Research Article

Optimization of Alkyl Imidazolium Chloride Pretreatment on Rice Straw Biomass Conversion

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Received: 28 February 2018; Accepted: 5 March 2018; Published online: 13 June 2018

Abstract
Conversion of lignocellulosic biomass to value-added biochemicals and biofuels have gained importance nowadays as a method to reduce environmental problems and to increase economical profits of wastes. One of the main bottleneck of this process is the ineffective hydrolysis of biomass to small sugars due to recalcitrant structure of lignocellulosic biomass. To improve enzymatic hydrolysis, ionic liquid pretreatment on rice straw was optimized to determine the operational condition. Here, two types of ionic liquids, including 1-Butyl-3-methyl imidazolium chloride (BMIM-Cl) and 1-Ethyl-3-methy limidazolium chloride (EMIM-Cl), were challenged with different pretreatment conditions based on Response Surface Methodology (RSM) and their pretreatment efficiencies were comparatively monitored. The pretreatment models representing the effects of BMIM-Cl and EMIM-Cl pretreatment parameters on sugar yields were generated with high R^2 value at 0.9720 and 0.9356, respectively, advocating the reliabilities of the models. Validation experiments were performed to determine the power of model prediction and results showed that there were only 6.3 and 4.86% error in the cases of BMIM-Cl and EMIM-Cl pretreatments, respectively. In this study, BMIM-Cl pretreatment had higher efficiency on improvement of rice straw saccharification compared to EMIM-Cl pretreatment for 35.39%. The results suggested the importance of optimization before selection of pretreatment condition to different types of lignocellulosic biomass.

Keywords: Ionic liquid pretreatment, Lignocellulose, Rice straw, Saccharification, Alkyl imidazolium chloride, Enzymatic hydrolysis

Please cite this article as: N. Junnienkul, M. Sriariyanun, T. Douzou, P. Yasurin, and S. Asavasanti, "Optimization of alkyl imidazolium chloride pretreatment on rice straw biomass conversion," *KMUTNB Int J Appl Sci Technol*, vol. 11, no. 3, pp. 199–207, Jul.–Sep. 2018.

1 Introduction

Lignocellulosic biomass is currently targeted to be one of the most potential raw bio-materials for biorefining process to produce valuable chemicals and biofuels due to its abundant availability worldwide. Nowadays, agricultural residues have been worthlessly disposed on the fields after harvesting seasons and have become environmental problems. In Thailand, 29.83% of electricity (2,814.7 MW) and 90.60% of heat (6.507 MT crude oil equivalent) of renewable energy were produced from agricultural biomass in 2016 [1]. In 2016, about 20% of total agricultural areas (104,000 km^2) in Thailand were used for rice plantation. About 24 MT and 25.45 MT of rice and rice straw were yielded, respectively. Rice straw with 10% humidity could be potentially converted to heat at 12.33 MJ/kg, therefore about 313,800 TJ of heat could be potentially produced from rice straw left in the field every year [2]. Currently, there is no official report about rice straw utilization to produce electricity or fuel in industrial scale, in Thailand. Additionally, submerged rice straw in the rice fields are naturally degraded by microorganisms and turned to CO_2, which subsequently released to environment and caused greenhouse effect.

To gain benefit from agricultural wastes, and reduce environmental problems, biorefining process has been intensively developed in this decade. Generally, the production of renewable energy from lignocellulosic biomass is composed of four steps namely, pretreatment, hydrolysis, fermentation and separation [3]. Among these four steps, the rate-limiting step of the process is the hydrolysis due to the presence of crystallinity of cellulose fibrils and inhibitors preventing the function of hydrolytic enzyme. To improve hydrolysis efficiency, various pretreatment methods are employed to modify the structures of cellulose fibrils and to remove inhibitors [4], [5]. However, each type of lignocellulosic biomass is composed of different proportions of cellulose, hemicellulose, lignin and other components. Therefore, selection of appropriate pretreatment method could not be done by one-for-all rule.

Ionic Liquids (ILs) are liquid salts at room temperature. Due to their properties, such as low flammability, low vapor pressure, good recyclability they have been applied in various applications, for examples, electrolites, hydrolic fluids, and extractive solvents [6], [7]. ILs has been applied in various purposes as green solvents to dissolve the cellulose in many studies because they are able to modify the molecular arrangement of crystalline celluloses. Therefore, ILs could improve the accessibility of hydrolysis enzymes to cellulose, and promote the conversion of cellulose to small molecule sugars [8], [9].

ILs could be tailor-made synthesized by mixing various types of cations and anions. Since 2002, ILs have been applied in pretreatment of lignocellulosic biomass because they are considered as green solvents [10]. The pretreatment efficiency of each IL varies depending on its physical and chemical properties, pretreatment condition, and compatibility to biomass. IL pretreatments have been demonstrated in many studies that they are comparatively better methods to enhance enzymatic hydrolysis or saccharification than other chemicals [11]–[13]. Using ILs in pretreatments, it could also reduce the use of other corrosive chemicals and reduce the release of chemical waste to environment.

Although the prices of ILs continuously decrease in these recent years, however ILs are relatively more expensive than other chemicals. Therefore, the process optimization should be performed to make the economically feasible process. This study aimed to apply two types of ILs, 1-Butyl-3-methyl imidazolium chloride (BMIM-Cl) and 1-Ethyl-3-methy limidazolium chloride (EMIM-Cl), for rice straw pretreatments. The optimum condition pretreatments of these ILs were achieved based on Response Surface Methodology (RSM). The effectiveness of the pretreatment conditions was evaluated in term of sugar yields released from enzymatic saccharification by using commercial cellulases.

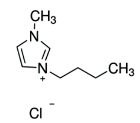
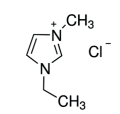
2 Materials and Methods

2.1 *Biomass materials, chemicals, and enzymes*

Rice straw was collected after a harvesting season from a local rice field in Phra Nakhon Si Ayutthaya province, Thailand. Rice straw was cut to 1-cm-long pieces and dried in a hot-air oven at 80°C for 48 h. Dried rice straw was milled to particle size between 10–20 mesh using aluminium sieve and stored in sealed plastic bags at room temperature until use. The compositions of rice straws in the forms of cellulose, hemicelluloses and lignin of rice straw were analyzed as described by Van Soest and Wine, 1967 [14].

The ILs used in this study, BMIM-Cl (CAS No. 79917-90-1) and EMIM-Cl (CAS No. 65039-09-0), were purchased from Sigma-Aldrich (St. Louis, MO, USA) (Table 1). Commercial cellulase, CelluClast 1.5 L, (produced by Trichoderma reesei ATCC 26921) and cellobiase (produced by Aspergillus niger) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Megazyme (Wicklow, Ireland), respectively. 3,5-dinitrosalicylic acid (CAS No. 609-99-4) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Others chemicals were purchased from Ajax Finechem (New South Wales, Australia).

Table 1: Properties of BMIM-Cl and EMIM-Cl

Properties	BMIM-Cl	EMIM-Cl
CAS No.	79917-90-1	65039-09-0
Empirical Formular	$C_8H_{15}ClN_2$	$C_6H_{11}ClN_2$
Molecular Weight	174.67	146.62
Melting Point (°C)	70	77–79
Molecular Structure		

2.2 *Optimization of biomass pretreatment*

Response Surface Method (RSM) with Box-Behnken design was applied to design the experiments to optimize the pretreatment condition, which yielded the maximum contents of sugars from rice straw as described in previous studies [15]–[17]. A three levels, three factors of Box-Behnken design (BBD) was employed as independent variables, including loading ratio of straw to ILs (X_1:5–15% (w/w)), pretreatment temperature (X_2: 90–140°C), and pretreatment time (X_3: 30–90 min), where Y is the reducing sugar yield (Table 2). The, regression analysis of RSM with 17 experimental runs, and estimation of the coefficients were conducted using Design-Expert software version 7.0.0 (Stat-Ease, Inc., Minneapolis, MN, USA). The reliability of generated model was estimated by the coefficient of determination (R^2). The second order polynomial regression model was generated to enhance the response by optimizing the three pretreatment parameters, as followed:

$$Y = \beta_0 + \sum_{i=3}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ii} X_i X_j$$

The dependent variable (Y) was reducing sugar yield (Y), i and j are linear and quadratic coefficients, and β_0, β_i, β_{ii}, and β_{ij} are the regression coefficients.

To perform biomass pretreatment based on RSM plan, milled rice straw was mixed with each IL, BMIM-Cl and EMIM-Cl in a glass screw-capped tube with different loading ratio ranging from 5–15% (w/w). The pretreatments were carried out in a hot air oven using temperature-time conditions as specified in Table 2. After pretreatment, solid residue was precipitated by drop-wise addition of anti-solvent, deionized water, with 1 : 1 (w/w) ratio. Then, IL-water mixture was discarded from pretreated rice straw. The sample was washed with deionized water for 5 times by centrifuging at 6,000g for 5 min to remove remaining IL and other residuals that are inhibitory to enzymatic saccharification. After that, the solid biomass residues were dried under the hot-air oven at 80°C until the constant weight were achieved. Then, samples were stored in sealed plastic bags at room temperature until use for subsequent enzymatic saccharification.

Table 2: RSM with Box-behnken design. Values of the three independent variables (X_1, X_2, X_3) and the dependent variable (Y) for each pretreatment

Run	Pretreatment Condition			Y: Reducing Sugar (mg)	
	X_1: Loading Ratio (%)	X_2: Temp (°C)	X_3: Time (min)	BMIM-Cl	EMIM-Cl
1	15	100	60	7.84	5.54
2	10	120	60	8.35	3.17
3	10	140	30	8.61	8.88
4	10	120	60	7.94	4.84
5	10	140	90	12.00	5.03
6	10	120	60	8.69	3.73
7	15	140	60	8.74	2.20
8	5	120	30	8.76	2.74
9	10	120	60	8.33	5.95
10	15	120	30	7.24	5.76
11	10	120	60	8.06	4.67
12	10	100	90	7.36	1.91
13	15	120	90	6.34	3.75
14	10	100	30	7.82	4.89
15	5	140	60	12.85	4.33
16	5	100	60	7.75	5.66
17	5	120	90	11.30	4.41

2.3 *Enzymatic saccharification*

Each hydrolysis mixture containing of 0.1 g of pretreated rice straw, 4 FPU/g-substrate of Celluclast® 1.5 L and 25 CBU/g-substrate of cellobiase, 40 µL of 2 m sodium azide in 4 mL of 50 mm sodium citrate buffer, pH 4.7 was set up in a screw-capped plastic vial [18]. Hydrolysis reaction was carried out in a 200-rpm shaking incubator at 45°C for 72 h. After incubation, supernatant fractions of samples were collected for reducing sugar analysis. The amounts of reducing sugars were measured using 3,5-dinitrosalisylic acid (DNS) [19].

The efficiency of enzymatic saccharification was expressed as yields of reducing sugars released from each pretreated biomass. The statistical analysis of the effect of each variable was conducted using analysis of variance (ANOVA). Probability of $p < 0.0001$ was used to indicate statistical significance of the model.

3 Results and Discussions

Based on lignocellulose composition analysis, the rice straw biomass was consisted of 42.35% (w/w) cellulose, 31.07% hemicellulose and 15.85% lignin, respectively. Total 17 runs of IL pretreatments were carried out according to various pretreatment conditions of three pretreatment parameters, including loading ratio, pretreatment temperature and pretreatment time (Table 2).

After pretreatment, each pretreated sample was subjected to enzymatic saccharification, and the contents of released reducing sugars were measured using the DNS method (Table 2). The yields of the reducing sugars were different in each pretreatment condition. The sugar yields obtained from BMIM-Cl pretreated biomass ranged from 7.24–12.85 mg. While, the sugar yields obtained from EMIM-Cl pretreated biomass ranged from 1.91–8.88 mg. The highest content of reducing sugars at 12.85 mg was obtained from BMIM-Cl pretreated biomass with run No.15. The highest reducing sugars at 8.88 mg was observed in EMIM-Cl pretreated biomass with run No.3.

To evaluate the effects of pretreatment parameters on the yields of reducing sugars, Regression analysis based on RSM was executed to statistically evaluate the relationships of independent variables (pretreatment parameters) and their interactions on the dependent variable (reducing sugars). Significance of each independent parameter effect was determined using ANOVA and expressed as F value (Tables 3–4). Quadratic mathematic models were suggested to represent the effects of BMIM-Cl and EMIM-C pretreatments with high coefficient of determination (R^2) values of 0.9720 and 0.9356, respectively, advocating the reliability of the models.

The significance of each generated model that represented the effects of pretreatment parameters on yields was indicated with the *p*-value (Prob. > F) of less than 0.01, while a cut-off *p*-value of less than 0.05 was applied to each of the model terms (Tables 3–4). Based on these cut-off criteria, the generated models of BMIM-Cl and EMIM-C pretreatments were interpreted as statistically significant with *p*-value < 0.0001 and 0.0005, respectively. Additionally, the *p*-value of Lack of Fit tests in BMIM-Cl and EMIM-C pretreatments were 0.1522 and 0.1871, respectively, which rejected the hypothesis of Lack of Fit, suggesting that the models have good reliability.

Table 3: ANOVA of the BMIM-Cl pretreatment model

Source	Sum of Squares	df	Mean Square	F-value	*p*-value Prob > F
Model	46.51	7	6.64	36.79	< 0.0001
A-Loading ratio	13.79	1	13.79	76.36	< 0.0001
B-Temp	16.38	1	16.38	90.71	< 0.0001
C-Time	2.62	1	2.62	14.48	0.0042
AB	4.43	1	4.43	24.55	0.0008
AC	2.95	1	2.95	16.35	0.0029
BC	3.7	1	3.70	20.50	0.0014
B^2	2.63	1	2.63	14.55	0.0041
Residual	1.63	9	0.18		
Lack of Fit	1.29	5	0.26	3.04	0.1522
Pure Error	0.34	4	0.085		
Cor Total	48.13	16			

In case of model terms, the BMIM-Cl pretreatment parameters that were statistically significant included loading ratio, temperature, time, loading ratio x temperature, loading ratio x time, temperature x time and temperature^2. While, in EMIM-Cl pretreatment, the statistically significant model terms were loading ratio, temperature, time, loading ratio x temperature, loading ratio x time, temperature^2 and time^2.

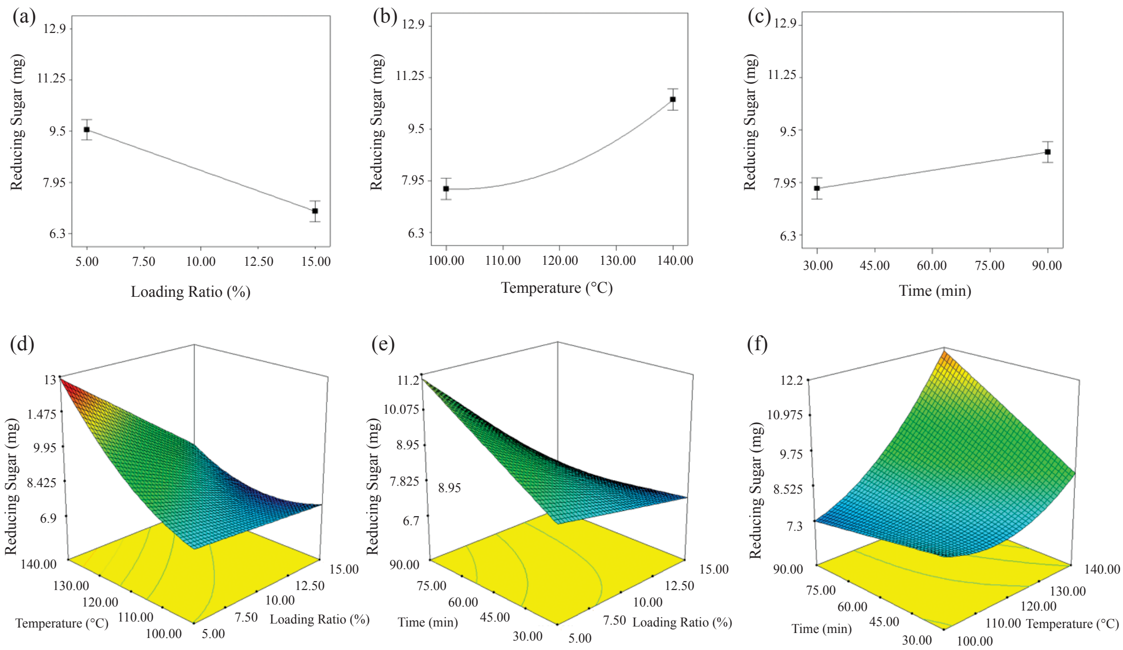


Figure 1: Response surface plots representing interaction effects of the independent variables on reducing sugar yield obtained from BMIM-Cl pretreatments. (a) loading ratio, (b) temperature, (c) time, (d) loading ratio x temperature, (e) loading ratio x time, and (f) temperature x time.

Table 4: ANOVA of the EMIM-Cl pretreatment model

Source	Sum of Squares	df	Mean Square	F-value	*p*-value Prob > F
Model	39.84	7	5.69	12.54	0.0005
A-Loading ratio	3.26	1	3.26	7.18	0.0252
B-Temp	3.48	1	3.48	7.67	0.0218
C-Time	5.62	1	5.62	12.38	0.0065
AB	4.13	1	4.13	9.11	0.0145
AC	2.36	1	2.36	5.20	0.0485
B^2	3.52	1	3.52	7.76	0.0212
C^2	18.29	1	18.29	40.30	0.0001
Residual	4.09	9	1.45		
Lack of Fit	3.13	5	0.63	2.61	0.1871
Pure Error	0.96	4	0.24		
Cor Total	43.93	16			

The response surface model was generated and visualized in the form of the contour plot to represent the effect of each pretreatment parameter on sugar yield (Figures 1–2). Additionally, the benefit of contour plot was to monitor the interactive effects between two pretreatment parameters at a time. In BMIM-Cl pretreatment, the model terms including loading ratio, temperature, time had different trends of impacts on sugar yields (Figure 1). It could be observed that the more loading ratio, the lower sugar yield was obtained. On the other hand, temperature and time parameter had positive effects on sugar yields [Figure 1(a)–(c)]. In case of the interactive effects, the highest sugar yield could be obtained when pretreatment was performed with low loading ratio and high temperature [Figure 1(d)]. For loading ratio x time, the highest sugar yield could be obtained at condition with low loading ration and high time [Figure 1(e)]. Lastly, temperature x time, both factors synchronizely increased sugar yields [Figure 1(f)]. These results were similar to other previous studies that time and temperature were important parameters in the pretreatment of lignocellulosic biomass [20], [21]. As the temperature increases and longer pretreatment time, the biomass solubility increases and subsequently improves the accessibility of hydrolysis enzymes [22].

In EMIM-Cl pretreatment, pretreatment parameters including loading ratio, temperature, time differently

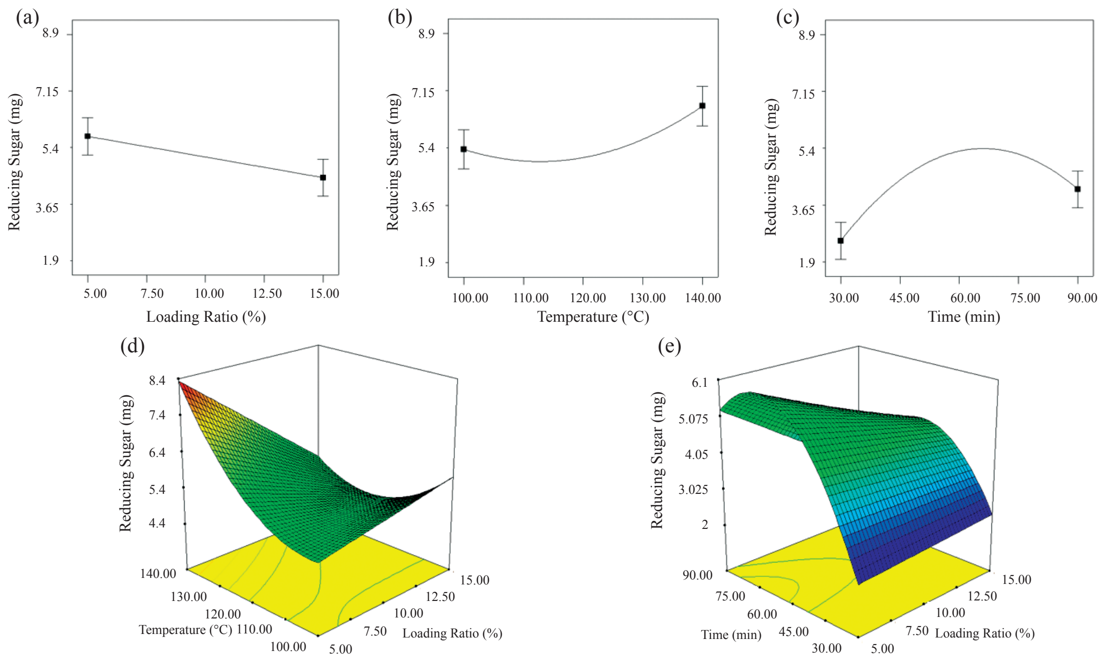


Figure 2: Response surface plots representing interaction effects of the independent variables on reducing sugar yield obtained from EMIM-Cl pretreatments. (a) loading ratio, (b) temperature, (c) time, (d) loading ratio x temperature, and (e) loading ratio x time.

affected sugar yields (Figure 2). Similar to BMIM-Cl, the sugar yields was increased when the lower loading ratio was used [Figure 2(a)]. IL functions as solvent to extract cellulose and remove lignin, therefore the selection of lower loading ratio with higher proportion of IL solvent increases extractibility and reduces hydrolysis inhibitors. In case of temperature factor, it had positive effects on sugar yields [Figure 2(b)]. Whereas, sugar yield was increased when pretreatment time rised, however the yield gradually dropped when time was higher than 60°C [Figure 2(c)]. For two interacting parameters, the highest sugar yield could be obtained when pretreatment was performed with low loading ratio and high temperature [Figure 2(d)]. For loading ratio x time, the highest sugar yield could be obtained at condition with low loading ratio and medium range of pretreatment time [Figure 1(e)].

The effects of all significant pretreatment parameters on sugar yields were expressed in mathematical equations (Table 5). Then, the optimum conditions of BMIM-Cl and EMIM-Cl pretreatments were predicted based on calculation of mathematical equations. The predicted optimum condition of BMIM-Cl was at 5.22% of loading ratio, 139°C of temperature of and 88.2 min of time. While, for EMIM-Cl, the optimum condition was predicted to be at 5% of loading ratio, 140°C of temperature of and 71.56 min of time. The predicted maximum sugar yields obtained from BMIM-Cl and EMIM-Cl pretreatments were 14.99 mg and 8.65 mg, respectively (Table 5).

To investigate the reliability of the model, the predicted optimum condition was experimentally validated with three repetitive runs. The reducing sugar yields obtained from BMIM-Cl and EMIM-Cl pretreatments were 14.04 mg and 9.07 mg, respectively (Table 5). The sugar yields obtained from the validating experiments were close to the predicted yields, which were about 6.34 and 4.86% difference, respectively. This result suggested that the RSM optimization model was a powerful tool to improve the efficiency of pretreatment process.

In this study, two types of ILs, BMIM-Cl and EMIM-Cl, were selected for pretreatment. Using the same optimization procedure, BMIM-Cl pretreatment had higher efficiency on improvement of rice straw saccharification compared to EMIM-Cl pretreatment

Table 5: Validation of mathematical model generated from RSM

IL	Optimum Pretreatment Condition			Released Reducing Sugar (mg)			Mass Loss (%)	
	Loading Ratio (%)	Temp (°C)	Time (min)	Predicted	Experimental	% Difference	Pretreatment	Hydrolysis
BMIM-Cl	5.22	139	88.2	14.99	14.04	6.34	28.89	20.00
	Optimum condition model: Reducing sugar (mg) = 25.05877 + 1.34448*Loading ratio – 0.39194*Temp – 0.11607*Time – 0.010528*Loading ratio*Temp – 5.72807 × 10^{-3}*Loading ratio*Time + 1.60346 × 10^{-3}*Temp*Time + 1.96902 × 10^{-3}*Temp^2							
EMIM-Cl	5	140	71.56	8.65	9.07	4.86	13.64	33.60
	Optimum condition model: Reducing sugar (mg) = 10.04477 + 1.39954*Loading ratio – 0.41557*Temp + 0.35669*Time – 0.010165*Loading ratio*Temp – 5.12299 × 10^{-3}*Loading ratio*Time + 2.28417 × 10–3*Temp^2 – 2.31274 × 10^{-3}*Time^2							

for 35.39% according to the reducing sugar yields. Interestingly, the optimum conditions of two IL pretreatments were sligtly different, for example 5.22 min and 5 min for pretreatment time and 139°C and 140°C for pretreatment tempearature in BMIM-Cl and EMIM-Cl pretreatment, respectively. This finding could be due to the differences in their chemical and physical properties (Table 1) leading to the variations in their extraction efficiencies. In facts, the pretreatments lead to improvement of enzymatic hydrolysis by solubilizing cellulose fibril, removing enzyme inhibitors and preventing the formation of inhibitory by-products [23]. Previously, cellulose solubilities in the form of Avicel® in BMIM-Cl and EMIM-Cl were comparatively observed. The results showed that Avicel® solubility in EMIM-Cl was better than in BMIM-Cl for 2.53 times [24]. Based on XRD analysis, EMIM-Cl pretreatment could reduce relative crystallinity degree of cellulose for 57.5% [24]. Based on our study, it could be hypothesized that BMIM-Cl pretreatment was a better method for rice straw pretreament might be due to its efficiency to remove enzyme inhibitor. After rice straw pretreatments, about 28.89% and 13.64% of biomass weights were removed during BMIM-Cl and EMIM-Cl pretreatment (Table 5). These biomass weight losses could be dissociated with the lignin contents in lignocellulose. The more loss of biomass weight in BMIM-Cl pretreatment could be hypothesized to be the more loss of lignin content, leading to the better enzyme efficiency, ultimately.

4 Conclusions

IL pretreatments have been applied in biomass refinery process due to their effectiveness to improve hydrolysis efficiency. Here, BMIM-Cl and EMIM-Cl were selected to pretreat rice straw biomass. Based on RSM with Box-behnken experimental design, the effects of pretreatment parameters on enzymatic saccharification were revealed based on mathematical model. The optimum pretreatment conditions were predicted and validated with experiments, suggesting the reliability of the model. The extent benefit of this optimization study could be the better design of pretreatment operation to make the feasible biorefining process.

Acknowledgments

The authors would like to thank King Mongkut's University of Technology, North Bangkok (Research Grant No. KMUTNB-61-GOV-03-47) for financial support of this work.

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