



Research article

A facile method for char elimination during base-catalyzed depolymerization and hydrogenolysis of lignin



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ABSTRACT

Lignin is a renewable source of phenolic compounds for the possible replacement of fossil fuels. However, severe char formation induced by the repolymerization is a crucial challenge for current lignin utilization. Herein, an efficient base-catalyzed depolymerization and in situ hydrogenolysis process of organosolv lignin depolymerization and char elimination was implemented using the synergic catalyst of NaOH and different hydrogenation catalysts. NMR (2D-HSQC and ^{31}P NMR), TG and GPC techniques were elaborately used to characterize the partly degraded lignin (DL) after catalytic hydrocracking. Meanwhile, the monomeric compounds were characterized and quantified by GC–MS technique. Under an optimal condition with the synergic catalyst of 0.025 mol NaOH coordinated with 5% Ru/C at 260 °C, a low yield of char (6.4%) and high yield of water-soluble fraction (95.4%), including 24.3% degraded lignin, 44.6% water-soluble product and 26.5% oil-soluble product, could be obtained. Additionally, the content of acetic acid was significantly high in the monomeric fraction among all degraded compounds of lignin. Furthermore, the DL exhibits excellent thermal stability, which can be suitable for developing lignin-based flame resistant material. In short, this proposed process extends the depolymerization methodology of lignin in aqueous NaOH system.

1. Introduction

With the excessive consumption of fossil fuels as a source for fuels, chemicals, and energy, the production of these commodities from renewable lignocellulosic biomass can be expected to increase in the near future [1,2]. Since lignin, along with cellulose and hemicelluloses, is one of the most abundant natural polymers, it constitutes 20%–30% (wt %) of lignocelluloses and carries the highest specific energy content of all the three fractions, the depolymerization of lignin into aromatic components is probably the most promising way to provide an alternative to the petrochemical industry [2–4]. Over the past few decades, researches on the production of value-added chemicals, alternative fuels and platform compounds from lignin have grown rapidly on account of the importance of lignin in the biorefinery [5–8]. However, efficient conversion of lignin into aromatic products is still a challenge due to structural complexity and natural recalcitrance of lignin to depolymerization process.

Currently, most reported processes suffered from obvious char formation, repolymerization of oligomer product and low yield of phenolic monomers. Barta et al. [9] provided a good example that an aldehyde product was identified as the main cause of side reactions under cleavage conditions and markedly suppresses such an undesired pathway

by capturing the aldehyde products with diols and by in-situ conversion of the reactive intermediates. Interestingly, there are no aldehydes products after reductive depolymerization of lignin produced, which don't need to capture the unstable compounds for inhibiting repolymerization. However, noble metals normally have excellent hydrogenation activity. For example, Xu et al. [10] reported that the molecular weight (M_w) of the lignin was reduced significantly from 10,200 to 1020 g/mol over noble metal catalysts (Ru/C or FHUDES-2 catalysts). Zakzeski et al. [11] used noble metals (Pt/Al₂O₃, Pd/C, and Ru/C) as hydrogenation catalyst in depolymerization process of lignin, and the liquid-phase was reformed to 17.6 wt% monomeric phenols. Yan's group [12,13] reported the hydrogenolysis of β -O-4 linkage in model compounds and in real lignin over a series of bimetallic catalysts, and bimetallic catalyst exhibited significantly higher activity in the direct conversion of lignin into monomeric aromatic chemicals. Besides that, hydrogen donor solvent, i.e., isopropanol, is employed in lignin depolymerization to stabilize free radicals that otherwise recombine to form char [14–16]. Rinaldi et al. [16] recently investigated the transformation of lignin in the presence of Raney Ni using isopropanol as a hydrogen-transfer initiator and it was found that the molecular weight of bio-oil decreased after the process.

Although base-catalyzed depolymerization is insignificant to carbon

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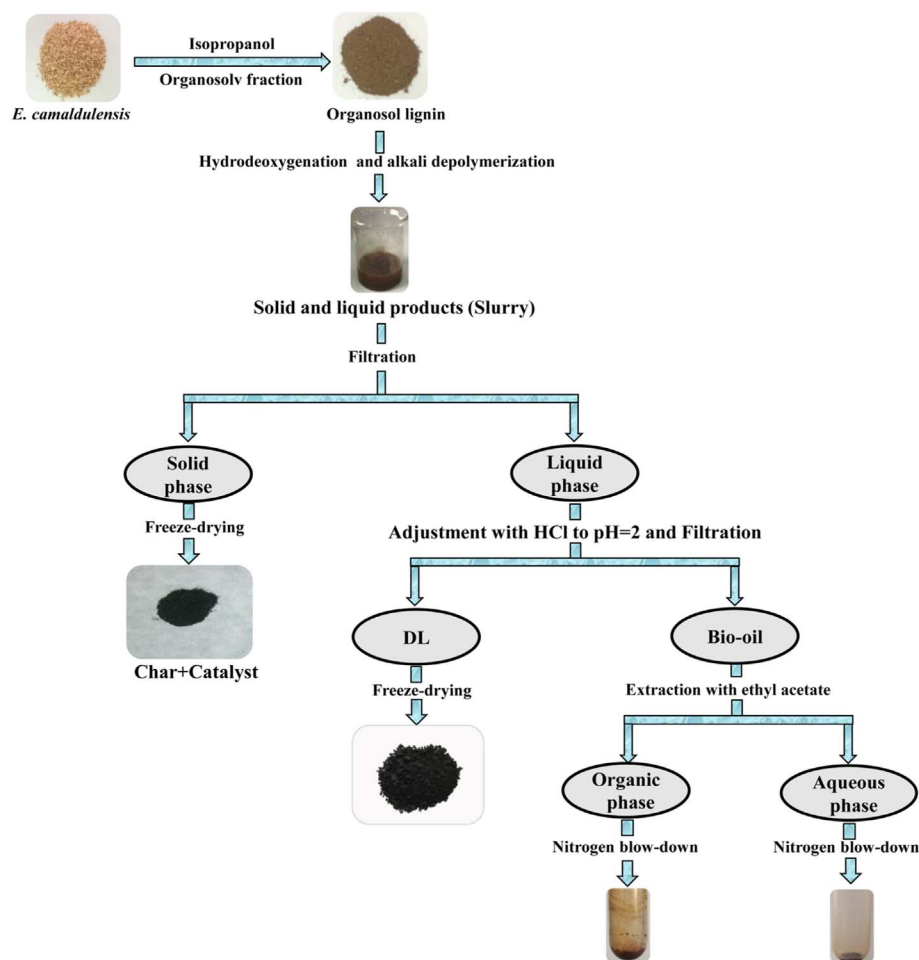


Fig. 1. Schematic illustration of the experimental procedure.

deposition, it is still a promising process for the chemical conversion of lignin into biofuels and biochemical such as phenolic monomers due to its excellent catalytic degradation performance. For example, Lavoie et al. [17] reported that 12% phenolic monomers compounds and 60% oligomers could be obtained after the NaOH catalyzed depolymerization of the steam-treated lignin under 300–330 °C. However, the base-catalyzed depolymerization process should be performed at high temperatures. A recent study showed that a series of base catalyst (KOH, NaOH and Na₂CO₃) and noble metal catalyst (Ru/C and Pd/C) is efficient on the lignin depolymerization and the results showed that 92.5% lignin was converted into monomers (18.81%), water-soluble oligomers (59.66%), and char (14.03%) under the optimal condition (260 °C, 4 h) [18]. However, the content of residual char was still high and long reaction time was needed under the given catalytic system. Moreover, the used feed lignin was extracted from pine wood based on acidic ionic liquid (IL) and a mixture of C₂H₅OH and water under high temperatures. Generally, softwood lignin is composed almost of guaiacol units (G) and its chemical structure is simple. Similarly, Yan's group [19] reported that alkali enhanced organosolv lignin depolymerization in Ni₇Au₃ nanoparticle catalyst system and suggested that alkali favored the formation of phenolate products, which prevented subsequent absorption and hydrogenation.

Herein, we establish an efficient and synergetic catalytic system for lignin depolymerization and char elimination under mild conditions using NaOH and noble metal catalysts (Ru/C, Pt/C, and Pd/C). The ether bonds of lignin were expected to be firstly cleaved and unstable oligomers were generated. These oligomers could be transformed into more stable chemicals in the hydrogen donor solvent (isopropanol) with the noble metal catalyst, thus reducing the char formation. To

detect the changes of molecular weight, chemical bonds, functional groups and structural changes of lignin during the depolymerization, the organosolv lignin (OL) and degraded lignin (DL) was comprehensively characterized by gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) techniques (2D-HSQC and ³¹P NMR). Additionally, the thermal degradation kinetics of OL and DL were also evaluated by the TG curves and the corresponding mathematical models were established. Furthermore, gas chromatography mass-spectrometry (GC–MS) was used for identifying the degraded small molecules (i.e. aromatic compounds) in the oil-soluble product.

2. Material and methods

2.1. Materials

Eucalyptus camaldulensis were harvested from Guangxi province, China. The preparation of *Eucalyptus* sawdust was according to a previous literature [20]. The composition of *Eucalyptus* sawdust, which was determined according to a previous literature [20], was 43.5% cellulose, 17.1% hemicelluloses and 26.3% Klason lignin in terms of dry weight. Sodium hydroxide, hydrochloric acid, ethyl acetate and isopropanol were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., and catalysts (Ru/C, Pd/C, and Pt/C) were purchased from Sigma-Aldrich.

2.2. Preparation of organosolv lignin (OL)

The preparation of organosolv lignin was carried out in a 1000 mL Parr reactor (Parr Instrument Company, USA). *Eucalyptus* powder (50 g)

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