Powerful peracetic acid–ionic liquid pretreatment process for the efficient chemical hydrolysis of lignocellulosic biomass

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HIGHLIGHTS

- A new method for efficient lignocellulosic biomass (LB) hydrolysis was proposed.
- LB was pretreated by peracetic acid (PAA) followed by ionic liquid-HCl hydrolysis.
- PAA treatment disrupted lignin fraction, and enhanced depolymerization of cellulose.
- At low molar HCl, [Bmpy][Cl]-HCl hydrolysis yielded 80–98% cellulose conversion.
- PAA-[Bmpy][Cl] treatment caused transformation from cellulose I to II.

GRAPHICAL ABSTRACT
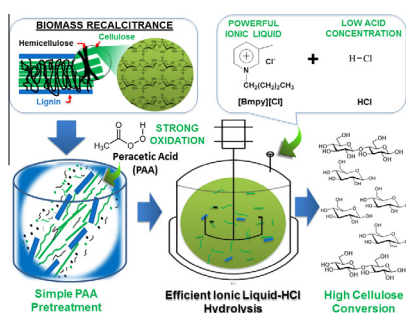
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ABSTRACT

The aim of this work was to design a new method for the efficient saccharification of lignocellulosic biomass (LB) using a combination of peracetic acid (PAA) pretreatment with ionic liquid (IL)-HCl hydrolysis. The pretreatment of LBs with PAA disrupted the lignin fractions, enhanced the dissolution of LB and led to a significant increase in the initial rate of the IL-HCl hydrolysis. The pretreatment of Bagasse with PAA prior to its 1-buthyl-3-methylimidazolium chloride ([Bmim][Cl])-HCl hydrolysis, led to an improvement in the cellulose conversion from 20% to 70% in 1.5 h. Interestingly, the 1-buthyl-3-methylpyridium chloride ([Bmpy][Cl])-HCl hydrolysis of Bagasse gave a cellulose conversion greater than 80%, with or without the PAA pretreatment. For LB derived from seaweed waste, the cellulose conversion reached 98% in 1 h. The strong hydrolysis power of [Bmpy][Cl] was attributed to its ability to transform cellulose I to II, and lowering the degree of polymerization of cellulose.

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1. Introduction

Lignocellulosic biomass contains cellulose (40–50%), hemicellulose (25%) and lignin (25%), with the relative amounts of these materials varying depending on the type of lignocellulosic biomass (Tadesse and Luque, 2011). In recent years, considerable research interest has been directed towards lignocellulosic biomass as a potential resource for biofuels and biochemical feedstocks.

Furthermore, some studies have reported that the global potential of lignocellulosic biomass could reach $1–50 \times 10^{10}$ ton/year (Alvira et al., 2010; Tadesse and Luque, 2011). In a similar manner to many first generation biofuel feedstocks, such as starch and simple sugars, the high cellulose and hemicellulose contents could be converted to biofuels and biochemical products through chemical and biological reactions. The main advantage of feedstocks derived from lignocellulosic biomass is their low price compared with other biofuel-based feedstocks, including starch-rich and sucrose-rich materials (Alvira et al., 2010). Furthermore, lignocellulosic biomass feedstocks could potentially replace several commercial biofuel and biochemical products, which are currently derived from food-based resources (sugar and starchy materials) such as corn and sugarcane. This is particularly important because the use of food resources for biofuel feedstocks has been blamed for recent rises in global food price as the world's population continues to grow, represent a threat to food security.

There are several challenges associated with the commercialization of lignocellulosic biomass, including the high resistance of this material to being hydrolyzed to mono- and oligosaccharides (Alvira et al., 2010). Cellulose is insoluble in water and most common organic solvents because of the strong hydrogen bonding interactions between the many glucose units making up its complex structure (Tadesse and Luque, 2011). Furthermore, lignin binds to cellulose and hemicellulose through a series of covalent bonds to form lignin–carbohydrate complexes. The formation of these lignin–carbohydrate complexes makes the structure of the lignocellulosic biomass much more resistant to the physical, biological and chemical treatment processes typically used to break down these structures (Hu and Ragauskas, 2012). To obtain valuable chemical compounds from lignocellulosic biomass with high cellulose conversion, the processing of lignocellulosic biomass needs extreme conditions such as high pressure, high temperature and high concentration for extended time periods due to the presence of lignin. For instance, it was reported that the dissolution of softwood and hardwood biomass using ionic liquids required the pretreatment for 24 h at 140–150 °C (Casas et al., 2012).

The results of several recent studies have shown that ionic liquids (ILs) can be applied to the treatment of lignocellulosic biomass feedstocks. It has been shown that the treatment of lignocellulosic biomass with ILs leads to a variety of interesting effects, including the swelling of its cell walls, the break down of intermolecular hydrogen bonding interactions, enhanced surface area and a reduction in the crystallinity of cellulose (Lee et al., 2009; Singh et al., 2009), all of which make the cellulose more accessible to water. In particular, imidazolium-chloride ILs, such as 1-butyl-3-metyl imidazolium chloride ([Bmim][Cl]) and 1-ethyl-3-methylimidazolium chloride ([Emim][Cl]), have been shown to assist in the enzymatic hydrolysis of cellulosic feedstocks when they are used for the pretreatment of these materials. Furthermore, the combination of ILs with strong acids has been shown to improve the hydrolysis performances of cellulosic feedstocks by increasing the cellulose conversion or total amount of reducing sugar (Binder and Raines, 2010; Iguchi et al., 2013; Li and Zhao, 2007; Morales-delaRosa et al., 2012). For instance, the hydrolysis reactions of cellulose with [Bmim][Cl] in the presence of 20 wt% HCl (1.66 M) at 125 and 105 °C produced glucose yields of 99.8% and 100%, respectively (Morales-delaRosa et al., 2012). However, the maximum glucose yield obtained for a lignocellulosic feedstock such as rice straw was only 70% (Binder and Raines, 2010). The lower cellulose conversion of lignocellulosic biomass compared with microcrystalline cellulose is caused by lignin, which inhibits the hydrolysis of cellulose (Lee et al., 2013; Wang et al., 2012). In contrast, there have been very few reports pertaining to the acid-mediated hydrolysis of lignocellulosic biomass using pyridinium-type ILs. The potential of pyridinium-chloride ILs as hydrolysis

agents has been reported previously (Binder and Raines, 2010; Uju et al., 2013b, 2012). In the previous report, the pretreatment of Avicel and Bagasse with 1-hexylpyridinium chloride ([Hpy][Cl]) without the addition of any other catalyst resulted in cellulose conversion of 19% and 6%, respectively (Uju et al., 2013b). Furthermore, a higher cellulose conversion (9%) was obtained following the pretreatment of Bagasse with 1-butyl-3-metylpyridinium chloride ([Bmpy][Cl]) at 120 °C for 1 h (Uju et al., 2012). Based on these results, development of a keen interest in exploring the potential of pyridinium-type ILs for the hydrolysis of lignocellulosic biomass, especially in combination with other hydrolysis methods was carried out.

In this study, evaluation of the performance of the pyridinium chloride IL [Bmpy][Cl] for the dissolution and subsequent hydrolysis of lignocellulosic biomass in the presence of HCl under various experimental conditions was validated. Furthermore, comparison of the performance characteristics of this IL with those of its imidazolium counterpart, [Bmim][Cl] was carried out. To minimize the inhibitory effect of lignin (i.e. its ability to prevent the penetration of the IL into cellulose) and accelerate its hydrolysis performance, we incorporated a peracetic acid (PAA)-pretreatment process. It was envisaged that the introduction of a pretreatment process prior to the dissolution step would reduce the lignin content (Gonçalves et al., 2015), making the structure of the lignocellulosic biomass more porous in nature (Uju et al., 2013a). Therefore, incorporating PAA pretreatment in the IL-acid hydrolysis process could enhance the conversion of lignocellulosic biomass to sugars. There have been no reports in the literature describing the combination of a PAA-pretreatment process with a [Bmpy][Cl]-HCl hydrolysis. In this paper, the potential agro-industrial residues of Bagasse and Seaweed waste biomass from carrageenan processing (SWBC) (Uju et al., 2015) were selected as suitable hydrolysis feedstocks. The performance characteristics of this combination process were evaluated in terms of the dissolved biomass fraction (DBF) in the ILs and the conversion of cellulose to saccharides (glucose and cellobiose). To develop a deeper understanding of the mechanisms of the cellulose dissolution and hydrolysis steps, we analyzed the regenerated biomass materials by FT-IR, XRD and SEM. The overall experimental design of this study is summarized in Fig. 1.

2. Materials and methods

2.1. Materials

[Bmpy][Cl] (>98% purity) and [Bmim][Cl] (>98% purity) were purchased from IoLiTec (Ionic Liquids Technologies GmbH, Heilbronn, Germany) and Kanto Chemical Co., Inc. (Tokyo, Japan), respectively. Peracetic acid (PAA) 40% (w/w) was supplied by Mitsubishi Gas Chemical Company, Inc. (Tokyo, Japan). SWBC (particle size $\sim$ 100 mesh with cellulose and lignin contents of 34% and 4%, respectively) (Uju et al., 2015) was obtained from CV Ocean Fresh (Bogor, Indonesia). Bagasse (particle size $\sim$ 200 μm with cellulose and lignin contents of 37.7% and 22.5%, respectively) (Gonçalves et al., 2015) was purchased from Toyota Tsusho Corporation (Nagoya, Japan). All of the reagents were used as received without further purification.

2.2. Glucose and cellobiose analyses

The saccharide content in the reaction mixture was measured by high performance liquid chromatography (HPLC) using an LC-10AT VP system (Shimadzu, Japan) equipped with a Honenpak C18 column (4.6 × 75 mm; J-Oil Mills Inc., Tokyo, Japan). The mobile phase consisted of deionized water containing 0.02% (v/v)