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Optimization of Oil Palm Fronds Pretreatment Using Ionic Liquid for Levulinic Acid Production

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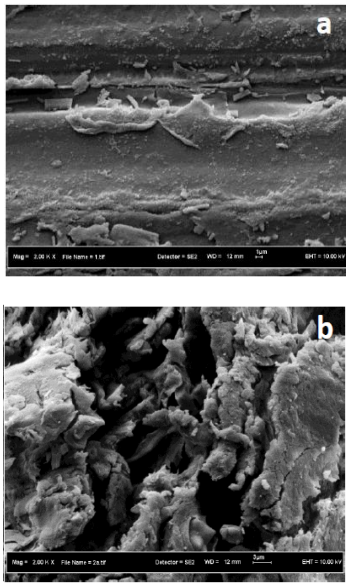
Graphical abstract



Abstract

The pretreatment of oil palm frond (OPF) has been carried out using 1-butyl-3-methylimidazolium bromide ([BMIM]Br) in the presence of aqueous sulphuric acid (H_2SO_4). The effects of reaction temperature, reaction time and [BMIM]Br loading on lignin degradation were investigated by applying Box Behnken Design of Response Surface Methodology (RSM). The optimized process condition for OPF pretreatment were 123°C, 175 min and 9.9 g of [BMIM]Br loading with an optimum lignin degradation of 88.2%. The experimental results fitted-well with the predicted value with less than 5% error. It was also demonstrated that lignin degradation using recycled [BMIM]Br gave sufficient performance for five successive runs. It was revealed from SEM and XRD analyses, that the pretreated OPF was porous and less crystalline after pretreatment. Consequently, the pretreated OPF renders 25.3% levulinic acid yield in acid hydrolysis compared to 18.2% yield for untreated OPF.

Keywords: Lignin degradation; oil palm fronds; ionic liquid; optimization; levulinic acid production

Abstrak

Prarawatan pelepah kelapa sawit (OPF) telah dijalankan dengan menggunakan 1-butil-3-metilimidazolium bromida ([BMIM]Br) dalam larutan akues asid sulfurik (H_2SO_4). Kesan suhu tindak balas, masa tindak balas, dan suapan [BMIM]Br terhadap degradasi lignin telah dikaji menggunakan reka bentuk Box Behnken Kaedah Gerak Balas Permukaan (RSM). Keadaan proses optima bagi prarawatan OPF adalah 123°C, 175 min dan 9.9 g suapan [BMIM]Br, dengan degradasi lignin optima 88.2%. Keputusan ujikaji adalah mematuhi nilai yang telah diramal dengan ralat kurang daripada 5%. Ia juga menunjukkan bahawa degradasi lignin menggunakan [BMIM]Br yang dikitar semula memberikan prestasi yang mencukupi untuk lima kitaran berturutan. Ia juga dibuktikan daripada analisis SEM dan XRD bahawa OPF yang telah dirawat adalah poros dan kurang kristal selepas prarawatan. Oleh yang demikian, OPF yang dirawat menghasilkan 25.3% hasil asid levulinik dalam hidrolisis asid berbanding dengan hasil 18.2% daripada OPF yang tidak dirawat.

Kata kunci: Degradasi lignin; pelepah kelapa sawit; cecair ionik; pengoptimuman; penghasilan asid levulinik

1.0 INTRODUCTION

The decreasing supply and increasing prices of fossil fuel have created great efforts in the search for a renewable and sustainable fuel source. In recent years, biofuels which can be derived from lignocellulosic biomass has been viewed as one of the potential replacements to the petrochemical resources.[1] Agricultural residues are most abundantly found lignocellulosic biomass especially in countries where agricultural activities are dominant. In Malaysia, oil palm is the agricultural sector that generates the most biomass residues around 30 million tons per year. The generated palm oil residues are in the form of empty fruit bunch, trunks and fronds. 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 levulinic acid, 5-hydroxymethylfurfural and biofuel.[2-4]

The complex matrix of lignocellulosic biomass unfavourably hinders its effective conversion into valuable chemical products. Thus, pretreatment is an important tool for biomass conversion processes, by altering the structure of biomass, increasing their surface area, removing the lignin content, reducing cellulose

crystallinity and increasing the accessibility of the catalysts to cellulose.[5-7] Several pretreatment technologies are currently utilized to overcome the recalcitrance of lignocellulose and to increase the efficiency of catalytic process for production of value added chemicals.[8,9]

In recent times, ionic liquid has been discovered and widely used to dissolve cellulose. It offers some advantages over the conventional acid pretreatment method. Besides being more environmental, ionic liquid pretreatment also gives considerably mild conditions.[10] Although ionic liquid pretreatment has gained attention as a green solvent and new technology, this process is too expensive due to high cost and large amount of ionic liquid required.[11] For that reason, ionic liquid has been combined with other pretreatment methods such as combination of ionic liquid with ammonia and oxygen.[12,13] These combined pretreatment processed managed to reduce cost, decreased lignin accumulation in the recycled ionic liquid stream, and enhanced process efficiency. The ionic liquid pretreated biomass reported reduced lignin content, lower degree of crystallinity and can be enzymatically hydrolyzed at a faster rate.[14] The recyclability of ionic liquid has also added advantage to this biomass pretreatment method.[11,15,16]

Optimization of a pretreatment process is a crucial step in determining the suitability and economic conditions to enhance the process efficiency. Statistical approach is suitable to quantify the relationship between the measureable response and a set of experimental factors, where the factors are assumed to affect the response. In addition, the best value of the response could be determined. Response surface methodology (RSM) is managed by certain rule that can be estimated by the relationship between the factors to optimize a desired output.[17] Many tools were used by the researchers to optimize different pretreatment processes including full factorial design, Central Composite Design (CCD) and Box-Behnken Design (BBD).[18-20] The effect of several reaction parameters on biomass pretreatment such as reaction temperature, reaction time, solid loading, have been extensively investigated by the researchers.[11,20,21]

To date, there are limited studies on the optimization of combined biomass pretreatment process. The objective of this study is to optimize the pretreatment of oil palm fronds (OPF) by using 1-butyl-3-methylimidazolium bromide ([BMIM]Br) ionic liquid in the presence of aqueous H_2SO_4. The effect of reaction temperature, reaction time, and [BMIM]Br loading on the lignin degradation from OPF was investigated for levulinic acid production. The experimental data were analyzed based on the Box Behnken Design to determine the optimum condition. In addition, the performance of regenerated ionic liquid on lignin degradation was investigated. The morphological and structural changes of OPF after pretreatment were also examined using FESEM, XRD and FTIR.

2.0 MATERIALS AND METHODOLOGY

2.1 Materials

Oil palm fronds (OPF) were supplied by the Malaysian Palm Oil Board (MPOB), Bandar Baru Bangi, Kajang Selangor. The OPF was air dried before further shredded and grinded grinded into smaller particle size in the range of 1–5 mm. Sulphuric acid (H_2SO_4, 98%), acetone (99%), and potassium permanganate ($KMnO_4$) were purchased from commercial sources (QRec New Zealand). Ionic liquid 1-butyl-3-methylimidazolium bromide (BMIMBr), and levulinic acid (98%) were purchased from Merck, Germany. Fe/HY zeolite catalyst was prepared through wet impregnation method.

2.2 Oil Palm Fronds Delignification Process

The delignification process was performed by charging 2 g of OPF samples, 1 ml of 0.4 M H_2SO_4 and BMIMBr at various loading into a 100 ml Schott bottle (batch reactor). The reactor and contents were heated and stirred in an oil bath at desired temperature with stirring speed, 200 rpm. After completing the incubation, 30 ml of water was slowly added into the slurry for regeneration of the dissolved cellulose from the OPF. The mixture was centrifuged at 3000 rpm for 5 min. The supernatant containing ionic liquid was removed, and the precipitate was washed with additional water to ensure the removal of excess ionic liquid. Subsequently, the solid sample was dried in oven at 105 °C to a constant weight. This biomass sample was then placed in 20 ml of a 1:1 v/v mixture of water and acetone, and vigorously stirred to dissolve lignin.[22] The suspension was filtered and the solid residue was collected. The residue was dried at 105 °C and collected for the determination of lignin degradation from the process.

2.3 Lignin Content Determination

0.1 g of delignified OPF was added into a mixture of 5 ml of 0.02 M $KMnO_4$ with 20 ml of 0.4 M H_2SO_4 and mixed well for three minutes. Solid sample was separated from the solution through filtration, while the filtrate was measured using UV-Spectrophotometer (Shimadzu, USA) at 546 nm. The kappa number was determined using Equation (1):

$$K = a/w\ (1 - A_e/A_o) \quad (1)$$

Where, K is Kappa Number, a is the volume of $KMnO_4$ used in the solution, w is weight of OPF sample used, A_o is spectral intensities before the sample is being added, and A_e is spectral intensities at the end of the reaction. Accordingly, lignin content in the OPF sample was calculated from the values of Kappa number, K using Equation (2), where the percent of lignin degradation is calculated based on Equation (3):

$$\text{Lignin content (wt\%)} = 0.15K \quad (2)$$

$$\text{Lignin degradation} = \frac{\text{Lignin content (untreated-treated)}}{\text{Lignin content (untreated)}} \quad (3)$$

2.4 Experimental Design

In this study, the Box-Behnken design was used to design the experiment with three variables. The variables; reaction temperature (X_1), reaction time (X_2), and [BMIM]Br loading (X_3), at three different levels (low, medium, and high) and coded as (-1, 0, +1) respectively are tabulated in Table 1. The variables were coded according to Equation (4) for statistical calculation.

$$x_i = \frac{X_i - X_o}{\Delta X_i} \quad (4)$$

Where x_i is the coded value of the independent variable, X_i is the real value of the independent variable, X_o is the real value of the independent variable at the center point and ΔX_i is the step change value. According to Box-Behnken design, with three independent variables, there were 15 sets of experiments.

Table 1 Experimental range and levels for the independent variables

Factors	Symbol		Range and level		
	Uncoded	Coded	-1	0	+1
Temperature (°C)	X_1	x_1	110	120	130
Time (min)	X_2	x_2	120	180	240
[BMIM]Br loading (g)	X_3	x_3	5	7.5	10

The statistical analysis of the response was carried out using Statsoft Statistica software version 8.0. The mathematical model for the OPF lignin degradation was fitted to second order polynomial model as in Equation (5):

$$Y_i = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (5)$$

Where Y_i is dependent variable (lignin degradation); x_1, x_2, and x_3 are the independent variables; β_o is the regression coefficient at the central point; β_1, β_2, and β_3, are the linear coefficients; β_{11}, β_{22}, and β_{33} are the quadratic coefficients; β_{12}, β_{13}, and β_{23} are the second order interaction coefficients.

The significant effect of each coefficient of the above equation was determined by *t*-test and *p*-values. The fitted polynomial equation was expressed as surface plots in order to visualize the relationship between the response and each factor. The surface plots were also applied to presume the optimum conditions. The mathematical model was tested with the analysis of variance (ANOVA) within 5% level of confidence. ANOVA was used to verify the significance of the second-order models which is determined by *F*-value. Generally, the calculated *F*-value should be greater than the tabulated *F*-value to reject the null hypothesis. The calculated *F*-value is defined as the ratio between the mean of square regression (MSSSR) and mean of square residual (MSSSE), where MSSSR and MSSSE are obtained by dividing sum of squares (SSR) and sum of residual (SSE) over degree of freedom (Df), respectively. Meanwhile, tabulated *F*-value is obtained from the *F* distribution based on Df of regression and residual.[17,23,24]

2.5 Levulinic Acid Production

The hydrolysis of delignified OPF for levulinic acid production was carried out by dissolving 1 g of OPF in 50 ml distilled water and mixed with 1g of Fe/HY catalyst. The catalyst was prepared using wet impregnantion method as reported in literature.[2] The solution was heated up in a 100 ml high pressure reactor at 170°C with stirring speed, 200 rpm. After 3 h the reaction mixture was cooled down to room temperature. A liquid sample was filtered before further analysis. The concentration of levulinic acid in the liquid product was determined using high performance liquid chromatography HPLC (Perkin Elmer) under the following conditions: column = Hi Plex H; flow rate = 0.6 ml/min, mobile phase 5mM H_2SO_4, detector = UV 220 nm; retention time = 40 min; column temperature = 60°C. Levulinic acid yield was calculated according to Equation (6) :

$$\text{Levulinic acid yield (\%)} = \frac{\text{Final levulinic acid amount (g)}}{\text{Initial OPF amount (g)}} \times 100\% \quad (6)$$

2.6 Characterization of Oil Palm Frond

X-ray diffraction measurements were performed on a Bruker D8 Advance diffractometer for biomass samples before and after ionic liquid pretreatment. The X-ray diffraction patterns with CuKα radiation (k = 1.5406 Å) were recorded over the angular range of 10–30°, with a step size of 0.02° and step time of 1 s. The morphology of oil palm frond before and after pretreatment were analyzed by a scanning electron microscope (SEM: JEOL, JSM-6390LA). The samples were coated with Aurum (Au) to make the biomass samples conductive before subjected into SEM instrument. SEM images were taken at 6000x magnification with SEM instrument operated at 10 kV accelerating voltage. The infrared spectra of the samples were recorded with a FTIR spectrometer (Perkin Elmer). The samples were analyzed in powder form in the absorption band mode in the range of 400–4000 cm^{-1}.

3.0 RESULTS AND DISCUSSION

3.1 Model Analysis

Response surface methodology and Box Behnken design were employed to analyze the interaction or relationship between the response and the variables. The experimental matrix for the design and analytical results of lignin degradation are given in Table 2. The lignin degradation (Y_1) was the response for the tested variables in coded units; reaction temperature (x_1), reaction time (x_2), and [BMIM]Br loading (x_3). The second order polynomial model for lignin degradation as in Equation (7):

$$Y_i = -1423.02 + 23.01x_1 + 1.22x_2 - 1.64x_3 - 0.10x_1^2 - 0.56x_3^2 + 0.13x_1x_3 - 0.02x_2x_3 \quad (7)$$

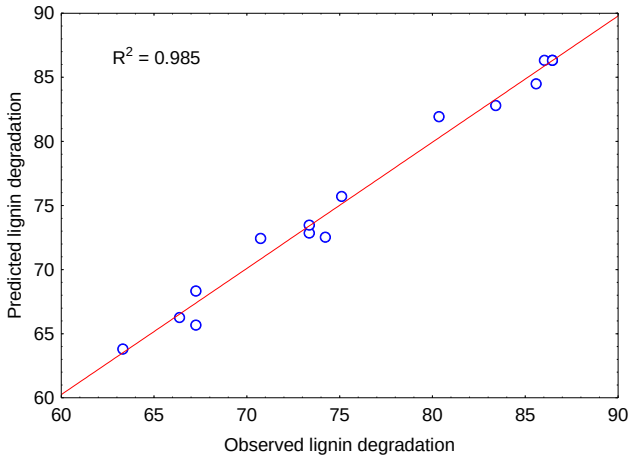


Figure 1 The coefficient of determination and predicted versus observed values for lignin degradation model

Table 2 Experimental data set for lignin degradation from OPF samples

Run	Variables						Response
	x_1, Reaction temperature (°C)		x_2, Reaction time (min)		x_3, [BMIM]Br loading (g)		Lignin degradation, Y_1 (%)
1	110	-1	120	-1	7.5	0	63.3
2	130	+1	120	-1	7.5	0	70.7
3	110	-1	240	+1	7.5	0	74.2
4	130	+1	240	+1	7.5	0	73.4
5	110	-1	180	0	5	-1	67.2
6	130	+1	180	0	5	-1	66.4
7	110	-1	180	0	10	+1	73.4
8	130	+1	180	0	10	+1	85.6
9	120	0	120	-1	5	-1	67.2
10	120	0	240	+1	5	-1	75.1
11	120	0	120	-1	10	+1	83.4
12	120	0	240	+1	10	+1	80.3
13	120	0	180	0	7.5	0	86.5
14	120	0	180	0	7.5	0	86.0
15	120	0	180	0	7.5	0	86.5

The model has shown the adequacy between the observed and predicted results where the coefficient of determination (R^2) was close to 1. The empirical model is adequate to explain most of the variability in response which should be at least 0.75. The value of R^2 for lignin degradation model was 0.985 as shown in Figure 1. The results indicate that 98.5% of the variability in the response can be explained by the model. Only 1.5% of the total variability was not explained in the regression model. A high R^2 value can explain that the model obtained is able to give a good estimate of the response within the process conditions range. Figure 1 also demonstrates the comparison between the predicted and the observed values of lignin degradation by using Equation (5). The results indicated that the observed lignin degradation was distributed relatively near to a straight line, and the sufficient correlation between these values was observed.

The analysis of variance (ANOVA) as tabulated in Table 3 was used to check the *F* values by comparing it with the tabulated *F*-value. The tabulated *F*-value was used at a high confidence level (95%) in order to obtain a good prediction model. The *F*-values for lignin degradation model is higher than the tabulated *F*-value by rejecting the null hypothesis at the 0.05 level of significance. The significance of each coefficient was determined by t-test and p-values as shown in a Pareto chart (Figure 2). Pareto chart is employed to understand the pattern of interactions between the factors. The greater the magnitude of the t-value and the smaller the p-value, the more significant was the corresponding coefficient. From Figure 2, it could be revealed that all coefficients have remarkable effects on the lignin degradation of OPF as the p-values were lower than 0.05. In this study, quadratic effects of x_1^2 and x_2^2, and linear effect of x_3 on lignin degradation were the most significant coefficients at approximately 99% of significant level with the p-values < 0.01 which are 0.00011, 0.00088, and 0.0002 respectively. There is also interaction between the parameters which is reaction temperature with [BMIM]Br loading (x_1x_3), and reaction time with [BMIM]Br loading (x_2x_3). With highest p-value (0.0588) and lowest t-value (2.438), it is confirmed that there is no interaction between reaction temperature and reaction time on lignin degradation from OPF by pretreatment in [BMIM]Br.

Table 3 Analysis of variance (ANOVA) for quadratic model of lignin degradation

Sources	Sums of square	Degree of freedom	Mean square	*F*-value	$F_{0.05,9,5}$
Regression	922.75	9	102.53	35.403	4.77
Residual	14.48	5	2.90		
Total	937.23	14			

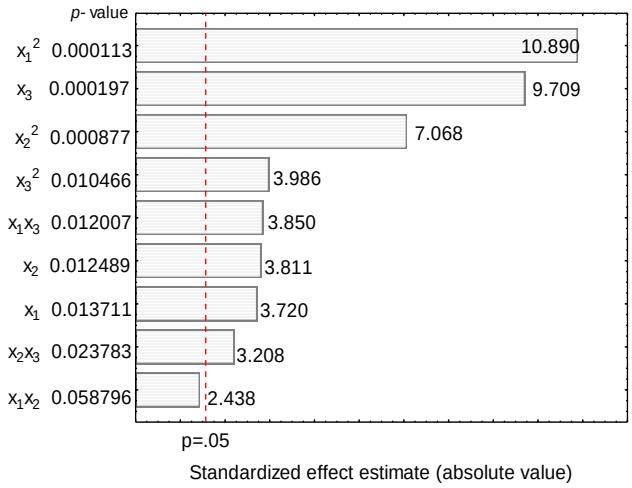


Figure 2 Pareto chart of lignin degradation model

3.2 Variables Effect on the Response

The three-dimensional (3D) response surface plots and contour plots for the interaction effects between two variables and the response are illustrated in Figure 3. These plots were drawn by varying two variables while the other variable was maintained at zero level. The interaction effects were considered within the range of respected variables. As shown in Figure 3a, the quadratic effect of reaction temperature and reaction time on the response was observed on OPF lignin degradation. Figure 3b illustrates the interaction of reaction temperature and [BMIM]Br loading. While the effect of [BMIM]Br loading and reaction time on OPF lignin degradation at constant reaction temperatures (120°C) is exhibited in Figure 3c.

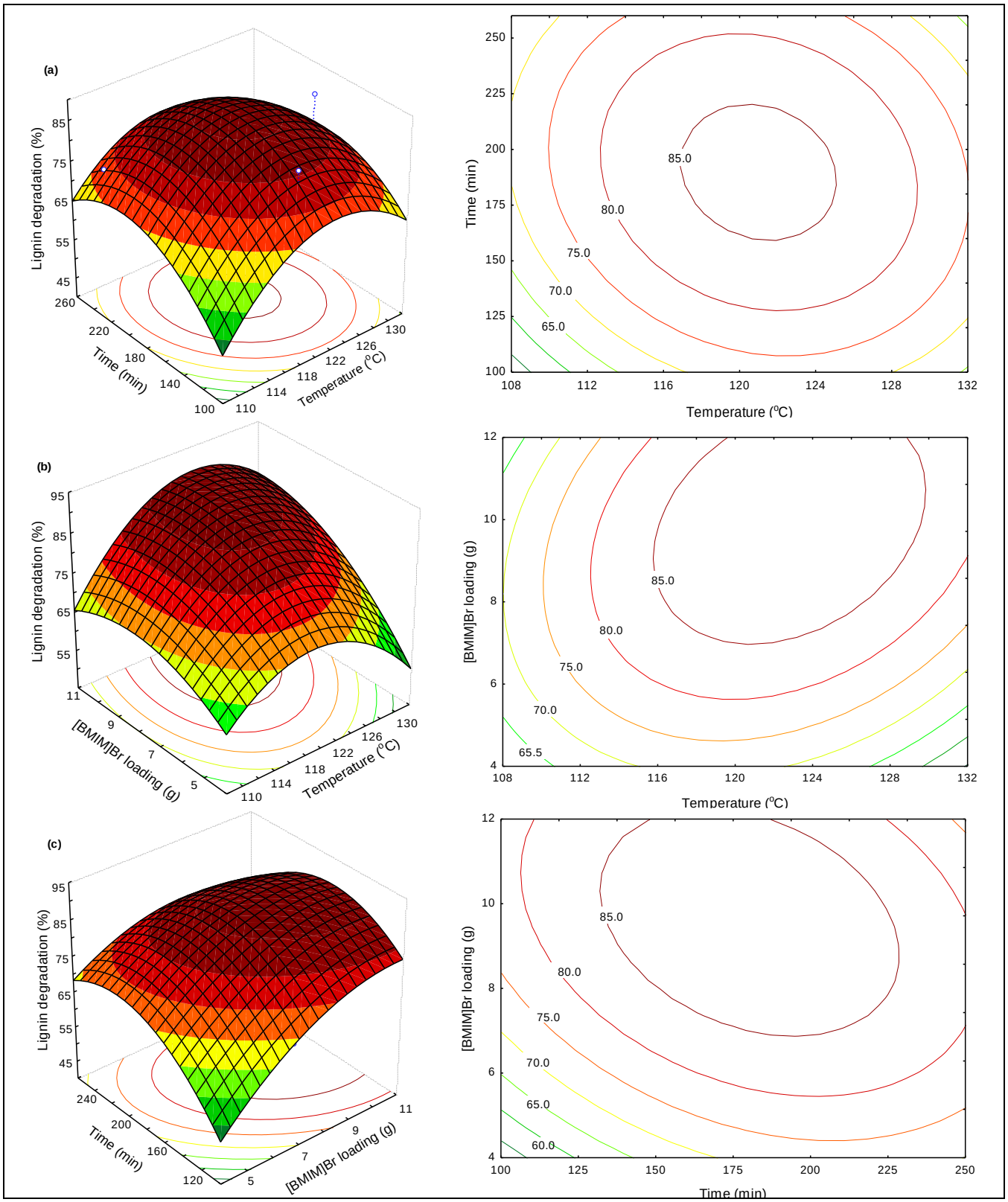


Figure 3 Response fitted surface area and contour plot for lignin degradation based on (a) reaction temperature and reaction time, (b) reaction temperature and and [BMIM]Br loading (c) reaction time and [BMIM]Br loading

From these figures (Figure 3a-b), lignin degradation increased with the reaction temperature up to the optimum temperature. At higher temperature, lignin in the OPF samples cannot be degraded well and this might be due to the disruption of ionic liquid properties at high temperature. This can be overcome with higher [BMIM]Br loading. However, high temperature and

high [BMIM]Br loading for higher OPF lignin degradation would cause in elevated operating cost. Hence, it is necessary to select an adequate amount of ionic liquid occupied in the process. On the other hand, pretreatment process at low temperature might cause the accumulation of lignin in the OPF. H_2SO_4 in [BMIM]Br did not have enough energy to distort the bonds in OPF since reaction rate is strongly dependent on the temperature. Moreover, at low reaction temperature, the increment of [BMIM]Br loading gives insignificant effects towards OPF lignin degradation.

The increase in [BMIM]Br loading gives a positive effect on OPF lignin degradation as reaction time is increased (Figure 3c). Sidik *et al*., (2013) reported that by increasing the ionic liquid amount, it will enhance the performance of the lignin production process from biomass.[25] Large amount of ionic liquid will increase the solubility of lignin from OPF and accelerated the efficiency of the pretreatment process. At longer reaction time, the solubility of anion in [BMIM]Br gave strong effect on the cellulose fibres.[26] As more cellulose is dissolved, higher lignin degraded from OPF is also attained.

From all 3D response surface plots, it can be seen that the quadratic effect of reaction temperature and reaction time was observed on OPF lignin degradation. This is consistent with previous researches.[25,27] They discovered that reaction temperature and time as the most essential conditions that affecting the efficiency of the ionic liquid pretreatment process. The surface confined in the smallest ellipse in the contour plots indicates the optimum values of variables at maximum predicted values of respective response.[28] From the contour plots, optimum lignin degradation could be obtained when the reaction temperature around 118 to 124°C, reaction time from 160 to 200 min, and [BMIM]Br loading was varied from 9 to 11 g.

3.3 Optimization of Lignin Degradation

Based on the model (Equation (7)), the lignin degradation was predicted at optimum conditions in order to obtain high amount of lignin degraded. The optimum conditions for prediction of high OPF lignin degradation indicated the reaction temperature, reaction time and [BMIM]Br loading were at 122.9°C, 175.0 min and 9.8 g, respectively corresponded to 89.5% of predicted lignin degradation (Table 4). Further analysis was performed at optimum conditions for the verification of the predicted lignin degradation.

The lignin degradation of the observed value was 88.2% indicating a 1.45% error between the observed and predicted values.

Table 4 Optimum conditions, predicted and observed values for lignin degradation

Optimum condition			Lignin degradation (%)		Error (%)
x_1 (°C)	x_2 (min)	x_3 (g)	Predicted	Observed	
122.9	175.0	9.9	89.5	88.2	1.45

3.4 Characterization of Untreated and Treated Oil Palm Fronds

A more crystalline structure was confirmed by XRD analysis (Figure 5) with the occurrence of a sharper peak at 2θ = 22° in the untreated OPF as compared to pretreated OPF. When compared to untreated OPF, OPF upon ionic liquid pretreatment possessed lower crystallinity. The intensity peaks resembling the crystallinity of the native biomass at around 2θ = 15° and 22° were decreased for the pretreated OPF. In addition to lower intensities obtained, the peaks were shifted to lower Bragg angles pretreated OPF; particularly the main peak shifted from 22° to 20°. This shift is an indicator of the modification of cellulose.[14,29] Lower crystallinity signifies that a larger amount of amorphous cellulose was present in the pretreated biomass.[30] This provides a larger surface area accessible for catalytic processes. Hence, an enhanced levulinic acid yield was obtained after acid hydrolysis of the pretreated OPF.

FTIR analysis was applied to study the changes in the chemical structure of OPF after [BMIM]Br pretreatment. The FTIR spectra of [BMIM]Br pretreated and untreated OPF were found to be similar as shown in Figure 6. The appearance of the lignocellulosic matrix in this biomass is confirmed from the bands at 3330 cm^{-1} and 2905 cm^{-1}, attributed to the presence of cellulose, hemicellulose, and lignin content in OPF.[31,32] The presence of crystalline cellulose in OPF characterized from band 1425 cm^{-1} diminished after the [BMIM]Br pretreatment. Meanwhile, the absorbance of amorphous cellulose at 897 cm^{-1} happened to be more intense after the pretreatment. This result implies the cellulose content in OPF was modified into a more amorphous structure that would give a higher levulinic acid yield after the hydrolysis of [BMIM]Br pretreated OPF. The peak at 1515 cm^{-1} that represents the lignin structure undergoes reduction in the intensity after the pretreatment. This finding might be the consequences of lignin depolymerization during pretreatment.[33] Other lignin peaks at 1634 cm^{-1}, 1375 cm^{-1} and 1328 cm^{-1} remained in the pretreated OPF; this, indicates that small amount of lignin is still present. Hemicellulose that characterized by the band at 1732 cm^{-1} was preserved in pretreated OPF and it indicates that [BMIM]Br pretreatment did not cause the elimination of hemicellulose content.

Figure 7 shows the SEM images of untreated and [BMIM]Br pretreated OPF. A relatively more porous structure can be observed for [BMIM]Br pretreated OPF. [BMIM]Br pretreated OPF has a more irregular and uneven surface with thinner fibres compared to the untreated OPF.

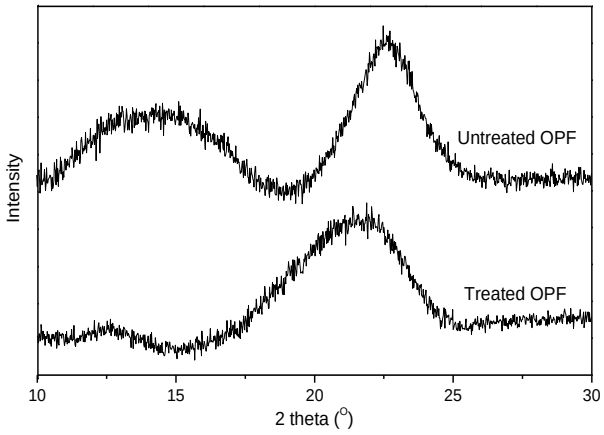


Figure 5 XRD patterns of (a) untreated OPF and (b) treated OPF using [BMIM]Br

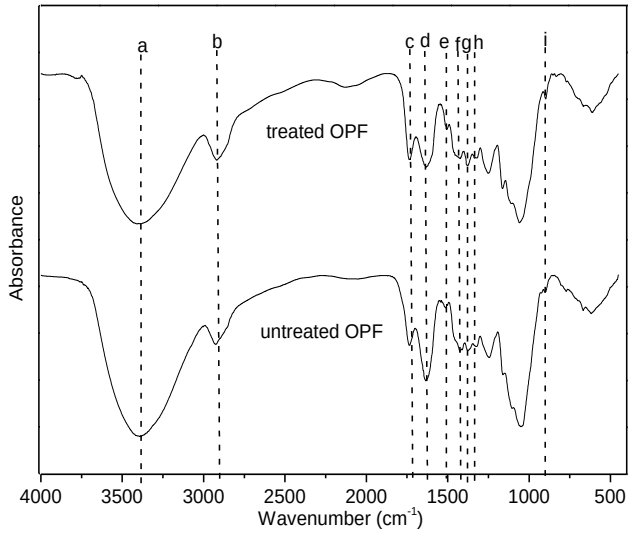


Figure 6 FTIR spectra of untreated OPF an treated OPF using [BMIM]Br. (a) 3330 cm^{-1}, (b) 2905 cm^{-1}, (c) 1732 cm^{-1}, (d) 1634 cm^{-1}, (e) 1515 cm^{-1}, (f) 1425 cm^{-1}, (g) 1375 cm^{-1}, (h) 1328 cm^{-1}, (i) 897 cm^{-1}

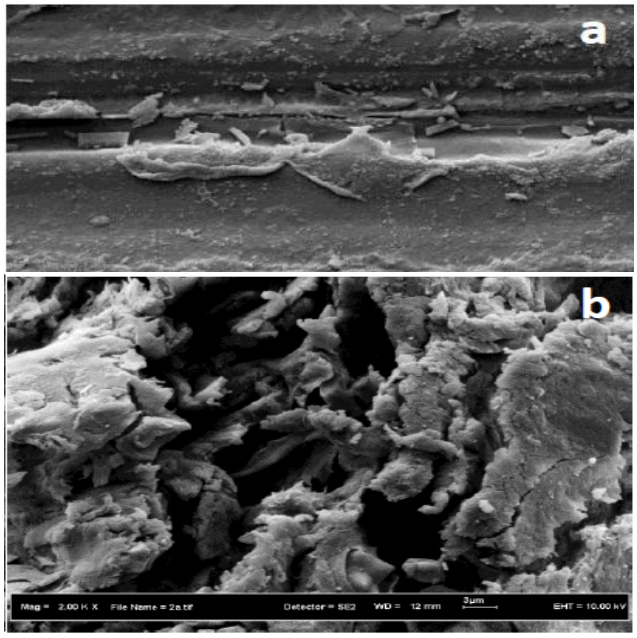


Figure 7 SEM images of (a) untreated OPF and (b) treated OPF using [BMIM]Br

3.5 OPF Lignin Degradation for Levulinic Acid Production

The pretreated OPF sample with 88.2% lignin degraded has been used for levulinic acid production and compared with the untreated OPF sample. Levulinic acid is considered as one of the valuable chemicals due to its potential as an important basic chemicals such as methyltetrahydrofuran (MTHF); a solvent and fuel extender.[34] The results show that the pretreated OPF was favourable for acid hydrolysis in the production of levulinic acid. The hydrolysis of untreated OPF gave 18.2% levulinic acid yield while the pretreated OPF gave higher levulinic acid yield; 25.3%. The recalcitrance of lignocellulosic biomass has made it difficult for the hydrolysis process in converting biomass to levulinic acid. The reduction in cellulose crystallinity and degradation of the lignin content by pretreatment method could enhance the product yield.[9,35] The amorphous cellulose in the lignocellulosic biomass could boost the acid catalyzed reaction due to high porosity of the materials, increasing the accessibility of catalyst to cellulose and the absence of inhibitor.

3.6 Reusability of [BMIM]Br

Another advantage of ionic liquid is the possibility to be recycled and reused.[12,36,37] In this study, [BMIM]Br was feasibly recycled 5 times while maintaining its activity as a biomass pretreatment solvent. The effect of recycled [BMIM]Br on lignin degradation and the effect of pretreated OPF using recycled [BMIM]Br on levulinic acid production are shown in Figure 8. From Figure 8, the difference between the first and fifth cycle for lignin degradation is 13%, while for levulinic acid yield is 11%. The decrease in levulinic acid yield for the later cycle was due to the extra amount of lignin content compared to the earlier cycle. The presence of lignin in the OPF has caused the less accessibility of catalyst to cellulose thus hinder the hydrolysis process for the production of levulinic acid.

Ionic liquids have been applied as solvent for lignocellulosic biomass pretreatment in recent years.[15,20,22,38] Regardless of its versatile properties, the usage of ionic liquid in biomass pretreatment has been restricted because of its high price. The pretreatment system with combination of ionic liquid with aqueous H_2SO_4 can clearly reduce the amount of ionic liquid used. The amount of biomass feedstock to ionic liquid used in our study was 20 wt%, which is much higher compared to previous studies.[11,39] On the other hand, the presence of aqueous H_2SO_4 could reduce the viscosity of the product for easier handling and recycling process.[25] Further studies on combined biomass pretreatment method are required in order to create an alternative route to enhance the efficiency of lignocellulosic biomass pretreatment.

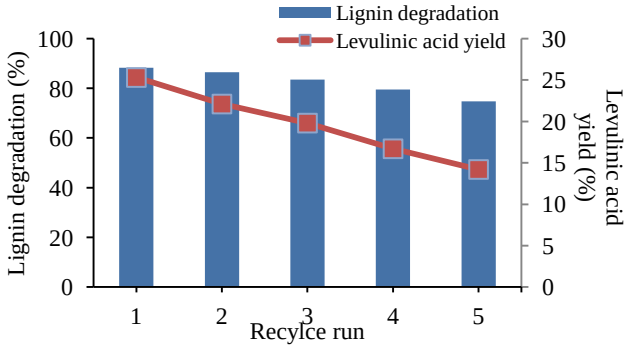


Figure 8 Reusability of [BMIM]Br for lignin degradation and levulinic acid production

4.0 CONCLUSION

This study examined the effect of reaction temperature, reaction time and [BMIM]Br loading on OPF lignin degradation by [BMIM]Br pretreatment in the presence of aqueous H_2SO_4 using Box Behnken design. Good correlations between the experimental and predicted lignin degradation were obtained. The optimum pretreatment conditions of 123°C, 175 min and 9.9 g [BMIM]Br loading has given 88.2% of lignin degradation. The pretreated OPF has a more porous and less crystalline structure which is a desired feature for subsequent hydrolysis step for levulinic acid production. In conclusion, the good performance of [BMIM]Br in

the presence of aqueous H_2SO_4 in enhancing the levulinic acid yield of the pretreated OPF has made this pretreatment process feasible. The feature of [BMIM]Br reusability was also investigated five times in order to improve the cost effectiveness of the entire pretreatment process.

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