[Letter]

Extraction and Modification of Lignin from Red Pine Using Ionic Liquid

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Pyridinium and imidazolium ionic liquids with different anions were synthesized and used to extract lignin from red pine. Based on the catalytic depolymerization activity and the recovery of lignin in different ionic liquids, N-allyl-pyridinium chloride ([Apy]Cl) was chosen to extract lignin from red pine. Cellulose was recovered from the [Apy]Cl solution with methanol, and lignin was recovered with water and acetonitrile, and the maximum recovery of lignin from red pine was 98.7 wt%.

Keywords: Lignin, Extraction, Ionic liquid, Recyclability, Depolymerization

Lignocellulose biomass is a renewable resource with the potential for conversion into liquid transport fuel and high value-added products. Many value-added products have been obtained from cellulose and hemicellulose, but relatively few studies have focused on the utilization of lignin\(^{1\,2}\). Lignin is a complex biopolymer that accounts for 25-35 % of potentially renewable carbon resources and is a potentially valuable source of aromatic compounds\(^3\), which form an important component in bio-oils. Clearly, efficient means of extracting and depolymerizing are required for the utilization of lignin to obtain aromatic compounds. However, conventional extraction methods, such as the kraft, sulfite, soda and organosolv processes, have several disadvantages including high energy cost, potential pollutant release, harsh conditions and significant modification of the lignin structure, which seriously impedes practical applications\(^4\)\(^-\)\(^6\).

Ionic liquids (ILs) are a type of superior green solvent useful in the lignin extraction with more advantages than conventional lignin extraction methods\(^7\)\(^-\)\(^9\). Different types of ILs have been investigated for the extraction of lignin from biomass. Use of 1-propionitrile-3-(2-hydroxyethyl) imidazolium chloride ([C2CN HEim]Cl) successfully extracted 53 % of lignin at 120°C for 24 h\(^10\). Use of 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) obtained 44 % lignin from corn stalks at 125 °C for 1 h\(^11\). Most extraction processes typically require long processing times with relatively low yield of lignin extracted from the biomass. Additionally, ILs are also promising solvents for lignin depolymerization, and our previous study\(^12\) indicated that N-allylpyridinium chloride ([Apy]Cl) could dissolve lignin effectively with partial conversion of lignin macromolecules into low molecular weight compounds with cleavage of methyl ary1 ethers and β-O-4 bonds, which further promoted the efficient catalytic depolymerization of lignin with SO\(_4^{2-}/ZrO_2\) catalyst under mild conditions. Therefore, selection of IL with high reactivity in lignin depolymerization and high lignin extraction ability is very necessary for the utilization of lignin, especially in a continuous flow reaction system.

The present study synthesized and tested a series of ILs with pyridinium- and imidazolium-based cations to identify an IL which could efficiently extract lignin from red pine, but also with high catalytic activity for lignin depolymerization. The catalytic activity of the ionic liquids for the depolymerization of alkali lignin was assessed using a model reaction with SO\(_4^{2-}/ZrO_2\) catalyst. ILs were synthesized as shown in the supporting information and the thermal stabilities of the fresh ILs are shown in Fig. S1. The effects of the amounts of antisolvents (e.g., methanol, water and acetonitrile) on the extraction of lignin under ambient pressure and low temperature were investigated. Based on the results, promising ILs were identified and used for lignin extraction from red pine. The extracted IL-lignin and cellulose-rich solids were characterized with Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), differential thermal analysis (DTG) and elemental analysis (CHN).

The effect of IL dissolution on lignin was investigated using alkali lignin as a model. The DTG curves of raw alkali lignin and extracted IL-lignin are shown in Fig. 1. The maximum decomposition

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temperature of raw alkali lignin was 350 °C, as different ILs had varying solubility for alkali lignin with disruption of the intramolecular hydrogen or β-O-4 bonds\(^{(15)}\). Maximum decomposition temperatures for \([\text{Apy}]\text{Cl}, [\text{Apy}]\text{Br}, [\text{Bpy}]\text{Br}, [\text{Bmim}]\text{Cl}\) and \([\text{Bmim}]\text{Br}\) were 235, 250, 264, 286 and 288 °C, which indicated that the extracted IL-lignin was more easily decomposed than raw alkali lignin, especially the extracted \([\text{Apy}]\text{Cl-lignin}\).

FT-IR analysis was performed for IL-lignin using raw alkali lignin as the standard as shown in Fig. S2. Different peaks characteristic of aryl ring stretching, aromatic skeleton vibration and aromatic C–H deformation were observed\(^{(13)-(15)}\). No significant difference was found between the raw alkali lignin and extracted IL-lignin.

All IL-lignin and alkali lignin samples were dominated by a wide band at 3418 cm\(^{-1}\), which is attributed to phenolic and aliphatic O–H groups. Bands around 1635 cm\(^{-1}\) are attributed to the C=C stretching vibration\(^{(19)}\). The absorbance intensity of the peak at 1635 cm\(^{-1}\) increased compared to raw alkali lignin after dissolution in \([\text{Apy}]\text{Cl}, [\text{Apy}]\text{Br}\) and \([\text{Bpy}]\text{Br}\), indicating that IL-lignin contains many more double bonds\(^{(19)}\), due to bond cleavage during the dissolution process, which promoted lignin depolymerization to a certain extent\(^{(12)}\). The absorbance intensity of the peak at 770 cm\(^{-1}\) increased after dissolution in ILs, which is assigned to the deformation vibrations of C–H bonds associated with aromatic rings, indicating that IL-lignin was more prone to the ary1 substitution reaction. Overall, all ILs used for dissolution had insignificant modification effects on the structure of alkali lignin.

To study the effect of ILs on lignin depolymerization, alkali lignin was dissolved into the IL and \(\text{H}_2\text{O}\) mixture, and catalytic depolymerization of alkali lignin in the presence of \(\text{SO}_4^{2-}/\text{ZrO}_2\); catalyst was carried out in a glass tube reactor at 200 °C for 3 h. After depolymerization, the main liquid products were quantified and identified by GC-FID and GC-MS. Figure S3 and Table S1 show the main liquid products and details of their structures after alkali lignin depolymerization using \([\text{Apy}]\text{Cl}\). Based on these characterizations, the products obtained using other ILs were analyzed and identified. The yields of the main products obtained by different ILs are summarized in Table S2. The peaks for (i) and (ii) were the extraction solvents and the pyridine residue formed in the process of the synthesis of ILs, respectively. Phenolic compounds showed higher yield and p-methy1guaiacol was the main product as shown in Table S2. In particular, \([\text{Apy}]\text{Cl}\) showed higher catalytic activity for lignin depolymerization than other ILs under mild conditions. Consistent with the results of the DTG analysis, \([\text{Apy}]\text{Cl-lignin}\) was more ready to decompose after dissolution. Considering the high reactivity of \([\text{Apy}]\text{Cl}\) for lignin catalytic depolymerization, modification of extraction of lignin from red pine under mild conditions was conducted using \([\text{Apy}]\text{Cl}\).

The preliminary studies showed that raw cellulose, alkali lignin and xylan could be dissolved into \([\text{Apy}]\text{Cl}\) completely, and almost all cellulose was extracted with the mass ratio of methanol:\([\text{Apy}]\text{Cl}\) was 1:1, but without xylan:\([\text{Apy}]\text{Cl}\) the solid extracted was decomposed completely. Most alkali lignin was extracted using the mass ratio of \(\text{H}_2\text{O}:[\text{Apy}]\text{Cl} 20:1\) and acetonitrile:\([\text{Apy}]\text{Cl} 20:1\). Therefore, the effect of the ratios of antisolvent (methanol, \(\text{H}_2\text{O}\) and acetonitrile)\([\text{Apy}]\text{Cl} 1:1\) from 1:1 to 20:1 was investigated for extracting lignin from the simulated mixture (model biomass, including cellulose, alkali lignin and xylan) and red pine. Simulated mixture or red pine 0.1 g was dissolved into \([\text{Apy}]\text{Cl} 3.3\text{ g}\) and the two-step process (Scheme 1) used to extract the lignin. Using methanol as the antisolvent and mass ratio of methanol:\([\text{Apy}]\text{Cl}\) of 1:1, precipitation of lignin ([Apy]Cl-M-lignin) from the simulated mixture increased as the mass ratio of antisolvent:IL increased from 1:1 to 20:1 as shown in Fig. 2. The recovery ratio of \([\text{Apy}]\text{Cl-M-lignin}\) achieved by adding \(\text{H}_2\text{O}\) and acetonitrile was proven to be the most efficient antisolvent with recovery ratios of 75.0 wt% and 66.1 wt% using the same mass ratio of 20:1. Due to the high recovery ratio of precipitated \([\text{Apy}]\text{Cl-M-lignin}\) and the significant change in the components compared to alkali lignin (Table 1), \(\text{H}_2\text{O}\) and acetonitrile with mass ratio of 20:1 were considered as the most promising antisolvents and were used for further extraction of lignin from red pine. Figure 2 shows that 99.5 wt% of cellulose-rich solids were precipitated with the ratio of methanol:\([\text{Apy}]\text{Cl}\) at 3:1, but almost all cellulose-rich solids were precipitated without lignin with the mass ratio of methanol:\([\text{Apy}]\text{Cl}\) at 2:1. Table 1 shows that the components of the extracted cellulose-rich solids were similar to raw cellulose, with almost the same thermogravimetry as raw cellulose (Fig. S4), which indicated that most xylan in the simulated mixture was decomposed during \([\text{Apy}]\text{Cl}\) dissolution. Therefore, extraction of cellulose-rich solids from red pine was investigated using methanol with a mass ratio of methanol:\([\text{Apy}]\text{Cl}\) at 2:1. A ground sample of red pine (250-106 μm, 0.1 g) was dissolved in \([\text{Apy}]\text{Cl} 3.3\text{ g}\) at 100 °C; then methanol, \(\text{H}_2\text{O}\) and acetonitrile were added with mass ratios of methanol, \(\text{H}_2\text{O}\) and acetonitrile to \([\text{Apy}]\text{Cl}\) of 1:3, 1:20 and 1:20, respectively. Cellulose-rich solids and \([\text{Apy}]\text{Cl-R-lignin}\) were extracted using the process...
shown in Scheme 1. Different dissolution times from 3 to 12 h were investigated and the yields of extracted cellulose-rich solids and IL-R-lignin (Table 2) were calculated based on the original content in red pine. Longer dissolution time from 3 to 6 h increased the total recovery ratio of [Apy]Cl-R-lignin, based on the original content of lignin (26.2 wt%, NREL method23) in red pine, from 56.9 to 98.7 wt%, and then decreased to 97.3 wt% after 12 h. In addition, the total recovery ratio of cellulose-rich solids was reduced from 104.7 to 76.4 wt% with increased dissolution time, possibly due to partial decomposition of hemicellulose and cellulose during [Apy]Cl dissolution.

Table 1 shows the [Apy]Cl-R-lignin and cellulose-rich solids extracted from red pine after [Apy]Cl dissolution at 100 °C for 6 h. The components of the [Apy]Cl-R-lignin showed insignificant changes compared to alkali lignin. Therefore, the extracted lignin basically maintained its original characteristics. The slight change in components was due to the breakage of partial bonds during dissolution, which was consistent with the finding for the extracted alkali lignin above. The extracted cellulose-rich solids had slightly larger carbon content compared to commercial cellulose, as part of the hemicellulose or decomposed macromolecules were precipitated during separation. The elemental analyses also showed a slight increase in the N amount for the extracted [Apy]Cl-R-lignin, which originated from the cation of [Apy]Cl, possibly due to a small amount of residual [Apy]Cl from the interaction between the ionic liquid and lignin molecules during the dissolution process.

Table 1 Elemental Analysis

| Content [wt%] | H   | C   | N   |
|---------------|-----|-----|-----|
| Cellulose a)  | 6.47| 42.89| 0.15|
| Cellulose-rich solids b) | 6.78 | 43.41 | 0.17 |
| Cellulose-rich solids c) | 6.83 | 46.77 | 0.20 |
| Alkali lignin  | 4.32| 50.23| 0.13|
| [Apy]Cl-M-Lignin b) | 4.01 | 50.00 | 0.16 |
| [Apy]Cl-R-Lignin c) | 4.14 | 49.97 | 0.21 |

a) Supplied by Sigma Aldrich; b) From dissolution of simulated mixture using [Apy]Cl; c) From dissolution of red pine using [Apy]Cl.

FT-IR analysis of the alkali lignin and [Apy]Cl-R-lignin found a wide band at 3401 cm⁻¹ assigned to the phenolic and aliphatic OH groups18,19, and bands for carbonyl stretching (1710 cm⁻¹), C=O stretching of syringyl groups (1390 cm⁻¹), C=O deformation of guaiacyl groups (1216 cm⁻¹), C–O absorption of the methoxy group on the benzene ring (1129 cm⁻¹) and C–O(C) stretching of ether groups (1036 cm⁻¹).20,21 Figure 3 shows the absorbance intensity of the peaks at 1710, 1216 and 1036 cm⁻¹ were increased compared to alkali lignin, indicating that [Apy]Cl-lignin had much higher content of unsaturated bonds. Additionally, the absorbance intensity of the peaks at 1390 cm⁻¹ and 1129 cm⁻¹ had decreased for [Apy]Cl-R-lignin, indicating that the demethylation reaction and breakage of the ether bond occurred during [Apy]Cl dissolution. Figure 4 shows the increased intensity of the peak at 1513 cm⁻¹ which was attributed to greater aromatic skeletal vibrations in lignin, indicating that lignin was partially precipitated with methanol extraction. The band at 1155 cm⁻¹ corresponded to the C–O–C asymmetric stretching vibration in cellulose/hemicellulose22, and the intensity decreased, indicating that cellulose or hemicellulose was partially decomposed in [Apy]Cl. The spectra of the extracted [Apy]Cl-R-lignin and cellulose-rich solids from red pine are compared to those of raw alkali lignin and cellulose in Figs. 3 and 4. The close similarity of the spectra indicates that lignin was extracted from red pine with only mild modification.

The TGA and DTGA curves of the raw alkali lignin and extracted [Apy]Cl-R-lignin from red pine are shown in Fig. S5. The maximum decomposition temperature was 350 °C for raw alkali lignin, and 231 °C for extracted lignin from red pine, due to the partial decomposition of [Apy]Cl-R-lignin during the...
dissolution of [Apy] Cl, which was consistent with our previous research results\(^\text{23}\). This finding indicates that the extracted [Apy]Cl-R-lignin was more easily decomposed.

The regenerated mass yield of the ionic liquid was 96.1 ± 0.5 wt%. The \(^{13}\)C-NMR spectra of the regenerated [Apy]Cl and fresh [Apy]Cl appeared to be around 232 °C (Fig. S6) and the overall thermal decomposition behavior of the regenerated [Apy]Cl was similar to that of fresh [Apy]Cl, which demonstrated potential recyclability.

In summary, to compare the catalytic activity of ILs for lignin depolymerization and the mild modification effect on the structure of alkali lignin, [Apy]Cl was chosen as a promising ionic liquid. Investigation of the effect of the amount of antisolvent on the recovery ratio of lignin found the optimum mass ratios of methanol:[Apy]Cl, H\(_2\)O:[Apy]Cl and acetonitrile:[Apy]Cl were 2:1, 20:1 and 20:1, respectively, which were used to extract cellulose-rich solids and [Apy]Cl-R-lignin from red pine. Extraction of lignin from red pine was successfully achieved at atmospheric pressure, with 98.7 wt% yield after 6 h of dissolution. The regenerated [Apy]Cl showed no change in structure and thermal stability, which demonstrated potential recyclability.

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**Supporting Information**

Supplementary data associated with this article can be found, in the online version, at https://jstage.jst.go.jp/browse/jpi/-char/en (DOI: doi.org/10.1627/jpi.63.102).