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Catalytic Conversion of Enzymatic Hydrolysis Lignin into Cycloalkanes over a Gamma-Alumina Supported Nickel Molybdenum Alloy Catalyst

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Abstract

The efficient depolymerization and hydrodeoxygenation of enzymatic hydrolysis lignin are achieved in cyclohexane solvents over a gamma-alumina supported nickel molybdenum alloy catalyst in a single step. Under initial 3 MPa hydrogen at 320 °C, the highest overall cycloalkane yield of 104.4 mg/g enzymatic hydrolysis lignin with 44.4 wt% selectivity of ethyl-cyclohexane was obtained. The reaction atmosphere and temperature have significant effects on enzymatic hydrolysis lignin conversion, product type and distribution. The conversion of enzymatic hydrolysis lignin was also investigated over different nickel and molybdenum-based catalysts, and the gamma-alumina supported nickel molybdenum alloy catalyst exhibited the highest activity among those catalysts. To reveal the reaction pathways of alkylphenol hydrodeoxygenation, 4-ethylphenol was tested as a model compound. Complete conversion of 4-ethylphenol into cycloalkanes was achieved. A two-step mechanism of 4-ethylphenol dihydroxylation - hydrogenation is proposed, in which the benzene ring saturation is deemed as the rate-determining step.

Keywords: Enzymatic hydrolysis lignin, Gamma-alumina supported nickel molybdenum alloy catalyst, Solvolysis, Cycloalkanes
1. Introduction

In recent years, the second generation (2G) bioethanol production from lignocellulosic biomass shows energetic, economic, societal and environmental advantages in comparison to the fermentation of starch and sugar (Alvira et al., 2010). The 2G biorefinery includes four major operations: feedstock harvest and storage, pretreatment, enzymatic hydrolysis, and fermentation (Ragauskas et al., 2014; Dale and Ong., 2012). As a primary byproduct of the enzymatic hydrolysis step, enzymatic hydrolysis lignin (EHL) is produced in large quantity and is becoming a challenging bio-waste due to the rapid development of the 2G biofuel industry (Zakzeski et al., 2010; Ponnusamy et al., 2019). It is foreseeable, as the improvement of the enzyme for lignocellulose hydrolysis, high lignin content agricultural and forestry wastes, will become the main feedstocks of the 2G production.

EHL is more active than the lignin materials obtained from other chemical routes because of the activation during enzymatic hydrolysis and has a more similar structure to the original lignin since EHL is obtained under the mild enzyme catalytic condition (Cho et al., 2012). EHL is cleaner than Kraft lignin, with much lower ash and sulfur contents, thus facilitating the application of the valorization products. However, EHL is presently used as a low-grade fuel. Efficient strategies for the conversion of EHL into high-quality fuels and value-added chemicals are urgently demanded (Kim et al., 2019; Tribot et al., 2019). Nevertheless, EHL has also been proposed to produce various products, such as lignosulfonates (Huang et al., 2018) and lignin-phenol-formaldehyde adhesive (Pei et al., 2020).

For lignin valorization, many technology routes, e.g., pyrolysis, hydrocracking, acid-catalyzed depolymerization, oxidation and solvolysis have been intensively explored
(Hepditch and Thring, 2000; Yan et al., 2008; Crestini et al., 2010; Song et al., 2012; Li et al., 2012). Among the proposed routes, solvolysis of lignin with a fuel compatible solvent has been proved to be an effective way for lignin to liquid fuel commodities because the concept potentially eliminates the need for separation of the solvent from the produced fuel molecules (Barta et al., 2010; Ma et al., 2014; Ma et al., 2015a; Yan et al., 2017; Chen et al., 2017a; Chen et al., 2017b; Huang et al., 2014, 2017). Due to the good performance and cheap cost, transition metal, especially Ni and Mo based catalysts, are widely utilized for the solvolysis of lignin, and a two-step reaction pathway was proposed for lignin alcoholyysis over transition metal based catalysts, in which lignin was firstly fragmented to medium sized molecules within molecular weight < 1600, and further depolymerized into monomers (Song et al., 2013; Ma et al., 2015b). However, the lignin alcoholyysis products still richly contain oxygen functional groups, lowering its heating value and stability (Kadarwati et al., 2016; Zhang et al., 2013; Wang and Rinaldi, 2012). The oxygen functional groups cause high viscosity, poor thermal and chemical stability, corrosivity (acidity) and immiscibility with hydrocarbon fuels (Yang et al., 2009). Cycloalkanes, the primary products of lignin-derived bio-oil HDO, have a few advantages as jet fuel molecules (Cheng and Brewer, 2017). Recently, direct conversion of lignin into cycloalkanes over Ni-based catalyst in methylecyclohexane and dodecane solvent shed some light for producing high heating value fuel, such as jet fuel, from lignin (Wang and Rinaldi, 2016; Kong et al., 2016). Among different types of lignin, EHL is becoming available in large volume as industrial waste and its utilization becomes a crucial link of the 2G bioethanol production chain. EHL conversion to high quality fuel draws a great curiosity.

In this work, a single-step conversion process of EHL in cyclohexane (CYH) over a
NiMo/γ-Al2O3 catalyst is carried out. The conversion was also investigated over different Ni and Mo catalysts supported on active carbon (AC) and γ-Al2O3. Effects of reaction atmosphere and temperature on the EHL conversion is examined. In addition, 4-ethylphenol is tested as a model compound to reveal the steps of alkylphenol deoxygenation and illuminate the reaction pathway.

2. Materials and Methods

2.1. Materials

The EHL was purchased from Shandong Longlive Biotechnology Co. Ltd., and the detailed characterization of the EHL was given in a published paper (Bai et al., 2019). Analytical grade chemicals and solvents, e.g., CYH and n-hexane (n-HEX), were purchased from Tianjin Yuanli Chemical Co., Ltd. The deionized water was prepared with an Ulupure ultrapure water purification machine (UPH-1-10). Nickel (II) nitrate hexahydrate (Ni(NO3)2·6H2O, 99.9%), ammonium molybdate tetrahydrate ((NH4)6Mo7O24·4H2O, 99.98%), 4-ethylphenol, MoO3 and gamma-alumina were purchased from Aladdin Co. Ltd and used as received. Activated carbon was purchased from Cabot Corporation. Nickel molybdate (NiMoO4) was purchased from Tianjin Heowns OPDE Technologies, LLC.

2.2. Catalyst preparation

The supported Ni and Mo and their alloy catalyst samples were prepared with an impregnation-reduction technique, which has been reported in our previous work (Bai et al., 2019). In short, the precursors with Ni and Mo or both were prepared by successive incipient-wetness impregnation on γ-Al2O3 or active carbon (AC) support with aqueous solution of ammonium molybdate ((NH4)6Mo7O24·4H2O) and/or nickel nitrate.
(Ni(NO$_3$)$_2$·6H$_2$O). The precursors were dried and calcined to form supported metal oxide. Then, the precursors were reduced under hydrogen atmosphere in a quartz tube. The obtained catalyst was used immediately after preparation. The unsupported NiMo catalyst was prepared by reducing NiMoO$_4$ under the same conditions. As blank tests, the activity of the supports, γ-Al$_2$O$_3$, AC and MoO$_3$ was also measured.

2.3. EHL conversion experiments

A batch reactor (Kemi Co. Ltd, 250 mL, made of Hastelloy) was used to conduct the EHL conversion experiments. The reaction was carried out under 320 ºC for the desired time, and 0.5 g EHL, 0.5 g catalyst and 100 mL solvent were added before reaction. Afterwards, the reactor was sealed and purged with N$_2$ for six times, then purged with H$_2$ or N$_2$ for another three times, and finally set at 3 MPa at a stirring rate of 600 rpm. After the reaction, the gas in the reactor was collected with an air bag, and the liquid products were obtained by filtration. Internal standard anisole was added to the liquid sample before GC analysis.

2.4. Product analysis

The analysis of liquid products was carried out using the same equipment and method as reported previously (Bai et al., 2019). The liquid products were identified and quantified using a gas chromatograph-mass spectrometer (GC-MS) and a gas chromatograph equipped with a flame ionization detector (GC-FID), respectively. The gaseous products were qualitatively analyzed with the Hiden Analytical HPR20 mass spectrometer.

The product yield, carbon mass balance, weight and molar selectivity of liquid products were calculated according to the following equations (1), (2) and (3), respectively:
Product yield (mg/g EHL) = \frac{\text{Weight of product}}{\text{Weight of input EHL}} \quad (1)

Carbon mass balance (%) = \frac{\text{Mass of the carbon in the products}}{\text{Mass of the carbon in the 4-ethylphenol reactant}} \quad (2)

Weight (or molar) selectivity (%) = \frac{\text{Weight (or Molar quantity) of the specific product}}{\text{Weight (or Molar quantity) of the overall product}} \quad (3)

The heating value of the samples was estimated by the Dulong formula:

Heating value (MJ/kg) = 33.8X_C + 142.8(X_H - 0.125X_O) \quad (4)

Where \( X_C, X_H \) and \( X_O \) are the weight percentage of carbon, hydrogen and oxygen elements in the material.

The molecular weight distribution of the product residue was analyzed using an Autoflex tof/tof III matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) made by Bruker Daltonics, USA. The matrix used for the samples was 2,5-dihydroxy benzoic acid (DHB) (SIGMA) dissolved in CAN-H_2O-TFA (666: 333: 1) with a concentration of 25.0 mg/mL. The samples (0.50 mL) were dropped onto the MALDI target plate and dried in air at room temperature. Then, the matrix solution was spotted on the sample point prior to analysis. The instrument was operated at an accelerating voltage of 20 kV. A 200 Hz pulsed ND: YAG laser (355 nm) was used for MALDI. Positive ion MALDI-TOF-MS spectra were collected from the signal average of 1500 laser shots in the linear detection mode. The laser intensity was
kept constant.

2.5. Characterization

The X-ray powder diffraction (XRD) patterns were collected with the Bruker D8-Focus diffractometer (Cu Kα, λ = 1.5406 Å) at 40 kV and 40 mA. The powder sample was scanned from 10° to 80° at a rate of 10°/min. The samples were pre-treated at 300 °C for 3 h under vacuum before sorption test. The surface and porosity data were measured with the nitrogen sorption at -196 °C and analyzed by the multipoint BET method (Quantachrome Auntosorb-1).

3. Results and discussions

3.1. Catalyst characterization

In the diffraction patterns of NiMo/γ-Al₂O₃ and NiMo/AC samples, the peaks of Mo₁.2₄Ni₀.7₆(PDF 47-1129) are observed. For the unreduced Ni/γ-Al₂O₃ catalyst precursor, the diffraction pattern shows the peaks of NiO (PDF 78-0423). For the Ni/γ-Al₂O₃ catalyst sample, the diffraction peaks of Ni (PDF 87-0712) are observed without the peaks of NiO, indicating that the Ni species was well reduced during the synthesis process. The texture data of the NiMo/γ-Al₂O₃ and NiMo/AC samples are given in Table 1. NiMo/AC has a larger surface area, but smaller pore volume and average pore diameter than those of the NiMo/γ-Al₂O₃ sample.

3.2. Catalytic activity

3.2.1. Catalytic activity

Table 2 exhibits the activity measurement results obtained with different catalyst samples. The reactions were carried out at 320 °C for 7.5 h, with an initial 3 MPa of H₂ in CYH solvent. NiMo/γ-Al₂O₃ gave the highest yield of cycloalkanes, 104.4 mg/g EHL
In comparison, unsupported NiMo catalyst exhibited much lower activity and only 12.7 mg/g EHL of cycloalkane was obtained (Entry 2). In blank test, the complete hydrodeoxygenation (HDO) of EHL did not take place without catalyst (Entry 3), and γ-Al₂O₃ and AC supports also failed to produce cycloalkanes (Entry 4-5). EHL conversion over the NiMo/AC sample was examined, the overall cycloalkanes yield as well as the molecular distribution exhibited no significant difference (Entry 6) compared with those obtained with using NiMo/γ-Al₂O₃. The diffraction peaks of Mo₁.₂₄Ni₀.₇₆ observed in both the XRD patterns of NiMo/γ-Al₂O₃ and NiMo/AC suggesting Mo₁.₂₄Ni₀.₇₆ is an important active species for the HDO of EHL. Moreover, the significant difference of surface area and average pore diameter between NiMo/γ-Al₂O₃ and NiMo/AC did not result in distinct difference of catalytic performance, indicating that mass transfer within the different pore structure of the two catalysts has little influence on EHL conversion. For the monometallic Ni and Mo supported on γ-Al₂O₃ or AC catalysts (Entry 7-10), only Ni/γ-Al₂O₃ as catalyst gave a cycloalkane yield of 43.0 mg/g EHL, and diffraction peaks of metallic Ni in the XRD pattern suggesting that metallic nickel was also efficient for EHL conversion and HDO, which is consistent with the literature results (Wang et al., 2016). Furthermore, MoO₃, as an effective catalyst for lignin conversion in supercritical ethanol (Chen et al., 2017a), was also tested in the reaction and failed to achieve the complete HDO of EHL (Entry 11).

In order to assess the effect of possible solvent conversion, CYH without EHL and n-NHX as the solvent with EHL experiments were carried out over the NiMo/γ-Al₂O₃ catalyst under 3 MPa H₂ at 320 °C for 7.5 h. The results are listed in Table 3. In the blank experiment without EHL input with only CYH as feedstock (Table 3, entry 1), no alkyl cycloalkane was detected in the liquid products, demonstrating that CYH remained stable
during the reaction atmosphere. With EHL as the feedstock in CYH (Table 3, entry 2), the yield of cycloalkanes reached 104.4 mg/g EHL under the same conditions. When using n-HEX as the solvent with the same amount of EHL (Table 3, entry 3), the product distribution was similar to that obtained with CYH as the solvent, while CYH gave higher yields for most of the measured compounds. In addition, HDO of lignin to cycloalkanes was reported in dodecane (Kong et al., 2016) and methylcyclohexane solvents (Wang and Rinaldi, 2016). Direct HDO of raw woody biomass into liquid alkanes was reported in the CYH solvent (Xia et al., 2016). The product molecule distributions are similar for the results obtained in CYH, dodecane and methylcyclohexane solvents. The results presented here indicate that the two C₆ alkane solvents, i.e. CYH and n-HEX possibly have similar performance on EHL conversion and verify that alkylated cycloalkane products were formed from EHL depolymerization instead of the alkylation of CYH solvent.

3.2.2. Effect of reaction conditions

The yield, selectivity and atomic ratio of liquid products obtained under different reaction conditions are listed in Table 4, and the reactions were carried out over the NiMo/γ-Al₂O₃ catalyst. Under inert nitrogen atmosphere (Table 4, entry 1), the overall product yield was 48.2 mg/g EHL without benzene ring saturation. The O/C and H/C atomic ratios are 0.145 and 1.15, respectively. For the liquid products obtained over the NiMo/γ-Al₂O₃ catalyst under hydrogen atmosphere (Table 4, entry 2), 7 kinds of cyclohexyl derivatives were obtained with the yield of 104.4 mg/g EHL. No oxygenated product was detected, and all benzene-rings were saturated, implying that the complete HDO of the product was achieved. After reaction over the NiMo/γ-Al₂O₃ catalyst, the H/C atomic ratio of the products increased to 1.99, and only hydrogen was detected in the
gaseous products, indicating that no gaseous alkane or alkene product was formed during the EHL conversion. In our previous work, \(^{32}\) when using ethanol as solvent, EHL was depolymerized into aromatic compounds without benzene-ring saturation over the same NiMo/γ-Al\(_2\)O\(_3\) catalyst under 2.76 MPa hydrogen pressure, indicating that both solvent and reaction atmosphere are crucial factors for EHL conversion. For the conversion process of EHL, gaseous H\(_2\) is deemed as the hydrogen source for the HDO and benzene ring saturation in CYH solvent, and CYH remained stable during the reaction.

Moreover, the influence of reaction temperature on the yield and distribution of liquid products obtained from EHL conversion over the NiMo/γ-Al\(_2\)O\(_3\) catalyst is also illustrated in Table 4. With the reaction temperature decreasing from 320 to 240 °C, the overall aromatic yield continued to reduce (Entry 3-6), indicating that when using NiMo/γ-Al\(_2\)O\(_3\) supported alloy catalyst, high temperature facilitates the conversion of lignin, which is consistent with our previous results (Bai et al., 2019). Furthermore, the distribution of the products shows no significant difference, and even at 240 °C, the complete HDO of the products was achieved with a low product yield. These results suggest that at low temperature, EHL depolymerization rather than product HDO restrained the production of cycloalkanes.

The element contents and heating values of the EHL and the reaction products are listed in Table 5. The heating value of EHL feedstock was 25.0 MJ/kg estimated by the Dulong formula, according to the result of the organic element analysis (Bai et al., 2019). After catalytic treatment in CYH over the NiMo/γ-Al\(_2\)O\(_3\) catalyst, the heating value of the alkylated cycloalkane products was estimated as 49.3 MJ/kg, comparing to the heating value 43.2 MJ/kg of BP Jet A-1 fuel. Nevertheless, the product still cannot be directly used as a jet fuel. Significant increase of H/C atomic ratio and complete HDO of the liquid
product are needed.

3.2.3. Molecular weight distribution of the residue

A matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) technique was employed to monitor the molecular weight of the EHL residue fragments after the experiments carried out with CYH solvent. Due to the procedure of sample preparation, all the volatile components such as the solvent and monomers are not included in the spectra, and the measurement was not quantitative. This analysis was done to verify the two-step lignin depolymerization mechanism, viz., lignin molecule is firstly fragmented to medium sized intermediates and then the intermediate is further scissored into monomers (Ma et al., 2014; Song et al., 2013; Ma et al., 2015b). In fact, compounds with molecular weight above 250 cannot be gasified effectively due to the high boiling point in the injection port of GC-FID and GC-MS systems. Therefore, only small molecule compounds were detected in GC analysis and regarded as products in Table 2. For the liquid product obtained under 3 MPa H$_2$ at 320 °C in CYH without catalyst, the molecular weight of the fragments fell mainly in the m/z range of 300-600, and no species with m/z above 800 was detected. When using NiMo/γ-Al$_2$O$_3$ as catalyst, the intensity of the response decreased but still in the similar m/z range under the same condition. In comparison, birch wood lignin was first fragmented into pieces with m/z in a range of 1100-1600 in methanol (Song et al., 2013), and Kraft lignin was firstly depolymerized into fragments in the m/z range of 700-1400 in ethanol (Ma et al., 2014; Ma et al., 2015b). Here, EHL in CYH, much smaller segments were formed in the first step. As shown in Figure 1, the reaction pathway can be also assumed as a two-step process: Firstly, EHL was converted into oxygenated aromatic products and oligomers within the m/z range of 300-600 via solvolysis. Then, NiMo/γ-Al$_2$O$_3$ catalyzed the
demethoxylation, further depolymerization and HDO of the monomers, and finally produced alkylated cycloalkanes. These results proved that EHL is more active than Kraft lignin. However, the MALDI-TOF-MS result also implies that even with the presence of the catalyst, the fragments to monomers step was incomplete during the reaction. The solution contains trace amounts of molecules in m/z range 300-600, which is out of the molecular weight range of liquid fuels. It arises the need of intensive investigation of the complete conversion of the residue to monomers and to characterize and quantify the reaction residue in the CYH and HEX solvents.

3.3. Catalytic conversion of 4-ethylphenol

Without the catalyst in CYH solvent, EHL was converted into oxygenated products, e.g., 4-ethylphenol. In the presence of NiMo/γ-Al₂O₃ catalyst, completely deoxygenated and saturated cycloalkanes were obtained and identified by GC-MS. It is reasonably to think that the NiMo/γ-Al₂O₃ catalyst facilitates the HDO and benzene-ring saturation of lignin-derived oxygenated products. Moreover, for EHL ethanolysis, alkylphenols are the major products with high yield (Bai et al., 2019; Mai et al., 2019). Hence, 4-ethylphenol is chosen as a model compound to investigate the underlying reaction pathway of alkylphenol HDO.

Under 3 MPa hydrogen at 320 °C in CYH for 0 h, viz. when the temperature reached 320 °C the reactor was cooled to ambient immediately, complete deoxidation of 4-ethylphenol was achieved over the NiMo/γ-Al₂O₃ catalyst. With a carbon mass balance of 88.6%, the selectivity of methyl-CYH and ethyl-CYH was 11.7% and 87.2%, respectively, while 1,3-dimethyl-CYH, 1-ethyl-3-methyl-CYH, propyl-CYH and 1,3-diethyl-CYH accounted for 1.1% in total. Two possible reaction pathways, as shown in Figure 2, are proposed for the HDO of 4-ethylphenol. Trace amount of ethylbenzene,
which is an intermediate in Pathway I, was identified in the liquid products, with the absence of ethyl-cyclohexanol. Accordingly, the reaction pathway of alkylphenol HDO is proposed as that, in the first step, alkylphenol was converted into alkylbenzene through dehydroxylation. Subsequently, the complete hydrogenation of benzene ring took place, resulting in the formation of alkylated cycloalkanes. Furthermore, in the short-time reaction, the complete conversion of 4-ethylphenol and existence of ethylbenzene suggested that the reaction rate of 4-ethylphenol dehydroxylation surpasses that of the ethylbenzene saturation. Therefore, the hydrogenation saturation of ethylbenzene is assumed to be the rate-determining step for the HDO of 4-ethylphenol.

4. Conclusions

EHL is efficiently converted into cycloalkanes in CYH solvent over a NiMo/γ-Al₂O₃ catalyst with a cycloalkane yield of 104.4 mg/g EHL and a 44.4 wt% selectivity of ethyl-CYH under initial 3 MPa hydrogen at 320 ºC for 7.5 h. The H/C ratio and heating value of the cycloalkane products increased by 51.9% and 97.2%, respectively, compared to those of the EHL feedstock. Additionally, complete conversion of 4-ethylphenol is achieved under the same reaction condition and the result suggests a two-step pathway for alkylphenol HDO, in which the dehydroxylation of alkylphenol precedes the benzene-ring hydrogenation, and thus the latter is rate-determining step.

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Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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Table 1. Texture data of the NiMo/Al and NiMo/AC samples.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Average Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NiMo/Al</td>
<td>122.2</td>
<td>0.4014</td>
<td>13.24</td>
</tr>
<tr>
<td>2</td>
<td>NiMo/AC</td>
<td>554.3</td>
<td>0.3687</td>
<td>3.53</td>
</tr>
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</table>
Table 2. The yields of cyclohexane derivatives obtained from EHL conversion in CYH over different catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Product Yield (mg/g EHL)</th>
<th>Overall Yield (mg/g EHL)</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>1</td>
<td>NiMo/Al₂O₃</td>
<td>15.2</td>
<td>46.4</td>
</tr>
<tr>
<td>2</td>
<td>NiMo</td>
<td>6.0</td>
<td>6.7</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Al₂O₃</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>AC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>NiMo/AC</td>
<td>16.9</td>
<td>57.0</td>
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<tr>
<td>7</td>
<td>Ni/Al₂O₃</td>
<td>9.3</td>
<td>26.3</td>
</tr>
<tr>
<td>8</td>
<td>Ni/AC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Mo/AC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Mo/Al₂O₃</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>MoO₃</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* No catalyst was added.
Table 3. Product yield of CYH blank experiment and EHL depolymerization in two different solvents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Reactant</th>
<th>Product Yield (mg/g EHL)</th>
<th>Overall Yield (mg/g EHL)</th>
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<tr>
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<td></td>
<td></td>
<td>I</td>
<td>II</td>
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<tr>
<td>1</td>
<td>CYH</td>
<td>- *a</td>
<td>-</td>
<td>-</td>
</tr>
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<td>2</td>
<td>CYH</td>
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<td>3</td>
<td>n-HEX</td>
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<td>12.2</td>
<td>39.6</td>
</tr>
</tbody>
</table>

*a No EHL was added.
Table 4. The yield, selectivity and atomic ratio of liquid products obtained from EHL conversion in CYH under different reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Atmosphere</th>
<th>Temperature (°C)</th>
<th>Reaction Selectivity (wt%)</th>
<th>O/C atomic ratio</th>
<th>H/C atomic ratio</th>
<th>Overall Yield (mg/g EHL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N₂</td>
<td>320</td>
<td>Cycloalkanes - ~100 Alkylphenols -</td>
<td>0.145</td>
<td>1.15</td>
<td>48.2</td>
</tr>
<tr>
<td>2</td>
<td>H₂</td>
<td>320</td>
<td>~100 - -</td>
<td>-</td>
<td>-</td>
<td>1.99</td>
</tr>
<tr>
<td>3</td>
<td>H₂</td>
<td>300</td>
<td>100 - -</td>
<td>-</td>
<td>-</td>
<td>2.00</td>
</tr>
<tr>
<td>4</td>
<td>H₂</td>
<td>280</td>
<td>100 - -</td>
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<td>H₂</td>
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<tr>
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<td>Catalyst</td>
<td>Atmosphere</td>
<td>Element content (wt%)</td>
<td>Heating Value (MJ/kg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-------------------</td>
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<td>-----------------------</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Carbon</td>
<td>Hydrogen</td>
<td>Oxygen</td>
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<tr>
<td>1*</td>
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<td>N₂</td>
<td>77.57</td>
<td>7.43</td>
<td>15.00</td>
<td>34.1</td>
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* EHL feedstock without treatment.
Figure 1. Possible reaction pathway for EHL conversion over NiMo/Al.
Figure 2. Possible reaction pathways of 4-ethylphenol HDO.
Highlights

1. Enzymatic hydrolysis lignin (EHL) is effectively depolymerized.

2. Complete hydrodeoxygenation cycloalkane molecules were obtained.

3. The H/C ratio and heating value were increased.

4. A two-step reaction pathway of alkylphenol HDO is proposed.