Structural Features of Lignins Extracted from Pine with a Protic Ionic Liquid

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Abstract

Protic ionic liquids have been recognized as promising agents that effectively fractionate lignocellulosic feedstocks into a cellulose enriched pulp and a lignin precipitate. Both materials introduce significant potential as low-cost and renewable precursors in the energy industry. Lignin with its highly functional and aromatic nature can provide the generation of a wide range of platform chemicals, fuels and materials. In this work, lignin recovered from pine through pretreatments with the low-cost protic ionic liquid, triethylammonium hydrogen sulfate ($TEAHSO_4$) were examined regarding their chemical and thermal properties. The effects of pretreatment parameters, biomass loading and recycling were investigated using characterizations via Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) and trivial changes were obtained between the samples. The findings demonstrated the use of cost-effective conditions and recycling for pretreatments using PILs as being among the most recognized lignin-selective strategies.

Keywords: *lignocellulosic biomass, pine, pretreatment, lignin, protic ionic liquids, recycling*

I. INTRODUCTION

Lignin is the second most abundant naturally occurring biopolymer on earth. It is a glue that holds fibrous material together and gives strength and defensive features to the lignocellulosic structure [1]. Its biosynthesis is basically provided by the polymerization of three phenylpropane units, p-coumaryl, conifer-

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yl, and sinapyl alcohols through different chemical bonds mainly, ß-O-4, ß -5, ß - ß, 5-5, and 5-O-4 [2]. The extent and the assembly of these linkages are determined by the biomass varieties and extraction conditions. Lignin platform introduces low-cost carbon fibers, plastics, commodity chemicals, diesel or gasoline ranged fuels, and quantum dots [3,4].

The chemically stable structure of lignin makes its valorization limited and therefore, renders its utilization for low-value applications [5]. Several strategies have been proposed to facilitate the recovery of lignin and unlock its hidden potential. Among them include the processing of lignocellulosic feedstocks with protic ionic liquids (PILs), which has received a lot of attention during the last decade because they are easier and less expensive to synthesize than their aprotic counterparts. Their synthesis is based on a single-step reaction between a BrØnsted acid and a Br?nsted base as a result of a simple proton exchange mechanism [6]. The PILs offer advantageous properties during their interaction with lignocellulosic biomass and post-processing because they principally remove lignin while leaving the cellulose largely intact [1]. Therefore, both components can be recovered with minimal losses as long as proper PILs are used and optimum conditions are applied. Following the recovery of biomass components, the PILs can be recycled and reused which is essential to maintain cost-effective conditions for the PIL-biomass interactions.

In other studies, the PILs have been shown to remove lignin from different feedstocks such as bagasse, *Miscanthus giganteus*, switchgrass, eucalyptus with recoveries as high as 80% [7–10]. The major mechanism that leads to lignin depolymerization has also been studied in which the PILs were shown to be effective on ß-o-4 linkages, which make up roughly 50% of all linkages in the polymer structure [11]. Structural investigation of the recovered material is vital to find a place for lignin in the right application. For instance, carbon quantum dots, which gained tremendous interest in solar cell applications, can be derived from lignin nanoparticles [12]. In this context, examining the sizes and functional groups of lignin is of vital importance to generate nanoparticles that yield desirable optical features.

For this reason, lignins extracted with the use of different techniques from various biomass sources have been studied to understand the variations in the chemical and physical structures of the aromatic polymer. A combination of quantitative 13C and 2D-HSQC NMR techniques, which has been useful to characterize lignins isolated from ball-milled poplar and abundancy of ß-O-4 aryl ether, resinol, and phenylcoumaran units, were monitored [13]. Degradation and condensation of lignin, which were detected during furfural production from corncob when milled wood lignin, was analyzed in terms of functional groups, molecular weight and thermal stability [14]. Besides, lignin extracted from *Miscanthus giganteus* via the PIL, 1-butylimidazolium hydrogen sulfate ($HBIMHSO_4$) was previously investigated with respect to its carbohydrate content, abundances of ether, ester, and glycosidic linkages, and its condensation [15]. Pin et al [7] also monitored the changes in the lignin extracted from sugarcane bagasse with different amine-functionalized PILs, in which they observed that the elemental composition, molecular weight, abundances of interunit linkages, and aromatic units were found strongly dependent on the type of anions and cations of PILs used. Besides, the impact of PIL recycling on the biomass pretreatment efficiency has been also under investigation regarding lignin removal, characterization of lignin precipitates, and saccharification of recovered biomass. PIL recoveries and lignin extraction percentages were maintained steadily after the reuse of $TEAHSO_4$ following the pretreatment of *Miscanthus giganteus* [16].

In this study, extracted lignins from pine via the protic ionic liquid, $TEAHSO_4$ was evaluated with respect to their chemical and thermal features. The Fourier-transform spectroscopy (FTIR), and thermogravimetric analysis (TGA) were used to understand the variations in $TEAHSO_4$ extracted lignins from pine with pretreatment conditions and evaluated the use of higher biomass loadings and the chance of recycling that render more economical conditions for the processes.

II. MATERIALS AND METHODS

Preparation of protic ionic liquid

An aqueous solution of triethylamine was combined with an aqueous sulfuric acid solution at equimolar amounts of acid and base under constant stirring and cooling according to the previously reported procedure [17]. Following the synthesis of PILs, the water content was reduced to 20 % by weight using a rotary evaporator operated at 80 °C. The final product was characterized with ^{1}H-NMR to ensure the completion of the PIL synthesis. The PIL was dissolved in DMSO-d_6 and the spectrum was obtained with a spectrometer (Bruker 300 MHz). Chemical shifts (δ) were reported in ppm; $TEAHSO_4$ (300 MHz, DMSO-d_6): 4.44 (s (br), HSO_4^-, N–H^+), 3.02 (q, 6H, N–CH_2), 1.13 (t, 9H, N–CH_2–CH_3).

Lignin extraction from biomass with protic ionic liquid

Prior to lignin extraction from the biomass, dried pine samples were sieved to a particle size <1.76 mm, stored in plastic bags at room temperature in the dark. Biomass samples were soaked into 10 g and 20 g of PILs at the loadings between 10 % and 30 %. All pretreatments were performed in duplicate. Pretreatments were conducted in 50 ml pressure tight tubes at 150°C for 3 hrs in a similar manner reported in the Ionosolv protocol [18]. Following the pretreatments, the tubes were brought to room temperature. Ethanol with a 3-fold higher volume of the PIL was added into the tubes. Cellulose enriched solid fraction was precipitated through centrifugation at 6000 rpm. The solid fraction was further washed with ethanol three times in a shaker for 15 min to remove and collect the residual PIL following the centrifugation of the solid material at 6000 rpm. The liquid fraction, which comprises PIL, ethanol and dissolved lignin was combined with the residual PIL and then subjected to rotary evaporation to remove ethanol. Later, water was added to precipitate lignin. The precipitated lignin was washed with water three times and centrifuged at 6000 rpm for 20 min each time. Finally, the lignin was dried under vacuum overnight prior to its characterization. The residual PIL and water solution was then placed in a rotary evaporator to remove water and recycle PIL.

Lignin characterizations

Fourier-transform infrared spectroscopy (FTIR) of the lignin samples were recorded with Thermo Scientific Nicolet İS5 FTIR operated at ATR mode. The samples were analyzed in the absorption band mode in the range of 4000–400 cm^{-1}. Thermal decomposition of lignin samples was observed in a STD650 Simultaneous DSC/TGA instrument by heating the samples up to 800°C at 10°C min^{-1} heating rate in a nitrogen atmosphere.

III. RESULTS AND DISCUSSION

Results

Fourier-Transform Infrared Spectroscopy Analysis

FTIR spectra of the lignins extracted with pristine $TEAHSO_4$ at biomass loadings, 10%, 20% and 30% and with recycled $TEAHSO_4$ at 20% biomass loading were examined in the absorption mode at wavenumbers between 600-1800 cm^{-1} and depicted in Figure 1. The peaks between 1500-1600 cm^{-1} are related to the characteristic aromatic skeletal vibrations. The peaks at around 900, 1105 and the shoulder at 1160 cm^{-1} are indicators of guaiacyl, p-hydroxy phenylpropane and syringyl units, respectively. Besides, the vibration at around 1030 cm^{-1} represents the methoxy groups in lignin. Moreover, the signals at 1210 and 1266 cm^{-1} are attributed to C-O stretching of syringyl ring and guaiacyl ring, respectively. Signals at 1420 cm^{-1} and 1461 cm^{-1} indicated the presence of aromatic and asymmetric C-H vibrations.

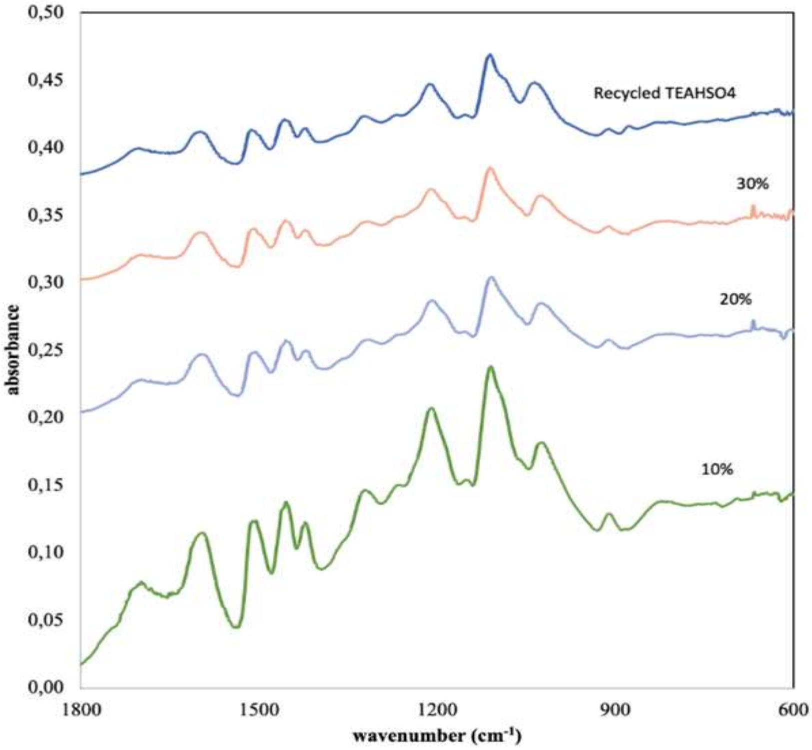

Figure 1. FTIR spectra of lignins recovered with pristine $TEAHSO_4$ at biomass loadings, 10%, 20% and 30% and with recycled $TEAHSO_4$ at biomass loading, 20%.

Thermogravimetric Analysis

The thermogravimetric analysis (TGA) of lignin samples is plotted (Figure 2), which represents the thermal degradation data of lignins extracted via $TEAHSO_4$ at 10%, 20% and 30% biomass loadings (Table 1).

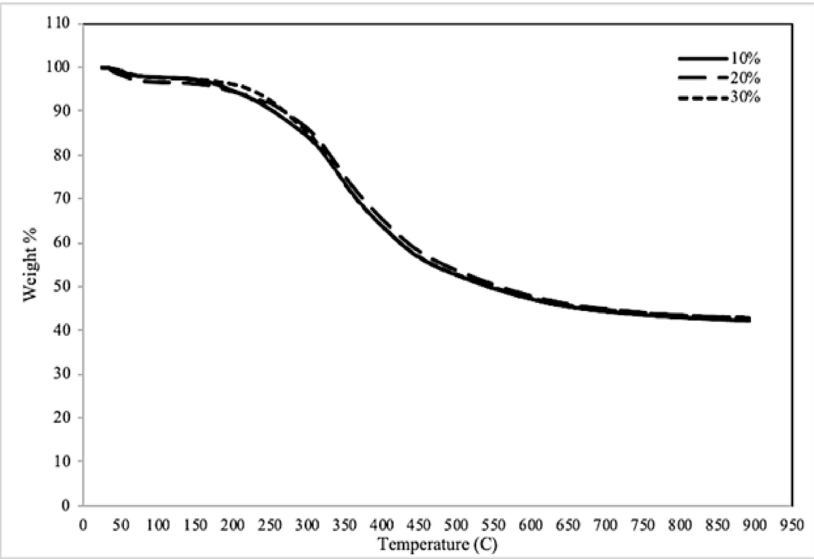

Figure 2. Thermal Degradation Curves for Lignin Samples.

Table 1. Thermogravimetric Data of Lignin Samples

Conditions	Weight loss at 890°C (%)	DTG_{max} (%)	Weight loss rate (%/min)
10% biomass loading with pristine $TEAHSO_4$	58	338	-2.4
20% biomass loading with pristine $TEAHSO_4$	57	338	-2.5
20% biomass loading with recycled $TEAHSO_4$	54	343	-2.2
30% biomass loading with pristine $TEAHSO_4$	57	335	-2.6

Discussion

The signal assignments in FTIR analysis are based on previously reported literature data [19, 20]. The peaks between 1500-1600 cm^{-1}, which are assigned to characteristic aromatic skeletal vibrations, were observed in all samples with different intensities. The lignin recovered at 10% loading with pristine $TEAHSO_4$ displayed narrower and steeper signals in that region. Considering the peaks at around 900, 1105 and the shoulder at 1160 cm^{-1}, there has been a change in the H-unit content of lignin with biomass loading. The vibration at around 1030 cm^{-1} that represents the methoxy groups in lignin was observed to be slightly influenced with loading and recycling. The decrease in the intensity of guaiacyl structure with an increase in biomass loading is less pronounced than the decrease in syringyl structure. The intensities of the peaks at around 1420 cm^{-1} and 1461 cm^{-1} were observed to be affected with biomass loading.

Aforementioned peaks were also identified for the samples extracted with recycled PILs. Although minor changes in the peak intensities were observed, a peak at around 1080 cm^{-1}, which is associated with deformation vibrations in C-O bonds of aliphatic ethers, appeared with PIL recycling. Lignin extracted from various with aprotic ILs (APILs) and PILs has been examined previously. Yan et. al. [21] investigated the chemical structure of lignins extracted from eucalyptus bark with amine-sulfonate functionalized ILs using FTIR. They monitored the presence of hemicellulosic material due to the bands assigned to C=C and C=O vibrations [21]. Recently, lignins extracted from sugarcane bagasse with ammonium-based PILs were characterized with FTIR to understand the variations in aromatic ring modifications and cleavage of ester linkages with PIL type [22]. In another study, chloride-based APILs were found more capable to regenerate lignin from pine and eucalyptus than acetate-based APILs according to the chemical structure of lignins evaluated with FTIR [23].

Regarding TGA analysis of lignins, the maximum rate of heat loss was observed at 338°C as -2.4%/min for 10% and 20% loadings, weight losses of 58% and 57% were obtained, respectively. On the other hand, the DTG peaked at a lower temperature, 335 °C and 57.1 % weight loss was obtained for the sample extracted at 30 % loading. The weight loss for the lignin extracted with $TEAHSO_4$ after its first recycle was 54 %. Accordingly, similar thermal degradation profiles were achieved with an increase in biomass loading and PIL recycle.

IV. CONCLUSION AND RECOMMENDATIONS

Lignins recovered with PIL, $TEAHSO_4$ under certain pretreatment conditions were examined with respect to the molecule's chemical and thermal features. Trivial variations were obtained between the structural features of lignin indicating the use of high biomass loadings and the possibility of recycling for the pretreatment of biomass. Overall, the findings provided a foresight to future studies on biomass fractionation performed under cost-effective conditions.

V. ACKNOWLEDGEMENT

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