Enhanced hydrolysis of bamboo biomass by chitosan based solid acid catalyst with surfactant addition in ionic liquid

Wenqing Si [a,b], Yichen Li [a], Jie Zheng [a], Shun'an Wei [a,*], Dan Wang [a,b,*]

[a] *Department of Chemical Engineering, School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, P.R. China*
[b] *State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, Shanghai, P.R. China*

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ABSTRACT

Surfactants were used for the hydrolysis of bamboo biomass to enhance lignocellulose hydrolysis. Tween 80, polyethylene glycol 4000 (PEG 4000), and sodium dodecyl sulfate (SDS) were tested as surfactants for improving the bamboo hydrolysis with a novel sulfonated cross-linked chitosan solid acid catalyst (SCCAC) in ionic liquid (IL). Compared to the use of only SCCAC in 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl), the surfactants facilitated hydrolysis and improved the yield of total reducing sugar (TRS) under the same conditions. Tween 80 was the most effective surfactant, with a TRS yield of 68.01% achieved at 120 °C after 24 h. Surfactants broke the lignocellulose structure, promoted lignin removal, and increased positive interactions between cellulose and the catalyst, which were favorable for hydrolysis. This novel surfactant-assisted hydrolysis strategy with SCCAC and IL as the solvent demonstrated a promise for the large-scale transformation of biomass into biofuels and bioproducts.

1. Introduction

Lignocellulosic biomass demonstrates promise as the most economical, highly renewable natural resource in the world. The development of renewable energy obtained from lignocellulosic biomass as an alternative to fossil fuel is ultimately essential for the survival of the human race (Ragauskas et al., 2006). Considerable research and development programs have been initiated worldwide to convert lignocellulosic biomass into various valuable products in biorefineries, where the liberation of reducing sugars from lignocellulose is a crucial step (Jäger & Büchs, 2012). However, lignocellulosic biomass is resistant to hydrolysis because of its complex hetero-matrix structure (Himmel et al., 2007), and cellulose fibers in the lignocellulose matrix are naturally protected by lignin and hemicellulose to resist microbial and enzymatic attack (Goshadroua & Lefsrud, 2017).

Ionic liquids (ILs) exhibit attractive properties such as chemical and thermal stability, high ionic conductivity, non-volatility, recyclability, and good dissolving capacity (Welton, 1999; Zhao, Xia, & Ma, 2005). Previous studies have indicated that ILs can decrease the crystallinity of cellulose, where hemicelluloses and lignin are partially removed; this partial removal leads to the chemical transformation of cellulose chains (Shafiei, Zilouei, Zamani, Taherzadeh, & Karimi, 2013; Swatloski, Spear, Holbrey, & Rogers, 2002). The dissolution of lignocellulosic substrates in various ILs as an effective pretreatment method has attracted significant attention worldwide (Bian et al., 2014; Silva, Lopes, Roseiro, & Bogel-Lukasik, 2013; Zavrel, Bross, Funke, Büchs, & Spiess, 2009).

From the viewpoint of green chemistry and industrialization, solid acid catalysts have become one of the excellent choices for the hydrolysis of lignocellulose into glucose. As these catalysts demonstrate tremendous potential to overcome limitations such as reactor corrosion, waste treatment, poor recyclability, isolating difficulty (Shen, Wang, Han, Cai, & Li, 2014), and energy- and cost-intensive pretreatment for enzymatic hydrolysis (Hu, Lin, Wu, Zhou, & Liu, 2015). Hara et al. (2004) and Suganuma et al. (2008) have independently reported that a carbon-based solid acid consisting of polycyclic aromatic carbon and functional groups, e.g., sulfonic acid, can act as strong solid acid catalyst for various acid-catalyzed reactions. Nata, Irawan, Mardina, and Lee (2015) have obtained highly sulfonated carbonaceous spheres in the presence of hydroxyethyl sulfonic acid and acrylic acid, which can be used as a solid acid catalyst for the hydrolysis of cornstarch. Zhong et al. (2015) have prepared a nanoscale catalyst, which can effectively hydrolyze hemicellulose while retaining cellulose and lignin. Chitosan is useful in many different applications (Deng et al., 2011; Huang et al., 2015; Xiao & Zhou, 2008; Xin et al., 2013), one of

which is to synthesize resin and catalyst. In our laboratory, preliminary studies have been conducted to synthesize a novel sulfonated cross-linked chitosan solid acid catalyst (SCCAC), and examine the effectiveness of it in ILs for the hydrolysis of lignocellulose, with a comparatively ideal yield obtained for TRS (Cheng et al., 2016). Nevertheless, the yield is predominantly attributed to the large amount of the added catalyst and the consumption of the IL. Consequently, the development of an auxiliary strategy is urgently required for the economical, efficient hydrolysis of lignocellulose using solid acid catalysts in ILs.

Surfactants exhibit hydrophobic and hydrophilic properties and enhance the removal of hydrophobic substances by decreasing the surface tension between the two liquid phases (Qing, Yang, & Wyman, 2010). Furthermore, surfactants can serve as emulsifiers and dissolve the extractives present in the wood structure. These properties make surfactants prospective additives for the pretreatment of lignocellulose (Kim, Kim, & Kim, 2007; Kurakake, Ooshima, Kato, & Harano, 1994). Recent studies have investigated the synergistic effect of surfactants and IL for the hydrolysis of lignocellulose. Chang et al. (2016) have indicated that surfactant-assisted IL ([BMIM]Cl) pretreatment enhances the removal of lignin during pretreatment and cellulose conversion during subsequent enzymatic hydrolysis as compared with pretreatment without surfactants. Nasirpour, Mousavi, and Shojaosadati (2014) have assessed the effect of Tween 80 and polyethylene glycol 4000 (PEG 4000) on the pretreatment of sugarcane bagasse using [BMIM]Cl, and the removal of lignin is enhanced by 12.5% as compared to the IL-only pretreated sample. Pandey and Negi (2015) have assessed the impact of surfactant assisted acid and alkali pretreatment on pine foliage, it was proved to be efficient for removal of lignin. However, to our best of knowledge, the combination of surfactant-assisted solid acid catalysis and ILs as a novel strategy for hydrolysis has not been reported.

In this study, surfactants (e.g., Tween 80, PEG 4000, and SDS) were added to improve the hydrolysis of bamboo with SCCAC in IL (i.e., [BMIM]Cl). Reaction conditions were optimized to choose the best surfactants suited for the hydrolysis of bamboo. Furthermore, Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analyses were conducted to discuss the mechanism of the addition of surfactants with SCCAC and IL on hydrolysis.

2. Experimental

2.1. Materials

Bamboo was readily obtained from a bamboo grove in Chongqing (China), sifted using an 80 mesh sieve. The main chemical composition of bamboo was determined by a two-step acid hydrolysis method developed by the National Renewable Energy Laboratory (NRTL) (Sluiter et al., 2008), with dry matter containing 20.3% of xylan, 22.3% of lignin, and 40.1% of glucan (Wang et al., 2014).

[BMIM]Cl used as a solvent in the system was purchased from Ke Neng Material Technology Co. Ltd (Linzhou, China). Table S1 lists the names and chemical properties of the surfactants used herein.

2.2. Preparation of sulfonated cross-linked chitosan solid acid catalyst

SCCAC was prepared in our laboratory via a multistep process involving crosslinking between chitosan and hydrochloric acid and sulfonation. Cross-linked chitosan was synthesized based on the procedures reported by Xiao and Zhou (2008). During the sulfonation, 2.0 g cross-linked chitosan was placed in a three-necked flask,

which was connected to a low-temperature pump, followed by dripping 2.5 mL H_2SO_4 solution (98%, w/v) slowly using a constant pressure funnel at −5 to 0 °C. The acid was mixed with the chitosan via periodic stirring (5 h), and then the reaction solution was diluted for suction filtration. After sulfonation and initial rinsing, the catalysts were subjected to additional washing until the pH was neutral. Finally, SCCAC was freeze-dried and stored for later use.

Vacuum freeze-drying was conducted for all synthetic methods.

2.3. Hydrolysis of bamboo

First, 4 g of [BMIM]Cl was added into a round-bottom flask and heated to 120 °C. Second, SCCAC (0.1 g) and 0.1 g bamboo were added, followed by the addition of an appropriate amount of surfactant. The mixture was stirred at a constant velocity for an appropriate time. At 2 h intervals, 0.1 mL (V_1) mixture was removed, cooled to room temperature with cold water, and then weighed and recorded as M_S. The sample was neutralized using a proper amount of 0.05 M NaOH and centrifuged at 10,000 rpm for 5 min for sugar analysis.

2.4. Analytical methods

2.4.1. Analysis of the total reducing sugars

TRS was measured by the 3,5-dinitrosalicylic acid colorimetric method (DNS method) (Miller, 1959; Wang et al., 2014) using a JASCO V-530 spectrophotometer at 540 nm. The concentration of TRS in the reaction sample was calculated on the basis of a standard curve obtained with a glucose standard. Monomeric sugars were analyzed by high performance liquid chromatography (HPLC), as Cheng et al. (2016) reported. Samples were centrifuged at 10,000 rpm for 10 min. Each of the supernatants was diluted with 10 vol of 5 mM H_2SO_4, and 20 μL of the diluted sample was injected (Sluiter et al., 2008). The column was eluted with 5 mM H_2SO_4 at a rate of 0.6 mL min^{-1} under 55 °C. The mass of TRS and the yield of TRS were calculated as follows:

$$M_T = M_1 \times \left(M_0/M_S \right) \qquad (1)$$

$$M_1 = \text{TRS concentration} \left(g/L \right) \times V_1 \qquad (2)$$

$$\text{TRS yield} = M_T / \left(100 \times A \times 1.1 \right) \times 100\% \qquad (3)$$

Here, M_T is the mass of TRS, M_1 is the mass of TRS in the reaction sample, M_0 is the total mass of the reaction solution, M_S is the mass of sample, 100 is the mass of bamboo biomass (mg), and A is the weight percentage of the polysaccharides contained in lignocellulose materials. For bamboo, A = 40.1% + 20.3% = 60.4%.

2.4.2. Fourier-transform infrared spectroscopy

FTIR spectra were recorded on a Nicolet iN10 FTIR microscope (Thermo Nicolet Corporation, Madison, WI) to identify the functional groups present in the bamboo powder after treatment for 24 h by SCCAC with or without Tween 80 in [BMIM]Cl at 120 °C. Sample spectra were recorded using an average of 64 scans over the range of 4000–500 cm^{-1} with a spectral resolution of 8 cm^{-1}.

2.4.3. SEM analysis

Surface morphologies of SCCAC were observed using a JSM-6700F (JEOL, Japan) SEM system operated at an accelerating voltage of 20 kV. The samples were pre-treated by gold sputtering before detection to make the fibers conductive and avert degradation.

2.5. Recovery of catalyst and IL

After the completion of hydrolysis, the residue was collected by suction filtration and dried for regeneration. Then, an anti-solvent