Biomass and Bioenergy 93 (2016) 243–253

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Comparing the influence of acetate and chloride anions on the structure of ionic liquid pretreated lignocellulosic biomass

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ARTICLE INFO

Article history:
Received 22 July 2015
Received in revised form
11 July 2016
Accepted 14 July 2016

Keywords:
Lignocellulosic biomass
Ionic liquid
Rheological behavior
Cellulose crystalline structure
Composition

ABSTRACT

The effect of the anion type, in an ionic liquid, on the transition of the crystalline structure when lignocellulose was pretreated in 1-ethyl-3-methylimidazolium acetate (EmimOAC) or 1-ethyl-3-methylimidazolium chloride (EmimCl) was studied. The influence of the pretreatment on the composition, the molecular structure, and the crystalline structure was observed using Fourier-transform infrared (FT-IR) compositional analysis, thermogravimetric analysis (TGA), rheological behavior, and X-ray diffraction (XRD). Compared to EmimCl, EmimOAC pretreatment substantially decreased the lignin and hemicellulose contents. The pretreatment also significantly changed the entanglement or cross-linking state of polymer chains in the lignocellulose solution. The changes in lignin content and the transformation from cellulose I to II were dependent on the anion type of the ionic liquid. The pretreated samples were recrystallized to cellulose II only in EmimOAC, whereas the samples pretreated with EmimCl had both cellulose I and II structures present at the same time.

1. Introduction

The need for alternative resources for fossil-based fuel has accelerated investigations on sustainable energy and bio-based materials. Lignocellulosic biomass, the most abundant material on the earth, is considered to be a promising candidate with great potential to serve as a substitute for fossil fuels. Lignocellulosic biomass (lignocellulose) is a complex composite of cellulose, lignin and hemicellulose as well as other materials. Among these components, cellulose is the major carbon-source for bio-fuel and sugar products. In particular, sugars obtained from cellulose are attractive starting materials for large-scale production in a bio-refinery [1–6], although the potential of lignocellulosic biomass has not been fully exploited due to poor accessibility of enzymes. Native lignocellulosic biomass is inherently recalcitrant to biodegradation, owing to the presence of lignin, high crystallinity of cellulose, and complex bonding between them. Lignin in lignocellulose acts as a physical or chemical barrier, protecting cellulose and hemicellulose from enzymatic degradation, and decreasing the efficiency of enzymatic hydrolysis [7,8]. The high crystallinity of the native cellulose structure (cellulose I) also hinders the accessibility of enzymes into polysaccharides. Accordingly, the conversion of the crystalline structure of cellulose I to other crystal forms such as cellulose II, cellulose III_{II} and cellulose III_{I} or to an amorphous structure, can significantly improve the susceptibility to hydrolysis [9]. Pretreatment of the biomass involving physicochemical, structural, and compositional changes is critical to overcome its recalcitrance to hydrolysis [10–12].

Ionic liquid-pretreatment for lignocellulosic biomass has emerged as a novel technology. Since Swatloski et al. [13] reported cellulose dissolution using ionic liquid, many ionic liquids have been synthesized and tested for lignocellulose dissolution. Representatively, superior solubility of those based on acetate and chloride anion combined with dialkylimidazolium cations was reported to dissolve high amounts of each components, such as cellulose, lignin and hemicellulose, in lignocellulose under mile condition [9]. Pretreatment of the lignocellulose by ionic liquids removes lignin as well as decreasing the level of crystallinity by weakening intra-/inter-molecular hydrogen bonds. In early studies, Dadi et al. [14] reported that the enzymatic hydrolysis yield of Avicel was dramatically improved after pretreatment with 1-buthyl-3-methylimidazolium chloride (BmimCl) since the resulting decrease in crystallinity improved enzyme accessibility to the substrate. Other researchers [15,16] studied the changes of

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http://dx.doi.org/10.1016/j.biombioe.2016.07.022
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crystalline structure and crystallinity using 1-ethyl-3-methylimidazolium acetate to pretreat various biomasses under a range of conditions. Although previous researches demonstrated the potential of ionic liquids for pretreatment in a bio-refinery, a systematic study on the influence of anion type remains to be done. In point of structural change of lignocellulose, the anion type in ionic liquids should be also considered due to its significance for disturbing the microstructure. Therefore, it is still required for an understanding on the physical state of the lignocellulose molecule associated differently with anion types of the ionic liquid in order to control the crystalline conversion.

In this study, we purposefully focused our investigation using typically used ionic liquids, 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium chloride, for the lignocellulose pretreatment. The selected ionic liquids are expected to represent properties of other ionic liquids consisting of similar anion, such as formate, iodide and bromide anions, due to their similar properties. Two types of ionic liquid with different anions were compared for pretreatment efficiency of lignocellulose: the influence of the anion type on the composition and the crystalline structure was investigated. The molecular interactions and the mobility were observed by considering the rheological behavior, which was used to demonstrate differences in crystalline change. This study provides a fundamental understanding of the action of ionic liquid and provides recommendations for which materials and conditions should be selected for pretreatment of the lignocellulosic biomass. In addition, the study is also expected to provide information concerning the mechanism of crystalline transition of lignocellulose by investigating the relationship between the dynamics of lignocellulose molecules and its composition.

2. Experimental section

2.1. Materials

Three different lignocelluloses were investigated in this study: cotton (*Gossypium arboretum*) stalks, hemp (*Cannabis sativa*) stalks and acacia (*Acacia auriculiformis*) pruning. Cotton and hemp were kindly provided by Hemplee korea Co., and acacia was provided by Moorim P&P Co. Microcrystalline cellulose (MCC, from Sigma Aldrich) was used as a control. 1-ethyl-3-methylimidazolium acetate (EmimOAC, ~95%, water content: 0.27 wt%) and 1-ethyl-3-methylimidazolium chloride (EmimCl, ~95%, water content: 0.22 wt%) were purchased from Sigma Aldrich. Anhydrous Lithium Chloride (LiCl) and N,N-dimethylacetamide (DMAc) were purchased from Daejung Chemicals & Methals Co. To remove moisture, DMAc was distilled over CaH_2 before use.

2.2. Pretreatment and recrystallization

The biomass samples were milled to 20 mesh (particle size: 200–800 μm) before pretreatment and were then incubated with EmimOAC or EmimCl at 4% (w/w) for 2 h at 80 °C or 120 °C. The temperatures were chosen to avoid thermal decomposition of the ionic liquid which could affect the efficiency of the pretreatment [17]. After the ionic liquid-pretreatment, the samples were transferred to a beaker, and acetone/water (1:1 v/v) was added in order to separate and remove the lignin from the cellulose [18]. The mixture was stirred for 1 h at room temperature and then the precipitated substrates were separated from the coagulant by filtration through a ceramic funnel with nylon filter paper, under vacuum. The material was washed with water at least four times to remove the ionic liquid and then dried in a vacuum oven for 2 days at 60 °C. The pretreatment conditions used for the lignocelluloses are summarized in Table 1.

2.3. Fourier-transform infrared spectroscopy (FT-IR)

The samples were subjected to FT-IR spectroscopy using a PerkinElmer spectrum BX spotlight spectrophotometer with diamond attenuated total reflectance attachment. Scanning was conducted from 4000 to 700 cm^{-1} with 64 repetitious scans averaged for each spectrum. Resolution was 4 cm^{-1} and interval scanning was 2 cm^{-1}.

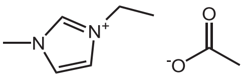
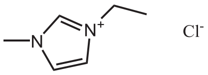
2.4. Lignocellulosic biomass composition

The composition of the samples before and after the pretreatment was determined according to the analytical procedure of the National Renewable Energy Laboratory (NREL) No. 002 [19,20]. Briefly, samples (150 mg each) were treated with 72% (v/v) sulfuric acid at 30 °C for 3 h, followed by diluted acid (4%) at 121 °C. Hydrolyzed products were analyzed by HPLC (Young-Lin Model YL9100, Korea) equipped with an RI detector and a Shodex sugar SP0810 column operated at 85 °C. The mobile phase consisted of deionized water with a flow rate of 0.6 ml/min. The amounts of cellulose and hemicellulose were calculated from the glucose and xylose contents multiplied by a conversion factor of 0.9 and 0.88 respectively [21]. The amount of acid-insoluble lignin after acid hydrolysis was measured as the mass of insoluble residue remaining [19]. The amount of acid-soluble lignin was measured by a UV–vis spectrophotometer at 205 nm with an extinction coefficient value of 110 Lg^{-1} cm^{-1} (NREL, 1996).

2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of the biomass samples was performed using a PerkinElmer instrument, Pyris Diamond TG/DTA. The thermal stability of 0.5 mg of each sample was studied from room temperature to 600 °C at a rate of 10 °C/min. The rate of purge gas (Nitrogen) flow was controlled at 70 mL/min.

Table 1
Pretreatment conditions and ionic liquids used in this study.

Sample code	Abbreviation	Structure	Name	Pretreatment temp. (°C)
EmimOAC 80 °C	EmimOAC		1-ethyl-3-methylimidazolium acetate	80
EmimOAC 120 °C EmimCl 80 °C EmimCl 120 °C	EmimCl		1-ethyl-3-methylimidazolium chloride	120 80 120