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Synergistic effects of surfactant-assisted ionic liquid pretreatment rice straw

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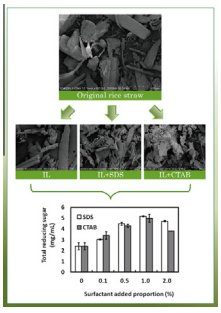
HIGHLIGHTS

- Surfactants-assisted ionic liquid pretreatment rice straw in a single system.
- Surfactant increased lignin removal by 32.53% compared with IL-only pretreatment.
- High total reducing sugar yield was obtained with IL + 1% SDS-pretreated rice straw.
- IL + 1% SDS-pretreated rice straw exhibited lower cellulose crystallinity.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work was to study an environmentally friendly method for pretreating rice straw by using 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) as an ionic liquid (IL) assisted by surfactants. Different temperatures, reaction times, and surfactant concentrations were studied. Compared with [BMIM]Cl only pretreatment, the addition of 1% sodium dodecyl sulfate (SDS) and 1% cetyl trimethyl ammonium bromide (CTAB) increased lignin removal to 49.48% and 34.76%, respectively. Untreated and pretreated rice straw was thoroughly characterized through FTIR, XRD, and FE-SEM. Cellulose crystallinity and surface morphology of the rice straw were substantially altered after surfactant-assisted IL pretreatment. In conclusion, surfactant-assisted IL pretreatment is an effective method for producing fermentable sugars from lignocellulosic substrates.

1. Introduction

During the past decades, the high energy demand has led to research on alternative energy sources, such as bioethanol and biobutanol. Converting abundant lignocellulosic biomass to biofuels as transportation fuels represents a viable option for improving energy security and reducing greenhouse gas emission. Effective production of sugars from lignocellulosic biomass is one of the greatest impediments in biofuel production (Koçar and Civaş, 2013; Singhvi et al., 2014). A pretreatment method that can facilitate lignin or hemicellulose removal and increase enzymatic access to cellulose is required to ensure favorable conversion efficiency. Effective pretreatment can reduce the downstream unit operation costs. Studies have investigated and proposed several pretreatment methods, such as acid (Zu et al., 2014), alkaline (Cabrera

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et al., 2014), steam explosion (Liu et al., 2014), ammonia fiber expansion (Zhao et al., 2014), ozonolysis (Bhattarai et al., 2015), freezing (Chang et al., 2011), and organosolv processes (Amiri et al., 2014). One of the most promising pretreatment processes for lignocellulosic biomass is ionic liquid (IL) pretreatment because of the unique physical and chemical properties of ILs, such as high thermal stability, nearly complete non-volatility, recyclability, low melting point and better dissolving capacity (Olivier-Bourbigou et al., 2010). Studies examining the pretreatment of lignocellulosic biomass by using various ILs have shown that ILs can reduce the crystallinity of cellulose, with partial hemicelluloses and lignin removal (Shafiei et al., 2013), without generating degradation products inhibitory to enzymes or fermenting microorganisms (Lee et al., 2009).

IL pretreatment methods are less energy demanding, easier to handle, and more environmentally friendly than other pretreatment methods are (Zhao et al., 2009). However, the residual lignin and hemicellulose in the IL-pretreated lignocellulosic biomass significantly affect enzymatic hydrolysis. A surfactant pretreatment method was recently proposed for improving enzymatic hydrolysis efficiency and reducing the amount of enzyme required. Surfactants have both hydrophobic and hydrophilic properties as well as enhance hydrophobic substance removal by reducing surface tension between two liquid phases. The effects of different surfactants on lignocellulosic substrates treated with ammonium hydroxide (Cao and Aita, 2013), dilute acid (Kapu et al., 2012), alkali (Pandey and Negi, 2015), ferric chloride (Chen and Fu, 2013), and microwave (Li et al., 2015) have been reported; however, studies evaluating the effect of surfactants on IL-pretreated lignocellulosic biomass are scant.

Nasirpour et al. (2014) investigated a novel and improved pretreatment method for sugarcane bagasse and demonstrated the effectiveness of adding surfactants before IL pretreatment. The authors used Tween 80 and polyethylene glycol 4000 as the additive surfactants and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) as the solvating IL. However, compared with a single system, IL addition after surfactant pretreatment and before enzymatic hydrolysis was time- and cost-intensive. Therefore, the present study evaluated the effectiveness of surfactants (sodium dodecyl sulfate [SDS] and cetyl trimethyl ammonium bromide [CTAB]) as additives for rice straw pretreatment with [BMIM]Cl in a single system. In addition, to gain insights into the mechanisms that may improve process efficiency, the structural features of rice straw pretreated using [BMIM]Cl with and without surfactants were examined through Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and field emission scanning electron microscopy (FE-SEM).

2. Materials and methods

2.1. Substrate, IL, and surfactants

Straw was obtained from 5-month-old japonica rice plants cultivated on the experimental farm (25°020′32.79″N, 121°360′47.40″E with 18-m elevation) located on the Academia Sinica campus, Taipei, Taiwan. The rice straw was dried, ground to powder, and stored in a sealed plastic bag at room temperature. The size distributions of the rice straw were determined through mesh sieving, and five fractions were obtained: <75 μm (12.63%), 75–106 μm (20.57%), 106–150 μm (15.52%), 150–300 μm (47.95%), and >300 μm (3.39%). [BMIM]Cl was purchased from Shanghai Chengjie Chemical Co. Ltd., China. SDS and CTAB were purchased from China Titans Energy Technology Group Co. Ltd., China, and Sigma–Aldrich, USA, respectively. All experiments were performed in duplicate under the same conditions, and average values were reported.

2.2. Surfactant-assisted IL pretreatment

SDS or CTAB was combined with [BMIM]Cl for pretreating rice straw. [BMIM]Cl (5 g), rice straw (40 mesh; 0.5 g), and 0.1%–2% (W/W, based on the weight of [BMIM]Cl) surfactants were mixed in 50-mL vials and heated at 70 °C–130 °C for 0.5–4 h with continuous stirring. After complete dissolution, 45 mL of deionized water was added to precipitate carbohydrate-rich materials. The mixture was centrifuged at 7000 rpm for 15 min, and the supernatants were stored. The carbohydrate-rich materials were washed with deionized water until the pH of the washing water was 7 and stored for enzymatic hydrolysis after drying. Untreated and [BMIM]Cl-pretreated rice straw samples were used as controls. The solid recovery and composition of the pretreated biomass were also analyzed.

2.3. Chemical composition analysis

The presence of cellulose, lignin, and holocellulose was determined using the 20% nitric acid–ethanol, 72% sulfuric acid, and sodium chlorite methods, respectively (Jung et al., 2015).

2.4. Enzymatic hydrolysis of rice straw

Enzymatic saccharification of pretreated and untreated rice straw was performed in 25-mL conical flasks. For each sample, 0.1 M sodium citrate buffer (pH 4.8) was added to an equivalent amount of 2.5% dry material. To prevent bacterial growth, 100 μL of 0.02% sodium azide was added. The substrates were hydrolyzed using a cellulase complex (Novozyme NS220086) at 50 FPU/g rice straw and β-glucosidase (Novozyme NS221118) at 40 CBU/g rice straw at 50 °C in a horizontal shaker incubator (150 rpm) for 72 h. Samples were collected at 0, 3, 6, 12, 24, 48, and 72 h and centrifuged at 7000 rpm. The reducing sugar was determined through the 3,5-dinitrosalicylic acid method. Cellulose conversion was calculated as follows:

$$\text{Cellulose conversion}\ (\%) = \frac{\text{Reducing sugar produced through enzymatic hydrolysis} \times 0.9}{\text{Holocellulose in pretreated biomass}} \times 100 \quad (1)$$

2.5. Sugar analysis

The reducing sugar content of the hydrolytic samples produced for each incubation time was analyzed by the dinitrosalicylic acid (DNS) method (Miller, 1959). The detection wavelength was 575 nm and the instrument was UV–vis spectro-photometer (UV 756CRT, Youke Co., Ltd, China).

2.6. FT-IR

FT-IR spectra for the samples were determined using a Nicolet 6700 spectrometer (Thermo Fisher Scientific, USA) within the wave number range of 400–4000 cm^{-1} with 20 scans at a 4-cm^{-1} resolution. The samples were mixed with potassium bromide (KBr) at a weight ratio of approximately 1:400 to form a pellet. Each FT-IR spectrum was recorded with a blank KBr pellet as the background.