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Ionic liquid-mediated solid acid saccharification of sago waste: Kinetic, ionic liquid recovery and solid acid catalyst reusability study

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ABSTRACT

Dissolved carbohydrate obtained from 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) pretreated sago waste was saccharified by Amberlyst 15 (A15) to study the kinetics of the ionic liquid-mediated solid acid saccharification of the lignocellulosic biomass. Besides the kinetics of both reducing sugars production and reducing sugars degradation reactions, emphasis was given to the recovery and reusability of the ionic liquid and solid acid catalyst. The hydrolysis reaction follows a first order sugars production-first order sugars degradation reaction that agreed well with the generalized Saeman kinetic model. Both the rates of reducing sugars production and degradation varied with temperature and catalyst loading. Higher temperature and catalyst loading promoted the rates of sugars production reaction more than the rate of degradation reaction. This is evident from the relatively larger rate constant of sugars production (k_1) than the rate constant of degradation (k_2). The activation energy for sugars production and degradation was 125.1 kJ mol^{-1} and 60.8 kJ mol^{-1} respectively. These values are lower than the literature reported values for sulfuric acid-catalyzed saccharification confirming its employment suitability for reducing sugars production. The good recovery of [BMIM]Cl and good reusability of A15 further substantiated the feasibility of the process. The recovery of ionic liquid was improved by employing a multiple step aqueous biphasic system in this study. Approximately 60% of the ionic liquid was recovered by 3-step aqueous biphasic system. This finding is on par with the reported literatures using aqueous biphasic system to recover ionic liquid. Equally robust, the solid acid catalyst regained its saccharification performance after regeneration for a total of three cycles.

1. Introduction

Sugars are abundantly available in the form of starch, cellulose and hemicellulose carbohydrates in lignocellulosic biomass. Generally, acid-catalyzed saccharification reaction is used to convert the carbohydrates to reducing sugars. With technological advancement, many efficient acid catalytic systems such as strong acidic cation exchange resins (Kim et al., 2005; Lanzafame et al., 2012; Marzo et al., 2012; Onda et al., 2008), H-type zeolites (Lanzafame et al., 2012; Onda et al., 2008), heteropolyacids (Lanzafame et al., 2012) and supported solid acids (Lanzafame et al., 2012; Onda et al., 2008) have been reported. However, even with the strong acidic cation exchange resins as powerful catalysts for saccharification (Kim et al., 2005; Kitano et al., 2009), the recalcitrant nature of biomass prevents chemical transformation and results in low saccharification rate (Ballesteros et al., 2008; Hu and Wen, 2008). This predicament has spurred the effort of researchers to employ ionic liquids in biomass dissolution (Fort et al., 2007; Haykir et al., 2013; Kilpeläinen et al., 2007; Li et al., 2010; Li et al., 2009; Mäki-Arvela et al., 2010; Sun et al., 2009; Yang et al., 2013; Zavrel et al., 2009) to assist solid acid saccharification of biomass in the production of reducing sugars (Dwiatmoko et al., 2010; Kim et al., 2010; Rinaldi et al., 2008; Watanabe, 2010; Lee et al., 2013).

Despite that the process scheme to produce reducing sugars via ionic liquid-mediated solid acid saccharification of lignocellulosic biomass has been reported viable (Dwiatmoko et al., 2010; Watanabe, 2010), the cost of ionic liquid and solid acid catalyst undermines the economic feasibility of the process concerned. To alleviate the cost constraint, aqueous biphasic systems (ABS) were attempted by researchers to separate and recover ionic liquid (Gutowski et al., 2003). The two phase system generated by adding kosmotropic salt into aqueous solution of ionic liquid was environmentally more benign than the conventional extraction using organic solvents (Hatti-Kaul, 2000; Zaslavsky, 1995). On the other hand, the reused solid acid catalyst regenerated with sulfuric acid

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(Rinaldi et al., 2010) to restore the active sites for saccarification process had also indicated positive recovery performance.

The reaction kinetics of catalytic reaction is essential for process optimization and reactor design. Hypothetically, solid acid saccharification of the dissolved carbohydrates in ionic liquid is expected to have distinct kinetics. The well-known cellulose hydrolysis model (Saeman, 1945) had been applied in hydrolysis of other carbohydrates such as starch (Barnali et al., 2008) and hemicelluloses (Lu and Mosier, 2008). Based on the model, the present work performed a kinetic study of a sequential ionic liquid-mediated solid acid catalytic reaction on sago waste that has not been reported elsewhere. The effects of temperature and catalyst loading on the production rate and degradation rate of reducing sugars were investigated. The generalized Saeman kinetic model applied to fit the experimental data to determine the kinetic parameters of the hydrolysis process. To study the overall process economic feasibility, the recovery efficiency and reusability of ionic liquid and solid acid catalyst were examined in this study.

2. Materials and methods

2.1. Materials

The sago waste supplied by CL Nee Sago Industries (Malaysia) was ground and sieved into desired size of approximately 500 μm. Ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl, □98.0% purity) was from Merck (Germany), Amberlyst 15 (A15) and potassium phosphate (≥98% purity) were purchased from Sigma-Aldrich (USA). The ultrapure water used was generated by Arium® 611UF system (Sartorius, Germany).

2.2. Saccharification of sago waste

Sago waste (15 mg) was dissolved in a test tube containing 1 g of [BMIM]Cl using an oil bath (MC, Julabo, Germany) at 160 °C for 1.75 h. The clear solution formed was added with 5 ml of ultrapure water and the mixture was evenly mixed. The resultant solution, known as prehydrolysate, was saccharified with A15 of 2% (w/v) to 10% (w/v) loading in the oil bath at a desired temperature, range of 100 °C to 140 °C for 5 h. The saccharified samples were collected at predetermined time of 5, 10, 15, 30, 60, 120, 180, 240 and 300 min. The liquid product, known as hydrolysate, once separated from the catalyst through gravity settlement, was determined for its reducing sugars content using 3,5-dinitrosalicylic acid (DNS) assay (Miller, 1959). All experiments were conducted in duplicate. The reducing sugars yield was calculated using Eq. (1):

$$\text{Reducingsugar yield}(\%) = \frac{w_{RS}}{[1.11(w_s + w_c) + 1.14w_h]} \times 100\% \qquad (1)$$

where w_{RS} represents the weight of reducing sugars, w_s, w_c and w_h represent the weight of starch, cellulose and hemicelluloses in sago waste, respectively. The values 1.11 and 1.14 are the multiplication factors that convert the respective carbohydrate to its equivalent sugars (Sluiter et al., 2011).

2.3. Measurement of protons concentration

The concentration of protons ([H$^+$]) in the hydrolysate was determined by measuring the pH of the solution according to Eq. (2):

$$\text{pH} = -\log_{10}[\text{H}^+] \qquad (2)$$

The pH of the reaction solution was measured at room temperature using a pH meter (827 pH lab, Metrohm, USA). Prior to use, the pH meter was calibrated using buffer solutions of pH 4.00, 7.00 and 9.00.

2.4. Hydrolysis kinetic model

The generalized Saeman model, i.e. two consecutive first order sugars production and sugars degradation reaction as expressed in Eq. (3), was applied to determine the kinetics of solid acid saccharification of dissolved carbohydrates in ionic liquid.

$$\text{Polymers} \xrightarrow{k_1} \text{Monomers} \xrightarrow{k_2} \text{Degradation products} \qquad (3)$$

The polymers and monomers expressed in the equation respectively represent the carbohydrates and the reducing sugars, while k_1 and k_2 are the rate constant for production and degradation of reducing sugars respectively.

For an irreversible first order reaction, the model shown in Eq. (3) can be described in two differential equations as expressed in Eq. (4) and (5):

$$r_S = -\frac{dS}{dt} = -k_1 S \qquad (4)$$

$$r_P = \frac{dP}{dt} = k_1 S - k_2 P \qquad (5)$$

where r_S is rate of degradation of carbohydrate, r_P is rate of production of reducing sugars, S is concentration of carbohydrate, P is concentration of reducing sugars and t is reaction time. By solving the differential equations, concentration of the reducing sugars as a function of time can be determined using Eq. (6):

$$P = P_o \times \exp(-k_2 t) + S_o \times \frac{k_1}{(k_2 - k_1)} \times (\exp(-k_1 t) - \exp(-k_2 t)) \qquad (6)$$

where the subscript o indicates the respective initial concentration.

The time required to reach maximum concentration of reducing sugars was calculated using Eq. (7). This equation is derived by setting the derivative of Saeman model, Eq. (6), to zero for maximum concentration of reducing sugars.

$$t_{\max} = \ln \frac{(k_2/k_1)}{(k_2 - k_1)} \qquad (7)$$

The dependence of the rate constants k on temperature can be expressed by Arrhenius equation as in Eq. (8):

$$k = A \times \exp\left(\frac{-E_a}{RT}\right) \qquad (8)$$

where A is the Arrhenius constant, E_a is the activation energy, R is universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature. The acid concentration and the rate constant k at constant temperature is related as shown in the equation below (Saeman, 1945):

$$k = W[\text{H}^+]^m \qquad (9)$$

where W is a constant, [H$^+$] is the proton concentration and m is the gradient of line in logarithm k against logarithm of [H$^+$] plot. The kinetic parameters of the model were determined using MATLAB R2009b (MathWorks Inc., USA).

2.5. Recovery of ionic liquid

Aqueous biphasic system (ABS) was employed to recover the ionic liquid from the hydrolysate. Potassium phosphate solution of 80% (w/w) concentration was added to the hydrolysate in a drop wise manner until a phase separation was observed via a change of clear to turbid solution. The turbid solution formed two phases after centrifuged (Centrifuge 5810R, Eppendorf, Germany). For each drop of potassium phosphate solution added, the mixture in the test tube was shaken and the resulting solution was examined for turbidity. The amount of potassium phosphate added was recorded and also the volumes of the two phases formed. A portion of the