

Efficient base-catalyzed decomposition and *in situ* hydrogenolysis process for lignin depolymerization and char elimination



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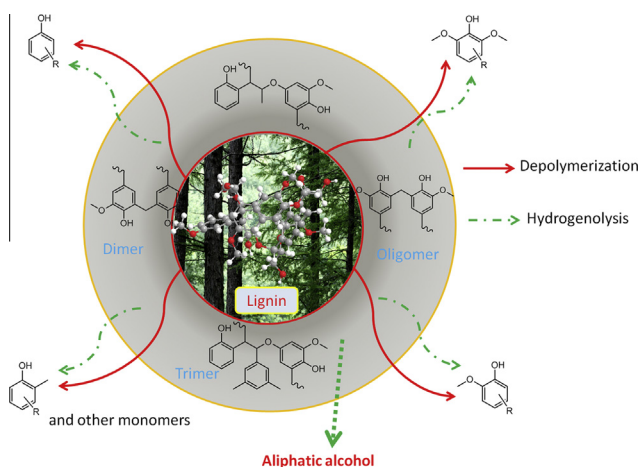
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HIGHLIGHTS

- A promising process for lignin depolymerization and char elimination.
- Lignin decomposition and *in situ* oligomer hydrogenolysis responds to char reduction.
- The unsaturated oligomer was converted to more stable aliphatic alcohol.
- 92.5% conversion, 12.69% phenolic monomer and 6.12% aliphatic alcohol were achieved.
- Less than 14% solid was shown, which was far lower than the single catalyst system.

GRAPHICAL ABSTRACT

A novel and promising strategy for the efficient lignin depolymerization and char elimination was achieved via base-catalyzed decomposition of lignin and the *in situ* hydrogenolysis of phenolic oligomer.



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ABSTRACT

Serious char formation caused by the repolymerization of unsaturated decomposition products is a considerable challenge for current lignin utilization. Here, a novel and efficient base-catalyzed depolymerization and *in situ* hydrogenolysis process for lignin decomposition and char elimination was proposed using the synergic catalyst of NaOH coordinated with Ru/C. In which, lignin was first depolymerized to phenolic monomer and its oligomer, and then the oligomer was further converted to more stable aliphatic alcohols simultaneously. The results showed that more than 92.5% of lignin was converted, giving 12.69% phenolic monomer, 6.12% aliphatic alcohol and less than 14.03% residual solid. This residual solid selectivity was far lower than it from the single catalyst condition. Furthermore, the products were analyzed using GC–MS, GPC, HPLC–MS and ¹H NMR. The synergistic effect between depolymerization and hydrogenolysis was also investigated through comparative analysis of the feed-stock, products, and the recovered lignin.

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1. Introduction

Lignin, a principal component of renewable biomass, consists of methoxylated phenylpropane structures and accounting for 15–30% of the weight and 40% of the energy of the lignocelluloses [1]. Therefore, lignin has been considered as a promising starting material for bulk aromatic chemicals and hydrocarbon (high quality biofuel) [2,3], considering on currently serious energy and resource crisis, CO₂ emission and air pollution. Unfortunately, this aromatic natural polymer is more recalcitrance than carbohydrate due to its complex structure and random chemical bonding. Most of it is combusted directly as a low value fuel, resulting in the significant deterioration of resource waste. Current technologies for this sustainable aromatic material include pyrolysis, liquefaction, hydrogenation and oxidation [4–8]. However, most of the reported processes suffer serious char formation, oligomer product repolymerization and relatively low phenolic monomers yield.

Compared with the acid catalyzed depolymerization, base-catalyzed process is insignificant carbon deposition [9–14]. For example, a series of alkali metal hydroxides such as KOH, CsOH and LiOH had proven to be efficient on the lignin depolymerization, but, it also exhibited more than 43% of ether insoluble char and tar [11]. Recently, Lavoie's study [14] showed that 10% phenolic monomers and 60% oligomer could be obtained after the NaOH catalyzed depolymerization of the steam-treated lignin at 300–330 °C, however, more than 30% of char was generated. More recently, we found that organosolv pine lignin can be efficiently depolymerized in the presence of solid alkali MgO and THF as well. More than 13.2% yield of phenolic monomer was obtained due to the excellent lignin dissolution capability and the catalyst promotion effect [15]. However, the repolymerization of oligomer resulting in residual solid producing cannot also be neglected. Furthermore, it was reported that the producing of char and tar during lignin depolymerization process is caused by the repolymerization and condensation of oligomer followed by dehydration on the catalytic activity center with the thermal effect [16,17]. This repolymerization product has a significantly tighter internal structure and chemical bonding than original lignin, and is more difficult to be degraded.

Generally, aliphatic alcohol is more stable than phenolic compound due to its saturated structure. Therefore, the exploitation of novel and efficient strategy for the hydrogenolysis of phenolic oligomer to more inert aliphatic alcohol would be a promising approach for the comprehensive utilization of lignin with reduced char formation. Here, we construct an efficient, novel and integrated catalytic system for lignin depolymerization and char elimination at mild condition, in which, the ether bond, such as β -O-4 and $-\text{OCH}_3$, was first degraded giving phenolic monomer and unstable oligomer. This oligomer can be converted to more stable chemicals such as aliphatic alcohol in the self H-donating reagent CH₃OH with the hydrogenation catalyst Ru/C, reducing the char formation by the elimination of the unsaturated intermediate. Furthermore, the *in situ* hydrogenolysis process can also promote the depolymerization balance through the product consumption, resulting in high lignin conversion and phenolic monomer yield at mild condition.

2. Materials and methods

2.1. Materials

5 wt% Ru/C and 5 wt% Pd/C were purchased from Aladdin (Shanghai, China) and were used as received. THF and CH₃CN (high performance liquid chromatography (HPLC) grade) were provided by Acros (Belgium). NaOH, KOH, Na₂CO₃ and HCl were analytical grade. The organosolv South China pine lignin was isolated accord-

ing to the reported procedure [18]. Fourier Transform Infrared spectroscopy (FT-IR) and Nuclear Magnetic Resonance (¹H NMR, ¹³C NMR) results showed no obvious absorbance of the carbohydrate. There was also not any sugar be detected by HPLC analysis from the dilute acid hydrolysis. Therefore, the purity of the lignin was more than 97%.

2.2. Depolymerization and *in situ* hydrogenolysis of lignin

The depolymerization and *in situ* hydrogenolysis of lignin was conducted in a 100 mL stainless batch autoclave reactor (316L stainless, Weihai Chemical Machinery Co., Ltd.). In a typical process, 1.0 g lignin, 0.030 mol NaOH and 0.20 g Ru/C were added into the autoclave along with 40 mL anhydrous methanol as solvent. The reactor was purged with H₂ for three times and pressurized to 4.0 MPa. After that, it was heated to 260 °C for 4 h under the stirring of 800 rpm. When the reaction was finished, the autoclave was cooled to room temperature using electron fan.

2.3. Production separation

The gaseous fraction was collected in a 200 mL reservoir bag. The product mixture was filtered, and the solid fractions (include catalyst and residue) were first washed three times with 30 mL CH₃OH (10 mL \times 3). Then, it was dried at 100 °C until constant weight. The filtrate was neutralized with 1.0 mol L⁻¹ HCl, then, 200 mL deionized water was poured to precipitate the undegraded and/or partly degraded lignin. Recovered lignin was obtained by the removal of solvent and freeze-drying overnight under vacuum. The phenolic monomers were extracted using CH₂Cl₂. The used catalyst (included in the residual solid fraction) was first neutralized by 1.0 mol L⁻¹ HCl, and then it was washed by deionized water for three times until no Cl⁻ was detected. After careful freeze-drying overnight under vacuum, the recycled Ru/C was used for the next run.

2.4. Analysis and measurement of the products

Detail product analysis could be found in the [supplementary data](#). The quality and quantitative analysis of the gaseous fraction were carried on an Agilent 7890 GC with both thermal conductivity detector (TCD) and flame ionization detector (FID). The gas chromatography mass spectrometer (GC-MS) analysis of the volatile products was conducted on an Agilent 7890 GC with an Agilent 5975 inert mass-selective detector and was identified according to the NIST MS library. The quantitative analysis of these chemicals was carried out on an Agilent 7890 GC with a FID using acetophenone as internal standard at the same capillary column and temperature program as the GC-MS analysis.

The FT-IR spectrum of water soluble fraction was obtained on a Nicolet is50 FT-IR spectrometer by KBr pelleting method. ¹H NMR experiment was performed on a Bruker Advance 400 III spectrometer, where D₂O was used as solvent. And the HPLC-MS analysis was carried out on a Quadrupole-time of flight Liquid Chromatography-Mass Spectrometry (LC-MS, Agilent, USA) equipped with HiP Sampler, Binary Pump and triple-quadrupole Mass Spectrometer (TOF/Q-TOF). The FT-IR analysis of the residual solid was conducted on a Nicolet is50 FT-IR spectrometer using KBr pelleting method.

The conversion of lignin was measured by the weight comparison between the recovered and the original lignin as shown in Eq. (1). The yield of aliphatic alcohol and phenolic monomer were measured according to the following Eqs. (2) and (3) respectively based on the GC results. The yield of residual solid was obtained by Eq. (4). According to above separation procedure, the products were separated into gas (less than 1% weight of lignin for each

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