Coupling of ionic liquid treatment and membrane filtration for recovery of lignin from lignocellulosic biomass

Gayatri Gogoi, Swapnali Hazarika

Chemical Engineering Group, Engineering Science and Technology Division, CSIR-NEIST, Jorhat 785006, Assam, India
Academy of Scientific and Innovative Research, CSIR-NEIST Campus, India

Abstract

The work demonstrates the pretreatment of lignocellulosic biomass (Rice straw) in imidazolium based ionic liquids. Three different imidazolium based ionic liquids, 1-ethyl-3-methyl–imidazolium acetate, 1-methyl-3-octylimidazolium chloride and 1-butyl-3-methyl-imidazolium tetrafluoroborate were used to dissolve the lignocelluloses of rice straw and the dissolution process was optimised under several conditions viz. time, temperature and particle size of biomass. The dissolution process was investigated by characterizing the biomass before and after treatment by FTIR, XRD, SEM and Zeta Potential analysis. From the pretreated lignocelluloses, cellulose and lignin were separated using chemical methods. On the basis of investigations, the role of ionic liquids on dissolution of lignocelluloses and effect of different imidazolium based ionic liquids for the regeneration of cellulose and lignin were discussed. After the separation process ionic liquid was recovered using nano filtration membrane and was reused for further study.

1. Introduction

Biomass provides alternative and renewable energy resources for sustainable production of organic fuels and chemicals. Furthermore lignocellulosic biomass from agricultural residues, forestry wastes, waste paper and crops which is a renewable, relatively carbon-neutral source of energy has come under intense research scrutiny due to its potential use as a starting material for bioproducts from biofuels to specialty chemicals [1–3]. In this study rice straw (Oryza sativa) collected from the North East India, one of the hotspots of biodiversity of the world was considered as the lignocellulosic biomass for processing and recovery of value added product by greener approach. Various pretreatment options are defined in literature such as dilute acid, concentrated acid, and organosolv pretreatment. However this study emphasizes the potential of certain ionic liquids as pretreatment solvents for lignocellulosic biomass.

Lignocellulosic biomass contains ~30–50% cellulose, a glucose polymer; 10–40% hemicelluloses, a sugar heteropolymer and ~5–30% lignin, a non-fermentable phenyl propene unit plus lesser amounts of minerals, oils, soluble sugars, and other components [4,5]. The dense network of intramolecular/intermolecular hydrogen bonds in cellulose, branched heteropolysaccharides of hemicelluloses with shorter chain lengths and three dimensional amorphous lignin provides a complex network in lignocellulosic biomass [6–8]. Because of this, new and efficient solvents and process technologies are needed to break the complex network of lignocellulosic biomass. Ionic liquid serves as a new class of designer solvents that can dissolve a large number of biomacromolecules such as cellulose, lignin, silk fibroin, and starch with high efficiency [9–11].

As an environment friendly material, the applications of ionic liquids have been extensively reported as solvent to facilitate green applications in reactions and separations due to their unique beneficial properties usually negligible vapour pressure, low flammability, high thermal stability over a wide range of temperatures and tuneable properties such as hydrophobicity, polarity and solvent power [12–16]. Due to the IL’s solvent power, their use in the development of alternative methods for the extraction and processing of carbohydrates and other compounds from lignocellulosic biomass was recently explored intensively [17,18]. In this study pretreatment of lignocellulosic biomass with ionic liquid was carried out to alter the structure of lignocellulosic biomass by breaking the lignin seal and disrupting the crystalline structure of cellulose. A typical deconstruction sequence for lignocelluloses is: size reduction to chips and pretreatment that solubilises the...
hemicelluloses and alters/removes lignin and cellulose [19]. To gain a greater insight into ionic liquid pretreatment, the effect of ionic liquids with different anionic groups on the structural changes of rice straw was investigated. Various ionic liquids such as 1-methyl-3-octyl imidazolium chloride, 1-ethyl-3-methylimidazolium acetate, 1-butyl-3-methyl-imidazolium tetrafluoroborate have been applied as solvents in pretreatment step.

Since ionic liquids are very expensive than the conventional solvents hence recycling and reuse of the ionic liquids is a crucial factor for the economic efficiency of the extraction process. Thus in our study recovery of ionic liquids has been studied using nano filtration membrane.

2. Experimental

2.1. Materials

The lignocellulosic feedstock used in this study was rice straw (Oryza Sativa) collected from the Jorhat district of Assam, India. The biomass was washed, air-dried and then finely grounded with a grinder and sieved (150 μm, 300 μm, 450 μm) before use. The prepared grounded rice straw samples were then stored in plastic bags at room temperature. The ionic liquids 1-methyl-3-octylimidazolium chloride, 1-ethyl-3-methylimidazolium acetate and 1-butyl-3-methyl imidazolium tetrafluoroborate were purchased from Sigma-Aldrich (USA) and were used without further purification. The standard lignin was purchased from TCI, Japan. The commercial polyamide thin film composite membranes (FilmTec NF 270-400) were used for further purification. The samples were collected every one hour interval of time and filtered and analysed by UV visible spectrophotometer. The UV absorption peak for lignin was noted at 280 nm. After dissolution of the biomass in ionic liquid percentage of biomass dissolved was calculated according to the equation:

\[
Diss = \left(1 - \frac{M_{\text{und}}}{M_0}\right) \times 100
\]

where \(M_{\text{und}}\) → Mass of undissolved residue recovered.

\(Mo\) → Mass of original biomass.

\(Diss\) → Dissolution %.

2.2. Dissolution of rice straw

0.2 g of the rice straw was taken for each experiment and 5 mL ionic liquid was added to each sample and stirred using a homogenizer with a constant speed of 400 rpm at different temperatures. The samples were collected every one hour interval of time and filtered and analysed by UV visible spectrophotometer. The UV absorption peak for lignin was noted at 280 nm. After dissolution of the biomass in ionic liquid percentage of biomass dissolved was calculated according to the equation:

\[
Diss = \left(1 - \frac{M_{\text{und}}}{M_0}\right) \times 100
\]

where \(M_{\text{und}}\) → Mass of undissolved residue recovered.

\(Mo\) → Mass of original biomass.

\(Diss\) → Dissolution %.

2.3. Lignocellulose recovery

Once the lignocellulose has been pretreated, it needs to be recovered and further processed. The first step is to separate the three major components—cellulose, hemicelluloses and lignin. Two prominent stages appear in separating the components. Firstly cellulose is precipitated by adding an organic solvent (acetone)-water mixture (1:1). As the cellulose is precipitated the lignin remains in the solution. After evaporating off the organic solvent lignin can be recovered. Since acidification reduces the basicity of the ionic liquids which in turn lowers the lignin solubility, thus 0.1 N H2SO4 was added to the lignin containing IL solution to increase the amount of lignin recovery [20,11,15]. The typical process for the separation of lignocelluloses with ionic liquids is represented schematically as shown in Fig. 1.

2.4. Recovery and recycle of ionic liquid

Due to high cost of ionic liquid it is important to recover the used IL from its aqueous mixture after recovery of lignin. Nano filtration, a pressure driven membrane process was carried out for recovery of ionic liquid in a standard experimental set up as described in our published work [21] in which a two compartment membrane cell was used for the study. Volume of each compartment of the cell was 150 mL. The commercial polyamide thin film composite membrane was placed between the compartments with silicone-rubber packing and the cell was connected with a reservoir of 500 mL. The solution of dissolved lignocelluloses in ionic liquid was stirred continuously and circulated by peristaltic pump that was connected to the reservoir applying a pressure 5 bar and flow rate 20 mL/min. Permeate flux was calculated by using the equation given as,

\[
J = \frac{V\Delta C}{A\Delta t}
\]

where \(V\) is the volume of permeate at time \(t\), \(\Delta C\) is the concentration variation in the corresponding aqueous solution at the time interval \(\Delta t\), A is the area of the membrane. Rejection of the membrane is given as,

\[
R\% = \frac{C_f - C_p}{C_f} \times 100
\]

where \(C_f\) is the concentration in feed and \(C_p\) is the concentration in permeate.

2.5. Analytical methods

Samples were analysed by UV–Visible Spectrophotometer (Thermo Scientific, EVOLUTION 201), IR (PERKIN Elmer System 2000), XRD (JDX-11P-3A, JEOL, Japan), surface morphology was studied by a scanning electron microscope (LEO 1427VP, UK), zeta potential and isoelectric point were determined by Electrokinetic Analyzer (Anton-Paar SurPASS).

3. Results and discussion

3.1. Dissolution of lignocelluloses

After ten hours of ionic liquid treatment the lignocelluloses content is high in the solution as is evident from the change in colour.
of ionic liquid shown in Fig. 2 which is a qualitative study. Dissolution of lignocelluloses in ionic liquid are known to be dependent on the ionic liquid, as well as on several conditions inherent to pretreatment, such as temperature, time, and particle size of biomass. Major effects of these parameters in the biomass pretreatment are described in the following sections, which contribute for a better understanding of pretreatment of lignocellulosic biomass with ionic liquids.

3.2. Influence of IL ions in the biomass dissolution

Because of the complex matrix of lignocelluloses, new and efficient solvents and process technologies are needed for dissolution and further separation of lignocelluloses. Several studies shown that imidazolium based ionic liquids could effectively dissolve lignocellulosic components [14,22]. Theoretical modelling has shown that cations based on imidazole are particularly well suited for dissolving lignin since the cation can favourably interact with aromatic phenyl rings of lignin [23]. In our study, three imidazolium based ionic liquids viz. 1-butyl-3-methyl-imidazolium tetrafluoroborate, 1-ethyl-3-methyl–imidazolium acetate, 1-methyl-3-octylimidazolium chloride shown in Fig. 3 are used for dissolution of rice straw at atmospheric pressure and elevated temperature (50–150 °C). On treating the rice straw with 1-butyl-3-methyl-imidazolium tetrafluoroborate at temperature range of 50–150 °C, no significant change in dissolution was observed. However the chloride and acetate based ionic liquid (1-ethyl-3-methylimidazolium acetate, 1-methyl-3-octylimidazolium chloride) resulted a significant dissolution as is evident from the change in colour intensity shown in Fig. 2. It has been shown that hydrogen bond basicity of the anion of the ionic liquid plays crucial role in dissolving lignocelluloses.

The viscosity and the melting point of ILs also play an important role in the dissolution of lignocelluloses because it can effect the mixing and mass transfer of lignocelluloses and IL itself. Studies showed that the low viscosity ILs undergoes for rapid extraction of cellulose and other carbohydrates due to the higher mobility of the ions [11,15]. However, in our case, among the three ILs, acetate based ionic liquids with medium viscosity shows good ability for pretreatment of lignocelluloses. This observation perhaps explained from the lowest melting point of the acetate based IL (>30°) whereas other ILs have melting point range from 285 to 402 °C as shown in the Table 1. This is due to the reason that IL having low melting point facilitates the better dissolution of biomass.

The effect of selected ionic liquids on the dissolution of rice straw and subsequent regeneration of cellulose and precipitation...
of lignin was investigated and it was concluded that among these ionic liquids, 1-ethyl-3-methyl-imidazolium acetate is more efficient for dissolution of lignin than the others.

3.3. Cellulose regeneration and recovery of lignin

From the study the amount of cellulose regenerated on dissolution with the ionic liquids were found to be 29%, 34% and 46% respectively from 1-butyl-3-methyl-imidazolium tetrafluoro-borate, 1-methyl-3-octylimidazolium chloride and 1-ethyl-3-methyl imidazolium acetate. Thus 1-ethyl-3-methyl-imidazolium acetate serves as the efficient solvent for the pretreatment of the lignocelluloses. Dissolution mechanism of cellulose in ILs is based on the capability of anions of ILs to effectively break the extensive intra- and inter-molecular hydrogen bonding network in cellulose. Dissolution of rice straw is influenced by the interaction between anion of the ionic liquid and hydroxyl group of the cellulose [24–26]. Anion of the ionic liquid acts as the hydrogen bond acceptor in dissolution where it interacts specifically with the hydroxyl protons of the celluloseic materials and facilitates the formation of hydrogen bonds between cellulose and ionic liquid [27,28]. Ionic liquids with a strong hydrogen bond basicity are effective in weakening the hydrogen-bonding network of the polymer chains. Among the three selected ionic liquids, the acetate based IL has higher hydrogen bond basicity due to which [EMIM]OAc is more effective for cellulose dissolution. Fig. 4 shows one of the proposed mechanisms of cellulose dissolution in ionic liquids [29,30].

After dissolution process, the reaction mixture was appeared dark brown in colour which is imparted by the dissolved lignin of the lignocellulosic matrix [9,11,24]. As with dissolution of cellulose, imidazolium cations of the ILs also plays role in the dissolution of lignin due to the n–π interactions between the cations and the aromatic rings (polyphenolic structure) of lignin [23,31]. On the basis of the results from the screening experiments, we selected IL [EMIM]OAc for the extraction of lignin from rice straw. Lignin extractability of the IL was recorded by UV absorption brated at 280 nm. The lignin extracted during pretreatment with ionic liquid was recovered by acid precipitation and was found to 43%. Among the three selected ionic liquids 1-ethyl-3-methyl-imidazolium acetate was found to be more efficient for extraction and recovery of lignin from the rice straw.

3.4. Temperature effect

The dissolution kinetics of rice straw in IL was studied over a wide range of temperatures (50–150 °C) which is shown in Fig. 5(a). The increase of temperature accelerates swelling and dissolution rates of lignocelluloses in ionic liquids which is due to destabilisation effect of temperature on the hydrogen bonds in the structure of cellulose and lignin [32,33]. On decreasing temperature longer times are required for an efficient swelling and dissolution of lignocelluloses.

3.5. Reaction time effect

To investigate the effect of reaction time on dissolution, biomass (rice straw) dissolution at 150 °C was conducted for five different residence times viz. 4 h, 6 h, 8 h, 10 h and 12 h and the extent of dissolution of the biomass was measured for each time which is shown in Fig. 5(b). Long pre-treatment times were reported to favour lignin extraction. As the pretreatment time increases the diffusion of ionic liquid into the biomass is improved and increases the dissolution and extraction of lignin from biomass [20].

3.6. Particle size of biomass

Particle size is one of the crucial factor which directly impacts on the contact and diffusion of ionic liquid into the lignocellulosic material and thus the solubilisation of lignocellulosic biomass. It was found that the solubility of finely milled biomass is higher than that of coarser material. Thus smaller the particle size of the biomass the greater is the solubilisation of lignocellulosic biomass as shown in Fig. 5(c).

3.7. Structural characterization

3.7.1. FT-IR

In order to see the effects of ionic liquid pretreatment, studies on the chemical and structural characteristics of the ionic liquid treated rice straw and untreated rice straw are essential. Ionic liquid treated rice straws have altered chemical and structural characteristics compared to the untreated rice straw. Table 2 gives the group frequencies of absorption bands assigned with the lignocellulosic components. The changes in the structural characteristics of the untreated rice straw and the cellulose regenerated from the different ionic liquids can be observed from the FTIR spectra as shown in Fig. 6. The untreated rice straw gives characteristic absorbances at 800–950 cm⁻¹, 1035 cm⁻¹, 1368 cm⁻¹, 1457 cm⁻¹, 1638 cm⁻¹, 2913 cm⁻¹, 3000–4000 cm⁻¹ that are assigned with characteristic groups of lignocellulosic components as shown in Table 2. IR spectra of all the regenerated cellulose from the three ionic liquids gives absorbances at 800 cm⁻¹, 1040 cm⁻¹, 1368 cm⁻¹, 1638 cm⁻¹, 2913 cm⁻¹ and 3000–4000 cm⁻¹ indicating assignments with C–H deformation, C–O asymmetric stretching vibration in cellulose, hemicelluloses and aryl group of lignin, symmetric C–H bending in cellulose and C–H stretching in cellulose respectively. On comparing the characteristics of the IR spectra of untreated rice straw and the regenerated cellulosic component of different IL treated rice straw it has been established that cellulose regenerated from [EMIM]OAc treated rice straw gives more intense absorbance peaks at the assigned bands compared to the other two ILs which indicates the highest dissolution and regeneration of

<table>
<thead>
<tr>
<th>IL</th>
<th>Melting point</th>
<th>Viscosity</th>
<th>Molecular weight</th>
<th>Density</th>
<th>Flash point</th>
<th>Partition coefficient</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EMIM]OAc</td>
<td>&gt;30 °C</td>
<td>162cp</td>
<td>170.21 g/mol</td>
<td>1.027</td>
<td>164 °C</td>
<td>&lt;0.3</td>
<td>n20/D 1.502</td>
</tr>
<tr>
<td>[BMIM]TfB</td>
<td>402 °C</td>
<td>114cp</td>
<td>226.02 g/mol</td>
<td>1.21 g/ml</td>
<td>288 °C</td>
<td>&lt;0.3</td>
<td>n20/D 1.52</td>
</tr>
<tr>
<td>[MOIM]Cl</td>
<td>285 °C</td>
<td>337cp</td>
<td>230.78 g/mol</td>
<td>1.01 g/ml</td>
<td>–0.31</td>
<td></td>
<td>n20/D 1.51</td>
</tr>
</tbody>
</table>

Table 1 Properties of ionic liquids.

Fig. 4. Dissolution mechanism of cellulose in 1-ethyl-3-methyl imidazolium acetate.
cellulose in [EMIM]OAc. The IR spectra of the lignin extracted from IL [EMIM]OAc treated rice straw and the commercial lignin shows a quite resemblance in their structural characteristics as shown in Fig. 7. Both the spectra gives characteristic absorbance at 1035 cm⁻¹/C which gives the assignment for aryl OH group of lignin while absorbance at 1457 cm⁻¹/C assigns the asymmetric bending of CH₃ and methoxy (−OCH₃) groups present in lignin. A sharp absorbance peak at 1510 cm⁻¹/C shows the C=O vibration in aromatic ring of lignin and a broad peak at 3450 cm⁻¹/C assigns the free and hydrogen bonded O−H stretching in lignin. Thus FTIR spectra of the lignin extracted from the [EMIM]OAc treated rice straw interprets the higher dissolution capacity of the ionic liquid for the extraction of lignin from the rice straw. This suggest that [EMIM]OAc effectively dissolves both cellulose and lignin of the biomass.

3.7.2. XRD characterization

The crystallinity of the rice straw was analysed by XRD by determining the crystallinity index. The crystallinity index is the measure of the relative degree of crystallinity which can be determined by XRD using relationship,

\[ CRI = \frac{I_{cr} - I_{am}}{I_{cr}} \times 100 \]

where \( I_{cr} \) is the maximum intensity of crystalline region and \( I_{am} \) is the maximum intensity of the amorphous region. As shown in

![Fig. 5. Effect of (a) temperature, (b) time and (c) particle size of biomass on the dissolution of rice straw with ionic liquid [EMIM]OAc.](image)

![Fig. 6. FTIR spectra of (a) untreated rice straw and cellulose regenerated from the ionic liquids, (b) [EMIM]OAc, (c) [BMIM]TFB, and (d) [MOIM]Cl.](image)

<table>
<thead>
<tr>
<th>Group frequency (wavenumber, cm⁻¹)</th>
<th>Origin</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>800–950</td>
<td>C−H</td>
<td>C−H deformation</td>
</tr>
<tr>
<td>~1035</td>
<td>C−O</td>
<td>C−O asymmetric stretching vibration in cellulose, hemicelluloses and aryl OH group of lignin</td>
</tr>
<tr>
<td>~1368</td>
<td>C−H</td>
<td>Symmetric C−H bending in cellulose</td>
</tr>
<tr>
<td>~1457</td>
<td>C−H</td>
<td>Asymmetric bending of CH₃ and methoxy (−OCH₃) groups present in lignin</td>
</tr>
<tr>
<td>~1509</td>
<td>C−C</td>
<td>Vibration in aromatic ring of lignin</td>
</tr>
<tr>
<td>~1638</td>
<td>O−H</td>
<td>O−H bending vibration of adsorbed water molecule</td>
</tr>
<tr>
<td>~1733</td>
<td>C=O</td>
<td>Stretching vibration in acetyl group of hemicelluloses</td>
</tr>
<tr>
<td>~2913</td>
<td>C−H</td>
<td>C−H stretching in cellulose rich material</td>
</tr>
<tr>
<td>2995–4000</td>
<td>O−H</td>
<td>Free and hydrogen bonded O−H stretching in lignin</td>
</tr>
</tbody>
</table>
Fig. 8 occurrence of a sharper peak at $2\theta = 24.5^\circ$ gives lower crystallinity of the regenerated cellulose after treatment with ionic liquid compared with the untreated rice straw. The lower crystallinity index of the regenerated cellulose is due to the presence of higher amount of amorphous cellulose.

From Table 3 it was observed that the crystallinity index of the regenerated cellulose of 1-ethyl-3-methyl imidazolium acetate treated rice straw was lowest (14%) followed by 1-butyl-3-methyl-imidazolium tetrafluoro borate and 1-methyl-3-octyl imidazolium chloride (29.8% and 31.45% respectively). A significant difference in the crystallinity index of the regenerated cellulose on treatment with different IL shows the different ability of the ILs to dissolve the cellulose. The acetate based IL disrupts the cellulose crystallinity of the rice straw more effectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated rice straw</td>
<td>35.85</td>
</tr>
<tr>
<td>1-Methyl-3-octyl imidazolium chloride based regenerated cellulose</td>
<td>31.45</td>
</tr>
<tr>
<td>1-Butyl-3-methyl-imidazolium tetrafluoro borate based regenerated cellulose</td>
<td>29.8</td>
</tr>
<tr>
<td>1-Ethyl-3-methyl imidazolium acetate based regenerated cellulose</td>
<td>14</td>
</tr>
</tbody>
</table>
3.7.3. SEM analysis

The SEM analysis of biomass before and after treatment demonstrates that surface structure disruption of the rice straw occurs on pretreatment with ionic liquids as shown in Fig. 9 which shows the significant changes in the morphology of biomass after treatment with ionic liquids. The untreated rice straw shows an even and smooth surface while the morphology of the rice straw after treatment shows a disordered and a loose surface. The disruption of the pretreated rice straw is due to the swelling of the lignocellulosic matrix caused by the solvating action of liquid [20].

3.7.4. Zeta potential analysis

The streaming potential analysis of lignocellulosic fiber shows porous structures with high swelling propensity. Fig. 10 (a) and (b) shows the pH dependence of the apparent zeta potential for rice straw before and after IL treatment. The isoelectric point, where zeta potential is zero, for untreated rice straw and IL treated rice straw corresponds to pH 1.11 and 2.001 which indicates the different surface chemistry of treated and untreated lignocellulosic biomass. The negative zeta potential at a higher pH reflects the enhanced swelling capacity of the IL treated rice straw that increases the accessibility of functional groups located at the inner surface of the biomass [34].

3.7.5. Recovery of ionic liquid by nano filtration

After separation of cellulose and lignin from the ionic liquid treated lignocellulosic mixture, ionic liquid is recovered from the mixture using nano filtration membrane. Fig. 11 shows the time versus flux and % rejection plot from which it is observed that about 95% rejection of IL is recovered using NF membrane.

4. Conclusion

From this study it has been demonstrated that ionic liquid can be used for the pretreatment of lignocellulosic biomass for the extraction and separation of the lignocellulosic components. Hydrogen bonding and II-II interactions between the complex structure of the lignocelluloses and IL effectively plays role in the dissolution process. Among the three selected ionic liquids 1-Butyl-3-Methyl–imidazolium tetrafluoroborate, 1-Ethyl-3-Methylimidazolium acetate and 1-Methyl-3-Octylimidazolium chloride, 1-Ethyl-3-Methyl-imidazolium acetate serves as the best solvent due to its certain physicochemical properties such as lower viscosity and melting point and higher hydrogen bonding basicity. Lignin was recovered by chemical method and after its recovery IL was recovered by using nano filtration membrane.

Acknowledgement

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