signals of original ether linkages in EHL also disappeared after the reaction at 280 °C under 2 MPa H_2 for 6 h, while the signals of C' structures were also detected (Fig. S4). The C-H cross signals of C'' structure, which could be formed from the dehydroxylation reaction of C' structure, were not detected in all the liquid products. In addition, some new C-H cross signals appeared at $\delta\text{C}/\delta\text{H}$ 67.4/3.9 ppm and $\delta\text{C}/\delta\text{H}$ 60.0/3.7-3.6 ppm when the reaction was conducted at 280 °C under 0 MPa H_2 for 6 h (Fig. 3(k)), and the signal at $\delta\text{C}/\delta\text{H}$ 67.4/3.9 ppm was also observed when the reaction was conducted at 300 °C under 2 MPa H_2 for 6 h (Fig. 3(e)), but these signals were not detected under other reaction conditions. As these signals appeared in the H-C-O-correlation region, they may be ascribed to the new type ether linkages formed during the reaction.

3.2.2. Infrared spectroscopy analysis

The FT-IR spectra of EHL and the liquid products obtained under different initial hydrogen pressures are presented in Fig. 4, and the corresponding band assignments are summarized in Table S1, according to the previous literatures²⁸⁻³⁰. The broad band 1 (3400 cm^{-1}) was ascribed to O-H stretching vibration. The bands 2 ($3000\text{-}2842\text{ cm}^{-1}$) were ascribed to C-H stretching in methyl and methylene groups. The band of unconjugated C=O (band 3, 1698 cm^{-1}) and conjugated C=O (band 4, 1640 cm^{-1}) stretching vibration were also observed. The band 5 (1603 cm^{-1}) and 6 (1513 cm^{-1}) were ascribed to the aromatic skeletal vibrations, and the band 7 (1462 cm^{-1}) was ascribed to the C-H deformation combined with aromatic ring vibrations. The weak band 8 (1370 cm^{-1}) was ascribed to the O-H deformation in phenols, and band 9 (1325 cm^{-1}) was ascribed to breathing of S ring and condensed G ring. Meanwhile, the band ascribed to aromatic C-H in-plane deformation in S ring (band 10, 1126 cm^{-1}) and G ring (band 11, 1031 cm^{-1}), and the band ascribed to the aromatic C-H out-plane deformation (band 13, 835 cm^{-1}) were distinguished. In addition, the band of -HC=CH- out-of-plane deformation (band 12, 980 cm^{-1}) was also observed.

In the spectrum of liquid products obtained under 2 MPa H_2 , the band of O-H stretching vibration (band 1) diminished due to the disruption of hydrogen bonds in EHL³¹. The band of conjugated C=O stretching vibration (band 4) and -HC=CH- out-of-plane deformation (band 12) disappeared. The band of O-H deformation in phenols (band 8) obviously strengthened. The band of breathing of S ring and condensed G ring (band 9) was significantly weakened, but the band of aromatic C-H in-plane

deformation in S ring (band 10) was not weakened. When the initial hydrogen pressure decreased to 0 MPa, although the band of conjugated C=O stretching vibration (band 4) disappeared, the weak band of -HC=CH- out-of-plane deformation (band 12) still detected. Meanwhile, the intensity of the band of C-H stretching in methyl and methylene groups (band 2) became stronger, while the intensity of the band of unconjugated C=O stretching (band 3) became weaker, compared with that obtained under 2 MPa H₂. Moreover, the band ascribed to the breathing of S ring and condensed G ring (band 9) strengthened as the initial hydrogen pressure decreased from 2 to 0 MPa.

3.3. The stability of the Ni (220H) catalyst

The used Ni (220H) catalyst was employed directly without treatment for EHL ethanolysis at 280 °C under 2 MPa H₂ for 6 h. The total monomer yield decreased from the 28.5 wt% of the first run to 26.0 wt% for the third run (Fig. S6(a)). In the third used catalyst, only metallic Ni phase was detected with XRD (Fig. S6(b)), and no carbon was detected with Raman spectrum analysis (Fig. S6(c)). Nevertheless, the average Ni particle size increased from 53.9 nm in the fresh catalyst (Fig. S1(b)) to 63.6 nm in the third used catalyst (Fig. S6(d)).

4. Discussion

4.1. The cleavage of linkages in EHL

The results of 2D-HSQC NMR analysis of liquid products showed that the signals of ether linkages completely disappeared at a low reaction temperature after long time

reaction (220 °C, 6 h) and at the beginning of the reaction at a high reaction temperature (280 °C, 0 h). Meanwhile, the signals of C' structure, which is associated with C-C linkages, gradually diminished with the increase of the reaction temperature or the prolongation of the reaction time. The dehydroxylation of C' also results in the disappearance of their C-H cross signals ²⁵, but the signals of C'' which forms from dehydroxylation of C' were not detected with 2D-HSQC NMR. Moreover, the β -O-4 linkages, which are believed mainly responsible for the formation of monomers ², were completely cleaved at 220 °C and 6 h or at 280 °C and 0 h, but the total monomer yield still increased obviously with the increase of the reaction temperature or the reaction time. These results indicate that not only the ether linkages but also the C-C linkages are cleaved during the EHL ethanolysis, forming monomers. The catalyst mainly responsible for the cleavage of C-C linkages, while the ether linkages were cleaved after the reaction without catalyst at 280 °C under 2 MPa H₂ for 6 h. Because of the higher bond dissociation energy of C-C linkages than that of the ether linkages ², the cleavage of C-C linkages needs a high temperature and gradually happens with the extent of reaction progress, while the ether linkages can be totally cleaved at 220 °C and 6 h or at 280 °C and 0 h. In addition, the decrease of the initial hydrogen pressure mainly suppresses the cleavage of the C-C linkages, but do not affect the cleavage of ether linkages. This is in accordance with those found by Cheng *et al.* ³² that the bond dissociation energy of C-C linkages in lignin model compounds was lowered on the Ni (100) surface involving the coverage of hydrogen.

The FT-IR results indicate that the band ascribed to the breathing of S ring and

condensed G ring was significantly weakened after EHL ethanolysis at 280 °C under 2 MPa H₂ for 6 h, which can not be completely attributed to the demethoxylation of S units as the NMR signal of methoxyls was only slightly weakened after the reaction. This indicates that the depolymerization of condensed G units occurred during the reaction. Decreasing the initial hydrogen pressure from 2 to 0 MPa H₂ led to the increase of the intensity of the band ascribed to breathing of S ring and condensed G ring, indicating that the decrease of the initial hydrogen pressure suppressed the depolymerization of condensed G units.

4.1. The repolymerization steps

The total monomer yield decreased when the reaction temperature increased from 280 to 300 °C under 2 MPa H₂. Meanwhile, the formation of char was observed at 280 °C under 0 MPa H₂. These results indicate that the repolymerization reaction become serious at 300 °C under 2 MPa H₂ or at 280 °C under 0 MPa H₂. The HSQC-NMR results show that new type ether linkages were formed at 300 °C under 2 MPa H₂ or at 280 °C under 0 MPa H₂, indicating that the phenolic hydroxyls may involve into the repolymerization steps. Huang *et al.*⁹ also reported that phenolic hydroxyl groups are the main actors in repolymerization. The ether linkages formed from repolymerization steps may be more difficult to be cleaved than the original ether linkages in EHL, and hence the rate of their formation may be faster than the rate of their cleavage at 300 °C under 2 MPa H₂ or at 280 °C under 0 MPa H₂. In contract to the reaction temperature and initial hydrogen pressure, the increase of reaction time had a minimal effect on the repolymerization reaction, which is in line with the published works^{33, 34}.

4.3. Monomer conversion steps

The yield of OA increased significantly with the increase of the reaction temperature from 280 to 300 °C under 2 MPa H₂ or the decrease of the initial hydrogen pressure from 2 to 0 MPa at 280 °C. It was reported that the alkylation of phenol happens in supercritical alcohols without a catalyst, mainly forming ortho-alkylphenols^{35, 36}. Meanwhile, alkyl radicals can be produced from the decomposition of supercritical ethanol, and this reaction is enhanced at above 280 °C^{37, 38}. Moreover, Hydrogen gas, as a free radical stabilizer, suppresses the radical reactions²⁰. Based on these reasoning, we propose that the ortho-alkyl side chains in OA come from the reactions between monomers and alkyl radicals from ethanol. High reaction temperature or low initial hydrogen pressure is favorable for the free radical reactions, and thus promotes the formation of OA.

The yields of PA increased with prolonging the reaction time to 8 h, while the yield of Pol decreased after 4 h. Song *et al.*¹⁷ verified that hydroxyls attached to the γ C of side chains can undergo dehydroxylation over Ni/C catalyst through isotopic labeling tests. Lan *et al.*³⁸ studied the Pol conversion, and found that dehydroxymethylation of Pol can occur over Ru/C, Pd/C and Ni/C. Therefore, Pol may undergo dehydroxylation and dehydroxymethylation reactions over Ni (220H), transforming into para-propyl and para-ethyl phenols, respectively. In addition, para-allyl phenols were detected at 220 °C, indicating that Pol also occur dehydration reaction. Para-allyl phenols disappeared at above 220 °C due to their hydrogenation into para-propyl phenols. Para-propyl and para-ethyl phenols were classified into PA-type monomers.

Therefore, the decrease of the yield of Pol may result from their further transformation into PA during the reaction.

The results of FT-IR analysis of liquid products obtained at 280 °C under different initial hydrogen pressure indicate that the hydrogenation of -HC=CH- was suppressed under 0 MPa H₂. Nevertheless, monomers containing -HC=CH- were not detected at 280 °C under 0 MPa H₂, which may be because that these monomers were prone to repolymerization at high reaction temperature^{39, 40}. The initial hydrogen pressure had a remarkable effect on the yield of Es which increased significantly from 0 MPa H₂ to 2 MPa H₂. Es are formed from pCA and FA through esterification and hydrogenation steps⁴¹, but pCA and FA also occur decarboxylation reaction with the formation of para-vinyl phenols^{42, 43}. Decarboxylation reaction of pCA and FA eliminates the conjugated C=O without forming unconjugated C=O. The FT-IR results show that the band ascribed to conjugated C=O stretching disappeared after reaction under 0 MPa H₂ at 280 °C for 6 h, but the intensity of the band ascribed to unconjugated C=O appeared under 0 MPa H₂ was weaker than that observed under 2 MPa H₂, indicating that decarboxylation reactions of pCA and FA were enhanced with the decrease of the initial hydrogen pressure from 2 to 0 MPa. Pol are formed from the hydrogenation of -HC=CH- in coniferyl and sinapyl alcohols (GA and SA)⁴⁰, and hence their formation were also suppressed under 0 MPa H₂. In contrast to Es and Pol, low initial hydrogen pressure facilitated the formation of Ph which contain no side chains. The elimination of side chains seems not through the cleavage of C-C linkages on the Ni (220H) catalyst, as the 2D-HSQC NMR analysis results demonstrated that the cleavage of C-C linkages

was suppressed under 0 MPa H₂. As reported, the phenolic compounds containing alkenyl side chains undergo alkenyl elimination step to remove their side chains in thermal reaction^{44, 45}. Therefore, the Ph may originate from the elimination of alkenyl side chains of intermediates. At 280 °C under 0 MPa H₂, the alkenyl elimination reaction was favorable because the hydrogenation of alkenyl side chains into alkyl side chains not readily occur, thus promoting the formation of Ph.

4.4. Pathways to stable monomers

Based on the above results and discussions, the pathways of EHL to stable monomers are proposed and illustrated as Scheme 1. The ether linkages are completely cleaved at the beginning of the reaction at 280 °C under 2 MPa H₂, forming primary monomers and lignin fragments. The lignin fragments are further depolymerized through the cleavage of C-C linkages with the progress of reaction. The primary monomers, including pCA, FA, GA and SA, occur secondary reactions, transforming into final products. The pCA and FA preferably transform into aromatic esters through hydrogenation and esterification under 2 MPa H₂, but the formation of para-vinyl phenols is favored under 0 MPa H₂ through a decarboxylation step. The GA and SA are hydrogenated into propanol-substituted phenols which further undergo dehydration, dehydroxylation and dehydroxymethylation steps. The alkenyl side chains in phenolic monomers are preferably hydrogenated to alkyl side chains under 2 MPa H₂, but the alkenyl elimination step is favorable under 0 MPa H₂, forming phenols without side chains. Alkylation of monomers with radicals from ethanol is promoted with the increase of the reaction temperature or the decrease of initial hydrogen pressure,

forming ortho-alkyl side chains of the monomers.

5. Conclusion

The reaction condition of EHL ethanolysis over Ni (220H) catalyst was examined. At 280 °C under 2 MPa H₂ for 6 h, the highest aromatic monomer yield of 28.5 wt% was achieved, and both the ether and C-C linkages of EHL were cleaved. The repolymerization reaction was promoted when the reaction temperature increased to 300 °C or the initial hydrogen pressure decreased to 0 MPa H₂, but was not affected obviously by prolonging the reaction time to 8 h.

The ortho-alkyl side chains of OA originated from free radical reaction of ethanol, and their formation was favorable at high reaction temperature or low hydrogen pressure. The Pol further transformed into PA, and hence their yield decreased after 4 h of reaction. Under 0 MPa H₂, the hydrogenation of -HC=CH- was not efficient, and hence the decarboxylation and alkenyl elimination reaction of side chains were favorable, which suppressed the formation of Es and promoted the formation of Ph, respectively.

Supporting information

Catalyst preparation and characterization, Total-ion chromatogram (TIC) of the liquid products, 2D-HSQC NMR spectra of the liquid products obtained without catalyst, band assignment in FT-IR, the effect of weight ratios of Ni (220H) to EHL, and the stability of the Ni (220H) catalyst.

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Table and Figure captions

Table 1. The structure and classification of main monomers obtained from EHL depolymerization.

Fig. 1. The effect of (a) reaction temperature within 6 h under 2 MPa H₂, (b) reaction time at 280 °C under 2 MPa H₂ and (c) initial hydrogen pressure at 280 °C within 6 h on the monomer yield. (Reaction conditions: 1.0 g EHL, 0.3 g Ni (220H), 60 mL ethanol, 600 rpm.)

Fig. 2. 2D-HSQC NMR spectra of (a) the EHL sample, and (b) the liquid products obtained from EHL depolymerization with Ni (220H) catalyst at 280 °C for 6 h under 2 MPa H₂.

Fig. 3. 2D-HSQC NMR spectra of the liquid products obtained from EHL depolymerization at (a-e) different reaction temperature under 2 MPa H₂ within 6 h, (f-g) different reaction time at 280 °C under 2 MPa H₂, and (i and k) different initial hydrogen pressure at 280 °C within 6 h.

Fig. 4. FT-IR spectra of (a) the EHL sample and the liquid products obtained at 280 °C for 6 h under (b) 2 MPa H₂ and (c) 0 MPa H₂

Scheme 1. The pathway of EHL depolymerization into stable monomers.

Table 1. The structure and classification of main monomers obtained from EHL depolymerization.

Structure	Type
Es
Pol
Ph
PA
OA

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Fig. 4. FT-IR spectra of (a) the EHL sample and the liquid products obtained at 280 °C for 6 under (b) 2 MPa H_2 and (c) 0 MPa H_2

Scheme 1. The pathway of EHL depolymerization into stable monomers.