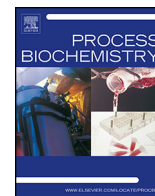




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Efficient pretreatment of lignocellulose in ionic liquids/co-solvent for enzymatic hydrolysis enhancement into fermentable sugars

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ABSTRACT

Ionic liquids (ILs) have been widely used as alternative solvents for biomass pretreatment, however, efficient methods that enable economically use of ILs at large scale have not been established. In this study, a new method in which ILs and polar organic solvents (ILs/co-solvent systems) was proposed for efficient pretreatment of lignocellulosic materials. The combination use of appropriate ILs and organic co-solvents can significantly enhance the solubility of lignocellulose due to the lower viscosity of ILs/co-solvent mixture as compared to those of pure ILs while the hydrogen bond basicity was maintained. In addition, the solubility of lignocellulosic materials in ILs/co-solvent system was found to be correlated with the Kamlet-Taft solvent parameters. Moreover, the use of microwave heating also enhances the efficiency of lignocellulose pretreatment. For example, the microwave-assisted [Emim][OAc]-DMSO (1:1 volume ratio) treated-rice straw could be hydrolyzed at least 22 times faster than that of untreated-rice straw by cellulase from *Trichoderma reesei*. This enhancement was attributed by several factors including more efficient lignin extraction, less crystalline cellulose and lower residual ILs in treated-rice straw. The produced sugars can be effectively fermented by *Pichia stipitis* for ethanol production. Moreover, [Emim][OAc]-DMSO mixture could be reused at least 5 times without significantly decrease in effectiveness demonstrated that the use of ILs/co-solvent was potential alternative method for large-scale biomass pretreatment.

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1. Introduction

Pretreatment is a vital step for the production of biofuels and platform chemicals from lignocellulosic biomass through enzymatic hydrolysis pathway. Pretreatment is required to reduce the crystallinity and increase the porosity of the lignocelluloses. A variety of pretreatment methods have been investigated, including biological, physical, chemical, and physicochemical processes [1]. These methods have been proved to provide hydrolysable sources of hemicelluloses and celluloses, however, none of these methods is able to sufficiently permit enzymatic hydrolysis at high solid loading, short residence time, and low enzyme loading concentrations

[2]. Moreover each of these methods has some drawbacks such as long treatment time (biological methods), high energy demand (physical methods), involved toxic and environmental unfriendly compounds (chemical methods), and high temperature/pressure (physicochemical methods).

Recently, ionic liquids (ILs), consisting entirely ions and having low melting point, have been used as alternative solvents for cellulose and lignocelluloses pretreatment [3,4]. In comparison to traditional molecular solvent, ILs exhibit very interesting properties such as broad liquid temperature, high thermal stability and negligible vapor pressure [5]. It is common acknowledged that carbohydrates and lignin can be dissolved in ILs. As a result of dissolution in ILs, the intricate network of non-covalent interactions among cellulose, hemicellulose, and lignin were effectively disrupted while minimizing formation of degradation products [4]. The use of ILs for cellulosic biomass pretreatment has been effectively demonstrated on several lignocellulosic feedstocks such as straw [6] and wood [7]. Despite their efficacy, using ILs for biomass pretreatment suffers several drawbacks, such as slow dissolution rate, high viscosity of the obtained polymer/IL solution, and high cost of ILs [8–10]. Thus, advances toward improved processes for

Abbreviations: [Emim]⁺, 1-ethyl-3-methylimidazolium; [Bmim]⁺, 1-butyl-3-methylimidazolium; [Cl]⁻, chloride; [OAc]⁻, acetate; [DMP]⁻, dimethylphosphate; DMSO, dimethylsulfoxide; DMF, *N,N*-dimethylformamide; DMA, *N,N*-dimethylacetamide.

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Table 1
Rice straw composition.

Cellulose	35.5%
Hemicellulose	20.7%
Acid insoluble lignin	14.3%
Acid soluble lignin	1.6%
Ash	10.5%
Moisture	8.9%
Others	8.5%

dissolution of cellulose are still necessary. In our previous work, the use of microwave irradiation on the dissolution of cellulose with different degree of polymerization (DP) in ILs has shown promising result. Microwave heating not only enhanced the dissolution of cellulose in ILs but also significantly decreased the DP of cellulose dissolved in ILs. In addition, dissolution pretreatment of cellulose in ILs by microwave heating also reduced the residual amount of ILs retained in regenerated celluloses, thus enhancing enzymatic hydrolysis of treated cellulose and recovery of ILs [11]. Furthermore, major drawbacks associated with high viscosity of ILs/cellulose solution and high cost of ILs could be improved by using polar organic solvents as additives or co-solvents to minimize the use of ILs. Several aprotic organic solvents (e.g., dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), 1,3-dimethyl-2-imidazolidinone (DMI), etc.) have been used as co-solvents on the dissolution of cellulose in ILs [12–16]. However, comprehensive data on the effect of co-solvent on the dissolution of lignocellulosic materials in ILs/co-solvent as well as the efficacy of ILs/co-solvent on the pretreatment of lignocelluloses are still limited [15–19].

In this study, the effect of ILs/co-solvents mixture on the dissolution of lignocellulosic materials as well as the synergetic effect of ILs/co-solvent and microwave heating on the pretreatment of lignocellulose was investigated. Additionally, the correlation between lignocellulose solubility and solvent properties was also examined. In other to evaluate the efficiency of the pretreatment method on lignocellulosic materials, rice straw (RS) was used as typical lignocellulose. RS is one of the abundant lignocellulosic waste materials in the world and has several characteristics that make it a potential feedstock for fuel production. For example, it has high cellulose and hemicelluloses content that can be readily hydrolyzed into fermentable sugars [20].

2. Material and methods

2.1. Material

[Emim][OAc] and [Bmim][Cl] were obtained from by C-Tri (Suwon, Korea). [Emim][DMP] was purchased from Sigma–Aldrich. All ILs were dried under vacuum at 90 °C for 24 h before use. Avicel PH-101, xylan (as major component of hemicelluloses) from birchwood and lignin (alkali, low sulfonate content) were obtained from Sigma–Aldrich. Rice straw (RS) from urban area of Suwon, Korea was used as representative lignocelluloses. The chemistry composition of RS is shown in Table 1. RS was cut, ground into small pieces and sieved through disk with size of 0.125–0.250 mm. RS samples were dried at 50 °C for 24 h before use. Cellulase from *Trichoderma reesei*, which activity of 421 FPU/g was obtained from Sigma–Aldrich. All other reagents were of analytical grade.

2.2. Lignocellulose dissolution and regeneration

For determining the solubility of cellulose, hemicelluloses and lignin in ILs/co-solvent, every 10 mg of the materials were gradually added in 5 mL glass vial containing 1 mL of ILs/co-solvent at 80 °C under nitrogen pressure and magnetic stirring at 500 rpm.

For RS pretreatment, 50 mg RS was dissolved in 1 mL of ILs/co-solvent at 110 °C (using oil bath) under nitrogen pressure and magnetic stirring at 500 rpm. For microwave-assisted RS dissolution, the ILs/co-solvent solution containing RS was placed under microwave irradiation using CEM discover microwave system (Matthews, USA) at constant power of 50 W for 1 min with magnetic stirring. The temperature of solution increased rapidly and the observed maximum temperature of RS/ILs/co-solvent solution was below 130 °C during microwave irradiation. After dissolution, 3 mL of acetone/water (1:1 v/v) was added to the RS/ILs/co-solvent solution. The solution was vigorously mixing by vortexer. The precipitated cellulose-rich materials were separated from the supernatant by centrifugation (1500 rpm for 5 min). The regenerated RS was washed thoroughly at least 5 times with acetone/water to remove residual ILs/co-solvent. The regenerated RS was dried under vacuum condition at 50 °C for 24 h before carrying out the enzymatic hydrolysis reaction. The lignin content in the combine supernatant was determined by the lignin precipitation with sulfuric acid and re-dissolution in 0.1 M NaOH. The absorbance of lignin in NaOH was measured at 280 nm with lignin as standard [21]. All experiments were duplicated.

2.3. Enzymatic hydrolysis of the regenerated rice straw

A suspension of 30 mg (untreated and regenerated) cellulose (3% w/v) in 1.0 mL citrate buffer (5 mM, pH 4.8) was incubated at 50 °C, 150 rpm. The reaction was started by adding 1.5 mg cellulase from *Trichoderma reesei* (20 FPU/g biomass). Twenty microliter of reaction aliquot was periodically withdrawn and the reducing sugars were determined by DNS method [22]. Glucose and xylose concentration were also determined by HPLC analysis. All experiments were duplicated.

2.4. Ethanol fermentation

The enzymatic hydrolysate of [Emim][OAc]-DMSO treated-RS with glucose and xylose content of 10.2 and 5.0 g/l, respectively, was used as carbon source for ethanol production by *Pichia stipitis* KCTC 7222 (Biological Resource Center, Korea) under batch condition. Fermentation was carried out in 500 mL Erlenmeyer flask containing 100 mL of RS hydrolysate, supplemented with 3.0 g/L yeast extract, 3.0 g/L malt extract and 5.0 g/L peptone. Culture flasks were inoculated with 5% (v/v) *P. stipitis* KCTC 7222 and incubated at 30 °C with shaking condition at 150 rpm. Sugar consumption and ethanol production were determined by HPLC and gas chromatography, respectively. All experiments were duplicated.

2.5. Analytical methods

The Kamlet-Taft solvent parameter (α : hydrogen bond donor/acidity, β : hydrogen bond acceptor/basicity, and π^* dipolarity/polarizability) of ILs, solvents and IL/co-solvent mixture were determined by using set of dyes including 4-nitroanisole, 4-nitroaniline and Reichardt's dye as described by Khodadadi-Moghaddam et al. [23].

The correlations between the lignocellulose solubility in IL/co-solvent mixtures and their corresponding Kamlet-Taft solvent parameters were analyzed by Multivariate Adaptive Regression Splines (MARS) methods [24]. It is a non-parametric regression technique and can be considered as an extension of linear models that automatically models non-linearities and interaction between variables. The MARS modeling was carried out using "earth" package in R program [25].

The crystallinity of cellulose was determined by X-ray diffraction (XRD) using Rigaku DMAX 2500 X-ray diffractometer. Cellulose samples were scanned from 10° to 30° at scan speed of 2°/min and

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