



Amination of biorefinery technical lignins using Mannich reaction synergy with subcritical ethanol depolymerization



Bing Wang^a, Tian-Ying Chen^a, Han-Min Wang^a, Han-Yin Li^a, Chuan-Fu Liu^b, Jia-Long Wen^{a,*}

^a Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083, China

^b State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

The alcoholic depolymerization and Mannich reaction were conducted to improve the chemical activity of biorefinery technical lignins and introduce amino groups into lignins, respectively. To understand the chemical structural transformations and examine the reaction mechanism, GPC and solution-state NMR techniques were performed. Element analysis was also used to quantify the amount of amine groups. The NMR characterization the depolymerized lignins indicated of the depolymerization, demethoxylation, and bond cleavage of linkages occurred during the depolymerization process. Results showed that the depolymerization temperature instead of the addition of capping reagents was the main factor for improving the reactivity of lignin under the given conditions. The Mannich reaction was very selective, primarily occurred at H_{3,5} and G₅ positions, and the H units present a higher chemical reactivity. It is believed that the understanding of the fundamental chemistry of lignin during depolymerization and Mannich reaction process will contribute to the extension of high value-added applications of biorefinery lignin.

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1. Introduction

With the gradual depletion of fossil fuels and the increase of awareness concerning the human impacts on the environment, there is a strong incentive to exploit alternative and sustainable energy sources for energy and material production [1]. At present, lignocellulosic biomass is considered to be one of the most promising renewable resources to replace fossil counterpart for the elaboration of biofuels and other bio-based products [2]. In lignocellulosic biomass, lignin is the most abundant biopolymer in plant cell wall besides cellulose, consisting primarily of three units: guaiacyl (G), sinapyl (S), and *p*-hydroxyphenyl (H) linked by aryl ether (β -O-4, α -O-4, and 4-O-5) and carbon-carbon (β - β , β -1, β -5, and 5-5) bonds [2–4]. With the development of the modern biorefinery industry (bio-ethanol, oligosaccharide, bio-diesel etc.) and the application of this concept in conventional biomass utilization, large amounts of biorefinery technical lignins have been generated. However, only an estimated 2–10% of the 50 million tons of lignin isolated from pulping processes was used for specialty products,

while the rest was burned as a low-value fuel or directly landfilled which seriously affected the environmental and economic benefit [5]. Actually, these globally abundant technical lignins have enormous potential to replace a significant portion of petrochemical feedstocks in the future.

In China, a successful story of biorefinery is the value-added applications of three components of corn cob in Shandong Longlive Bio-technology Co., Ltd. The general production processes for corn cob were as follows: (i) the corn cob was subjected to hydrothermal pretreatment to degrade the hemicelluloses into xylo-oligosaccharides; (ii) a diluted alkaline treatment was used to fractionate the residues into lignin and cellulose-rich substrates; (iii) the obtained substrates were deemed as a feedstock for the bio-ethanol production. The previous research from our group have verified that the separated corn cob lignin containing a considerable purity and presenting a tremendous potential to be utilized as a feedstock for the production of various bio-based materials, such as lignin-based phenol-formaldehyde resin adhesive, polyurethane, surfactant, and bio-sorbent [6–8]. Although the corn cob lignin has a high purity and relatively unscathed structures as compared to other industrial lignins, such as Kraft and industrially alkali lignin, its low chemical reactivity and macromolecule structures still impeded synthesizing the lignin-based materials with

* Corresponding author.

E-mail address: wenjialonghello@126.com (J.-L. Wen).

excellent performance as compared to similar products totally prepared from petrochemical feedstocks [6]. Thus, for value-added applications, structural modifications of the original lignin are imperatively required.

As phenolic polymers, technical lignins with physical and (or) chemical modification are considered to be potential renewable sources for industrial applications. Generally, lignin modification could decrease brittleness, increase solubility in organic solvents, and improve process ability by means of esterification, etherification, carboxymethylation, and epoxidation, which was mainly occurred at the phenolic hydroxyl groups [9,10]. In addition, amination, hydroxyalkylation, and other graft copolymerization were also the important modification methods. However, among these various approaches, ammonification is one of the most promising modification methods because the introduced amine groups are ionizable and positively charged under acidic conditions [11]. Chemically, there are many applicable methods for the introduction of amine groups, e.g., for polymeric materials (cationic surfactant, bio-adsorbent) [12], as a reagent for enzyme immobilization [13], and for use as slow-release fertilisers [14]. Among the ammonification methods, Mannich reaction is the simplest and most straightforward method, which is a condensation reaction that introduces amine groups to designated reactive sites. Traditionally, the Mannich reaction is one of the most important fundamental reactions in organic chemistry [15]. For example, this reaction is a powerful method that is typically used for the synthesis of various-amino ketones or esters, which are useful synthetic building blocks for the preparation of many biologically important nitrogen-containing compounds. Unfortunately, the native low chemical reactivity of lignin restricted the efficiency of chemical reaction. Therefore, the enhancement of chemical reactivity of lignin is also extremely significant for its further modification. To realize this purpose, phenolation, demethoxylation, and depolymerization methods were developed in the past few decades. As compared to other two approaches, depolymerization is much more effectively, simply, and environmentally friendly for improving the reactivity of lignin. Meanwhile, understanding the chemical structural transformations of lignin during the depolymerization and chemical modification processes, which was lack of sufficient study in previous literatures, is also significant for the extensive utilization of lignin.

In the present study, alcoholic depolymerization served as a green process was developed to improve the reactivity of industrial alkali lignin, and the depolymerized lignin was further modified through the Mannich reaction under acidic conditions. Meanwhile, the state-of-the-art NMR techniques, such as ^{31}P , ^{13}C , and 2D-HSQC NMR were performed to investigate the structural transformations of lignin during the depolymerization and chemical modification process. In addition, elemental analysis was also used to quantify the introduced amine groups. It is hoped that the current study can extend the approaches of lignin depolymerization and its chemical modification, which facilitate the value-added transformations of biorefinery technical lignins into valuable sustainable biomaterials.

2. Methods

2.1. Materials and chemicals

Alkali lignin (L) was acquired from Shandong Longlive Biotechnology Co., Ltd, China and used without any purification. The reagents used in this study, such as ethanol, phenol, 2-isonaphthol, 1, 4-dioxane, formaldehyde aqueous solution (37%), and dimethylamine aqueous solution (33%) were all purchased from Sigma-Aldrich (Beijing, China). All chemicals were analytical grade and used without further purification.

2.2. Alcoholic depolymerization of alkali lignin

Alcoholic depolymerization of alkali lignin was conducted in a laboratory-scale reactor (Parr Instrument Company, Moline, IL, USA) with a maximal volume of 1000 mL. For the alcoholic depolymerization reaction, 30 g lignin and 300 mL specified solvent (50% ethanol/water or 100% ethanol solution) was added to the tank. The depolymerization was performed with consistent output of the electric band heater under the given temperatures (200 and 240 °C), and maintained the targeted reaction time of 30 min. As a control, 3 g phenol or 2-isonaphthol was added in the reaction system of 50% ethanol/water at 200 °C for 30 min. The detailed conditions of alcoholic depolymerization are shown in Table 1. After the depolymerization process, the reaction mixture was cooled to room temperature and filtrated with a Buchner funnel. The filtrate was concentrated with a rotary evaporator under reduced pressure, dropped into 10 vols acidic water (pH = 2.0, adjusted by 2 M HCl) to precipitate lignin, and then washed with deionized water until neutral to purify lignin. The depolymerized lignins (DLs) were obtained by centrifugation and freeze-dried, which were named as EL₂₀₀ (100% ethanol, 200 °C), EWL₂₀₀ (50% ethanol, 200 °C), EWPL₂₀₀ (50% ethanol, phenol, 200 °C), EWNL₂₀₀ (50% ethanol, 2-naphthol, 200 °C), and EWL₂₄₀ (50% ethanol, 240 °C) according to the different depolymerization conditions.

2.3. Mannich reaction

The L or DL (1 g) and dioxane (10 mL) were added to a 50 mL three-necked flask. The mixture was vigorously stirred at room temperature to ensure that the lignin was fully dissolved. After 15 min, 7.5 g 33% dimethylamine aqueous solution, 4.5 g 37% formaldehyde aqueous solution, and 0.2 mL acetic acid was successively mixed with the lignin solution. Then, the mixture was heated up and kept at 60 °C for 4 h under stirring. As the Mannich reaction completed, the mixture was dialyzed with dialysis bag ($M_w = 500$ Da) to remove the low molecular organic and inorganic residues. After that, all the aminated lignins (AMLs) were freeze-dried and then stored in a dry ambient condition for further characterization. The prepared AMLs were named as AL, AEL₂₀₀, AEWL₂₀₀, AEWPL₂₀₀, AEWNL₂₀₀, and AEWL₂₄₀, respectively, according to the corresponding samples of L, EL₂₀₀, EWL₂₀₀, EWPL₂₀₀, EWNL₂₀₀, and EWL₂₄₀, respectively.

2.4. Characterization of DLs and AMLs

The weight average molecular weight (M_w) and number average molecular weight (M_n) of L and DLs were detected by GPC with an ultraviolet (UV) detector at 280 nm on a PL-gel 10 mm mixed-B 7.5 mm i.d. column, which was calibrated with PL polystyrene standards according to a previous publication [4]. GPC analyses were performed twice and the results presented in Table 1 were the average values. In addition, the elemental analysis (C, H, and N) for AMLs was subjected to be measured by an Element Analyzer (PE 2400 II).

NMR spectra were recorded on a Bruker AVIII 400 MHz spectrometer at 25 °C in DMSO- d_6 . The quantitative ^{31}P NMR spectra were performed as described in the literatures [16,17]. 20 mg of all lignin samples were dissolved in 0.5 mL of A solvent (anhydrous pyridine and deuterated chloroform 1.6:1, v/v) under vibrating. After exhaustive dissolution, 0.1 mL of cyclohexanol (10.85 mg/mL in A solvent) was added as an internal standard (IS), and 0.1 mL of chromium(III) acetylacetonate solution (5 mg/mL in A solvent) was as a relaxation reagent. Finally, the mixture was reacted with 0.1 mL of the phosphorylating reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) and was transferred into a 5 mm NMR tube for analysis. The standard parameters of

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