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Understanding the relationship between the structure and depolymerization behavior of lignin

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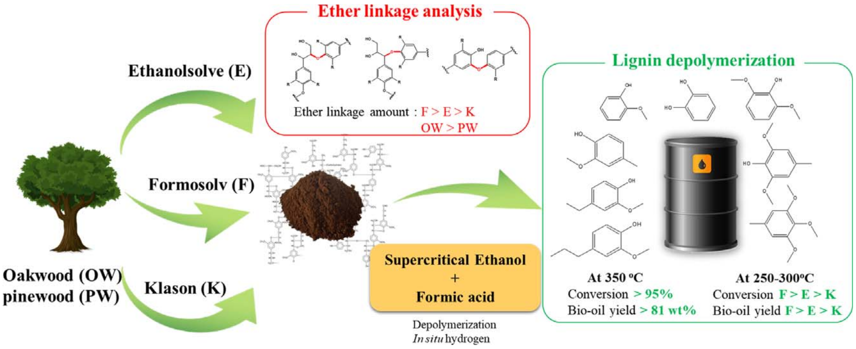
GRAPHICAL ABSTRACT



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ABSTRACT

Various lignin depolymerization methods have been proposed. Nevertheless, the relationship between the structure of lignin and its depolymerization behavior has not been widely investigated. Herein, six types of lignin samples were produced from oakwood (OW, hardwood) and pinewood (PW, softwood) using three different delignification techniques (ethanolsolv, formasolv, and Klason). The content of ether linkages in the OW-derived lignins was approximately three times higher than that in the PW-derived lignins because of the presence of the sinapyl alcohol unit in the former. The contents of ether linkages in the lignin isolated via the different methods followed the order: formasolv > ethanolsolv > Klason. The lignin samples were depolymerized in a mixture of supercritical ethanol (scEtOH) and formic acid at temperatures of 250–350 °C. At 350 °C, regardless of the lignin type, high conversion (> 95%) and a high bio-oil yield (> 81 wt%) could be achieved, demonstrating that the combined use of scEtOH-HCOOH was very effective for the depolymerization of various types of lignin. At the low temperatures of 250–300 °C, the lignin conversion and bio-oil yield were highly dependent on the amount of ether linkages; for example, at 300 °C, the use of OW-derived formasolv lignin resulted in a high bio-oil yield (86.2 wt%), whereas the use of OW-derived Klason lignin resulted in a very low bio-oil yield (27.9 wt%). The properties of the bio-oils produced from the different types of lignin were discussed.

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1. Introduction

Lignocellulosic biomass is considered one of the most promising non-edible renewable resources for producing bio-derived fuels and chemicals because of its natural abundance and global availability [1–4]. In a typical sugar platform pathway for producing biofuels and biochemicals (e.g., cellulosic bioethanol and biobutanol), it is necessary to separate lignin from cellulose using an appropriate pretreatment method [5–7]. When the current, active commercialization status of lignocellulosic biofuels worldwide is taken into account, a huge amount of lignin (which corresponds to 25–35 wt% of lignocellulosic biomass [8]) is generated from biorefinery plants as a byproduct [3,9]. Approximately 40% of the lignin produced from cellulosic biofuel plants would be required as a source of internal energy from combustion [10]; thus, the development of effective techniques for lignin valorization to produce liquid fuels and value-added chemicals is highly desired. The production of surplus lignin in the near future and its rich aromatic structure make it a promising alternative to petroleum-based aromatic chemicals. Nowadays, however, only a very small fraction (1–2%) of the lignin produced from pulping liquors is used to produce specialty chemicals [11]. One reason for the limited use of lignin as a feedstock for producing liquid fuels and chemicals is the highly recalcitrant and complex nature of lignin, which makes depolymerization very difficult. Moreover, the presence of various types of chemical bonds in the lignin derived from different wood sources and the unpredictable changes in the chemical bonding during delignification make it difficult to develop a "generalized" depolymerization technique; a depolymerization method that is effective for a certain type of lignin is not necessarily effective for other types of lignin. Therefore, it is crucial to understand the relationship between the lignin structure and its depolymerization behavior to develop an efficient valorization technique for ultimate utilization of various types of lignin.

Various methods of separating lignin from cellulose have been developed, including the steam explosion, Kraft, alkali, concentrated strong acid hydrolysis, and organosolv approaches [7]. During the pretreatment of lignocellulosic biomass, the structure of "native" lignin is ultimately changed; the degree and extent of the structural change is highly dependent on the pretreatment method selected for lignin separation. Most of the pretreatment methods proceed at elevated temperatures of 100–200 °C in the presence of acid or base catalysts. Under these conditions, C—C coupling reactions tend to occur, making the isolated lignin more recalcitrant to depolymerization [12,13]. Therefore, the chemical nature of isolated lignin (phenyl propanol monomers, ether and condensed linkages, bonding energies, substituent groups, etc.) is not only dependent on the lignin source (e.g., hardwood, softwood), but also on the separation technique. This makes it very difficult to develop a generalized depolymerization method for the effective production of value-added aromatic chemicals and fuel additives from various types of lignin.

Various lignin depolymerization approaches have been proposed, including fast pyrolysis [14], the ionic liquid-assisted method [15], biological degradation [16], and hydrothermal/solvothermal reactions with or without a catalyst [17,18]. Among these approaches, the hydrothermal/solvothermal technique is considered very promising because of its high liquid yield (up to 95 wt%) with low char formation (5–20 wt%) [19]. To enhance the conversion of lignin under hydrothermal/solvothermal conditions, various types of solvents (e.g., water, methanol, ethanol, isopropyl alcohol (IPA), acetone [20–22]) and catalysts (e.g., NaOH [23], KOH [24], H-USY (ultra-stable zeolite Y, Si/Al = 15) [25], $CuMgAlO_x$ [22], Pt/Al_2O_3 [26]) have been evaluated. To develop a versatile method for the depolymerization of lignin produced from various lignocellulose sources and using different pretreatment methods, it is necessary to gain comprehensive understanding of the relationship between the lignin structure and its depolymerization behavior. However, only a few studies have been dedicated to understanding the depolymerization behavior using different lignin sources; for example, Xabier et al. compared the depolymerization behavior of three types of organosolv lignin (acetosolv, formosolv, and acetosolv/formosolv) produced from a single wood resource using supercritical acetone, ethanol, and methanol [27]. In supercritical acetone at 300 °C and 6.6–6.7 MPa, the use of an acetosolv/formosolv lignin for 40 min resulted in a higher oil yield (38 wt%) than obtained with individual acetosolv and formosolv lignin (32–34 wt%). One of the key parameters determining the oil yield is the molecular weight of lignin; the oil yield was found to be lower when the molecular weight of lignin was lower. Jun et al. studied the catalytic solvolysis of organosolv lignins produced from Chinese fir and maple in a mixture of supercritical ethanol and 1-butanol in the presence of a Ru/C catalyst at 300 °C under a pressure of 40 MPa for a reaction time of 40 min [28]; the lower oil yield from Chinese fir lignin (32 wt%) than that from maple lignin (41 wt%) was attributed to the different lignin origins according to the wood types. Although the previous studies illustrated a plausible relationship between the lignin sources and bio-oil yields, there is still a lack of understanding of the fundamental properties of lignins and their depolymerization behaviors.

Herein, we investigate the chemical and physical properties of lignin produced by using two different types of lignocellulosic biomass (oak (hardwood) and pine (softwood)) and three different lignin separation methods (ethanolsolv, formasolv, Klason). The produced lignin was depolymerized in a supercritical mixture of ethanol (scEtOH) and formic acid (HCOOH) to gain fundamental understanding of the properties of lignin and its depolymerization behavior. The yields and properties of the lignin-derived oils from the depolymerization of oakwood-derived and pinewood-derived lignins are discussed in detail.

2. Materials and methods

2.1. Materials

Oakwood (*Ouercus*, OW, hardwood) and pinewood (*Pinus*, PW, softwood) were purchased from a local market in South Korea. The cellulose, hemicellulose, and lignin content were analyzed by using the Van Soest method [29], as listed in Table S1. HPLC grade ethanol, acetone, and dichloromethane (DCM) were purchased from Burdick & Jackson (USA). Aqueous sulfuric acid (H_2SO_4, ≥99.5%, ACS reagent grade) was purchased from Sigma-Aldrich (USA). Formic acid (reagent grade) and HCl (35%, extra pure grade) were purchased from Daejung Chemical & Metal (South Korea). Distilled-de-ionized (DDI) water was prepared by using an AQUAMax™-Basic 360 water purification system (Younglin Instrument Co., Ltd., South Korea). High-purity N_2 (99.999%) for purging the reactor was purchased from JC Gas Company (South Korea).

2.2. Lignin separation methods

To produce the ethanolsolv lignin, a batch reactor with an inner volume of 140 mL was filled with 10 g of wood, 80 mL of ethanol/water mixture (50:30 v/v), and 1 g of sulfuric acid as a catalyst. The reactor was heated to 190 °C by using cartridge heaters and a heating furnace and kept for 1 h. After delignification, the solid and black liquid products were collected from the reactor and separated by centrifugation at 4000 rpm for 10 min. The solid products contained cellulose and a small fraction of unreacted lignin. A 240-mL aliquot of water was then added to the recovered filtrate to precipitate the fragmented lignin in the black liquid. This precipitated lignin was then dried in a drying oven overnight at 80 °C. The ethanolsolv lignin samples produced using oakwood and pinewood are designated as OW-E and PW-E, respectively. For the production of formasolv lignin, the batch reactor was filled with 10 g of wood, 80 mL of a formic acid/water mixture (80:20 w/w), and 0.2 g of HCl as a catalyst. The reactor was then heated to 120 °C and kept for 1.5 h. After the reaction, the same separation protocol that was employed to recover the ethanolsolv lignin was used to obtain the