Selective Separation and Recovery of the Lignin from Lignocellulosic Biomass Using Ionic Liquid

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Abstract

Lignocellulosic biomass represents a potentially key and sustainable source for transformation into biofuels and other commodity chemicals. However, efficient means of separating and depolymerising the hard components are required. The use of ionic liquids (ILs) in biomass pretreatment has attracted significant attention as promising green solvents for its effectiveness at decreasing biomass recalcitrance. In this study, an efficient pretreatment method using the low-cost IL 1-butyl-3-methylimidazolium acesulfamate [BMIM]Ace and organic solvents for the extraction of lignin and recovery of carbohydrate-enriched materials (CEMs) from Eucalyptus. The lignin was recovered from the IL by precipitation with acetone, allowing the IL to be recycled. The results showed a synergy effect with exceeding 89.6% of the CEMs recovery and 14.1% of the lignin obtained. It was found that the presence of some organic solvents have affected the extraction efficiency, probably due to the difference of dielectric constants of the organic solvents. The regenerated ionic liquid showed good retention of structure and properties. The purity of the lignin fractions were characterized by high-performance anion exchange chromatography (HPAEC). Moreover, the lignin fractions were characterized with Fourier transform infrared (FT-IR). The recovered CEMs can be serving as a valuable source for enzymatic saccharification. These results indicates a potential approach in further optimization of the choice of low-cost ILs and organic solvents systems for the efficient utilization of the lignocellulosic biomass, and all constituents can be fully recovered and further processed.

Keywords: Lignocellulosic biomass; Lignin; Ionic liquid; Organic solvents; Extraction
Introduction
The depletion of the world’s petroleum supply and environmental issues associated with crude oil usage increase a demand for developing alternative, environmental friendly, and non-petroleum dependent energy sources [1]. An alternative and sustainable source for chemicals, materials, and fuels is lignocellulosic biomass. However, the structure of the lignocellulosic biomass is very complex; the rigid structure makes it highly resistant to biological and chemical degradation [2]. Lignocellulosic biomass consists mainly of cellulose (35-50%), hemicelluloses (20-35%), and lignin (5-30%) [3]. Cellulose is a linear polymer of β-1,4-linked d-glucopyranose monomers, and there are large amount of intra- and intermolecular hydrogen bonds in the cell walls [4]. However, cellulose is traditionally material used as a raw material for the production of paper, paperboard, fiberboard, and other similar products. Hemicelluloses are consisted of different five or six sugars, which can be further produced of xylitol and furfural. Hemicelluloses can also be hydrolyzed and used for fermentation, but the usage is more complicated due to the fact that xylose, which is the dominating monosaccharide released, is difficult to ferment [5]. Lignin is a stubborn polymer, which formed covalent bond with hemicelluloses. Lignin is a three dimensional network, and the complex structure is difficult for chemicals and microbial attack. All these factors make lignocellulosic biomass usage limitation. Recently, ionic liquid (IL) has received growing interest as green solvents for lignocellulosic biomass pretreatment [6]. IL is salts that melting point blow 100°C, and can be design for different cation and anion. It has several advantages, such as negligible volatility, wide liquid range, and relatively high thermal stability as well as ability to solubilize organic, inorganic, or polymeric substances [7,8]. In this paper, the ball-milled wood was dissolved in a new IL named 1-butyl-3-methylimidazolium acesulfamate [BMIM]Ace to extract lignin. Organic solvents were firstly added in this IL solution. The lignin obtained was characterized by high-performance anion exchange chromatography (HPAEC) and Fourier transform infrared (FT-IR).

Methods

Materials and Reagents. Eucalyptus was received from Guangdong province, China, Leaves and bark were removed, and the stems were chipped into small pieces (1-3 cm). After drying at 60°C for 16 h in an oven, the chips were ground using a mortar and sieved through a 40-60 mm mesh. The sawdust was milled for 3 h. The content of acid-insoluble lignin was 30.1% according the procedure of the National Renewable Energy Laboratory (NREL/TP-510-42618, TP-510-42622). The ionic liquid [BMIM]Ace was synthesized according to the literature [9]. The chemicals used were of analytical or reagent grade.

Wood Dissolution and Regeneration. 2.0 g of ground wood was added to 30 g of [Bmim]Ace, and 10mL of DMSO, dimethylacetamide (DMAc), dioxane, and methanol were added in the mixture, respectively. The mixture was mechanically stirred at 120°C for 3 h in an oil bath in open atmosphere. After that, the wood was regenerated in hot water, and the solution was added into acetone to precipitate lignin after remove water. Lignin was separated
by filtration. The acetone was evaporated for the recycle use of IL.

Sugar Analysis. The sugar content of the lignin fractions were detected by high-performance anion exchange chromatography (HPAEC). A 4-6 mg sample was hydrolyzed with 1.475 mL of 10% H_2SO_4 for 2.5 h at 105°C. The mixture was filtered and diluted. The sample was injected into the HPAEC system. L-arabinose, D-glucose, D-xylose, D-rhamnose, D-mannose, D-galactose, uronic acids were detected. All experiments were performed at least in duplicate, and the average values calculated for all of the lignin fractions.

FT-IR Analysis. The Fourier-transform infra-red (FT-IR) spectra of the samples were recorded using a Thermo Scientific Nicolet iN10-MX FT-IR chemical imaging microscope (Thermo Scientific, America) fitted with a narrow-band liquid nitrogen cooled MCT detector. Spectra were recorded with 64 scans at a resolution of 4 cm⁻¹ between the wave numbers of 4000 and 700 cm⁻¹.

Results and Discussion

Yield of Lignin. The yield of the lignin was showed in Table 1. Interestingly, different organic solvents resulted in different yields. The dioxane + IL mixture released a higher content of lignin (14.1%), while the methanol + IL mixture yield 3.0% of lignin. The neat IL extraction resulted in 11.5% of lignin released. The results indicated that some organic solvents such as dioxane can increase the lignin extraction efficiency, while DMSO, DMAc, and methanol will decrease it. This results probably due to the difference of dielectric constants of the organic solvents [10]. Meanwhile, adding of organic solvents is that the anions become more delocalized and the strength of the interaction with lignin decreases with increasing the polarity parameter.

| Table 1. Yield of lignin (% Klason lignin) released in different solvents systems. |
|----------------------------------------|------------------------------|-------------------------------|----------------|-----------------|-----------------|
| Solvent                               | DMSO+IL                      | DMAc+IL                       | Dioxane+IL     | Methanol+IL     | Neat IL         |
| Yielda (%)                            | 8.6                          | 11.8                          | 14.1           | 3.0             | 11.5            |

a The yield was based on the Klason lignin

Purity Analysis. To characterize composition of the IL/IL+ organic solvents systems, the five lignin preparations were prepared for determination of their carbohydrate content, and the results are given in Fig. 1. As can be seen, all lignin fractions contained different amount of sugars. The total content of sugars detected in the lignin fractions were in the order of the extraction systems of methanol+IL>dioxane+IL>neat IL>DMSO+IL>DMAc+IL, indicating that IL+methanol mixture result in a high content of carbohydrate loss. The DMAc +IL system has a weak effect on the hemicelluloses moiety in the wood cell. Glucose and xylose were the mainly sugars detected in the five lignin fractions. Moreover, we should note that neat IL extraction released more xylose (7.6%) than glucose (2.8%). Therefore, the results suggest that the hemicellulosic polymers in the cell walls might be degraded during the treatments with different organic solvents combined with IL under the conditions given.

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FT-IR Analysis. To identify the isolated extracts as lignin, the IR spectra of the five extracts obtained were analyzed (Fig. 2). As can be seen from the spectra, all the five spectra have typical bands at 1572, 1509, and 1431 cm\(^{-1}\), corresponding to aromatic skeletal vibrations. The band at 2961, 2874, and 1462 cm\(^{-1}\) arise from the C-H stretching and asymmetric vibrations of CH\(_3\) and CH\(_2\), respectively [11]. The wide absorption band at 3395 cm\(^{-1}\) originated from the O-H stretching vibration in aromatic and aliphatic OH groups. However, the bands at 1648 and 1738 cm\(^{-1}\) are assigned to the presence of conjugated and nonconjugated carbonyl groups in the lignin structure. The ILL (extracted with neat IL) spectra has a strong absorption band at 1738 cm\(^{-1}\), indicating that more C=O groups present in the lignin fraction, adding organic solvents in IL could decrease the C=O group. Syringyl and condensed guaiacyl absorptions are obviously observed at 1313 cm\(^{-1}\), whereas guaiacyl ring breathing with C=O stretching appears at 1265 cm\(^{-1}\). The absorption at 1055 cm\(^{-1}\) is owing to the C-H in-plane deformation. In addition, aromatic C-H out of plane bending appears at 938 and 853 cm\(^{-1}\).

Fig. 1. The monosaccharide rare (wt\%) of the different extraction systems.
Fig. 2. The FT-IR spectra of the extracted lignin: IOL-1, ionic liquid+methanol extracted lignin; IOL-2, ionic liquid+DMSO extracted lignin; IOL-3, ionic liquid+DMAc extracted lignin; IOL-4, ionic liquid+Dioxane extracted lignin; ILL, neat ionic liquid extracted lignin.

Conclusion

It was proved that imidazolium acesulfamate ILs has the ability to dissolve wood lignin in an open atmosphere. Different organic solvents+IL systems released different content of lignin from the lignocellulosic biomass. This was probably due to the difference dielectric constants of the organic solvents. The IL+methanol system resulted in a relatively high content of carbohydrate loss. The recovered carbohydrate-enriched materials (CEMs) can be used as a valuable source for enzymatic saccharification. These results indicated a potential approach in further optimization of the choice of low-cost ILs and organic solvents for the efficient utilization of the lignocellulosic biomass.

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References


