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Regression analysis on ionic liquid pretreatment of sugarcane bagasse and assessment of structural changes

Li Wan Yoon, Teck Nam Ang, Gek Cheng Ngoh*, Adeline Seak May Chua

Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

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ABSTRACT

This study aims to perform a regression analysis which leads to the optimization on the operating conditions of ionic liquid (IL), 1-ethyl-3-methylimidazolium acetate ([EMIM]oAc) pretreatment on sugarcane bagasse (SCB). The structural changes on SCB during pretreatment were also examined. The effects of temperature, time and solid loading on reducing sugar (RS) yield obtained from enzymatic hydrolysis of pretreated SCB were investigated by applying Central Composite Design (CCD) of Response Surface Methodology (RSM). Results from CCD were modeled into a second order polynomial equation and the model shows a good correlation between predicted and experimental values. The optimized condition for [EMIM]oAc pretreatment were 145 °C, 15 min and 14 wt% of solid loading with an optimum RS yield of 69.7%. Characterization of SCB was carried out and there were no significant difference between the chemical composition of untreated and [EMIM]oAc-pretreated SCB. Pretreated SCB was found to be porous, less crystalline and favorable to enzymatic hydrolysis as proven by Scanning Electron Microscopy (SEM), X-ray Powder Diffraction (XRD) analysis and Fourier Transform Infrared (FTIR) analysis. In short, [EMIM]oAc pretreatment shows good performance in improving the RS yield after enzymatic hydrolysis besides giving desirable structural modification on pretreated SCB. These are of great benefit to the subsequent downstream processes.

1. Introduction

The dwindling supply of fossil fuel has generated great efforts in the search for a renewable and sustainable fuel source. In the recent years, biofuel which can be derived from lignocellulosic biomass has been viewed as one of the potential substitutes for fossil fuel [1]. Agricultural residues are the most abundantly found lignocellulosic biomass especially in countries where agricultural activities are dominant. Like many lignocellulosic biomass, these low cost residues are made up of cellulose, hemicellulose and lignin [2]. Among the components, cellulose and hemicellulose are the well-known raw materials for a wide range of value-added products such as fermentable sugars and biofuel [3].

The complex matrix of lignocellulosic biomass unfavorably hinders the effective conversion of agricultural residues into value-added products. Thus, pretreatment process is necessary to alter the structure of biomass by increasing their surface area, removing the lignin content, reducing cellulose crystallinity or depolymerizing the hemicellulose, depending on the pretreatment methods employed [4,5]. Pretreatment would enhance the sugar yield from enzymatic hydrolysis of pretreated biomass due to the increasing accessibility of enzymes to cellulose and hemicellulose [6].

Recently, ionic liquid (IL) has emerged as one of the promising pretreatment reagent for lignocellulosic biomass. IL exhibits outstanding ability in dissolution of cellulose at considerably mild conditions [7]. Besides, some of the ILs are

* Corresponding author. Tel.: +603 79676879; fax: +603 79675371.
E-mail address: ngoh@um.edu.my (G.C. Ngoh).
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environmentally benign, attributed to their non-volatile and non-flammable properties [8]. The IL-pretreated biomass was reported to have a reduced content of lignin, lower degree of crystallinity and can be enzymatically hydrolyzed at a faster rate [9–11]. The recyclability of IL has also added a credit to this particular pretreatment method [8,12].

Optimization of pretreatment process is an essential step in determining the most suitable and economical condition to enhance the yield of products. Many tools such as full factorial design, Central Composite Design (CCD) and Box-Behnken Design (BBD) were used by the researchers to optimize different pretreatment processes [13–15]. Among the tools, CCD is the most popular design used for fitting second order models and therefore it is extensively applied in the optimization of pretreatment process [16]. Temperature and reaction time are the widely explored optimization parameters by the researchers [10,13,15]. Other factors such as concentration of the reagent, pressure and solid loading might also affect the process significantly [15,17,18].

To date, there are limited studies on the optimization of ionic liquid pretreatment process. The objective of this work is to perform a regression analysis on the pretreatment of sugarcane bagasse (SCB) by using IL 1-ethyl-3-methylimidazolium acetate ([EMIM]oAc). [EMIM]oAc was determined to be the most suitable pretreatment medium for SCB [19]. SCB was employed due to its relatively high cellulose content of approximately 50% [3]. The effect of pretreatment temperature, time and solid loading on reducing sugar (RS) yield was investigated and the pretreatment process was optimized by applying CCD. The RS yield obtained from enzymatic hydrolysis of pretreated SCB was used as a parameter to evaluate the effectiveness of [EMIM]oAc in pretreating SCB under different operating conditions. The morphological and structural changes of SCB after [EMIM]oAc pretreatment was also examined.

2. Materials and methods

2.1. Materials

Sugarcane bagasse (SCB) was collected from Purecane Manufacturing Sdn. Bhd., Johor, Malaysia. SCB was thoroughly washed and dried. It was ground and sieved into 250 μm–500 μm prior to use. Ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate ([EMIM]oAc) was purchased from Sigma Aldrich (St. Louis, USA). Cellulase Onozuka R-10 from *Trichoderma viride* (EC 3.2.1.4) was purchased from Merck (Darmstadt, Germany).

2.2. Ionic liquid pretreatment

Ionic liquid pretreatment was carried out by adding [EMIM]oAc into the test tube which contains SCB. The [EMIM]oAc-SCB mixture was heated in an oil bath (Julabo Labortechnik GmbH, Seelbach, Germany) and subsequently, deionized water was added to regenerate the dissolved cellulose after the reaction. The mixture was briefly centrifuged before subject to filtration. The retentate which consists of regenerated cellulose and the insoluble residue of SCB was washed by deionized water and acetate buffer solution. Pretreated bagasse was then dried prior to enzymatic hydrolysis, characterization, scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and Fourier transform infrared (FTIR) analysis.

2.3. Enzymatic hydrolysis

IL-pretreated SCB was hydrolyzed by using cellulase with a loading of 30 FPU/g substrate. Acetate buffer solution of pH 4.8 was used to buffer the mixture of SCB and cellulase enzymes. Enzymatic hydrolysis was conducted at 50 °C for 48 h. After the reaction, the samples were centrifuged and the concentration of RS in supernatant was determined by using DNS method [20,21]. All experiments were performed in duplicate. The RS yield obtained from enzymatic hydrolysis was computed by applying the equation as suggested by Li et al. [10].

2.4. Experimental design and regression analysis

Central Composite Design (CCD) of response surface methodology (RSM) was applied in regression analysis to determine the optimum condition of [EMIM]oAc pretreatment. Regression analysis was carried out with the aid of Design Expert 6.0.6 software (STAT-EASE Inc., Minneapolis, USA). The α value of 1 was applied in the experimental design and 20 experimental runs were conducted to optimize the process. The effect of three independent variables, i.e. pretreatment temperature (°C), time (min) and solid loading (wt%) on RS yield were investigated. Selection on the range for each independent variable was based on preliminary studies, i.e. pretreatment temperature from 120 °C to 160 °C, duration from 15 min to 45 min and solid loading from of 3 wt% to 15 wt%.

The experimental response, Y (RS yield, %) was fitted into a second order polynomial equation as stated in equation (1) [22]. Evaluation on the statistical significance of the model developed was done by using analysis of variance (ANOVA) method.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i<j}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2 \quad (1)$$

where, x_i, x_j = coded independent variables; β_0 = intercept effect; β_i = linear effect; β_{ij} = linear-by-linear interaction; β_{ii} = quadratic effect.

2.5. Characterization of SCB

Analysis of the chemical compositions in SCB was conducted by adopting the methods from National Renewable Energy Laboratory (NREL) [23]. The compositions of cellulose, hemicellulose, acid soluble lignin (ASL), acid insoluble lignin (AIL) and ash in SCB were determined.

SCB (300 mg) was first hydrolyzed with 72% sulfuric acid (H_2SO_4) for 1 h at 30 °C. After the reaction, the acid was diluted to 4% concentration by deionized water. The mixture was then autoclaved at 121 °C for 1 h. Filtration of the autoclaved solution was carried out and the solid residues remained after filtration was collected to determine the AIL and ash contents