Video Article

A Novel Method for the Pentosan Analysis Present in Jute Biomass and Its Conversion into Sugar Monomers Using Acidic Ionic Liquid

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Abstract

Recently, ionic liquids (ILs) are used for biomass valorization into valuable chemicals because of their remarkable properties such as thermal stability, lower vapor pressure, non-flammability, higher heat capacity, and tunable solubility and acidity. Here, we demonstrate a method for the synthesis of C5 sugars (xylose and arabinose) from the pentosan present in jute biomass in a one-pot process by utilizing a catalytic amount of Brønsted acidic 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate IL. The acidic IL is synthesized in the lab and characterized using NMR spectroscopic techniques for understanding its purity. The various properties of BAIL are measured such as acid strength, thermal and hydrothermal stability, which showed that the catalyst is stable at a higher temperature (250 °C) and possesses very high acid strength (H_o 1.57). The acidic IL converts over 90% of pentosan into sugars and furfural. Hence, the presenting method in this study can also be employed for the evaluation of pentosan concentration in other kinds of lignocellulosic biomass.

Video Link

The video component of this article can be found at https://www.jove.com/video/57613/

Introduction

Biomass has great potential as a renewable energy and chemical source because it is sustainable, inexpensive, and equally distributed unlike fossil resources, which makes it one of the promising candidates to replace fossil feedstocks. The estimated production of lignocellulosic biomass is 146 billion metric tons per year[1]. The lignocellulosic biomass is mainly comprised of lignin, cellulose, and hemicellulose as its three major constituents. Lignin is an aromatic polymer made from phenylpropanoid units; on the other hand, cellulose and hemicellulose are the polysaccharide parts of the lignocellulosic biomass. Cellulose is composed of glucose units connected by β(1→4) glycosidic linkage, whereas hemicellulose is made up of C5 sugars, C6 sugars, and sugar acids linked together by β (1→4), β (1→3) and β (1→6) glycosidic bonds[2,3]. Along with various lignocellulosic biomass (bagasse, rice husk, wheat straw, *etc.*), the jute lignocellulose biomass is also produced in very large quantities (*ca.* 98% in 2014) in Asia compared to the total jute production in the world. India produces 1.96 x 10^6 metric tons of jute biomass while Bangladesh produces 1.34 x 10^6 metric tons of jute biomass compared to the total production of jute biomass in the world (3.39 x 10^6 metric tons) in 2014[4]. The utilization of this non-edible biomass will not conflict with food demand. Hence, it is beneficial to use it as a stock for synthesizing a variety of value added chemicals (xylose, arabinose, furfural, 5-hydroxymethylfurfural (HMF), *etc.*). According to the U.S. Department of Energy, furfural and HMF are considered as some of the top 30 building block chemicals derived from biomass[5]. Furfural is obtained from xylose or directly from hemicellulose and can be converted to many important chemicals. Furfuryl alcohol, methyl furan, and tetrahydrofuran are important chemicals obtained from furfural[6]. Hence, conversion of lignocellulosic biomass such as jute biomass into C5 sugars and other important chemicals is an important topic.

Extensive reports are available on the various catalytic methods for the conversion of lignocellulosic biomass into value added chemicals. The mineral acids (HCl and H_2SO_4) and heterogeneous catalysts (Amberlyst, HMOR, HUSY, SAPO-44, *etc.*) were used significantly for the conversion of hemicellulose and lignocellulosic biomass into sugars (pentose and hexose sugars) and furans (furfural and HMF)[7,8]. The reusability and corrosiveness of mineral acid is a major issue. However, with the solid acid catalyst, higher temperature and pressures are required because the reaction occurs at the surface of the catalyst. To overcome these issues, recently ILs are reported for the valorization of biomass as a catalyst or solvent[9,10,11,12,13,14]. The use of IL as a solvent is not a better method because of its higher cost and the lower vapor pressure of ILs that creates difficulty in product separation. Therefore, it is imperative to use recyclable IL as a catalyst (in small amounts) in a water solvent system for the biomass conversion to value added chemicals.

Here, we present a method to use 1-methyl-3-(3-sulfopropyl) imidazolium hydrogen sulfate acidic IL as the catalyst for the direct conversion of pentosan present in jute biomass into sugar monomers without any pretreatment. Commonly, ILs are reported for the pretreatment of lignocellulosic biomass[10,15,16,17] whereas the very large quantity of ILs is used for the biomass pretreatment. Hence, it is always advantageous to use IL as the catalyst and to convert lignocellulosic biomass into chemicals without any additional treatment. Moreover, in the present work, the lignin concentration presented in jute biomass is calculated using Klason method which could be converted into various aromatic monomers[18].

Protocol

Several chemicals used in the presenting work are toxic and carcinogenic. Please use all appropriate safety practices when performing synthesis of IL and biomass processing.

1. Preparation of Acidic IL

1. Add 7.625 mmol of 1,3-propane sultone in a 50 mL round bottom flask and then close the flask with a rubber septum.
2. Add 7.625 mmol of 1-methylimidazole into 7.625 mmol of 1,3-propanesultone slowly (10 min) at 0 °C using a syringe (1 mL).
3. After the complete addition of 1-methylimidazole and 1,3-propanesultone, add 15 mL of dry toluene and reflux the mixture for 16 h at 120 °C to get the solid zwitterion.
4. Separate the zwitterion from toluene using filtration and then wash the zwitterion with 40 mL of toluene. For drying the zwitterion, set the oven temperature to 80 °C. Once the oven temperature reaches 80 °C, keep the sample in the oven for 4 h and then use the dried zwitterion in the next step.
5. Add sulfuric acid into the round bottom flask containing the zwitterion (equal moles of zwitterion and sulfuric acid) using a 1,000 μL micropipette. Then connect the round bottom flask to a reflux condenser. Heat and stir the mixture at 110 °C for 12 h to get the desired IL.
   NOTE: The reaction between sulfuric acid and zwitterion is carried out without any solvent.
6. After synthesis of acidic IL, characterize it using ^{1}H and ^{13}C NMR spectroscopy.

2. Determination of Hammett Acidity (H_o)

1. Add 10 mg of the *p*-nitroaniline indicator in a 1 L volumetric flask and then add distilled water to make a 1 L solution. Shake the solution well by hand for 2 min and leave the solution for 1 h to mix the *p*-nitroaniline in water (Blank solution).
2. Add 1.59 mmol of H$^+$ ion of the acid catalyst (HCl/H$_2$SO$_4$/acidic IL) to 50 mL of *p*-nitroaniline indicator solution and shake the solution by hand for mixing (Sample solution).
   Note All acid catalysts used in the present work (HCl, H$_2$SO$_4$, and acidic IL) are added individually in the 50 mL indicator solution (**Table 1**) for the determination of Hammett acidity (H_o).
3. Perform the UV measurement of blank solution (*p*-nitroaniline solution) and sample solution (catalyst containing *p*-nitroaniline solution) and determine the Amax of *p*-nitroaniline.
4. Finally calculate the molar concentrations of the unprotonated [I] and protonated [IH$^+$] indicator solutions using the Amax value of *p*-nitroaniline and sample solutions. Then calculate the H_o using the equation below[2]

$$H_O = \mathrm{pK(I)aq} + \log \left(\frac{[\mathrm{I}]}{[\mathrm{IH}^+]} \right)$$ **Equation 1**

where pK(I)$_{aq}$ is the pKa of the *p*-nitroaniline indicator in water (pKa = 0.99), and [I] and [IH$^+$] are the molar concentrations of the unprotonated and protonated indicator solutions, respectively.

3. Analysis of Jute Biomass

1. **Analysis of pentosan**
   NOTE: The jute biomass is oven dried at 105 °C for 16 h in the oven.
   1. Add 3 g of oven dried jute biomass in a 1 L round bottom flask, and then add 100 mL of 3.85 N HCl solution into it.
   2. Connect the flask to the distillation apparatus and start the stirring and heating so that the solution starts boiling.
   3. Add 250 mL of 3.85 N HCl dropwise using a funnel to the round bottom flask containing the jute biomass and the HCl solution.
   4. Maintain a constant volume (100 mL) in the round bottom flask during the distillation by adding 3.85 N HCl solution dropwise.
   5. Stop the experiment when 220 mL of distillate is collected. Then dilute the collected distillate to 500 mL with distilled water.
   6. Analyze the sample using UV-visible spectrometer and record the absorbance at 280 nm.
   7. Determine the Pentosan % according to the following formula using the absorbance and dilution value:

   $$\mathrm{Pentosan}\ (\%) = \frac{\mathrm{Absorbance\ at\ 280\ nm\ x\ Dilution\ x\ 1.563\ x\ 0.5\ x\ 100}}{151\ \mathrm{x\ Oven\ dried\ weight\ of\ jute\ biomass}}$$ **Equation 2**

   NOTE: This method is called the Technical Association of the Pulp and Paper Industry (TAPPI) method for pentosan analysis[9,19]. Repeat the experiment two to three times and take the average value of pentosan %. If necessary, dilute the collected distillate to get the absorbance to the optimum limit.

2. **Analysis of lignin**
   NOTE: Remove the moisture present in the jute biomass before using it for lignin analysis. Keep the jute biomass in an oven at 105 °C for 16 h to remove moisture.
   1. Add 1 g of jute biomass into a 50 mL vial, and then add 15 mL of 72 *wt*% H$_2$SO$_4$ in the vial containing jute biomass. Stir the mixture using a hot plate with stirring facility at 30 °C for 2 h.
   2. Add 150 mL of distilled water in a 1 L round bottom flask and transfer the digested biomass sample (present in the vial) to the flask.

3. Wash the vial with 195 mL of water and transfer the washed liquid into a 1 L round bottom flask containing digested biomass.
4. Reflux the solution for 4 h and then cool the round bottom flask to room temperature. Wait 12 h for the insoluble lignin and ash to settle down.
5. Filter the solution using a G2 crucible to obtain the insoluble lignin with ash. Then wash the insoluble solid with 150 mL of hot water to make it acid-free.
6. Dry the solid (lignin + ash) at 60 °C for 16 h in the oven and further dry it 105 °C for 1 h in the oven.
7. Keep the sample in the desiccator and take the weight when the sample is cooled. The lignin obtained at this stage contains ash and hence is called uncorrected lignin.
8. Perform the ash correction by heating the obtained sample at 650 °C for 5 h in the presence of air. Determine the ash correction using the formula below:

$$\text{Lignin ash correction } (\%) = \frac{[\text{wt. of uncorrected lingin} - \text{wt. of ash}]}{\text{wt. of dry jute biomass}} \; x \; 100 \qquad \textbf{Equation 3}$$

4. Conversion of Pentosan from Jute Biomass into Sugars

1. Add 2 g of oven dried jute biomass to a high pressure and high temperature batch reactor (160 mL Parr reactor). Add 60 mL of water along with 0.24 g of acidic IL and increase the temperature to 160 °C.
2. Set the stirring speed to 200 rpm while the reactor is heating up to 160 °C. Once the 160 °C temperature is reached, increase the stirring speed to 600 rpm.
3. Continue the reaction for 1 h. Then, decrease the stirring speed to 200 rpm and stop the heating.
4. Allow the reactor to cool down to room temperature. Stop the stirring, open the reactor, and separate the solid from the reaction mixture. Perform the analysis of reaction mixture using HPLC.

Representative Results

The exact amount of pentosan and lignin recovered from the biomass depends on the type of lignocellulosic biomass. Similar types of lignocellulosic biomass collected from different places can have different concentration of pentosan and lignin. The jute biomass used in this study contains 20 wt% pentosan and 14 wt% lignin.

Figure 1 shows the comparison of the catalytic activity of mineral acids (H_2SO_4 and HCl) and acidic IL for the conversion of jute biomass into C5 sugars. The reactions were carried out in water at 160 °C (1 h) using the same acid amount of the acid catalysts (*i.e.*, 1.59 mmol of H^+). The non-acidic IL and acidic IL are used at a similar molar concentration (0.79 mmol). The catalytic activity is further compared with an IL without any Brønsted acidity (1-butyl-3-methylimidazolium chloride).

Figure 2 illustrates the ^{1}H and ^{13}C NMR characterization of the acidic IL used in this study. The NMR (^{1}H and ^{13}C) spectra of the acidic IL shows no extra peaks other than the acid IL; this confirms that the acidic IL synthesized is pure. **Figure 3** shows the XRD of the jute biomass before lignin separation and the XRD of the separated lignin from the jute biomass.

Table 1 presents the Hammett acidity function (H_o) analysis of all the catalysts. The analysis was performed using the *p*-nitroaniline indicator that provides the information about acid strength.
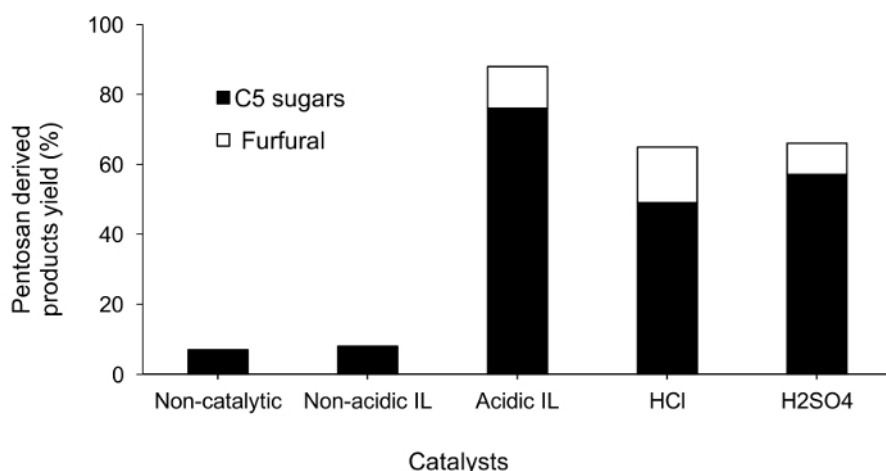

Figure 1: Conversion of pentosan present in jute biomass to C5 sugars and furfural. Reaction condition: Jute biomass 2 g, catalyst 1.59 mmol of H^+ (the IL and acidic IL are used with same mole *i.e.*, 0.79 mmol), 60 mL of water, 160 °C, 1 h. Please click here to view a larger version of this figure.
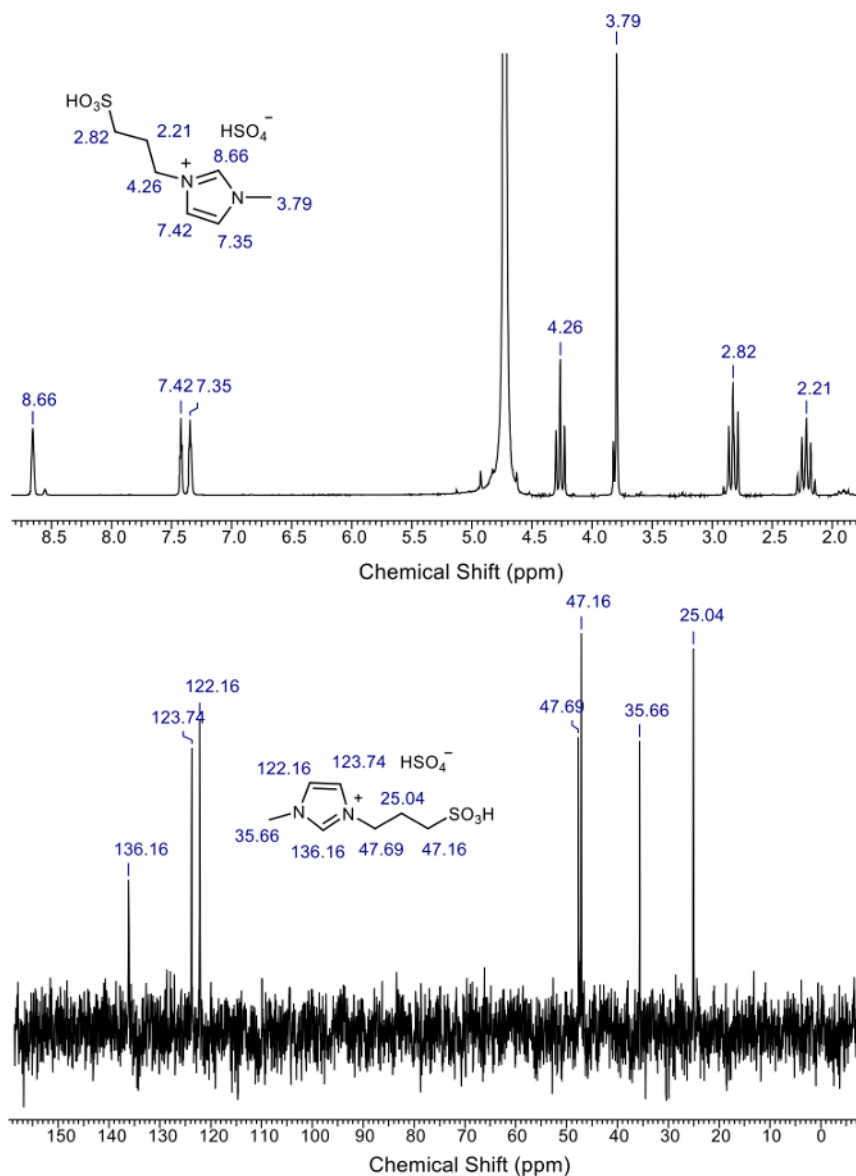
Figure 2: ^{1}H and ^{13}C NMR of acidic IL (1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate). Please click here to view a larger version of this figure.

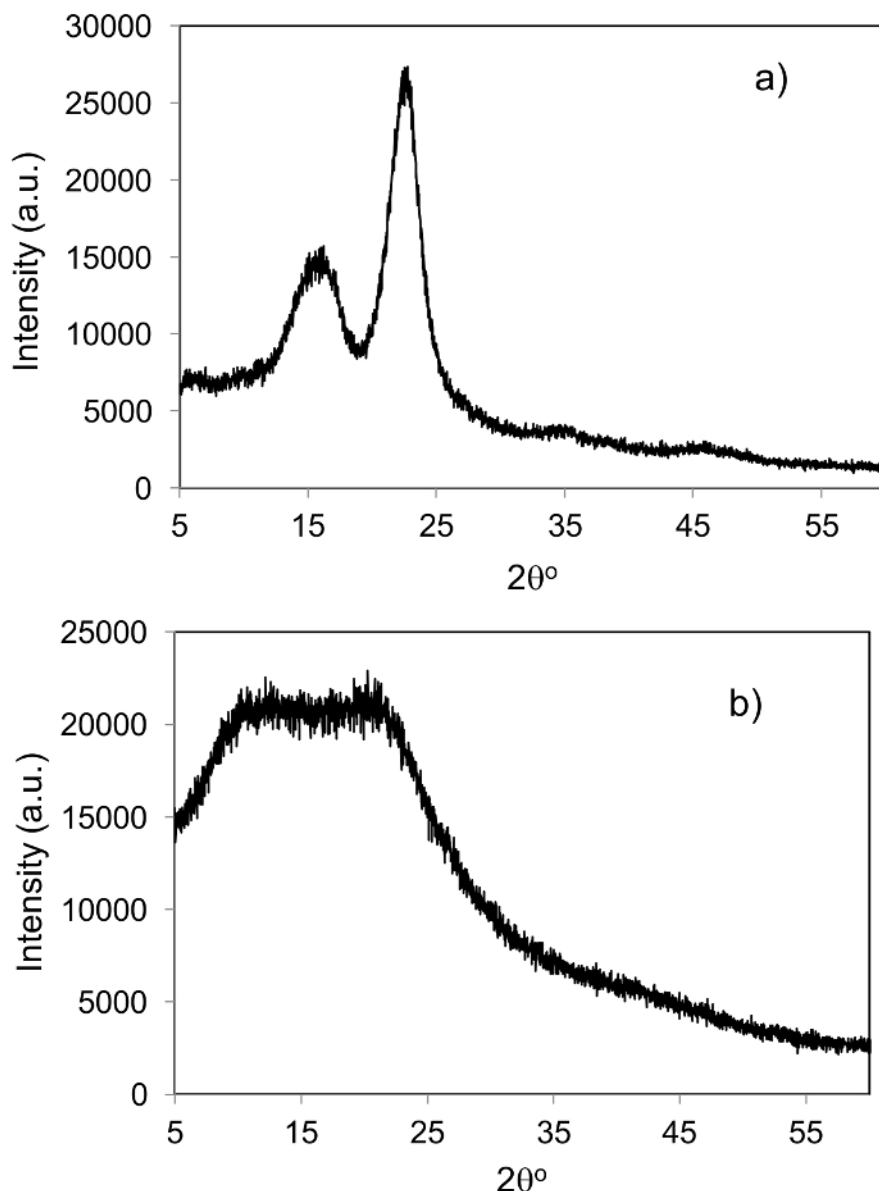**Figure 3: X-Ray Diffraction.** (**a**) XRD of jute biomass and (**b**) XRD of lignin extracted from jute biomass. Please click here to view a larger version of this figure.

Catalyst	A_{max}	[I]%	[IH$^+$]%	H_0
Blank	0.991	100	0	--
HCl	0.753	76	24	1.5
H$_2$SO$_4$	0.8	80.72	19.28	1.62
Acidic IL	0.787	79.4	20.6	1.57
Non-acidic IL	0.991	100	--	--

Table 1: Determination of Hammett acidity function (H_o) of various catalysts. In all measurements, the catalyst (1.59 mmol H$^+$) is mixed with 50 mL of *p*-nitroaniline solution in water (10 mg of *p*-nitroaniline was added in 1 L of water, pKa of *p*-nitroaniline = 0.99).

Discussion

The pentosan present in jute biomass conversion into C5 sugar monomers is demonstrated using various homogeneous Brønsted acidic catalysts such as H$_2$SO$_4$, HCl, and acidic IL. Furthermore, the catalytic result of the acidic IL was compared with the IL without acidity (1-butyl-3-methylimidazolium chloride). All reactions were performed in a Parr autoclave at 160 °C in water. The usage of acidic IL showed the highest pentosan conversion when compared to homogeneous acids used in this work (mineral acids H$_2$SO$_4$ and HCl). The results indicate that acidic

IL exhibits higher C5 sugar yield (76%) whereas mineral acids show lower yields (HCl 49% and H_2SO_4 57% of C5 sugar yield) for pentosan conversion into sugars. The mineral acid catalyst and acidic IL are used at similar acid amounts (1.59 mmol of H^+) to avoid the consequences of dissimilar catalyst acidity. The reaction carried out using non-acidic IL and without catalyst showed very low C5 sugar yields. This implies that acidic IL is the better catalyst for pentosan conversion into sugar monomers compared to mineral acids. Moreover, the acidity of IL is essential for this reaction because a similar type of non-acidic IL is not active in this reaction.

The acidic IL can also be used for the analysis of pentosan present in the lignocellulosic biomass because it produces a very high yield of C5 sugar monomers (76%) and furfural (12%). This method is more superior compared to the method described in section 3.1 that uses 3.85 N HCl and a longer reaction time (*ca.* 24 h). The sugars obtained using acidic IL can be further converted into furans (furfural and various furan derivatives) or hydrogenated into xylitol or arabitol. More importantly, using this method it is possible to recover C5 sugars as pentosan hydrolysis products. However, recovery of pentosan is not possible from the method described in section 3.1 because pentosan degrades into furans in concentrated HCl[19]. The ILs have lower vapor pressure and hence, there is a decreased possibility of IL evaporation during the process, which makes this process environmentally safer. Moreover, the corrosiveness and recyclability of HCl is the major issue with the HCl pretreatment[20,21]. On the other hand, the use of catalytic amounts of acidic IL in the process of pentosan conversion can be recycled.

The Hammett acidity (H_o) results showed that the acidic IL has the higher acid strength (H_o = 1.57) compared to H_2SO_4 (H_o = 1.62); therefore, it performs better than the H_2SO_4 catalyst. However, the acidic IL has a lower acid strength compared to HCl. Nevertheless, it performs better than the HCl catalyst because it is beneficial for better ion-dipole interaction with polysaccharides present in the lignocellulosic biomass[2]. Furthermore, the acidic IL used in the present work is thermally stable below 300 °C temperature (analyzed using thermogravimetric analysis) while it is hydrothermally stable below 180 °C temperature (0.6 g acidic IL heated in 60 mL water at 180 °C for 3 h)[2].

Additionally, the separation of lignin from jute biomass is carried out using the Klason method (section 3.2). The jute biomass used in the present work contains 14 *wt*% lignin. The lignin separated from the jute biomass is pure and contains much less ash (< 1%), which further could be converted into aromatic monomers.

Analysis of pentosan and lignin concentration is accomplished using mineral acid (HCl and H_2SO_4). Moreover, acidic IL used for the conversion of pentosan present in jute biomass showed an excellent yield of C5 sugars (76%) and furfural (12%) along with 5-10% oligomers, and the reaction was conducted in water using a small quantity of acidic IL without any external pressure and pretreatment. Moreover, the acidic IL exhibits over 90% pentosan conversion (the conversion of pentosan was calculated with the help of the yields of C5 sugars, furfural, and oligomers).

We have developed the method for the conversion of pentosan present in jute biomass into C5 sugars, but this method also could be applied for the determination of pentosan concentration present in the jute biomass. Additionally, the pentosan concentration present in other various lignocellulosic biomass can be determined using the present method.

Disclosures

We have nothing to disclose.

Acknowledgements

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