Process optimization and performance evaluation on sequential ionic liquid dissolution–solid acid saccharification of sago waste

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HIGHLIGHTS

▶ Effective sequential ionic liquid dissolution–solid acid saccharification process.
▶ 98.3% reducing sugars yield was achieved under optimized conditions.
▶ The quadratic models developed are of good predictive accuracy.
▶ The process is of better yield compared to other saccharification schemes.
▶ It offers high reaction rate, ease products separation and catalyst reusability.

ARTICLE INFO

ABSTRACT

The production of reducing sugars from sago waste via sequential ionic liquid dissolution–solid acid saccharification was optimized in this study. Ionic liquid dissolution of sago waste with 1-butyl-3-methyl-imidazolium chloride ([BMIM]Cl) was conducted prior to the solid acid saccharification with Amberlyst 15 (A15). The effect of time, temperature and substrate loading during dissolution reaction; and the effect of time, temperature and catalyst loading during saccharification reaction were examined by applying central composite design (CCD) separately. Both dissolution and saccharification reactions were respectively modeled into quadratic polynomial equations with good predictive accuracies. A high reducing sugars yield of 98.3% was obtained under the optimized conditions, i.e. dissolution at 1.75 h, 160 °C, 1.5% substrate loading, and saccharification at 0.5 h, 130 °C, 4% catalyst loading. From comparison studies of different saccharification schemes, the sequential ionic liquid dissolution–solid acid saccharification has proven to be a potential method in reducing sugars production from the lignocellulosic biomass.

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1. Introduction

Ionic liquids have attracted tremendous attention in chemical processing attributing to their numerous advantages, including low volatility, low toxicity, and high thermal and chemical stability (Feng and Chen, 2008; Wang et al., 2011; Zhu et al., 2006). Their applications have been found in the field of catalysis, electrolytes, advanced materials and polymer systems (Dwiatmoko et al., 2010). In recent years, ionic liquids have been used to dissolve lignocellulosic biomass (Fort et al., 2007; Kilpeläinen et al., 2007; Li et al., 2009, 2010; Sun et al., 2009; Zavrel et al., 2009) as the solvents have the ability to disrupt the extensive hydrogen network of the carbohydrate polymers in biomass. Through dissolution in ionic liquid, the carbohydrate polymers in the biomass is susceptible to chemical and biological transformation into biofuels and other valuable products such as enzymes and cellulose composites.

Prior to the biofuels production, lignocellulosic biomass needs to be saccharified to glucose or other fermentable sugars. Acid and enzymatic saccharifications are the two well known saccharification processes. Although they have been reported to be effective in saccharification, related shortcomings such as the need of expensive corrosion-resistant equipments and acid waste disposal problem have been encountered in acid saccharification (Dadi et al., 2006; Li and Zhao, 2007; Zhang and Zhao, 2009); while low saccharification rate and incomplete conversion of reducing sugars are common in enzymatic saccharification (Rinaldi et al., 2010). A better solution to the mentioned drawbacks could be the employment of solid acid catalyst in saccharification. The solid form of the catalyst can reduce equipment corrosion problem apart from offering facile catalyst separation from products mixture. Besides, the thermal stable solid acid catalyst enables the saccharification reaction to be conducted at higher temperature to facilitate a higher saccharification rate than the enzymatic saccharification.

Several studies incorporating both ionic liquid and solid acid catalyst in saccharification of cellulose or lignocellulosic biomass

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have been reported in recent years (Dwiatmoko et al., 2010; Kim et al., 2010; Rinaldi et al., 2008, 2010; Watanabe, 2010). The effective ionic liquid–solid acid catalyst combination commonly used was 1-butyl-3-methylimizalium chloride ([BMIM]Cl)-Amberlyst 15 (A15) (Rinaldi et al., 2008). In most of the studies conducted, the carbohydrate source, ionic liquid and solid acid catalyst were mixed together for saccharification to take place in a single step reaction. As a consequence, the reaction of ionic liquid in carbohydrate dissolution and the activity of solid acid catalyst in saccharification becomes complex. In addition, single step reaction is having poor sugars conversion.

Therefore, sequential ionic liquid dissolution–solid acid saccharification was proposed to convert the sago waste into reducing sugars in this study. Sago waste has been selected as the subject of investigation in view of its high carbohydrate content (Chew and Shim, 1993; Kumoro et al., 2008; Vikineswary et al., 1994). The effects of the parameters that influence both the dissolution and solid acid saccharification were examined by using central composite design (CCD) of response surface methodology (RSM). The ultimate aim of the work is to optimize the sequential ionic liquid dissolution–solid acid saccharification process and to evaluate its performance through comparison studies with other process schemes.

2. Methods

2.1. Materials

Sago waste, supplied by CL Nee Sago Industries (Malaysia) was ground and sieved to desired size of 500 μm. Ionic liquid [BMIM]Cl (⩾98.0% purity), 3,5-dinitrosalicylic acid (DNS) (⩾98.0% purity) were purchased from Merck (Germany) and solid acid catalyst A15 was purchased from Sigma–Aldrich (USA).

2.2. Sequential ionic liquid dissolution–solid acid saccharification

The first step of the sequential process in present study is the ionic liquid dissolution, which was modified from the dissolution procedure of Sun et al. (2009). Sago waste was dissolved in 1 g of [BMIM]Cl in a screw cap test tube in an oil bath (MC, Julabo, Germany). The amount of sago waste used and the reaction conditions applied during the dissolution reaction were tabulated in Table 1. Upon completion of reaction, the collected sample was cooled to room temperature, followed by the addition of 5 ml of deionized water (Arium® 611UF, Sartorius, Germany). The reaction mixture was evenly mixed prior to centrifugation (Centrifuge 5810 R, Eppendorf, Germany) for solid residue separation. The solid residue refers to the undissolved sago waste from ionic liquid dissolution reaction. The liquid product (hereafter named as prehydrolysate) obtained after centrifugation was subjected to solid

Table 1
Independent variables and their coded and actual levels.

Variable	Coding	Unit	Level				
			−1	−α[a]	0	α[a]	1
1st set of CCD (Ionic liquid dissolution)							
Time	A	h	0.5	1.0	1.5	2.0	2.5
Temperature	B	°C	140	145	150	155	160
Substrate loading[b]	C	% (w/w)	0.5	1.0	1.5	2.0	2.5
2nd set of CCD (Solid acid saccharification)							
Time	D	h	0.5	1.0	1.5	2.0	2.5
Temperature	E	°C	100	110	120	130	140
Catalyst loading	F	% (w/v)	2	4	6	8	10

[a] α, the distance from the center point was set at 0.5.
[b] Substrate loading 0.5, 1.0, 1.5, 2.0 and 2.5% (w/w) were corresponding to 5, 10, 15, 20 and 25 mg of sago waste used during dissolution

acid saccharification using A15 in the second step of the sequential process. The solid acid saccharification was conducted in test tube and the reaction mixture was heated in the oil bath according to reaction conditions presented in Table 1. After the reaction, the catalyst was allowed to settle and the liquid product from saccharification, hereafter named as hydrolysate, was analyzed for reducing sugars using DNS assay (Miller, 1959). The yield of reducing sugars was defined as the percentage of reducing sugars produced from sago waste, which was computed using Eq. (1) as suggested by Watanabe (2010).

$$\text{Yield}(\%) = \frac{\text{Amount of reducing sugars produced}}{\text{Amount of sago waste}} \times 100 \qquad (1)$$

2.3. Experimental design and optimization

Two different sets of CCD were performed for the ionic liquid dissolution and solid acid saccharification reactions in the sequential ionic liquid dissolution–solid acid saccharification. The CCD design matrix was generated with the aid of Design Expert 7.0.0 software (STAT-EASE Inc., Minneapolis, USA).

In the first set of CCD, the effect of three independent variables, i.e. dissolution temperature, time and substrate loading on carbohydrate dissolution capability of the ionic liquid were investigated. The studied ranges for these independent variables were based on the preliminary study and are listed in Table 1. The dissolution capabilities of the ionic liquid were evaluated based on the yield of reducing sugars obtained from the subsequent solid acid saccharification at a fixed condition, i.e. saccharification temperature of 120 °C, duration of 1.5 h and catalyst loading of 10% (w/v).

In the second set of CCD, dissolution was first conducted at the optimized conditions determined from the first set of CCD, followed by solid acid saccharification of the prehydrolysate at different temperature, time and catalyst loading as outlined in Table 1. The saccharification performance was evaluated based on the yield of reducing sugars.

The experimental response, y (yield of reducing sugars) was fitted into a second order polynomial regression model as shown in Eq. (2):

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j \qquad (2)$$

where x_i and x_j are the independent variables studied, β_0 is the constant coefficient, β_i is the ith linear coefficient, β_{ii} is the quadratic coefficient and β_{ij} is the ijth interaction coefficient. Second order polynomial regression model was chosen in this study as it is commonly applied by researchers (Tan et al., 2010; Yoon et al., 2012) to study the role of individual variable and their second order interactions on the response. The significance of the model was determined by performing analysis of variance (ANOVA). Three-dimensional response surface plots and contour plots generated by the program were used to provide some graphical illustration of the interaction between the operational variables. To evaluate and verify the predicted optimum reducing sugars yield, three experiments were conducted at the suggested optimum conditions. The optimum reducing sugars yield is defined as the reducing sugars yield achieved by incorporating both optimum operational conditions of ionic liquid dissolution and solid acid saccharification reactions.

3. Results and discussion

3.1. Statistical analysis

The experimental design for ionic liquid dissolution and solid acid saccharification process are tabulated in Tables 2 and 3