Zhihao Li, Zhihao Bi and Lifeng Yan*

Two-step hydrogen transfer catalysis conversion of lignin to valuable small molecular compounds

Abstract: As the major composite of biomass, lignin can be utilized as feedstock for valuable chemicals, especially phenols. Catalysis hydrogenation of lignin is an attractive route for the conversion. However, most of them require hydrogen gas under high pressure which is dangerous. Hydrogen transfer reaction provides an alternative route to degrade and hydrogenate lignin or its units to small molecular compounds. Here, a two-step method has been employed using Raney Ni and Pd/C catalysts consecutively for hydrogen transfer catalysis for lignin. The results reveal that lignin can be degraded efficiently about 90% during conversion, and the major products are phenols with ~30% in yield. It provides a new green method for converting natural lignin to valuable chemicals.

Keywords: biomass; catalysis; degradation; hydrogenation; lignin.

1 Introduction

Lignin, together with cellulose and hemicellulose, forms the main structure of plants cell wall, and is the second largest class of natural polymers in nature. The annual global amount of synthesized bio-lignin reaches 6×10^{14} t, and the current global production of industrial alkali lignin in paper-making industry is about 30 million tons per year. However, lignin has not been widely utilized. Less than 10% of alkali lignin has been well utilized, and most of them were burned. Lignin contains many aromatic groups [1, 2], which can be degraded in extremely harsh conditions (requiring hydrogen atmosphere and high temperature above 300°C) [3]. A number of innovative approaches both in homogeneous as well as heterogeneous catalysis exist and have been summarized in recent literature [4–6].

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However, the complexity of the lignin structure makes it difficult to be degraded and hampers its effective utilization for large-scale industrialization. Fast pyrolysis and catalytic pyrolysis are robust liquefaction technologies commonly used to depolymerize biomass [7]. Typically, the dry raw material is rapidly heated to a high temperature (over 450°C) under anerobic environment and the condensation of the pyrolysis steam results in liquid product. Lignin is generally thermally depolymerized to phenols, aromatic hydrocarbons, or aliphatic hydrocarbons during pyrolysis [8, 9]. Catalytic pyrolysis is the other method used to deoxygenate pyrolysis biomass [10]. Unlike fast pyrolysis, catalytic pyrolysis can avoid unstable bio-oil secondary reactions during condensation and revaporization [1]. Due to the very large annual yields of alkali lignin and Kraft lignin, using a common catalyst for lignin conversion under mild conditions would significantly increase the likelihood that biomass to chemicals is economically competitive in industrial production. Catalysis is regarded as the key enabling technology for fulfilling the promise of lignin conversion. Lignin polymer can be degraded to aromatic hydrocarbons by contact with a powerful catalyst under hydrogen gas atmosphere. Due to the high cost and risk when high pressure hydrogen gas (30–100 bar) is used, it is critical that lignin polymer can be converted into aromatic compounds at high conversion rate and selectivity under mild conditions without using hydrogen gas [11, 12]. At present, there have been reports that lignin or its model compounds can be converted or degraded by hydrogen transfer reactions in absence of hydrogen gas. Raney nickel is a typical catalyst for hydrogen transfer reaction which can effectively depolymerize organosolv lignin to low molecular weight liquid [13]. The noble metal catalyst may break the functional groups of the lignin model compound in the presence of hydrogen donor reagent (such as isopropanol), thereby depolymerizing it [14]. However, from the previous studies, when Raney Ni was used, although organosolv lignin could be effectively depolymerized, the major products are oligomers, which require furthermore degradation by the catalyst at 180°C while lignin with very large molecular weight could not be worked well. It is well known that Pd/C is an efficient catalyst for degradation of low molecular weight lignin, which may be used as a catalyst for furthermore degradation of the primary products of the hydrogen transfer reaction over Raney Ni catalyst [15].

Here, in case when using single catalyst cannot get good result of degradation of large molecular lignin, a new two-step catalytic route has been designed. At first, Raney Ni was utilized to reduce the molecular weight of lignin for oil-like products, and then Pd/C was used for furthermore depolymerization of small molecular compounds. The overall process concept is shown schematically in Figure 1.

2 Materials and methods

2.1 Material

Industrial lignin was purchased from Lanxu Biotechnology Co. Ltd. (Hefei, China) and washed with deionized water three times. Fresh lignin was obtained in the laboratory by acidic hydrolysis and removal of the polysaccharides of biomass. Deionized water with resistivity of 18 MΩ cm was produced by Milli-Q equipment (Millipore, USA) and was used for solution preparation. Other chemicals, including 2-propanol, ethyl acetate, and phenol, were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). In addition, H_2SO_4 (98%) was purchased from Shanghai Chemical Reagents Company and was used directly without further purification. The gas chromatography (GC) standard samples, such as 4-ethylphenol, 4-ethyl-2-methoxyphenol, 2,6-dimethoxyphenol, guaiacol, 2-methoxy-4-propylphenol, and 2,6-di-tert-butylphenol were purchased from Aladdin Chemical Reagent Co., Ltd (Shanghai, China).

2.2 Characterization of lignin and product

Lignin was characterized by means of Fourier transform infrared spectroscopy (FT-IR), gel permeation chromatography (GPC), elemental analysis, thermogravimetric analysis-differential scanning
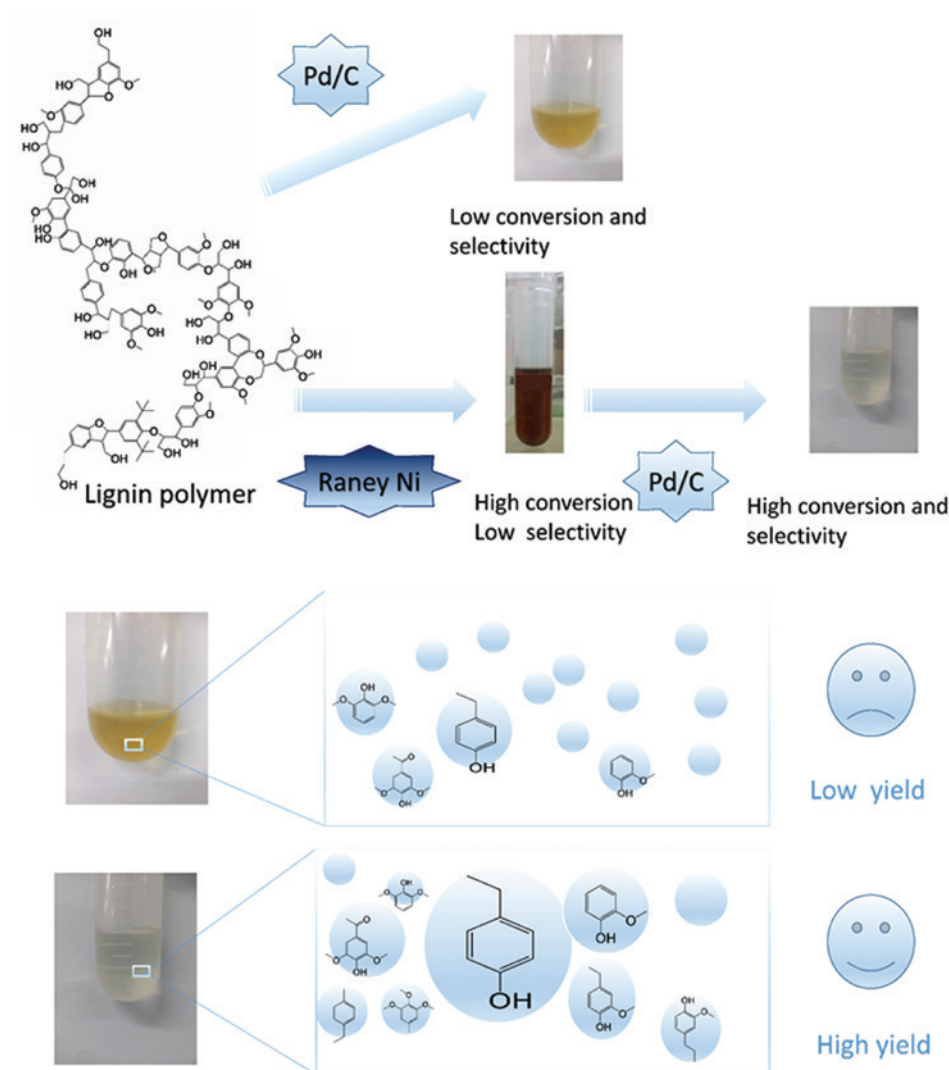

Figure 1: The overall process concept.

calorimetry (TGA-DSC), and UV-Vis spectroscopy. Reaction products were analyzed using GPC (dimethyl formamide, DMF), gas chromatography-flame ionization detector (GC-FID), gas chromatography-mass spectrometer (GC-MS), transmission electron microscopy, elemental analysis, UV-Vis, and FT-IR. FT-IR spectra were recorded on a Bruker spectrometer (EQUINOX 55, Bruker, UK) applying the potassium bromide (KBr) assay method. GPC, (LC-20AD, Shimadzu, Japan) with a Shimadzu Shodex GPC KD-804 column and a refractive index detector (RID-10A) was used to compare the molecular weights of the samples. The measurement was achieved at 60°C using DMF as the mobile phase at a determined sample concentration (5 mg/ml). UV-Vis spectra were record on a Shimadzu UV-2401 PC ultraviolet instrument. GC was conducted on a Thermo Fisher UV1800 instrument for quantitative analysis of the product.

2.3 Synthesis of Raney Ni catalyst

Raney Ni catalyst was prepared using the W-2-type preparation method [16]. A total of 10 g of sodium hydroxide was dissolved in 50 ml of distilled water cooled to 10°C in an ice bath. Twelve grams of Ni-Al alloy was added in small portions to the liquid with stirring to ensure that the solution temperature was maintained between 10°C and 15°C. After the addition was complete, the flask was removed from the ice bath, and the reaction was allowed to warm to room temperature. When hydrogen generation was slow, it could be heated slowly in an oil bath, and the heating was continued until the occurrence of bubbles became slower again. This process lasted for approximately 2 or 3 h. Then, the flask was put aside, after the formation of the nickel precipitates, and the supernatant was removed. Distilled water was added to the original volume, and then the solution was stirred to suspend the nickel powder. Again, the nickel powder precipitated, and the supernatant was discarded. This step was repeated three times. Next, the Raney Ni was washed three times with 2-propanol. The prepared Raney Ni was stored in 2-propanol avoiding contact with air.

2.4 Depolymerization of lignin over catalyst

Conversions of lignin were performed in a 50-ml polytetrafluoroethylene autoclave. When Raney Ni was used as the catalyst, 800 mg of the substrate and 800 mg of the catalyst were uniformly stirred and dispersed in 24 ml of isopropanol (isopropanol: $H_2O = 7:3$). Nitrogen gas was then introduced at ambient temperature for 2 h to remove oxygen. The vessel was closed, and the reactor was heated from room temperature to 180°C at a heating rate of 5°C/min for 180 min on a magnetic stirrer. After reaction, 20 ml of isopropanol was added to the liquid, and the obtained mixture was filtered, and the filtrate was washed with anhydrous sodium sulfate and then diluted with isopropanol to 50 ml for analysis. Next the product obtained by Ni catalysis was used for the Pd/C catalysis, and 900 mg of substrate, 150 mg of catalyst, and 1.5 ml of $NaBH_4$ solution (0.092 M) were homogeneously stirred and dispersed in 7.5 ml of ethyl acetate solution. Nitrogen gas was then introduced at ambient temperature for 2 h to remove oxygen. The vessel was closed, and the reactor was heated from room temperature to 180°C at a heating frequency of 5°C/min for 180 min on a magnetic stirrer. Then, it was allowed to stand at room temperature. After reaction, the liquid was subjected to suction filtration, and the filtrate was washed with a fixed amount of anhydrous sodium sulfate in 50 ml of ethyl acetate to carry out the analysis.

3 Results and discussion

3.1 Analysis of lignin

It is well known that the composition of lignin internal elements, functional groups, and various aromatic units is determined by the types of biomass. To further analyze the composition and structure of lignin and compare them with those of the products after the reaction, the lignin was analyzed by a wide variety of techniques, such as FT-IR, GPC, UV, calcinations, and CHNO elemental analysis. The CHNO elemental analysis and calcinations experimental results are listed in Table 1.

3.2 Hydrogen transfer reaction of lignin over Raney Ni catalysis

Raney Ni catalyst has a very wide range of applications in industry [17]. When lignin polymer is catalyzed by Raney Ni by the hydrogen transfer reaction, the conversion from solid to liquid is efficient. Table 2 lists the results of the conversion of lignin at 180°C for 18 h. It was found that alkali lignin has a better conversion than that of Klason lignin because of different preparation processes. The

Table 1: The content of the lignin used in this study.

Cᵃ (wt%)	Hᵃ (wt%)	Nᵃ (wt%)	Oᵃ (wt%)	Ashᵇ (wt%)
48.93	4.32	1.54	29.23	14.27

ᵃCalculated by elemental analysis. ᵇCalculated by calcinations.

Table 2: Conversion of the lignin under hydrogen transfer reaction over Raney Ni catalyst.

Types of lignin	Solution ratio	Reaction temperature (°C)	Reaction time (h)	Lignin conversion (%)
Alkali lignin	3:7	180	12	87.85
Alkali lignin	3:7	180	6	26.00
Alkali lignin	3:7	180	18	93.50
Alkali lignin	5:5	180	12	22.10
Alkali lignin	1:9	180	18	57.10
Alkali lignin	3:7	160	12	28.95
Alkali lignin	3:7	200	18	70.15
Alkali lignin	3:7	160	18	80.55
Klason lignin	3:7	180	18	70.50

role of high concentrations of acid in the Klason lignin preparation process resulted in condensation reaction. However, the occurrence of alkaline hydrolysis caused reduction molecular weight in the preparation process of alkali lignin. Lignin solids can be successfully converted to liquefied products, which still have high molecular weight. In other words, the reaction product of Raney Ni catalysis has a higher conversion but lower selectivity for small molecules. Conversion (C%), Total Yield (TY%), and Yield (Yi%) are defined as Eqs. (1–3), respectively.

hydrogen provided from $NaBH_4$ still caused the lignin to degrade by hydrogenation reaction in the absence of catalyst.

3.4 Hydrogen transfer reaction of lignin by the two-step catalysis

From the earlier studies, it was found that the two types of catalysts exhibited different characteristics in the process

$$C\% = \left(1 - \frac{\text{The weight of total detected unreacted solid residue}}{\text{The weight of lignin}}\right) \times 100\% \tag{1}$$

$$TY\% = \frac{\text{The total weight of products can be measured in GC} - \text{FID}}{\text{The total weight of feedstock}} \times 100\% \tag{2}$$

$$YI\% = \frac{\text{The weight of certain product measured by means of GC} - \text{FID}}{\text{The total weight of feedstock}} \times 100\% \tag{3}$$

3.3 Hydrogen transfer reaction of lignin over Pd/C catalysis

Like the Raney Ni catalyst, Pd/C catalyst plays an important role in industrial applications such as pharmaceutical production [18, 19]. It can be also used as a catalyst for hydrogen transfer reaction. Here, lignin was directly used as feedstock for hydrogen transfer reaction over Pd/C, and the reaction has a low conversion and liquefaction rate as shown in Figure 2, indicating Pd/C is not suitable as catalyst for direct conversion of lignin. In addition, the
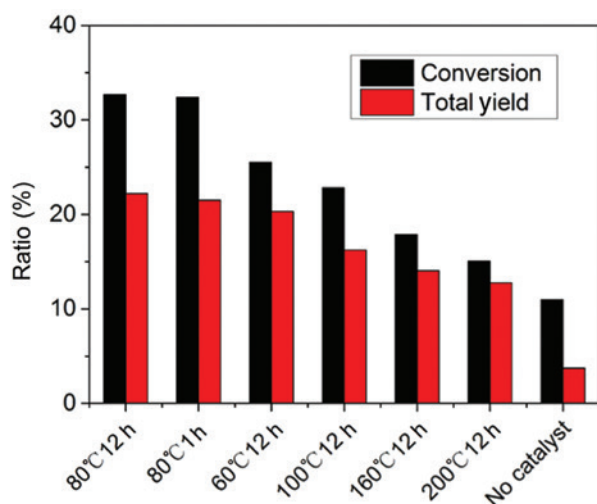
of lignin depolymerization. When Raney Ni catalyst was used, the conversion from solid to liquid was higher, but the total yield was low. When Pd/C catalyst was used, the conversion of lignin to liquid was low, but most of the degradation products had low molecular weights (Figure 3). The results are similar to the previous results of Ferrini and Galkin, who successfully liquefy unprocessed lignin through Raney Ni, while Galkin used Pd/C to convert low molecular weight model compound to monomer (~30% in selectivity). Therefore, the use of two-step catalytic (TSC) process is proposed. First, the Raney catalyst was used for liquefaction, and then the Pd/C catalyst was used to degrade high molecular weight liquid lignin to monomer. Figure 3 shows the GPC curves of products obtained from alkali lignin under different catalysts. For comparison,
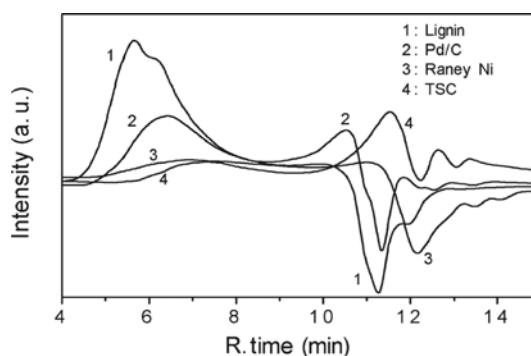

Figure 2: Conversion and total yield of the 12 compounds of alkali lignin degradation over Pd/C catalyst.

Figure 3: Gel permeation chromatograms obtained from alkali lignin. The products are degraded using two different catalysts separately or degraded using TSC.

two catalysts were utilized separately or in combination. It can be clearly seen that the original lignin has a relatively large molecular weight. When Pd/C is used as the catalyst, two peaks occur, in which the unreacted lignin peak is higher than the peak of the small molecular weight product. When using Raney Ni as the catalyst, the molecular weight distribution of the lignin depolymerization product is average and does not exhibit obvious peaks. However, the degradation peak with low molecular weight is very obvious after using both catalysts, while the height of the high molecular weight peak is very low. These results clearly demonstrate that the two catalysts used in combination are significantly better than using a single catalyst alone (Supplemental Figure S1).

Degradation of lignin can also be verified by the FT-IR studies. Figure 4 shows the FT-IR spectra of the lignin and the liquid phase of products for different catalytic processes. A strong, broad band is seen at 3400 cm^{-1}, indicating the presence of hydroxyl groups in large quantities in the liquid phase, as large amounts of hydroxyl groups are produced by degradation [20]. The main differences are observed for the C–O and C=O bonds. The increase of carbonyl group and the decrease of carbon-oxygen single bond actually indicate the degradation of lignin because of the breaking of the carbon-oxygen bond during catalysis, and the results also support the result that two catalysts system is efficient for lignin degradation.

The mass fraction of products after each stage of the reaction is shown in Figure 5. The solvent of the products was completely removed in the rotary evaporator. It can be seen that the content of hydrogen is lower than that of the hydrogen in the lignin when using a single hydrogen
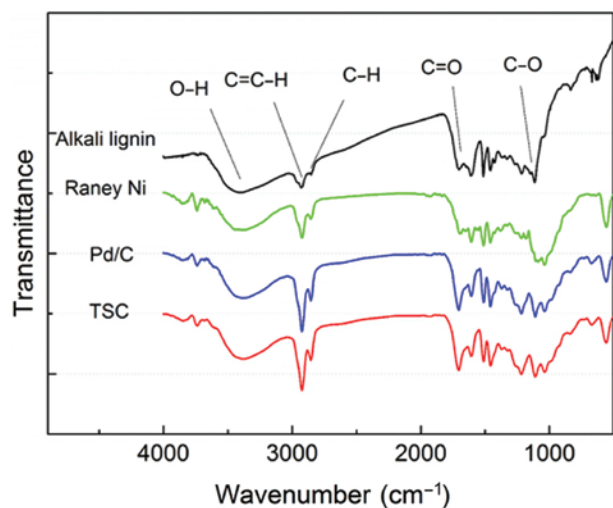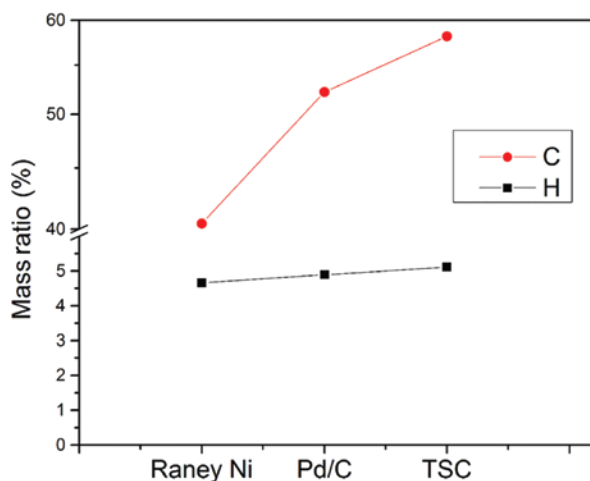

Figure 5: Elemental analysis of alkali lignin degradation products over different catalysts.

transfer catalyst, such as Raney Ni or Pd/C. However, when using the two-step method, the hydrogen content is much higher, indicating that as the reaction proceeds, hydrogen ions enter the lignin and break its chemical bonds, which improves the hydrogen mass ratio and promotes the degradation of lignin. As the reaction continues, the mass ratio of C element increases, indicating that the content of O element in the reaction product decreases.

Thermo gravimetric (TG) and deferential thermo gravimetric analysis (DrTGA) curves of the alkali lignin and the solid residue after reaction at each stage of the reaction are shown in Figure 6. The degree of charring of the reactants during the reaction can be deduced by analyzing the reaction residue. It can be seen that the weight loss peak of lignin is approximately 350°C, and when the temperature reaches 400°C, the pyrolysis is complete. Both catalysts lead to partial carbonization of the lignin, causing the weight losing peak to move to a high temperature. However, when the two catalysts are used sequentially, the degradation of the residue after the reaction is sufficient, the degree of carbonization is low, also indicating the efficient degradation of lignin.

The GC-MS was used to analyze the components of the liquid products, as shown in Figure 7. The major products include 4-ethylphenol (**1**), acetosyringone (**2**), 4-ethyl-2-methoxyphenol (**3**), 3,4,5-trimethoxytoluene (**4**), 2,6-dimethoxyphenol (**5**), guaiacol (**6**), 4-ethyltoluene (**7**), ethylbenzene (**8**), 2-methoxy-4-propylphenol (**9**), phenol (**10**), 2,6-di-tert-butylphenol (**11**), and *p*-tolualdehyde (**12**), and contents of compounds **1**–**6** are relatively high.

Figures 8 and 9 show the quantitative analysis of the products. It can be seen that among the degradation products, compounds **1, 7, 8, 10,** and **12** are derived from

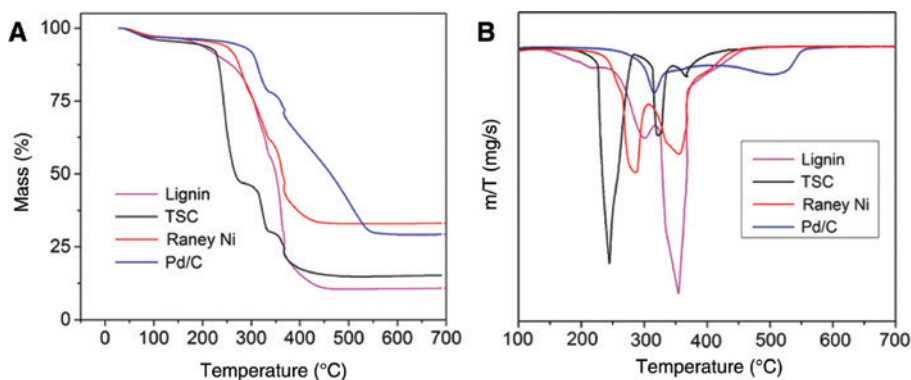**Figure 4:** FT-IR spectra of alkali lignin and the degradation products.

Figure 6: TG (A) and DrTGA (B) curves of alkali lignin and the degradation products.
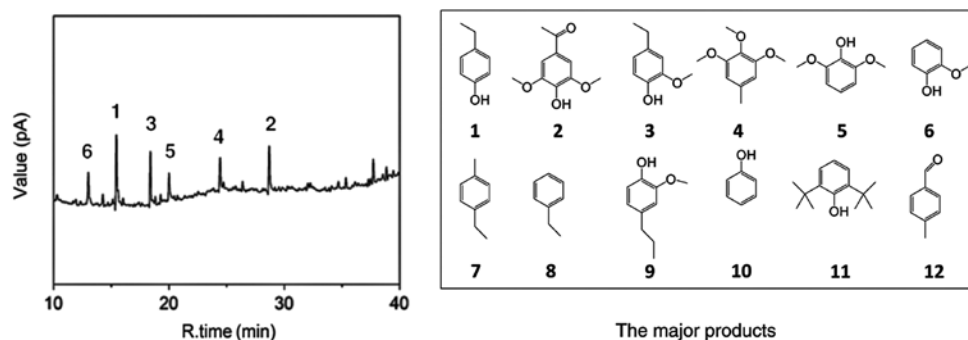

Figure 7: GC-FID of the final products and compounds found in products: 4-ethylphenol (**1**), acetosyringone (**2**), 4-ethyl-2-methoxyphenol (**3**), 3,4,5-trimethoxytoluene (**4**), 2,6-dimethoxyphenol (**5**), guaiacol (**6**), 4-ethyltoluene (**7**), ethylbenzene (**8**), 2-methoxy-4-propylphenol (**9**), phenol (**10**), 2,6-di-tert-butylphenol (**11**), and *p*-tolualdehyde (**12**).
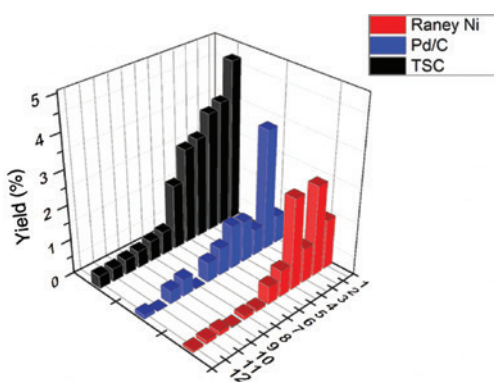

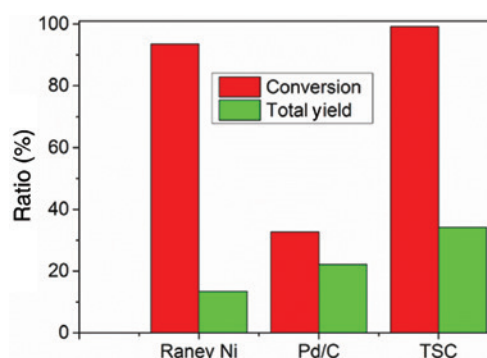**Figure 8:** Quantitative analysis of the products over different catalysts.

Figure 9: Conversion and total yield of the 12 compounds in the degradation product.

the *p*-hydroxy-phenyl lignin structure. In addition, compounds **6, 3, 9** and other degradation products are derived from the guaiacyl lignin structure. Compounds **2, 4, 5**, and **11** are derived from the syringyl lignin structure. The three structural units of lignin are all effectively degraded [21]. The representative alkali lignin structure is shown in Figure 10. Blue color shows the syringyl unit, red color and

green color display the *p*-hydroxy-phenyl unit and guaiacyl unit.

The main pathway for the lignin hydrogenation reaction is the cleavage of ether linkages connecting α, β, and γ carbon atoms of a side chain and position **4** of a phenolic ring unit. Depending on reaction conditions, carbon-carbon linkages may also be disrupted during
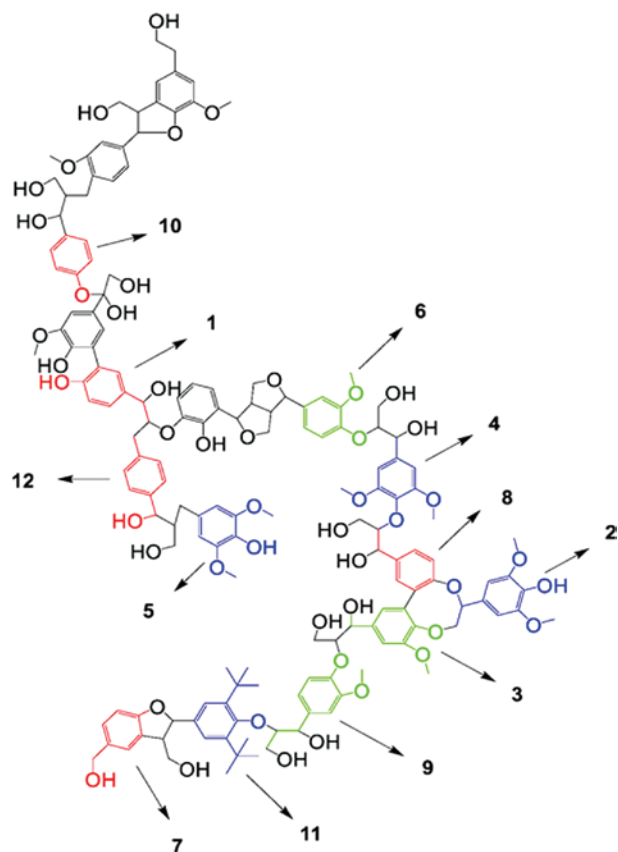
Figure 10: Representative alkali lignin structure and possible degradation mechanism.

hydrogenolysis, especially at α, β, and γ sites. As shown in Figure 10, compounds **1, 2, 3, 6, 9**, and **10** seem to have been generated from ether linkage bond cleavage, followed by carbon-carbon breakdown reactions that lead to compounds **4, 5, 7** and **8**, GC-MS studies for degradation products also support the mechanism (Supplemental Figure S2). Hydrogenation reactions can cause the disappearance of methoxy groups in compound **11** (particularly at positions 2 and 6 of the phenolic ring), which leads to the production of methyl groups. Compounds **2** and **12** exhibit a carbonyl group at a position (ketone or aldehyde) that could have originated from further reactions of the intermediates formed during the ether linkage cleavage between an aliphatic carbon and oxygen from the ether bond (generally in position 4) [20].

4 Conclusion

First, we found that when Raney Ni catalyst and Pd/C catalyst were used as the hydrogen transfer catalysts, the effects were different. When lignin polymer was catalyzed by Raney Ni under the hydrogen transfer reaction, the conversion from solid to liquid was higher. It was proven that the reactants had a low conversion rate and liquefaction rate for Pd/C catalysis. Then, when the lignin was hydrogenated by the two-step method, the natural lignin was successfully degraded into monomer. The liquefaction yield was more than 90%, and the selectivity was more than 30%. In using natural lignin as a renewable raw material to produce valuable chemicals, the conversion rate and selectivity are essential. In addition, the new environmentally friendly pathway has the competitive advantage of biomass lignin degradation and application.

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Bionotes

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