



Protic ionic liquids as effective agents for pretreatment of cotton stalks at high biomass loading

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ABSTRACT

This work demonstrated the performances of different protic ionic liquids (PILs) with respect to their effects on the pretreatment of cotton stalks at a relatively high biomass loading. Among the investigated PILs, 1-butylimidazolium hydrogen sulfate (HBIMHSO₄) employed in the presence of 20% (w/w) water at 15% biomass loading and 120 °C for four hours resulted in significant structural changes in the biomass. The lignin content of the cotton stalks was reduced by 35% and the cellulose content increased from 36% to 55% through HBIMHSO₄ pretreatment. Enzymatic hydrolysis of the biomass was enhanced almost 5-fold despite an increase in the biomass crystallinity. Morphological changes in the cotton stalks observed through SEM analysis verified the differences in the composition and enzymatic accessibility of the biomass samples subjected to PIL pretreatment. The results successfully revealed the potential of the PIL, HBIMHSO₄ for the valorization of cotton stalks, as a significant industrial crop waste, for the first time in the literature.

1. Introduction

Utilization of lignocellulosic feedstocks as self-replenishing resources for the production of fuels and chemicals is limited by the natural resistance of the biomass to enzymatic attacks. Crystalline cellulose and lignin-carbohydrate linkages are the leading factors that contribute to this natural resistance which is often referred to as biomass recalcitrance (Himmel et al., 2007). Several strategies have been implemented to tackle the recalcitrant lignocellulose structure and enhance the enzymatic accessibility of carbohydrate fractions of the biomass. These strategies mainly include chemical pretreatment methods, such as acidic, alkaline, organosolv pretreatments and ammonia fiber explosion, in combination with physical methods (milling or extrusion) as the initial step of the process that is involved in the transformation of biomass into biofuels (Alvira et al., 2010).

Though proven very effective for the deconstruction of lignocellulosic structure, conventional techniques often lead to conditions that are environmentally destructive and result in the loss of valuable carbohydrate fractions of the biomass (Jönsson and Martín, 2016). At this point, biomass pretreatment with ionic liquids (ILs) emerges as worthy of investigation. In principle, ionic liquids are salts with poorly coordinated cations and anions and melting point below 100 °C. The use of ILs for the deconstruction and valorization of lignocellulosic

feedstocks has gone through significant advancement in the last fifteen years. One of the major reasons underlying this advancement is the low vapor pressure exhibited by a majority of ILs, making their handling and recycling easy during pretreatment (Lopes et al., 2013). Another attractive point is their tuneable characteristic that provides flexibility for making modifications in the ILs' cations and anions (Tadesse and Luque, 2011). This enables the synthesis of different ILs that target different biomass components. Despite the aforementioned advantageous features, high cost of ILs is a major concern that hinders the economical viability of processes.

Since the striking exploitation of Swatloski et al. (2002) comprising cellulose dissolution in the IL, 1-butyl-3-methylimidazolium chloride (BMIMCl) and showing the structural changes in cellulose, various ILs have been investigated in this field. Most of the research to date on lignocellulose deconstruction with ILs involved significant findings obtained through the use of 1-ethyl-3-methylimidazolium acetate (EMIMAc) and similar aprotic imidazolium ILs for the pretreatment of a variety of lignocellulosic feedstocks (Yoo et al., 2017). A remarkable study by (Cruz et al., 2013) showed that increased biomass loadings as high as 50% (w/w) in EMIMAc provided superior changes in the structure of switchgrass compared to those attained at lower loadings. They emphasized on the economic viability of IL pretreatment conducted at high biomass loadings. Similarly, the potential of BMIMCl for

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the pretreatment of *Eucalyptus durni* at roughly 20% loading was demonstrated and pretreated biomass was converted into ethanol with 70% yield (Reina et al., 2016). Lately, the researchers developed a compatible IL-enzyme system for the conversion of wheat straw into fermentable sugars, because such strategy led to less separation steps and enhanced recycling for the IL (Husson et al., n.d.). While some researchers as mentioned above favor cost-effective routes through either one-pot process or minimization of the amount of IL in order to adapt the processes to large scales for aprotic imidazolium ILs; utilization of less expensive ILs such as protic ionic liquids (PILs) for large scale biomass deconstruction might be more reasonable for others.

PILs, as a unique class of ILs, are cheaper and faster to synthesize compared to their aprotic counterparts and generated through one step reaction between a Brønsted acid and a Brønsted base as a result of a simple proton exchange mechanism (Greaves and Drummond, 2008). This mechanism, which leads to lignin extraction from the lignocellulosic biomass and substantial changes in the aromatic polymer's structure, could promise the generation of lignin derived value-added products (Achinivu, 2018; Achinivu et al., 2013; Rashid et al., 2016, Rashid et al., 2018). It was shown that pyrrolidinium acetate (PyrAc) extracted more than 70% of lignin present in the corn stover along with a minimal impact on cellulose (Achinivu et al., 2013). Imidazolium based PILs such as 1-methylimidazolium chloride (HMIMCl) and 1-methylimidazolium hydrogen sulfate (HBIMHSO₄) were investigated in terms of their impacts on lignin model compounds (Jia et al., 2010) and lignin in *Miscanthus giganteus* (Brandt et al., 2015), respectively. Both PILs were found effective on β -O-4 linkages in the lignin. Moreover, delignification of cashew apple bagasse with 2-hydroxy ethylammonium acetate (2-HEAA) enhanced the enzymatic saccharification of the biomass remarkably (CLB et al., 2017). 2-HEAA used in an aqueous solution was also found very effective for the delignification of sugarcane bagasse with lignin solubilization more than 55% (Rocha et al., 2017). Recently, triethylammonium hydrogen sulfate (TEAHSO₄) was found to be quite successful to extract hemicellulose and lignin from hardwood willow through pretreatment at a biomass loading as high as 20% (w/w) (Weigand et al., 2017).

Cotton stalks make up the largest portion of the wastes generated during cotton growing and processing (Akhmedov et al., 2017). The other types are cotton gin trash and crushed seeds after oil extraction (Egbuta et al., 2017). Cotton wastes all together is estimated to have 4-fold higher production capacity than the cotton production (Mythili and Venkatachalam, 2013). Based on the statistics by Food and Agriculture Organization of the United Nations (FAO STAT) in the year 2014 (Food and Agriculture Organization), Turkey is recognized to be one of the leading five countries producing cotton lint and cottonseed with a total production of 2.2 million tones. The negative effects of left cotton stalks on the field such as autotoxicity and unstable crop plantation render removal of this waste inevitable (Akhmedov et al., 2017). Though the most straightforward approach to make use of cotton stalks is incineration, the attractive structure of the biomass with a cellulose content of 30–40% offers the production of a variety of fuels (Kantarelis and Zabaniotou, 2009; Keshav et al., 2016; Sharma-Shivappa and Chen, 2008; Wang et al., 2016), platform chemicals (Li et al., 2010), and materials (Reddy and Yang, 2009).

Regarding the previous work including PILs for the pretreatment of lignocellulosic feedstocks, favorable conditions that induced substantial changes in the biomass structure were either at elevated temperatures $\geq 150^\circ\text{C}$ and high biomass loadings $\geq 10\%$ (w/w) (Weigand et al., 2017) or relatively low temperatures $\leq 120^\circ\text{C}$ and low biomass loadings $\leq 10\%$ (w/w) (Achinivu et al., 2013; Brandt et al., 2017; Rashid et al., n.d.; Verdía et al., 2014). In this study, we report the deconstruction of cotton stalks with low cost PILs at a relatively high biomass loading, 15% (w/w) and a moderate temperature, 120° for the first time in literature. 1-butylimidazolium hydrogen sulfate (HBIMHSO₄), 1-methylimidazolium hydrogen sulfate (HMIMHSO₄), triethylammonium hydrogen sulfate (TEAHSO₄), and triethylammonium methanesulfonate

(TEAHSO₃) with IL:H₂O weight ratio of 4:1 were synthesized and explored with respect to their impacts on the enzymatic hydrolysis of cotton stalks, and the compositional and structural changes in the biomass.

2. Materials and methods

2.1. Materials

Cotton stalks obtained from Manisa, Turkey were air dried and ground with a hammer mill to a particle size less than 1 cm. The particles were then sieved to a size between 0.15–2 mm and stored at room temperature. Ethanol, trisodium citrate dihydrate, citric acid monohydrate, sulfuric acid, calcium carbonate, D-glucose and D-xylose were purchased from Merck (Darmstadt, Germany). Avicel cellulose, alkali lignin, methane sulfonic acid, triethylamine, 1-methylimidazole and, 1-butylimidazole were purchased from Sigma-Aldrich (St. Louis, MO, USA). The cellulase enzyme, Cellic Ctec2 was kindly provided by Novozymes (Denmark).

2.2. Synthesis and characterization of PILs

The synthesis of PILs was conducted through an acid-base reaction using the acids, sulfuric acid and methanesulfonic acid and the bases, triethylamine, 1-methylimidazole, and 1-butylimidazole. Both the acid and the base were used in equimolar amounts. The base was placed in a round bottom flask and mixed with an equal volume of water. The round bottom flask, which was cooled by an ice bath, was put on a magnetic stirrer. An aqueous solution of acid with a three-fold higher volume of water was prepared and added dropwise to the base solution that was under constant stirring and cooled with an ice bath. The IL solution was stirred overnight. In order to remove water, the resultant solution was kept in a rotary evaporator at 70°C . $^1\text{H-NMR}$ was used to characterize the final product. For $^1\text{H-NMR}$ analysis, IL samples were dissolved in deuterated dimethyl sulfoxide and the data was recorded with a Bruker 300 MHz spectrometer. $^1\text{H-NMR}$ spectra of PILs are provided in the supplementary data (Fig. S1). Their chemical shifts are given below.

HBIMHSO₄ (300 MHz, DMSO-d₆): δ 9.09 (s, 1H, C(2)H), 8.18 (s, 1H, C(4)H), 7.68 (dt, 1H, C(5)H), 4.21 (t, 2 H, NCH₂), 1.65 (m, 2 H, NCH₂CH₂), 1.12 (m, 2H, N(CH₂)₂CH₂), 0.73 (t, 3H, N(CH₂)₃CH₃).

HMIMHSO₄ (300 MHz, DMSO-d₆): δ 8.85 (s, 1H, C(2)H), 8.14 (d, 1H, C(4)H), 7.55 (d, 1H, C(5)H), 3.86 (s, 3H, NCH₃).

TEAHSO₄ (300 MHz, DMSO-d₆): δ 3.03 (q, 6H, NCH₂CH₃), 1.10 (t, 9H, NCH₃).

TEAHSO₃ (300 MHz, DMSO-d₆): δ 9.13 (s, 1H, NH), 3.08 (q, 6H, NCH₂CH₃), 2.41 (t, 3H, CH₃SO₃), 1.17 (t, 9H, NCH₃).

2.3. Pretreatment of cotton stalks with PILs

Pretreatment of cotton stalks with aqueous solutions of PILs was conducted in a similar manner reported in the Ionosolv protocol (FJV et al., 2016). All pretreatments were conducted in 50 mL Pyrex tubes with teflon-lined screw caps. 10 g of PIL with IL:H₂O weight ratio of 4:1 was combined with 1.5 g of oven-dried cotton stalks. The pretreatment was held at 120°C for 4 h. Following the pretreatments, the samples were allowed to cool to room temperature and ethanol was added to precipitate the pretreated biomass, in other words, the solid fraction. Solid fraction, which was washed with ethanol three times for 15 min in a shaker to remove the residual PIL, was recovered by filtration. Finally, the recovered biomass was dried at 70°C under vacuum for 24 h before it was subjected to enzymatic reaction and characterization. Solid weight was recorded to determine the percentage solid recovery (SR) as follows: $SR (\%) = (W_{\text{PRT}} / W_{\text{UT}}) \times 100$, where W_{PRT} is the weight of biomass recovered after pretreatment (g) and W_{UT} is the weight of untreated biomass subjected to pretreatment (g). All pretreatments were performed in duplicate (Haykir et al., 2013).

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