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Impact of lignin structure on oil production via hydroprocessing with a copper-doped porous metal oxide catalyst

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HIGHLIGHTS

- Lignins structure is linked to the oil composition obtained after hydroprocessing.
- Cu-PMO catalyst is effective on hydrogenolysis of low M.W. lignin fractions.
- Catalyzed hydroprocessing can provide aromatic monomers of commercial interest.

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ABSTRACT

A copper-catalyzed depolymerization strategy was employed to investigate the impact of lignin structure on the distribution of hydroprocessing products. Specifically, lignin was extracted from beech wood and miscanthus grass. The extracted lignins, as well as a commercial lignin (P1000), were then fractionated using ethyl acetate to provide three different portions for each source of lignin [total of 9 fractions]. Each fraction was structurally characterized and treated with a copper-doped porous metal oxide (Cu-PMO) catalyst under 4 MPa H_2 and at 180 °C for 12 h. The reaction conditions provided notable yields of oil for each fraction of lignin. Analysis of the oils indicated phenolic monomers of commercial interest. The structure of these monomers and the yield of monomer-containing oil was dependent on the origin of the lignin. Our results indicate that hydroprocessing with a Cu-PMO catalyst can selectively provide monomers of commercial interest by careful choice of lignin starting material.

1. Introduction

Lignocellulosic biomass, including hardwoods, softwoods and grasses, are abundant and renewable resources that are mainly composed of cellulose, hemicelluloses and lignin. Since lignocellulose is non-digestible by humans, its utilization as a chemical feedstock does not compete with food production and so lignin, hemicellulose and cellulose constitute promising alternatives to petrochemical fossil resources. Moreover, lignin is the only abundant source of aromatics found in nature and has the potential to be a major aromatic resource of a bio-based economy. While cellulose and hemicellulose have been extensively studied and used for the production of biofuels and bio-based products (Zakzeski et al., 2010), lignin, however, has not yet found large volume applications. To date, three major approaches to lignin valorization have been investigated: (1) the energy path through power production, green fuels or syngas; (2) the application of lignin as a macromolecule for selected materials; and (3) the production of aromatic compounds for the chemical industry (Bozell et al., 2007) as a direct replacement of petrochemical feedstocks. Considering the abundance of lignin and the uniqueness of its aromaticity within renewable feedstocks, the production of aromatic chemicals via lignin depolymerization as a drop-in solution within the pervasive petrochemical industry is very advantageous. With its unique polyaromatic structure and chemical properties, a wide variety of aromatic compounds are potentially obtainable from lignin.

Structurally, lignin is an amorphous, tridimensional polymer composed of three primary units: syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) (See ESI, Fig. S3).

Abbreviations: Cu-PMO, copper-doped porous metal oxide; EAS, ethyl-acetate soluble; EAI, Ethyl Acetate Insoluble; CL, crude lignin; S, syringyl; G, guaiacyl; H, p-hydroxyphenyl.

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Thermochemical methods for depolymerization of lignin are described in detail in a review published by Pandey & Kim (Pandey and Kim, 2011) and include such methods as pyrolysis, chemical oxidation and hydrogenolysis. Today one of the most popular and efficient depolymerization strategies for lignin is hydroprocessing, which involves lignin reduction by hydrogen to form simpler, monomeric compounds such as phenols and benzene, toluene, or *p*-xylene (BTX), depending on the reaction conditions (Pandey and Kim, 2011). These simple aromatic compounds can then be hydrogenated to alkanes for fuels or used as platform chemicals for the synthesis of fine chemicals and materials using technology previously developed in the petrochemical industry (Zakzeski et al., 2010). Three main reactions occur during catalytic hydroprocessing, namely, hydrogenolysis, hydrodeoxygenation and hydrogenation. Hydrogenolysis is an important reaction for lignin upgrading, particularly in cleaving the abundant ether bonds in lignin, thereby generating aromatic monomers. This reaction usually occurs between 90 °C and 200 °C in presence of a catalyst (Li et al., 2015; Zakzeski et al., 2010).

Catalysis is the basis for many improvements towards sustainable chemical transformations since catalysts reduce the energy and material inputs of the industrial processes that are required by society (Anastas et al., 2000, 1999; Anastas, 1998). Many studies have been conducted on model lignin compounds to study the action of metal catalysts such as Pt, Ni, Ru, Pd, Co, Mo, or W on the reductive cleavage of the ether bonds. These investigations are summarized in several reviews (Laskar et al., 2013; Li et al., 2015; Zakzeski et al., 2010). Investigations of the action of combination catalysts such as Ni-Ru, Ni-Rh and Ni-Pd, used in aqueous medium for the transformation of lignin to monophenols have also been performed (Li et al., 2015; Wang and Rinaldi, 2012; Zhang et al., 2014). However, catalytic methods commonly use noble metals or require forcing conditions that result in low product selectivity. Furthermore, the preparation of such catalysts can employ several equivalents of a toxic reagent or is energy intensive (Petitjean et al., 2016). Thus, easily synthesized green catalysts based on earth abundant elements could provide promising solutions for the large-scale applications of catalytic hydrogenation and hydrogenolysis (Petitjean et al., 2016). Previous work in our laboratories and others has revealed that a copper-doped porous metal oxide (Cu-PMO) is capable of very selective reactions. The Cu-PMO catalyst has the advantage of being composed entirely of earth-abundant materials and can operate at very low loadings of Cu (0.3 mol%). Moreover, when compared to other earth-abundant metal catalysts, Cu-PMO has other advantages, such as resiliency to phenolic units, the ability to accommodate electron-rich and sterically-hindered substrates, and durability - it was recycled 11 times before a noticeable decrease in activity (Barta et al., 2014; Petitjean et al., 2016; Warner et al., 2014). The Cu-PMO also catalyzes methanol reforming and the water gas shift reaction, producing hydrogen. The resulting hydrogen from the shift reaction in supercritical methanol can provide the reducing equivalents necessary both to cleave aromatic ethers and for further reduction and deoxygenation (Macala et al., 2009; Matson et al., 2011). More importantly, the Cu-PMO catalyst is also effective in converting lower molecular weight lignin into a mixture of aromatic products in high yield and without char formation (Barta et al., 2014). Notably, the reaction proceeds under relatively mild conditions (180 °C, 4 MPa H_2) and the aromaticity of the products is preserved. This is evidence of the high selectivity of Cu-PMO towards cleavage of C–O bonds (Barta et al., 2014).

Efficient and selective production of aromatic monomers from such a structurally diverse and complex material as lignin is a formidable challenge. Production of oxygenated aromatic compounds from lignins, rather than focusing on BTX, by mild and sustainable hydroprocessing is economically and environmentally appealing. In effect, oxidation steps have historically been the most environmentally polluting steps in all of petrochemical transformations (Anastas, 1998). The creation and design of new compounds with new properties and applications as well as the research of new markets for these products are capital opportunities to develop a more sustainable chemical industry that is consistent with green chemistry principles.

The majority of lignin depolymerization studies are carried out on model compounds and focus on the development of new catalysts for the optimization of yields and selectivity (Li et al., 2015; Zakzeski et al., 2010). There have been fewer hydroprocessing studies using lignin due to its complex structure and the poor solubility in conventional solvents.

Investigations on lignin itself have mainly targeted the optimization of reaction settings (temperature, pressure, time) or the testing of new catalysts (Li et al., 2015; Zakzeski et al., 2010) and have not focused on the source of lignin until last year (Guo et al., 2017; Jiang et al., 2016; Liu et al., 2016; Shu et al., 2016; Wang et al., 2017). These studies focus on either the pyrolysis or hydroprocessing depolymerization behaviors of different lignins. The hydroprocessing studies harness the activity of different catalysts and most employ noble metals (Bouxin et al., 2015; Shu et al., 2016; Wang et al., 2017). the effect of the starting lignin on product composition and yield was studied, using Ni/C in methanol under hydroprocessing conditions (Klein et al., 2015; Song et al., 2013), but not in detail how each component variable of the lignin structure affects product distribution and yield. Although these few studies evidence the importance of parameters such as the relative abundance of β-O-4 inter-unit linkages (Bouxin et al., 2015), molecular weight, and degree of unsaturation (Shu et al., 2016), more research is still necessary to elucidate more clearly the correlation between lignin structure and aromatic product yield and composition. In addition, no studies correlating lignin structure to reactivity has been done utilizing a copper–doped catalyst. Furthermore, we ensure to utilize conditions that are relatively mild, in combination with a heterogeneous catalyst composed entirely of earth-abundant elements, therefore providing mechanistic understanding of a green and industrially relevant methodology.

While the variable and complex structure of lignin highlights the diversity of useful products that could be derived from this naturally occurring polymer, the heterogeneity of lignin structure is a well-established challenge to valorization on an industrial scale. Understanding the influence of structure on the composition and yield of hydroprocessing products is important to the translation of this method into an industrial process and the design of integrated bio-refineries. We have therefore studied the impact of the lignin structure on liquefied aromatic product distribution obtained by mild hydroprocessing. The depolymerization of three different lignin structures, isolated from different raw biomass was investigated. All lignin samples were fractionated in organic solvent prior to the Cu-PMO reductive treatment. The crude, organic soluble, and insoluble portions were analyzed individually to elucidate the impact of lignin structure on its liquefied aromatic products.

2. Materials and methods

2.1. General Experimental

Chemicals and solvents were purchased from Sigma-Aldrich, Alfa-Aesar, JT Baker or TCI and used as received. Protobind™ 1000 (P1000) was obtained from ALM India Pvt. Ltd., Chandigarh, India. All hydroprocessing reactions were performed in a 100 mL stainless-steel Parr vessel equipped with a mechanical stirrer and temperature controller (Parr Instrument). The reactions were pressurized under ultra-high purity hydrogen atmosphere (Airgas).