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Ionic Liquid Pretreatment of Woody Biomass To Facilitate Biorefinery: Structural Elucidation of Alkali-Soluble Hemicelluloses

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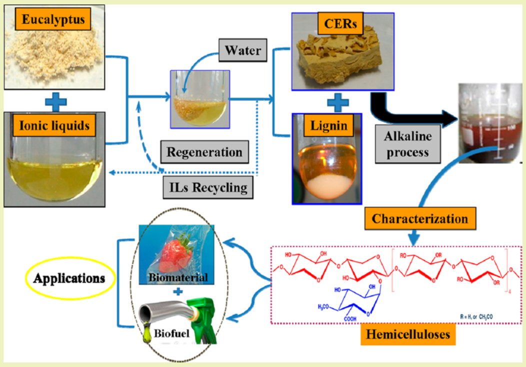
ABSTRACT: Woody biomass, eucalyptus, was submitted to pretreatments with five types of ILs followed by alkaline ethanol extraction for isolating hemicelluloses. The structural properties of these hemicelluloses obtained in high yields were compared with the corresponding alkaline fraction extracted from untreated eucalyptus. It was found that the yield of alkaline hemicelluloses increased remarkably after 1-butyl-3-methylimidazolium bromide ([BMIM]Br) pretreatment. Neutral sugars and molecular weight analyses of these hemicelluloses revealed that the molecular weights and distribution of branches along the xylan backbone are different among the hemicelluloses based on different IL pretreatments. The less branched hemicelluloses with lower yield were obtained by 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac) pretreatment, while the more branched and acidic polymers were obtained by 1-allyl-methylimidazolium chloride ([AMIM]Cl) pretreatment. The results showed that these fractions prepared with IL pretreatments exhibited relatively higher molecular weights (50,595−62,090 g/mol) than the hemicelluloses isolated from untreated eucalyptus (49,325 g/mol). No apparent transformation occurred for the main chain of hemicelluloses during these different IL pretreatment processes, which had a backbone of (1→4)-linked β-D-xylopyranosyl with 4-*O*-methyl-α-D-glucuronic acid attached to O-2. In addition, thermal analysis demonstrated a higher thermal stability of hemicelluloses from IL-pretreated eucalyptus as compared to the fraction obtained from the untreated sample.



KEYWORDS: *Hemicelluloses, Ionic liquids, Biorefinery, Pretreatment, Structure*

■ INTRODUCTION

Because of diminishing reserves and the fluctuating price of crude oil, woody biomass is drawing a great deal of attention as an economical and a sustainable source of future energy. Woody biomass refers to an important portion of biomass that can be sustainably produced in a broad fashion around the world.[1] It has several advantages for the future biobased economy, such as high density that reduces transportation cost, flexible harvesting time that eliminates long-term storage, and low ash content that reduces processing dead load.[2] Woody biomass, a heterogeneous polymeric material, is composed of three major components: carbohydrate-based cellulose and hemicelluloses and polyphenol-based lignin.[3] Deconstruction of woody biomass into three pure streams of chemical components is a promising alternative strategy to explore an economically viable biorefinery by providing a saccharide fraction to produce liquid fuels and a lignin stream that can be converted into high-value products. Among these components, hemicelluloses have emerged as an immense and readily renewable resource of biopolymers. They have the potential to be integrated in a wide variety of applications, such as film-former substances, thickeners, emulsifiers, stabilizers, and binders in the food, biomedical, and cosmetic industries.[4]

The term hemicelluloses refers to a type of heterogeneous polysaccharide with a complex structure containing several different sugar units arranged in different ratios and with diverse substituents.[5] Hemicelluloses rank second to cellulose in abundance in plant cell walls. Effective separation and recovery of hemicelluloses from woody biomass are critical toward valorizing the forest biorefinery. Unfortunately, a major impediment in utilizing woody materials is their inherent recalcitrance to destruction due to their polymeric nature and because they are physically large and structurally tough. Moreover, separation of hemicelluloses from this resilient structure is restricted by the presence of a lignin network, lignin−hemicellulose linkages, and the physical intermixing between hemicelluloses and cellulose. To improve the efficiency of separation and recovery of hemicelluloses, the first impediment to be resolved is the efficient removal of physical and chemical barriers through a cost-effective pretreatment process. Several pretreatment methods have been advocated over the years, including steam explosion,[6] organosolv,[7] ammonia fiber explosion,[8] lime,[9] dilute acid,[10] and sulfite.[11] It is well known that each of the pretreatment processes has its own particular advantages and limitations, for example, they often consume a considerable amount of energy,

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require extreme conditions, generate poisonous gas, and form undesired byproducts.[8,12] Low melting point ionic liquids (ILs) are however attracting increasing attention as a new class of solvents for the pretreatment and homogeneous processing of biomass because they are thermally stable, environmentally friendly, recyclable, and have low volatility.[13−19] Dissolution of woody biomass or its subcomponents in ILs provides a new platform for the effective fractionation of woody biomass and comprehensive utilization of its subcomponents.

At the current stage, most IL pretreatment processes focus on the versatility of cellulose, especially the subsequent conversion of cellulose into ethanol for production of second-generation biofuels. Nevertheless, less attention has been paid to the chemistry and application of hemicelluloses.[19,20] The development of value-added products from hemicelluloses would greatly enhance the economic growth in the biorefinery. However, the inherent heterogeneity and complicated structure of hemicelluloses are responsible for impairing their applications as biopolymers. Moreover, their chemical interactions within the cell walls and structures could be changed during IL pretreatments. Thus, the scientific examination of the structure and chemical composition of hemicelluloses is fundamental toward molecular-level understanding of how the various IL pretreatment processes affect cell wall components. This work aims to unveil the influences of the pretreatment stage with different ILs on physicochemical properties of hemicelluloses. There are comparative studies on the structural features of the hemicellulosic fractions obtained from different IL-pretreated eucalyptus for facilitating biorefinery and further utilization. The hemicellulosic fractions were extensively characterized by high-performance anion exchange chromatography (HPAEC), gel permeation chromatography (GPC), Fourier transform infrared (FT-IR) spectroscopy, two-dimensional solution-state heteronuclear single quantum coherence nuclear magnetic resonance (2D HSQC NMR) spectroscopy, and thermogravimetric analysis.

■ EXPERIMENTAL SECTION

Raw Materials and Chemicals. Eucalyptus was obtained from Guangdong province in China. The stalk of the wood was collected and dried in an oven at 50 °C. The dried stalk was then ground and screened to prepare 20−40 mesh size particles (450−900 μm). The dried material was milled in a planetary ball mill (FritschGMBH, Idar-Oberstein, Germany) for 4 h.

The different types of ILs used were purchased from Lanzhou Institute of Chemical Physics (Chineses Academy of Sciences, Lanzhou, China). Chemical structures and abbreviations of different ILs used for dissolution of eucalyptus are displayed in Figure 1. All standard chemicals were chromatographically pure, and other chemical agents are analytically pure.

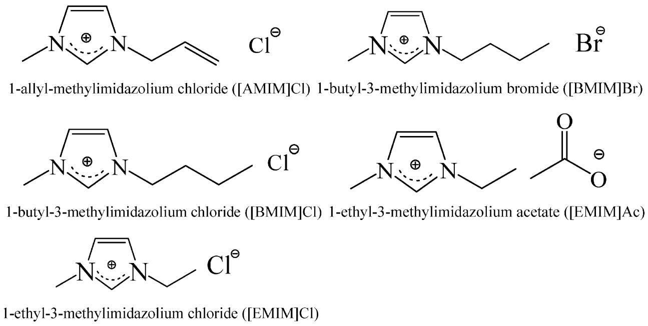

Figure 1. Structures and abbreviations of different ionic liquids used for pretreatment of woody biomass.

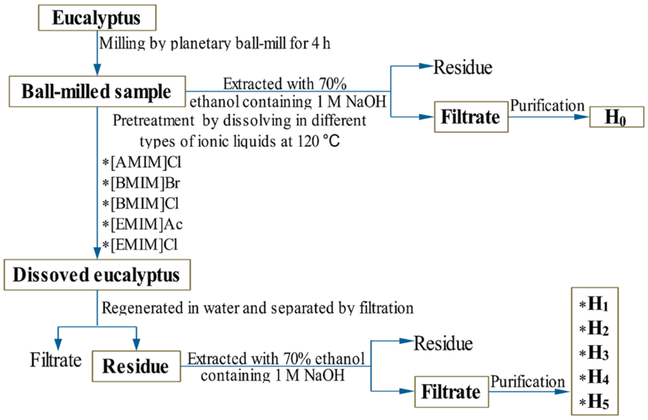

Figure 2. Overall scheme for this research.

Pretreatment and Preparation of Hemicelluloses. The overall experimental design of this study is summarized in Figure 2. Thirty grams of ILs was weighed into a 100 mL conical flask and preheated in an oven at 100 °C for 30 min to remove any moisture in the ILs that may influence its performance during wood dissolution. A magnetic stirrer and dried wood meal (for 5 wt % solid loading) was charged into the flask containing the ILs. The mixture was then placed into a preheated oil bath (120 °C) and stirred at 380 rpm for 3 h. After that specified time, the resulting reaction mixture was removed from the oil bath and immediately cooled to room temperature. Thirty milliliters of deionized water was added as an antisolvent to the mixture to precipitate the carbohydrate-enriched residue (CER). The mixture was again stirred for another 15 min and then filtered. The CER was repeatedly washed with hot water until a colorless filtrate was obtained to ensure complete removal of the ILs. The residue was then dried overnight at 50 °C and weighed. Subsequently, the dried residue was soaked in 70% aqueous ethanol containing 1 M NaOH at 75 °C for 3 h with a solid to liquid ratio of 1:25 (g/mL). Each of the insoluble residues was filtered off and washed thoroughly with distilled water until the filtrate was neutral. The combined supernatant was neutralized with 6 M HCl to pH 5.5, concentrated on a rotary evaporator under reduced pressure to about 50 mL, and then poured to three volumes of 95% ethanol for isolating solubilized hemicelluloses. The hemicellulosic fractions isolated from CERs that were pretreated with [BMIM]Br, [EMIM]Ac, [AMIM]Cl, [BMIM]Cl, and [EMIM]Cl were freeze-dried and labeled as H_1, H_2, H_3, H_4, and H_5, respectively. In addition, the hemicellulosic fraction H_0 was directly extracted by alkaline ethanol solvent from the untreated material as a reference.

Analytical Methods. The monosaccharide composition of all hemicellulosic fractions was determined by HPAEC according to the procedure described in a previous paper.[4] The molecular weights of all preparations were analyzed by GPC with a refraction index detector (RID) according to a previous method with some modifications.[4] The FT-IR spectra of all hemicellulosic fractions were recorded using a Thermo Scientific Nicolet iN10 FT-IR microscope in the range from 4000 to 700 cm^{-1} with a resolution of 4 cm^{-1}. All NMR spectra of hemicelluloses were conducted on a Bruker AVIII 400 MHz spectrometer at 25 °C using D_2O as the solvent. For the $^{1}H-^{13}C$ correlation 2D (HSQC) NMR spectrum, 60 mg of hemicelluloses was dissolved in 0.5 mL of D_2O. The parameters for data acquisition were set according to previous literature.[4] The ^{1}H NMR spectra of the fresh and recovered ILs (dissolved in 0.5 mL of DMSO-d_6) were acquired on the same spectrometer. Thermal stability of hemicelluloses was performed using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer.

RESULTS AND DISCUSSION

Yield and Chemical Composition. The yield and compositional analysis of the six hemicellulosic fractions are summarized in Table 1. As shown in Table 1, the yields of hemicelluloses (15.1−26.4%) obviously increased after IL pretreatment in contrast with H_0 (13.1%). The results could be related to the deconstruction of wood, reconstitution of the cell wall components, and the disruption of some chemical linkages between lignin and hemicelluloses during IL pretreatments.[18] The pretreatments with different types of ILs facilitated the swelling of the cell walls and thus slightly improved the dissolution of hemicelluloses in the following alkaline ethanol extraction processes. The increasing dissolution of hemicelluloses may suggest a relatively higher accessibility of components and more successful fractionation.[14] In addition, extensive hydrogen bonding between the individual polysaccharides cell wall components will hinder the extraction of hemicelluloses, which can be broken during the pretreatment processes.[15] Considering the different types of ILs used in the pretreatment stage, they have a diverse disruption degree of chemical linkages and dissolution abilities of organic components as they penetrate the cell wall, and the essential resistance of plant cell walls to chemical reagents eventually resulted in different yields of hemicelluloses. The reason for this discrepancy can be attributed to the hydrogen bond basicity of ILs as well as their polarizability; thus, these ILs differ greatly in disrupting the cell wall.[21] In comparison with other ILs, a relatively low yield of hemicelluloses was obtained from the [EMIM]Ac-pretreated eucalyptus. The explanation of this phenomenon can probably be ascribed to the fact that minor degradation of hemicelluloses occurred in [EMIM]Ac pretreatment, and hence, a relatively small percentage of hemicelluloses remained in the reconstructed wood available to be extracted and recovered. It should be noted that H_1 and H_4 presented a high yield of hemicelluloses, suggesting that [BMIM]Br and [BMIM]Cl under the condition used could cleave the chemical linkages between lignin and hemicelluloses significantly and destroy the crystal area by swelling the cellulose, which resulted in substantial dissolution of hemicellulosic polysaccharides in the next step. Taken together, excellent solubility and disruption ability, as well as minor degradation of polysaccharides, are the prerequisites for selection of ILs in the pretreatment processes, which depend on the proper combination of anion and cation. Furthermore, the extraction by alkaline organic solution could liberate a larger amount of hemicelluloses from the recovered CERs because the organic solvent primarily acts on the promotion of tissue impregnation, and then the alkali may break the bonds between the lignin and carbohydrates.[22]

Table 1. Yield and Chemical Composition of the Hemicellulosic Fractions

	hemicellulosic fractions[a]					
	H_0	H_1	H_2	H_3	H_4	H_5
arabinose	3.77	2.77	1.69	1.57	2.76	2.57
galactose	9.04	8.41	6.69	8.20	8.12	8.53
glucose	6.68	3.52	6.13	13.06	4.88	4.56
mannose	1.48	0.27	0.85	0.73	0.95	1.17
xylose	71.23	76.35	80.65	68.96	73.77	75.51
uronic acids	7.80	8.68	3.99	7.66	9.52	7.66
yield (%)[b]	13.06	26.39	15.12	18.52	26.01	22.64

[a] H_1, H_2, H_3, H_4, and H_5 represent the fractions obtained from [BMIM]Br, [EMIM]Ac, [AMIM]Cl, [BMIM]Cl, and [EMIM]Cl-pretreated eucalyptus, respectively. The hemicellulosic fraction H_0 was directly extracted from raw material without IL pretreatment. [b] Based on the amount of initial eucalyptus sample.

The sugar composition of the fractions is described as a relative content of the entire sugars. Sugar analysis facilitated the identification and quantification of monosaccharides present in the hydrolysates. As shown in Table 1, no significant differences were documented in the relative content of neutral sugars and uronic acids of the hemicellulosic fractions. This supported the hypothesis that the fundamental structures of hemicelluloses were reserved after the IL pretreatments. Xylose was the dominant sugar component in all of the hemicelluloses, comprising 69.0−80.7% of the total sugar. Small amounts of glucuronic acid (4.0−9.5%), galactose (6.7−9.1%), and glucose (3.5−13.1%) were detected in the six hemicellulosic fractions. Additionally, minor quantities of arabinose (1.6−3.8%) and mannose (0.3−1.5%) were also detected. The results obtained potentially suggested that the hemicelluloses have a xylose backbone that was substituted by other sugars. Apart from this unit, small amounts of glucuronic acid, galactose, and glucose are shown to be integral parts of the hemicelluloses. This structural type and the broad range of Xyl/GlcA ratios are similar to the hemicelluloses in hardwoods.[23] According to the previous literature,[23] the ratios of uronic acids (mainly glucuronic acid) to xylose for the hemicellulosic fractions extracted from hardwoods ranged between 6.2% and 25.0%. However, in this study, the ratio of uronic acids to xylose for H_2 was just 5.0%. It suggested that some uronic acids substituted in the side chain of hemicelluloses were disrupted during [EMIM]Ac pretreatment. This result was also explained by the fact that a slight degradation of hemicelluloses occurred during the IL pretreatment. This phenomenon also happens to be in accordance with the results of the low yield of hemicelluloses extracted from the [EMIM]Ac pretreatment. On the contrary, the hemicellulosic fraction H_3 exhibited a higher amount of glucose than other fractions, indicating a relatively higher degree of glucose substitution and complex structure of this hemicelluloses based on the [AMIM]Cl pretreatment. It was also found that all of the hemicelluloses obtained in the present study were mainly composed of xylan. Interestingly, the amount of galactose was almost the same as that of glucuronic acid in the hemicellulosic fractions, indicating some these xylan residues may be substituted with α-D-galactose.[24] Therefore, it can be concluded that there was a slight variation in composition and structure of these hemicellulosic fractions. That is, relatively linear hemicelluloses could be recovered using [EMIM]Ac pretreatment, while the more branched and acidic polymer were obtained by [AMIM]Cl pretreatment.

Molecular Weight. In order to investigate the extent of degradation that occurred during the IL pretreatment processes, all the hemicellulosic fractions were analyzed by GPC. The weight-average (M_w) and number-average (M_n) molecular weights, as well as the polydispersity (M_w/M_n) of all fractions are presented in Table 2. All of the fractions exhibited weight-average molecular weights varying from 49,325 to 62,090 g/mol. These results confirmed that no apparent degradation occurred for the main chain of hemicelluloses during the IL pretreatments in the present study. Evidently, the hemicellulosic fraction prepared with IL pretreatments showed relatively higher molecular weight (50,595−62,090 g/mol) than that of fraction H_0 prepared without pretreatment (49,325 g/

Table 2. Weight-Average (M_w) and Number-Average (M_n) Molecular Weights and Polydispersity (M_w/M_n) of Hemicellulosic Fractions

	hemicellulosic fractions[a]					
	H_0	H_1	H_2	H_3	H_4	H_5
M_w	49,325	57,150	53,785	50,595	54,125	62,090
M_n	26,775	32,100	31,695	31,655	28,975	26,904
M_w/M_n	1.84	1.78	1.70	1.59	1.87	2.31

[a] Corresponding to the hemicellulosic fractions in Table 1.

mol). This result suggested that pretreatment with ILs that have a strong penetrating ability for the cell wall results in the release of hemicelluloses with high molecular weights in alkaline ethanol extraction. The M_w of the hemicellulosic fractions H_1 and H_5 showed similar molecular weight distributions, but these are relatively higher than other fractions. This was probably due to the fact that a small amount of hemicelluloses was partially degraded into smaller molecules during the pretreatments and were washed out in the IL aqueous solutions during the washing step.[25] In addition, it is implied that different ILs show diverse solubility for hemicelluloses. The results also implied that less degradation of hemicelluloses occurred during [BMIM]Br and [EMIM]Cl pretreatments than other ILs. The reason for this can be related to the weak hydrogen bond basicity of [BMIM]Br and [EMIM]Cl as well as their low dipolarity.[21] Furthermore, hemicellulosic fraction H_5 has a relatively broader molecular weight distribution, corresponding to the polydispersity index of 2.31 as compared to other fractions (1.59−1.87), which illuminated the structural heterogeneity of the separated hemicelluloses. Generally, the polysaccharides with molecular weights in excess of DPn 50 and polydispersity below 3 are indicative of molecular uniform polymers with potential commercial utility.[26] Thus, on the basis of molecular weights and the polydispersity index, most hemicelluloses with relatively uniform structures possess commercial utility.

FT-IR Spectra. The partial structure and functional groups of the hemicellulosic fractions were studied by FT-IR. As shown in Figure 3, the six spectra clearly illustrated the typical signal pattern for hemicellulose moiety. FT-IR spectral analysis demonstrated that no significant difference was observed between all of the fractions, except for a subtle difference in the intensity of bands. The wide absorption at 3362 cm^{-1} due to the hydroxyl stretching vibrations and the absorption bands at 2934 cm^{-1} (asymmetrical stretching) and 2880 cm^{-1} (symmetrical stretching) originated from the C−H stretching of methyl and methylene groups, respectively. The absorptions at 1460, 1406, 1331, 1264, 1151, 1079, 1039, 985, 896, and 797 cm^{-1} are associated with hemicelluloses; and among them, the two bands at 1331 and 1264 cm^{-1} represent the C−H and C−O bending or stretching frequencies.[27] The presence of the uronic acid was also manifested mainly by the appearance of stretching from the −COOH group band at 1569 cm^{-1}. This band showed discrepancy in spectral shape and intensity depending on the branched at O-2 and O-3 positions, which caused by the pretreatments with different ILs. This phenomenon was in line with the observed variation in the content of uronic acids obtained from sugar analysis. It is known that the absorption bands in the 1200−800 cm^{-1} region may give information about the certain types of polysaccharides.[28] As shown in Figure 3, the FT-IR spectra of all hemicellulosic fractions show a similar pattern in accord with their similar sugar composition (Table 1). The bands at 1542 and 1460 cm^{-1} originated from aromatic skeletal vibrations, indicating that the polysaccharides isolated were possibly contaminated with small amounts of lignin.[29] Among them, the band at about 1406 cm^{-1} represented the C−H bending vibration of $-CH_2$. The two low intensity shoulders at 1151 and 985 cm^{-1} indicated the presence of the arabinosyl side chains, which have been reported to be attached only at positions of the xylopyranosyl constituents.[30] In spectrum H_1, the band shape at 1079 cm^{-1} can be explained by a small amount of the galactan from the side chain,[31] which is in accordance with the data obtained by sugar analysis. It should be noted that in the six alkali-soluble hemicellulosic fractions, the prominent band at 1039 cm^{-1} is attributed to the C−O, C−C stretching, or C−OH bending typical of xylans.[32] The band at 896 cm^{-1} corresponded to the C-1 group frequency or ring frequency, which was characteristic of β-glycosidic linkages

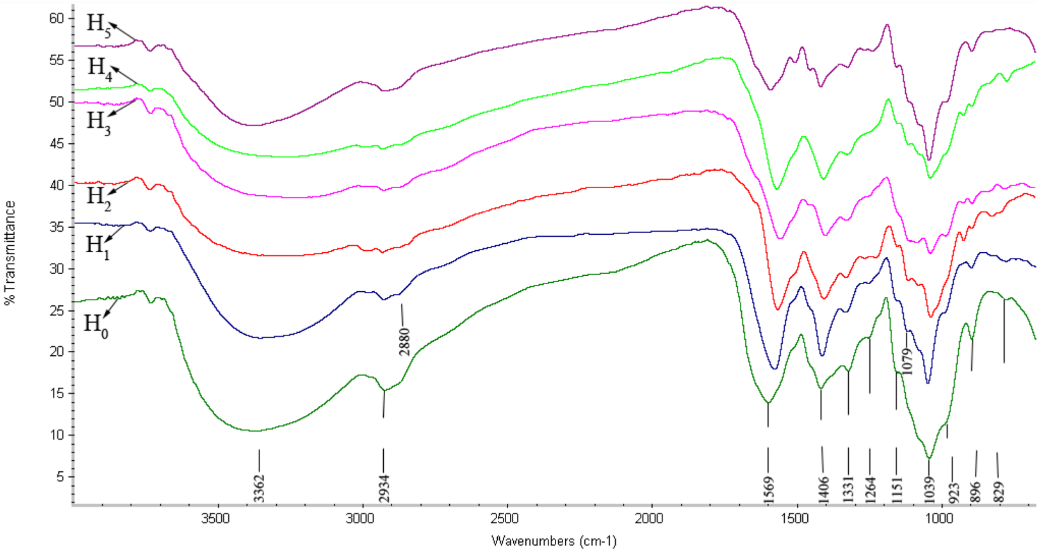

Figure 3. FT-IR spectra of the hemicellulosic fractions.

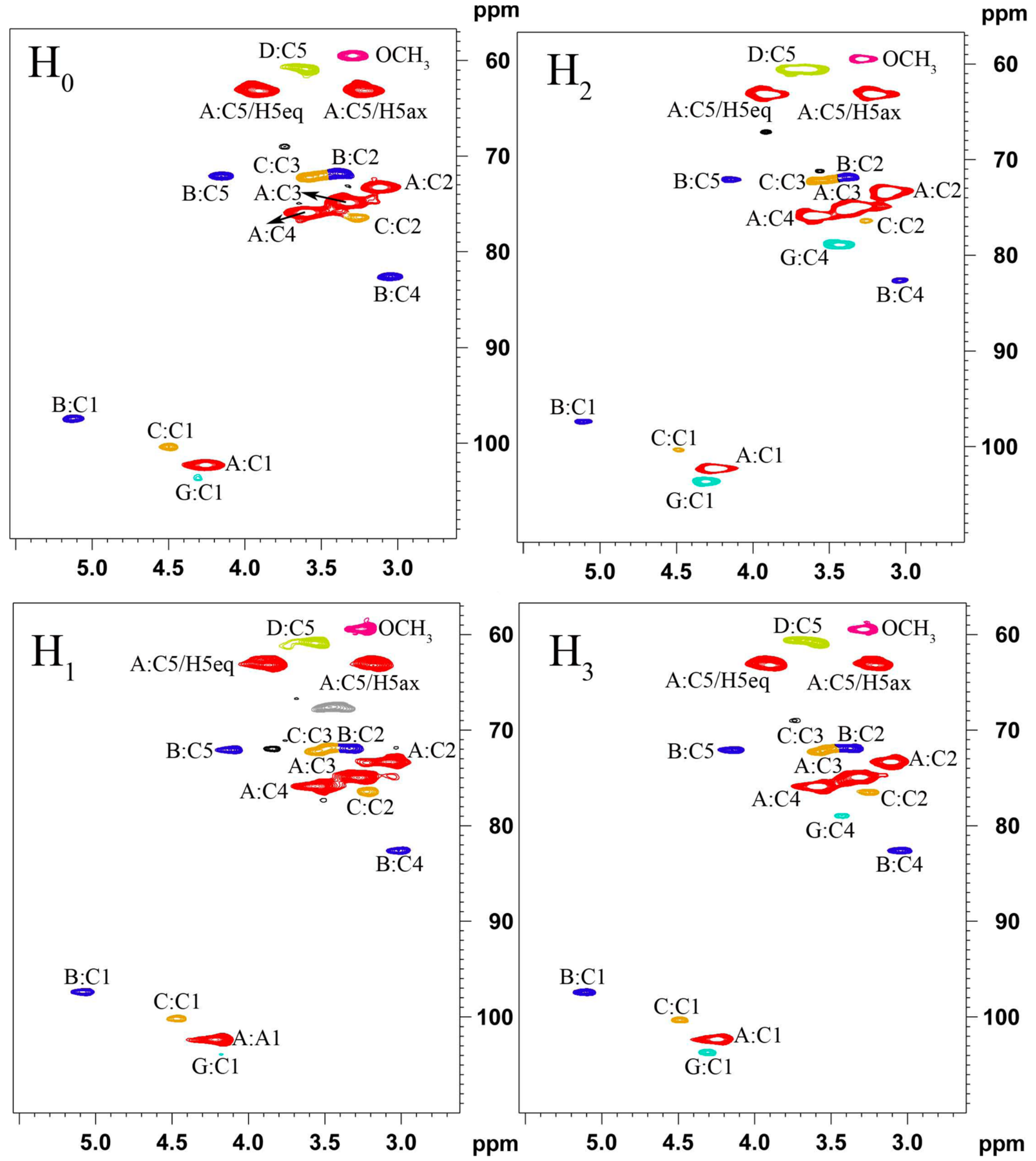

Figure 4. HSQC spectrum of the hemicellulosic fractions H_0, H_1, H_2, and H_3. (A) (1→4)-*β*-D-Xyl*p*, (B) 4-OMe-*α*-D-Glc*p*A, (C) (1→4)-*β*-D-Xyl*p*-2-*O*-(4-OMe-*α*-D-Glc*p*A), (D) (1→3)-*α*-L-Ara*f*, and (G) (1→4)-*β*-D-Glc*p*.

between the sugar units.[33] The symmetrical stretching vibration of C−O−C of glucopyranose was observed at about 797 cm^{-1}.

NMR Spectra. To explore the detailed structures and comparative analysis of these alkali-soluble hemicelluloses, four hemicellulosic fractions (H_0, H_1, H_2, and H_3) were characterized by 2D HSQC NMR techniques, which allowed for the resolution of otherwise overlapping resonances observed in either the ^1H or ^{13}C NMR spectra. The HSQC spectra of the hemicelluloses are illustrated in Figure 4. Most of the resonances were assigned according to the previous reports.[34−36] The HSQC spectra were rather similar, indicating a similar chemical structure of the hemicelluloses isolated. In the HSQC spectra, the signals from the *β*-D-Xyl*p* units were the most prominent, with its C_1−H_1 (anomeric), C_2−H_2, C_3−H_3, C_4−H_4, and C_5−H_5 correlations at δ_C/δ_H 102.1/4.25, 73.1/3.16, 75.1/3.32, 76.2/3.63, and 63.2/3.24 and 3.97, in which chemical shifts of δ 3.97 and δ 3.24 are assigned to the equatorial and axial protons linked at C−5, respectively. The signals from 4-OMe-*α*-D-Glc*p*A units were also clearly observed, with its C_1−H_1 (anomeric), C_2−H_2, C_4−H_4, and C_5−H_5 correlations at δ_C/δ_H 97.3/5.13, 71.6/3.39, 82.5/3.05, and 72.3/4.18, respectively. The methoxyl group of these units was observed at δ_C/δ_H 59.7/3.33. In addition, the signals at 103.7/4.31, 76.6/3.28, and 72.4/3.55 ppm were assigned to C_1−H_1, C_2−H_2, and C_3−H_3 of (1→4)-*β*-D-Xyl*p*-2-*O*-(4-OMe-*α*-D-Glc*p*A) units. However, the signals from (1→4)-linked *β*-D-Glc*p* units could only be detected of their C_1−H_1 (anomeric) and C_4−H_4 at δ_C/δ_H 103.6/4.32 and 78.9/3.53, respectively. This phenomenon can be ascribed to the low molecular weight cellulose and the degraded products from glucomannans. Moreover, a weak signal from (1→3)-linked *α*-L-Ara*f* units was observed at δ_C/δ_H 61.0/3.61. This was in agreement with the results obtained from sugar analysis. A clear signal of the residual IL from the pretreatment process was observed at δ_C/δ_H 67.8/3.48 in the spectra of H_1. The NMR analysis showed the facts that all of the fractions had similar structures, and thus, no apparent degradation occurred for hemicelluloses during different IL pretreatments. Summarizing the results of the

NMR analysis, the spectra presents the straightforward structure of hemicelluloses as revealed by five major signals corresponding to (1→4)-linked *β*-D-Xyl*p* residues and other less intense signals characteristic of 4-*O*-methyl-*α*-D-glucuronic acid residues as well as a L-Ara*f* residue and *β*-D-Xyl*p* units substituted with 4-*O*-methyl-*α*-D-Glc*p*A in position 2 or 3 (C-2 or C-3). Overall, the structural feature of hemicelluloses seems to be mainly influenced by the type and nature of ILs utilized in the pretreatment process.

Thermal Stability. Thermal analysis as the most effective and common measurement of weight loss allows us to describe the distinct thermal events recorded during the process. As shown in Figure 5, the TGA curves showed that the thermal decomposition of hemicelluloses takes place in three major stages. In the first stage, the samples just lost absorbed water, which was physical change. The endothermic peaks appear on the DTA curves at about 100 °C and suggest that the moisture absorbed by hemicelluloses was evaporated during heating. The second stage took place in the temperature range of 200−400 °C, which involved the dehydration fragmentation of the main and side chains of hemicelluloses. In this stage, the hemicellulosic fractions were degraded into CO, CO_2, CH_4, CH_3COOH, HCOOH, etc.[37] The decomposition rates of hemicellulosic fractions H_1 and H_2 were slower than the decomposition rate of fraction H_0 obtained without pretreatment. At the point about 300 °C, exothermal peaks appear in this stage on the DTA curves. In the third stage (more than 400 °C), the char residues at 600 °C were 40% for H_1, 24% for H_2, and 7% for H_0. The fractions H_1 and H_2 prepared with IL pretreatments showed a relatively higher weight of residues compared to fraction H_0 at the same temperature in this decomposition stage. This was probably due to the fact that the structure of the char residues obtained at the higher heating rate is more stable and inhibits the cracking of the cross-linked molecules.[38,39] A higher molecular weight of the hemicelluloses resulted in more thermal energy needed for the bond cleavage. According to Jin et al.,[40] the thermal stability of the hemicelluloses decreased with declining molecular weight. The remaining char residues at 600 °C for all of the hemicelluloses were presumed to be due to the end products of the decomposition of hemicelluloses.[40] The exothermal peaks of H_0 and H_1 change into relatively smooth ones; this means that the rates of heat released slow down. However, the endothermic peaks at 350 °C can be observed from the DTA curve of H_1, which could be regarded as the same effect that occurred at 300 °C because of the small temperature range covered by such reactions.[41] Overall, the thermal stability of the hemicellulosic fractions prepared with IL pretreatments was higher than that of fraction H_0 obtained without pretreatment, and the reason for this phenomenon should take many factors into consideration, such as the different types of sugar, degree of substitution, impurities, and molecular weight.

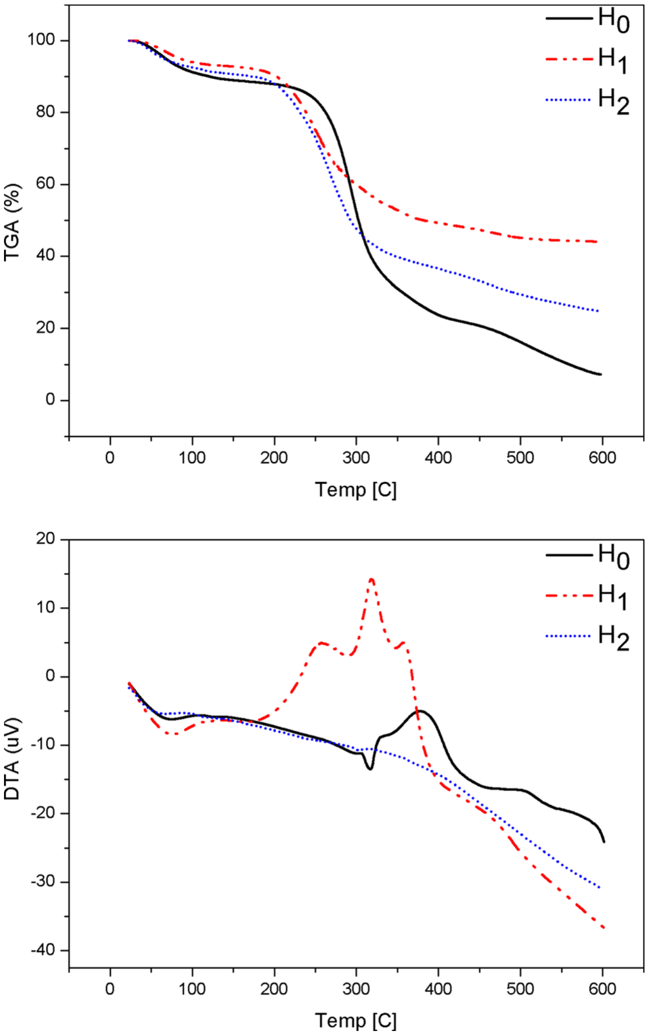

Figure 5. TGA/DTA curves of the hemicellulosic fractions H_0, H_1, and H_2.

Recovery of IL. Pretreatment and fractionation of lignocelluloses with ILs will be feasible if the ILs can be recovered and recycled because of the high solvent cost. Depending on the IL recovery process, the dissolved compounds can be recovered if further fractionation steps are applied. For instance, lignin could be precipitated by acidification of the liquid stream after the regeneration process. Therefore, IL recovery is largely dependent on the antisolvent used, as well as on the pretreatment conditions applied that guides to a certain extent carbohydrate dissolution, lignin removal, and biomass degradation products present in the liquid stream. In the present study, almost all the ILs used could be recovered by evaporation of water under reduced pressure. The resulting liquors were dried at 75 °C under vacuum for 24 h to obtain recovered ILs. The color of the recovered ILs became dark, which was probably due to the contaminants, such as the minor degradation of carbohydrates and lignin. The ^{1}H NMR spectra of the fresh [AMIM]Cl and recovered [AMIM]Cl are shown in Figure 6. It was found that there was no obvious difference from these two spectra except some new impurity peaks, indicating that small amounts of carbohydrates and lignin fragments accumulated in the liquor. As shown in Figure 6, the spectrum for recovered ILs shows a significant peak of 3.52 ppm in comparison with that of fresh ILs, suggesting an increased content of water in the recovered [AMIM]Cl. The chemical shifts of protons of the imidazolium ring (9.74, 7.95, and 7.93 ppm) for fresh [AMIM]Cl moves upfield slightly (9.45, 7.81, and 7.79 ppm) after recovery, which is likely due to the hydrogen-bonding interactions between recovered [AMIM]Cl and cellulose. Results of investigations show that there is no significant impact of impurities on the fundamental structure of this IL, and therefore, the nature and property of the IL remain unchanged essentially. This result also demonstrated that the original impurities present in this IL

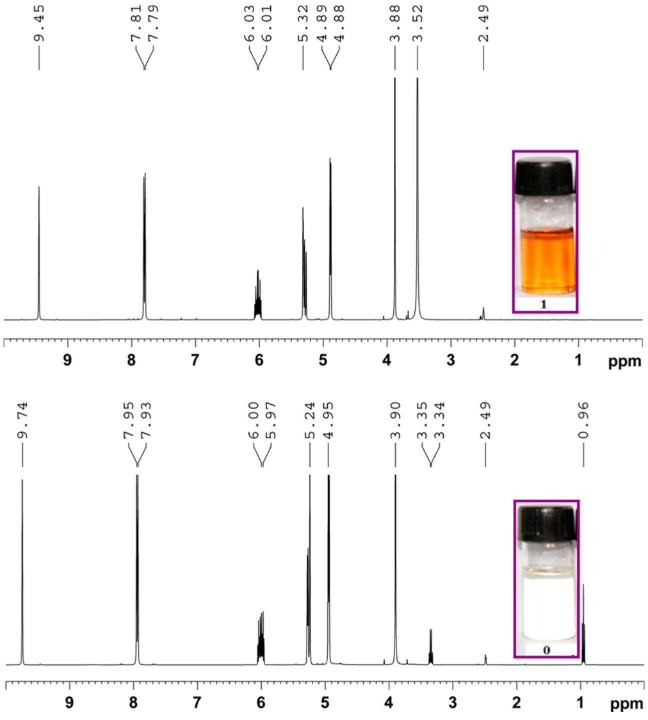

Figure 6. ^{1}H NMR spectra of the fresh [AMIM]Cl (bottom row) and recovered [AMIM]Cl (top row).

are at greatly reduced levels. This was in accordance with the results obtained by Wang et al. during the study of recovery of [AMIM]Cl from biomass pretreatment.[42] They reused [AMIM]Cl once after a dissolution treatment of 5 wt % wood and did not detect any reduction in performance. However, the reuse of ILs was not conducted in this research. It is well known that the recovery of ILs by evaporation is an energy-intensive and time-consuming procedure. On the basis of IL pretreatments and fractionation, therefore, a facile and economic technique for the recovery of ILs is crucial for the biorefinery.

■ CONCLUSIONS

In this study, it could be concluded that pretreatment of eucalyptus with ILs can swell the cell wall and increase the extraction efficiency of hemicelluloses. The detailed physicochemical properties of the isolated hemicellulosic fractions, which are obtained in high yield, have been comparatively analyzed. Combined use of [Bmim]Br pretreatment and alkaline ethanol extraction, which was screened as the best option for isolating hemicelluloses, were found to increase the yield significantly. No apparent distinctions can be observed for the main structures of these hemicelluloses after the different IL pretreatments, which had a backbone of (1→4)-linked β-D-xylopyranosyl decorated with branches of mainly 4-*O*-methyl-α-D-glucuronic acid at the O-2 position. In addition, the fractions prepared with IL pretreatments exhibited slightly higher thermal stability compared to the fraction without pretreatment. It is believed that the high molecular weight, high yield, and high purity of hemicelluloses obtained can serve as raw materials for the preparation of value-added products. ^{1}H NMR spectra indicated that the structure of recycled [AMIM]Cl remained essentially unchanged. The potential of tailoring the functionalities of ILs to maximize the yields of desired products while facilitating product separation and reuse of the ILs should be further investigated.

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Notes

The authors declare no competing financial interest.

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