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Ball milling pretreatment and diluted acid hydrolysis of oil palm empty fruit bunch (EFB) fibres for the production of levulinic acid

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ABSTRACT

Oil palm empty fruit bunch (EFB) fibres were pretreated by ball milling (BM) at different durations of times. The pretreated fibres were characterised by wide angle X-ray diffraction analysis, particle-size distribution and scanning electron microscopy while the effectiveness of the pretreatment was correlated with the yield of acid hydrolysis to produce levulinic acid (LA). The obtained results showed that the highest yield of LA (10.4 g/L, 52.08%) can be achieved from the 12 h BM pretreated EFB fibres. Further BM pretreatment exceeding 12 h has no significant effect on the LA yield. Optimisation process was further carried out by applying central composite with rotatable design to verify the optimum parameter (H_2SO_4 concentration, temperature, and time) to produce LA. The optimal conditions for the LA production from the EFB fibres were 0.57 N H_2SO_4, 185.98 °C, and 195.77 min for producing 10.77 g/L (53.93 %) of LA.

1. Introduction

The increasing demand on fossil fuel has dramatically risen up price of crude oil and caused great challenge to economic growth worldwide. This has encouraged researchers to search for alternative resources that can be converted into products, such as fine chemicals, bioethanol, and biofuel [1,2]. In this case, lignocellulosic biomass has been well reported as a promising resource [3,4].

Malaysia is the second largest palm oil producers in the world. Accompanying the production of 1 kg of palm oil, approximately 4 kg of dry biomass is generated, in which one third of the biomass is oil palm empty fruit bunch (EFB) [5]. Data provided by the Malaysian Palm Oil Board (MPOB) shows that a total of 17.86 million tonnes of crude palm oil was produced in Malaysia in 2009, revealing that there was 100 million dry tonnes of solid biomass including oil palm empty fruit bunches (EFBs), mesocarp fibres (MF), palm kernel shells (PKS), oil palm trunks and fronds were produced in that particular year [6]. The high carbohydrate content (42.7–65% cellulose, 17.1–33.5% hemicellulose) in oil palm EFB, mainly cellulose and xylan, makes it an attractive raw material to be converted into fermentable sugars or other basic chemical feedstocks [7,8].

Similar to other lignocellulosic materials, oil palm EFB fibres contain high amount of lignin which could be recalcitrant to conversion process via chemical and biological approaches. Pretreatment is an important process to remove lignin and increase accessibility of cellulose and hemicellulose in the lignocellulosic biomass prior to hydrolysis processes. Over the years, various pretreatment methods were studied, including chemical, physical, biological and chemical–physical pretreatments [9,10]. Chemical pretreatment mainly involves the usage of chemicals, such as acid, alkaline and organic solvent, which is normally performed at high temperature and high pressure. Utilisation of aggressive chemicals at high temperature possesses disadvantages such as the requirement of equipment with high resistant to corrosion, treatment of effluent and formation of inhibitors [11].

Ball milling (BM) has been proven to be an effective method to pretreat lignocellulosic biomass [12]. Several previous studies reported the enhancement of acid hydrolysis yield by conducting BM pretreatment on lignocellulosic biomass [13–15]. BM helps in reducing crystalline region of the cellulose, thus increases the accessibility of catalysts to the β-1,4-glycosidic bonds of cellulose [13,16].

Besides fermentation process to produce bioethanol from lignocellulosic biomass, chemical applications are also attractive. Practically, acid hydrolysis is one of the effective processes in converting lignocellulosic biomass into various fine chemicals, such as sorbitol, 5-HMF, levulinic acid (LA), and γ-valerolactone (GVL). LA is one of the platform chemicals which can be directly produced from lignocellulosic biomass via acid hydrolysis process. In the past few years, LA has been studied extensively by acid hydrolysis and produced from various types of lignocellulosic biomasses, such as sugarcane baggase, wheat straw, water hyacinth plant and

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Miscanthus giganteus [17–20]. LA is a highly versatile chemical with numerous industrial uses to produce resins, plasticisers, textiles, animal feed, coatings and antifreeze. Furthermore, LA can be reduced to produce GVL, which has been well known as a versatile molecule for the production of fuels and chemicals [21,22]. In our previous study, acid hydrolysis of oil palm EFB fibres was conducted using a microwave reactor to understand the conversion process of the EFB fibre [23]. In the present study, BM was conducted to pretreat the oil palm EFB fibres before the acid hydrolysis process to produce LA. This work is mainly focussing on the effect of BM pretreatment on the physical properties of the EFB fibres, which were then correlated with the yield of LA obtained from the acid hydrolysis process. Further optimisation studies were conducted to investigate the effect of hydrolysis parameters, *i.e.*, acid concentration, temperature, and time which can significantly affect the yield of LA.

2. Experimental

2.1. Materials

Oil palm EFB fibres were purchased from Szetech Engineering Sdn. Bhd. The fibres were sieved into size ranging from 150 to 500 μm, followed by drying at 105 °C before BM process. Analytical grade chemicals, sodium hydroxide, NaOH (purity ≥99%) and sulphuric acid, H_2SO_4 (purity 95–98%) and LA (purity ≥99.5%) was purchased from Merck (Darmstadt, Germany). Glucose (purity ≥99.5%) and xylose (purity ≥99.5%) were purchased from Sigma–Aldrich (Shanghai, China).

2.2. Composition analysis

The EFB fibres were analysed for the contents of glucan, xylan, lignin, water extractives, ethanol extractives, and ash using NREL's Laboratory Method [24,25]. Sugars (glucose and xylose) were measured by HPLC (LC-20A, Shimadzu, Japan) with an Aminex HPX-87P column (300 × 7.8 mm, Bio-Rad, California) equipped with a refractive index detector (RID-10A, Shimadzu) operated at 80 °C and flow rate 0.6 ml/min using ultra-pure water as mobile phase. Sugars were calibrated using standard sugar solution with different concentrations. Elemental analysis was carried out using an organic elemental analyser (Elementar Analysensysteme GmbH D-63452 Hanau, Germany) via combustion under oxidised condition at temperature 950 °C. All composition analyses were conducted in duplicates.

2.3. Methods

2.3.1. Pretreatment

A SHQM planetary ball miller (Chun Long instrument, Lianyungang City, Jiangsu Province, China), with four ceramic milling cylinders (50 mL), was used to carry out the BM pretreatment. Five gram of EFB fibres was placed into each cylinder with 10 (Ø = 10 mm) and 40 (Ø = 6 mm) ceramic balls. The mill rotated horizontally at a constant speed of 230 rpm for a total time of 6–24 h at room temperature. After the BM process, the EFB fibres were stored in a dessicator for further use. While, moisture content of the EFB fibres was measured using a moisture analyser (AND MX-50, New York).

2.3.2. Acid hydrolysis

Acid hydrolysis of the EFB fibres was carried out using a 60 mL capacity local fabricated high pressure stainless steel autoclave with Teflon-lined at 160–200 °C in a furnace. For a typical run, 0.25 g EFB fibres was mixed with 5 mL of 0.5 N H_2SO_4 and heated at 160–200 °C for various reaction times (60, 120 and 180 min). After the hydrolysis process, the autoclave was quickly immersed into an ice water bath to stop the reaction. The hydrolysate was centrifuged at 12,000 rpm for 15 min to separate the solid and liquid phases. The obtained solution was then neutralised with 0.25 N NaOH solution before further chemical analyses to determine the concentration of LA using a high performance liquid chromatography (HPLC; Agilent 1260 series, United States and Zorbax Sb-Aq column with a refractive index (RI) detector operated at 35 °C and flow rate 0.6 mL/min using 5 mmol H_2SO_4 as mobile phase.

Table 1
Main chemical components of oil palm EFB fibres.

Components	Mass fraction in percentage (%)
Lignin (acid soluble)	5.78 ± 0.02
Lignin (acid insoluble)	18.68 ± 0.19
Glucan	39.94 ± 0.96
Xylan	27.06 ± 0.63
Ash	1.57 ± 0.20
Extractives	9.49 ± 0.51
Elements	**Percentage (%)**
Carbon	46.83 ± 0.83
Hydrogen	6.20 ± 0.35
Nitrogen	0.53 ± 0.04

2.4. Characterisation

2.4.1. X-ray diffraction

Powder X-ray diffraction of the raw and pretreated EFB fibres was obtained using an X-ray diffractometer (Bruker AXS D8 Advance, United States). The sample was scanned at a range of 5-60°. The degree of crystallinity (*CrI%*) of the EFB samples was determined using Segal's equation as follows:

$$CrI\% = [(I_{002} - I_{AM})/I_{002}] \times 100\% \quad (1)$$

2.4.2. Scanning electron microscope (SEM)

Morphology of the raw and pretreated EFB fibres was observed using a scanning electron microscope (SEM-Philips XL-30, United States).

3. Results and discussion

3.1. Composition elemental analysis

The major components of lignocellulosic materials are made up of carbohydrates and lignin. Therefore, these components must be determined for the analysis of lignocellulosic biomass and the conversion yield of fine chemicals. Table 1 shows the components and the element analysis of EFB fibres. The main fractions of EFB fibres composed of xylan and glucan with 27.04% and 39.94%, respectively. High content of glucan makes EFB fibres a suitable raw material for the production of LA and other fine chemicals.

3.2. Average size and degree of crystallinity of EFB fibres after BM pretreatment

Table 2 presents the particle size and CrI (%) of the EFB fibres after BM for time ranging from 6 to 24 h. The particle size of the EFB fibres was determine using sieve shaker (Octagon) stacked column of standard sieve-test trays of different mesh sizes. During the first stage of

Table 2
Size and degree of crystallinity of EFB fibres.

Sample	Size (μm)	CrI (%)
Raw	125–500	57.16
BM6	125–150	57.09
BM12	80–106	49.49
BM18	63–80	47.25
BM24	<63	42.83

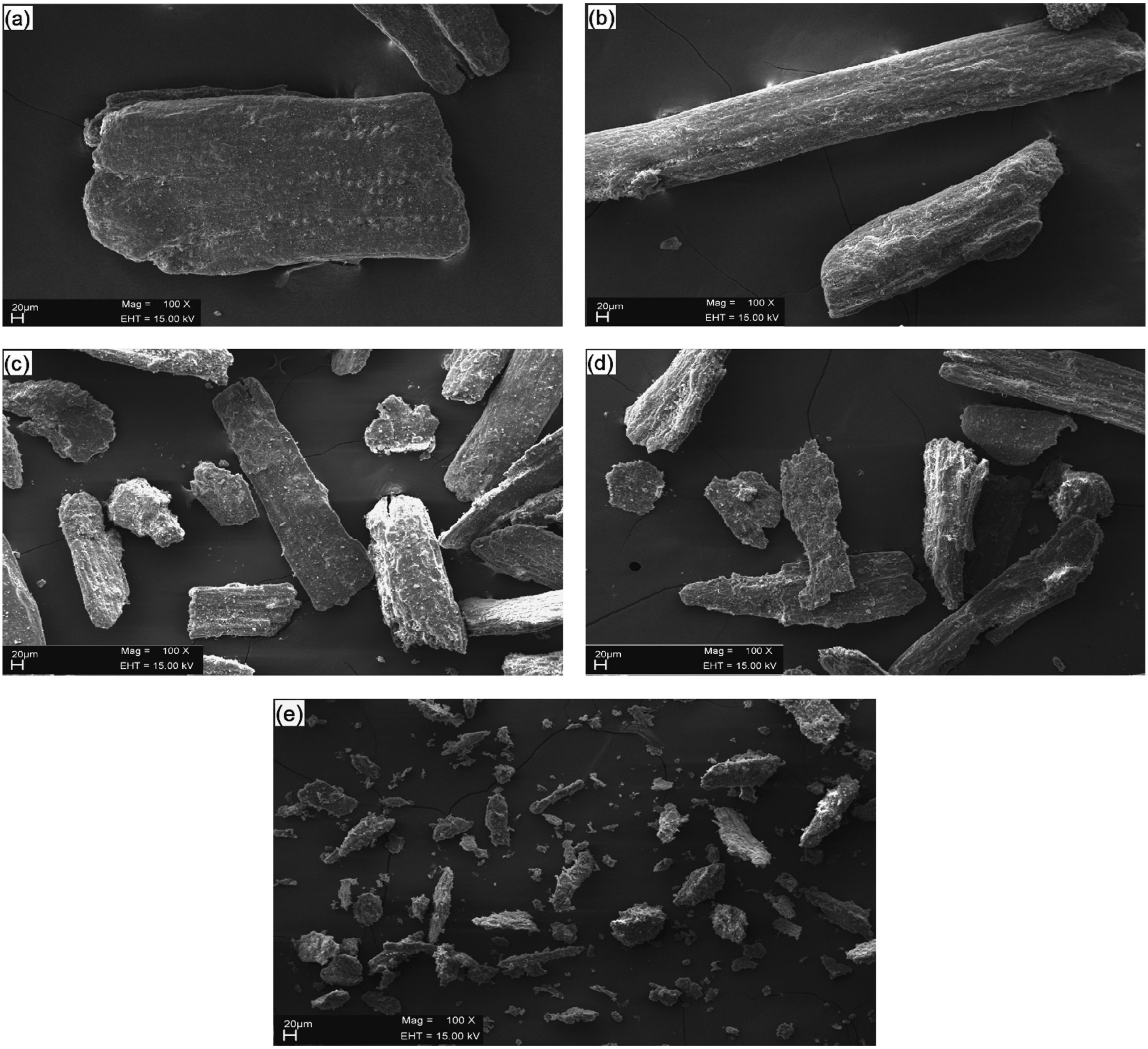

Fig. 1. SEM micrographs of BM pretreated EFB fibres: (a) 0 h, (b) 6 h, (c) 12 h, (d) 18 h and (e) 24 h.

the BM (6 h) the average particle size of the fibres remained practically unchanged as compared to the raw EFB fibres. However, the particle size of the EFB fibres has been reduced significantly as the durations of BM increased further. Besides, the CrI (%) of the EFB fibres obtained from the diffraction peak of cellulose decreased with the BM time. This suggested the diminishing of cellulose crystalline region during the BM process and it has been proven that ball milling produces fine particles with reduced crystallinity of the cellulose [12,16,26,27].

3.3. *Scanning electron microscope (SEM)*

The morphology of the ball milled EFB fibres is shown in Fig. 1a–e. As can be seen from Fig. 1a, the surface of the untreated EFB fibres is smooth and rigid. As the time of BM increased, a progressive reduction in the particle size of the EFB fibres was observed (Fig. 1b–e). After being ball milled for 24 h, the structure of the EFB fibres was completely disrupted resulted in rougher fibre surface [16,28].

3.4. *Effect of BM on the acid hydrolysis conversion of EFB fibres to levulinic acid*

After the BM pretreatment, the EFB fibres underwent acid hydrolysis reaction using 0.5 N H_2SO_4 at different temperature (160–200 °C) to produce LA. The yield of LA obtained at different temperature and hydrolysis time is shown in Fig. 2. As expected, BM time increases the reaction rate of EFB fibres into LA as in Fig. 2a. BM will cause changes in the physical structural of EFB fibres thus weakening the hydrogen bond network between hemicellulose, cellulose and lignin, making the cellulose within the EFB fibres more accessible [13,27]. This is consistent with the XRD, particles size and SEM results where the decrease in crystallinity of cellulose will enhance the hydrolysis process. Overall, BM time was advantageous for acid hydrolysis to produce LA. From Fig. 2a, the effects of BM pretreatment are significant for both acid hydrolysis reaction for 60 and 120 min. However, reaction for 180 min the effect of BM pretreatment reached a plateau in

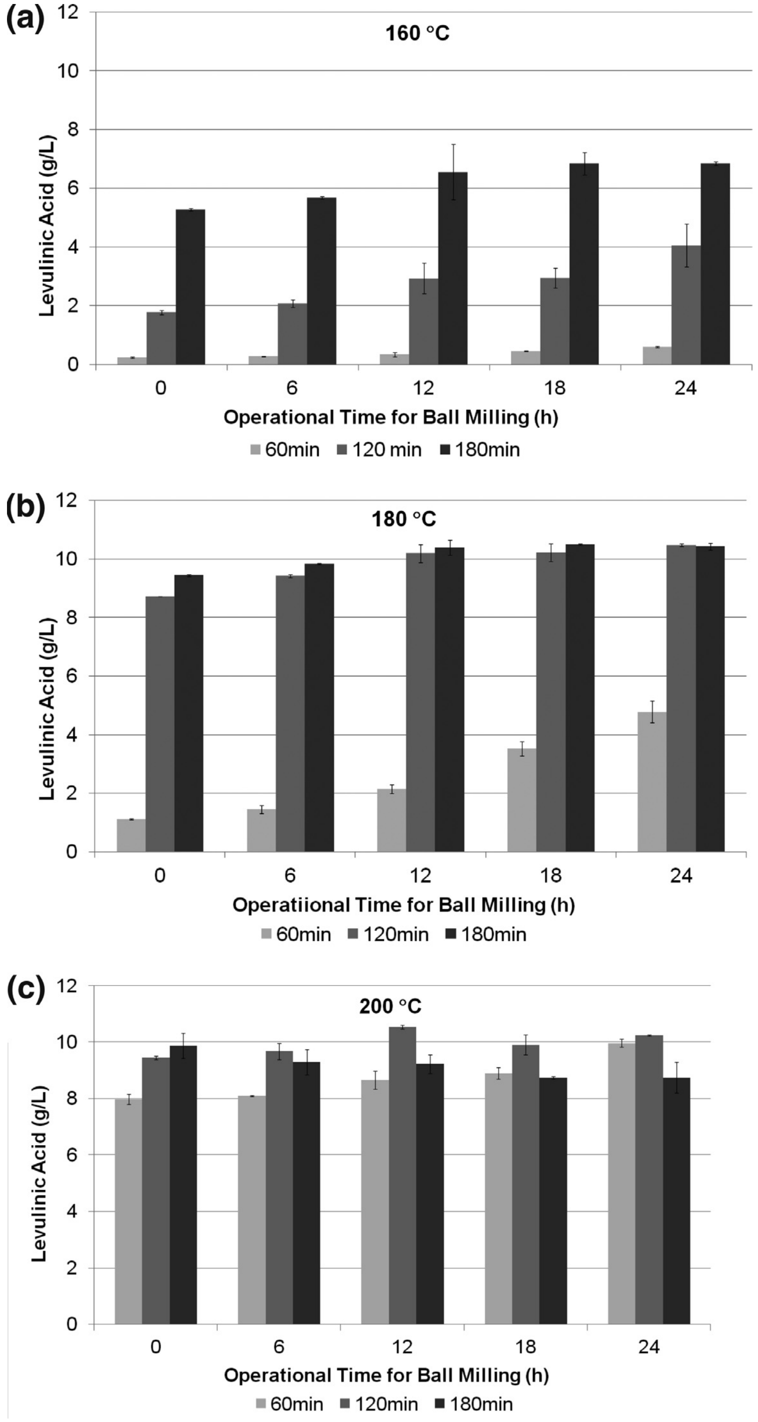

Fig. 2. LA yields of BM pretreated EFB fibres for different durations of time using 0.5 N H_2SO_4: (a) 160 °C, (b) 180 °C and (c) 200 °C.

producing LA (BM > 12 h). This indicates that at longer reaction time, energy required to disrupt the crystalline domains of EFB fibres before acid hydrolysis process to occur to produce LA is not significant.

Fig. 2b shows the yield of LA when acid hydrolysis carried out at 180 °C. Similar trends of LA yield as compared with Fig. 2a. However, the formation of LA from EFB fibres was faster at higher reaction temperature. Reaction temperature has a significant effect on the hydrolysis product yield. In which, higher temperature tends to enhance the rate of hydrolysis thus shortens the reaction time [29]. The overall acid hydrolysis reaction carried out at 180 °C gives higher yield of LA as compared with reactions carried out at 160 °C.

Fig. 2c shows the yield of LA for acid hydrolysis at 200 °C. The effect of BM at this reaction temperature is less significant than that of 160 and 180 °C. In this case, it can be observed that ball milled pretreated EFB fibres with different CrI (%) and particle size play only a minor role in the reaction of EFB fibres to produce LA. This could be explained that at higher reaction temperature, *i.e.*, 200 °C, energy required to disrupt the crystalline domains of the EFB fibres before acid hydrolysis process to occur to produce LA is not significant. Which mean that the effect of particle size of EFB fibres in the conversion to produce LA is less significant as the reaction temperature increases. Besides, as shown in Fig. 2c, the yield of LA decreases as the reaction

Table 3
Experimental design and response of yield of LA.

Factor	Symbol	Levels		
	Coded	–	0	+
Acid concentration (*N*)	X_1	0.25	0.5	0.75
Temperature (°C)	X_2	180	200	220
Time (min)	X_3	90	150	210

time increases. Theoretically, higher temperature and longer reaction time are favourable to the hydrolysis of EFB fibres to LA. However, unwanted side reactions also built up at the same time [18, 30]. Moreover, at 180 °C, glucose converted from the EFB fibres' cellulose was almost completely converted into LA. Hence, higher temperature (200 °C) will not further enhance the yield of LA. Therefore, the optimal BM time for EFB fibres is 12 h.

3.5. *Optimisation (design of experiment)*

Further optimisation of the acid hydrolysis of the EFB (RSM) was conducted out using response surface morphology. As above, it can be concluded that the optimal BM time for EFB fibres is 12 h. Therefore, the BM12 EFB fibres were selected for this study.

Two-level full factorial design (2^3) was applied in this study with three factors: X_1 (acid concentration, *A*), X_2 (temperature, *T*), and X_3 (time, *t*). Each factor was tested at three levels as shown in Table 3. These variables were coded according to Eq. (2).

$$X_i = \frac{x_i - x_0}{\Delta x_i} \tag{2}$$

where X_i, x_i and x_0 are the coded value, real value and centre point for the independent variable, respectively. While Δx_i is the step change value. the specific codes are as shown in Eqs. (3), (4) and (5).

$$X_1 = \frac{A - 0.5}{0.25} \tag{3}$$

$$X_2 = \frac{T - 200}{20} \tag{4}$$

$$X_3 = \frac{t - 150}{60} \tag{5}$$

A central composite with spherical design was employed to demonstrate the effect of independent variables on the response in the experimental region, *i.e.*, acid concentration, temperature and reaction time. In spherical design (rotatability), the properties of rotating points of the design are about the centre of the factor space where the variance of prediction depends only on the scaled distance from the centre of the design. This causes the axial points to be more extreme than the range of the factor. A total of 18 runs of experiments with four centre points and rotatabilility points was designed as ±alpha ($\pm\alpha$; ±1.682) were carried out. Centre point is important in relating the variance of a predicted value and to verify the prediction to be reliable throughout the region.

A second order polynomial model for the predicted response of LA yield (*Y*) was then developed, as shown in Eq. (5), where β_0 is the offset term, β_1, β_2, and β_3 are the linear effect terms, β_{11}, β_{22}, and β_{33} are the squares effects, and β_{12}, β_{13}, and β_{23} are the interaction effects.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \tag{6}$$

This polynomial equation is to describe the relationship between the independent variables and the response variables. The significance of each equation coefficient was determined by *P*-values. The quality of the fit of the polynomial model equation was evaluated by the coefficient of determination R^2, its statistical and regression coefficient significance were checked with *F*-test and *t*-test, respectively. Meanwhile, the fitted polynomial equation was expressed by surface plots in order to visualise the relationship between the independent variables and the response variables to deduce optimum conditions for this acid hydrolysis reaction.

Table 4
Central composite design and results of the LA yield obtained from acid hydrolysis of EFB fibres.

	Pattern	Acid (*N*)	Temperature (°C)	Time (min)	LA (g/L)
1	$-\alpha00$	0.08	200	150	4.76
2	$---$	0.25	180	90	2.79
3	$--+$	0.25	180	210	9.98
4	$-+-$	0.25	220	90	5.49
5	$-++$	0.25	220	210	7.90
6	$0-\alpha0$	0.5	166.36	150	8.00
7	$00-\alpha$	0.5	200	49.09	4.14
8	000	0.5	200	150	10.25
9	000	0.5	200	150	10.20
10	000	0.5	200	150	9.98
11	000	0.5	200	150	10.01
12	00α	0.5	200	250.91	9.00
13	$0\alpha0$	0.5	233.64	150	7.90
14	$+--$	0.75	180	90	8.94
15	$+-+$	0.75	180	210	10.11
16	$++-$	0.75	220	90	9.45
17	$+++$	0.75	220	210	8.45
18	$\alpha00$	0.92	200	150	8.83

3.5.1. *Experimental design and statistical analysis*

The experimental matrix for the design and the responses for the production of LA from EFB fibres are shown in Table 4.

A quadratic model was fitted to the experimental data for LA yield as follows:

$$Y = 10.0618 + 1.2926X_1 - 0.0513X_2 + 1.3141X_3 - 0.9627X_1^2 - 0.5548X_2^2 - 1.0407X_3^2 - 0.2225X_1X_2 - 1.1803X_1X_3 - 0.8696X_2X_3 \tag{7}$$

where *Y* is the responses (LA yield) for the testes variables in coded units, *i.e.*, X_1 (acid concentration), X_2 (temperature) and X_3 (time).

Fig. 3 shows that the fitted model accounted for over 95.42% of the variation in production of LA for EFB fibres via diluted acid hydrolysis and the adjusted R^2 is 90.27%. Only 4.58% of the total variability was not explained in the regression models. Both coefficient of determination (R^2 and adjusted R^2) demonstrates the agreement between the experimental and predicted yield of LA which can provide a good estimate of the response within the process conditions range [31,32].

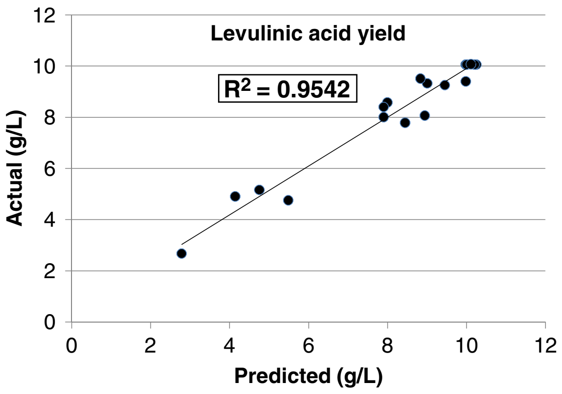

Fig. 3. The coefficient of determination and predicted *versus* observed values for LA yield.

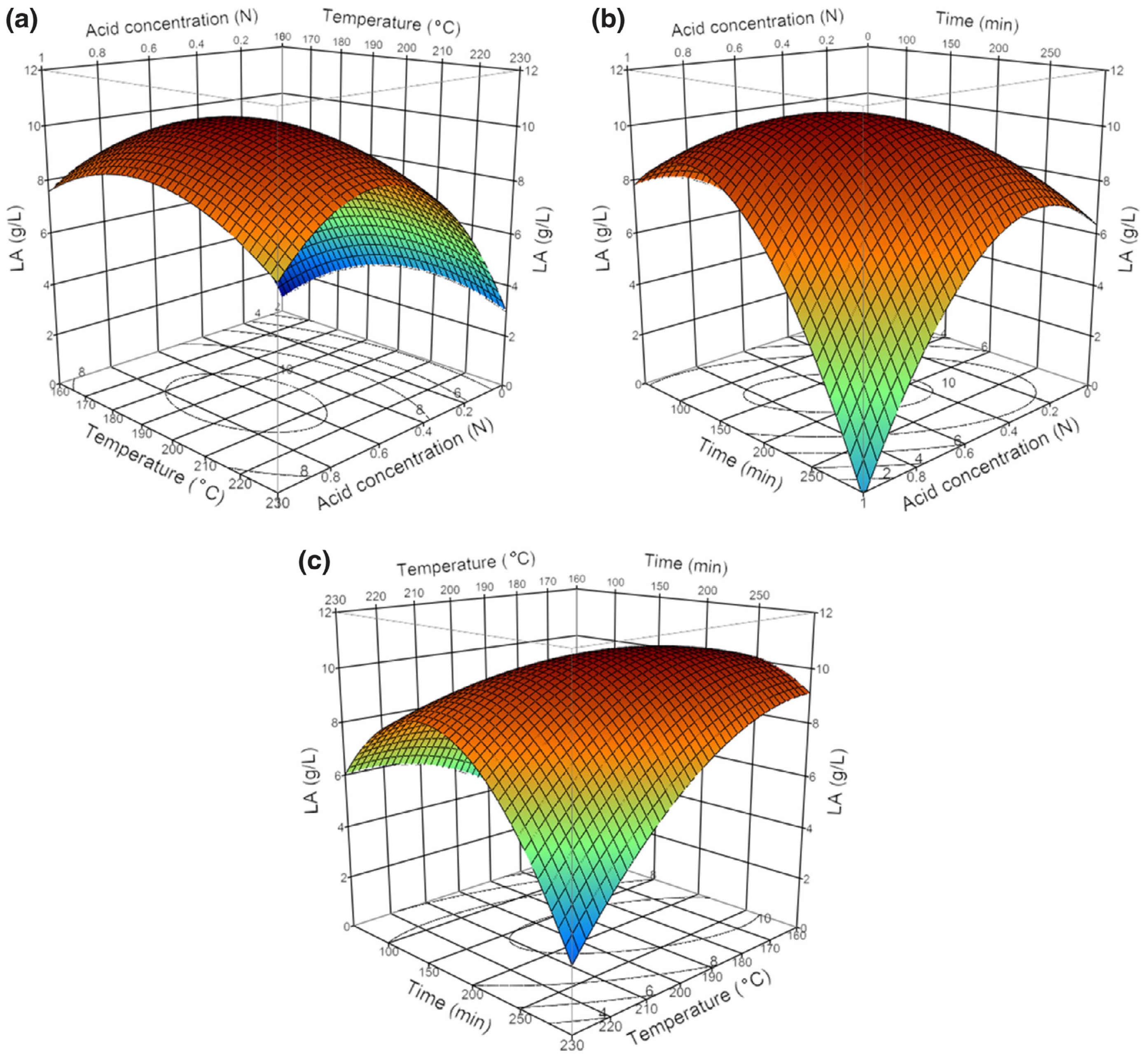

Fig. 4. 3D response surface plots of acid hydrolysis optimisation for LA yield: (a) LA yield *versus* acid concentration *versus* temperature, (b) LA yield *versus* acid concentration *versus* time and (c) LA yield *versus* temperature *versus* time.

The coefficients obtained from Eq. (6) are shown in Table 5. The estimated parameters show the coefficients and significance of the linear, cross product and quadratic terms on each response. From Table 5, absolute magnitudes in relation to the statistical significance *P*-level of 0.05 are showed. The greater the magnitude of the *t*-value and the smaller the *P*-value, the more significant was the corresponding coefficient [18,33]. For instance, the main variable of acid concentration (X_1) and time (X_3) has remarkable effects on the yield of LA with the largest *t*-value (6.66 and 6.77) and smallest *P*-value (0.0002 and 0.0001). Besides, it can be seen the conversion of EFB fibres to LA also significantly affected by the cross product of acid concentration × time ($X_1 \times X_3$) and temperature × time ($X_2 \times X_3$) and quadratic of acid concentration (X_1^2), temperature (X_2^2) and time (X_3^2). This means that the productions of LA from EFB fibres were directly related to these three main factors. This can be further correlated with the contour plot as shown in Fig. 4a–c. In which the shape of

Table 5
Significance of regression coefficient of LA yield.

Parameter estimates				
Variables	Regression coefficient	Standard error	*t* value	Significance level, *P*-value
Intercept	10.06177	0.357897	28.11	<0.0001*
X_1	1.292595	0.193977	6.66	0.0002*
X_2	−0.05127	0.193977	−0.26	0.7982
X_3	1.314126	0.193977	6.77	0.0001*
X_1X_2	−0.22248	0.253444	−0.88	0.4056
X_1X_3	−1.18025	0.253444	−4.66	0.0016*
X_2X_3	−0.86964	0.253444	−3.43	0.0089*
	−0.96265	0.201556	−4.78	0.0014*
	−0.55481	0.201556	−2.75	0.0250*
	−1.04067	0.201556	−5.16	0.0009*

* Significance variables.

Table 6
Analysis of variance and canonical analysis.

Source	DF	Sum of squares	Mean square	*F*-value	Probability > *F*	R^2
Model	9	85.653749	9.51708	18.5204	0.0002*	0.9542
Error	8	4.110954	0.51387			R^2 adjusted
C. total	17	89.764704				0.9027
			Canonical analysis			
	X_1	X_2	X_3	Predicted yield of LA at solution: 10.7650 g/L		
Eigen value	−0.2100	−0.6191	−1.7290			
Actual value	0.5712 N	185.9759 °C	195.7746 min			

the corresponding contour plots can indicate the significance level for the interactions between variables. Elliptical contours can be achieved when there is a good interaction between independent variables [34].

Furthermore, a significance testing on the regression models via analysis of variance (ANOVA), which focussed on the relationship between dependent and independent variables were performed using the obtained experimental data and the results are shown in Table 6. The ANOVA with low probability 0.0002 shows that the fitted model is highly significant [35].

3.5.1.1. Variables effect of acid concentration on LA yield. The predicted optimal conditions for the acid hydrolysis of EFB fibres to produce LA are illustrated in Fig. 4a–c which was obtained based on the regression equation (Eqn. (6)). These 3D response surfaces and the corresponding contour plots are generated to illustrate the interactive effects between the independent variables on the reaction response. From Fig. 4a–c, the maximum predicted yield of LA was indicated by the surface confined in the smallest ellipse in the contour diagram.

Fig. 4a and b shows that acid concentration is an important effect in the production of LA from the EFB fibres in which the linear and quadratic effect of acid concentration is significant (*P*-value). At the beginning, LA yield increased with the increase in acid concentration in which higher acid concentration will tend to enhance the rate of hydrolysis [17]. However, a quadratic of acid concentration on the response was observed from Fig. 4a and b in which higher acid concentration (>0.57 N) will not further enhance the yield of LA. This is because higher acid concentration might create an adverse effect on the yield of LA where higher acid concentration might enhance the formation of humic products or unwanted side reactions might occurred at the same time [18,30]. According to Yang et al. [29], higher acid concentration is bad for the formation of LA because of remarkable dehydration reaction. Besides, there is also a significant interaction between acid concentration and reaction times where at low acid concentration, a longer reaction time was required to obtain high yield of LA and *vice versa*.

Fig. 4a and c shows the effect of temperature on the yield of LA. Basically, temperature is one of the main effects that influence the yield of hydrolysis. Previous studies also proved that temperature is important in disrupt the rigid structure of lignocellulosic materials during hydrolysis, in which higher temperature could enhance the rate of hydrolysis [17,36]. In this study, the main effect of temperature is not significant. This is because the range of temperature in this optimisation is from 180 to 220 °C. However, maximum yield of LA can be achieved at 185.98 °C. This can be correlated with the quadratic effect of temperature (X_2^2) on the response was observed when temperature >185.98 °C will not boost the yield of LA, thus showing the similar trends as that of the acid concentration. This indicated that temperature is actually one of the key factors in enhancing the degradation of lignocellulosic materials during acid hydrolysis process. The interaction effect between temperature and time was significant ($P = 0.0089$) towards the yield of LA. In which the yield of LA is dependent on pairs of temperature and reaction time. Obviously, the higher the reaction temperature the shorter the reaction time is required to obtain high yield of LA and *vice versa*. According to Girisuta et al. [19], the activation energy of glucose to be degraded into humic products is 161.41 kJ/mol, for glucose into 5-HMF, the activation energy is 152.14 kJ/mol. This shows that higher temperature gives negative effect in the production of LA because the formation of humic favourable than that of 5-HMF, which will then be dehydrated into LA.

Fig. 4b and c shows the effect of reaction time on the LA yield. In this study, reaction time is highly significant affecting the yield of LA. In which the main variables, cross product and quadratic product are highly significant as shown in Table 5 (P-value). Again, quadratic effect of reaction time on the yield of LA was observed which indicated that longer reaction times cannot increase the yield of LA. This is because longer reaction times will favour the formation of humic and enhance unwanted side reactions. Besides, it was found that the yield of LA started to decrease after reaching a certain degree of optimisation. This result is in agreement with the previous studies [18,30]. The interaction effects between temperature and reaction time have revealed that the formation of LA increase linearly increased with increasing reaction temperature and reaction time. However, higher reaction temperature and time are not recommended because as the rate of hydrolysis increases, this will enhance the formation of side products [37]. Therefore, both reaction time and temperature reach an optimum point to give the highest yield of LA and the yield of LA started to decrease as the reaction time and temperature prolonged. Same phenomena can also be observed for the interaction effect between acid concentration and time, in which acid can increase the yield of LA until certain extend incorporating with appropriate reaction time [18].

3.5.1.2. Canonical analysis and optimum reaction conditions. Canonical analysis was further conducted and the results obtained are shown in Table 6. Canonical analysis is a multivariate technique which is focussed on determining the relationships between groups of variables in a data set. As can be seen, all the Eigen values were negative. This indicated that the stationary point was maximal [18]. The optimum parameters to achieve the highest LA yield are with acid concentration 0.57 N, reaction temperature 185.98 °C, and reaction time 195.77 min. The predicted maximum LA yield calculated to be 10.77 g/L (53.93% based on total percentage of cellulose in EFB fibres).Two confirmation runs, based on the predicted optimum conditions was performed to verify the stability of the model. The LA yield were 10.20 g/L and 10.26 g/L (51.08% and 51.38%), respectively. This is close to the predicted yield of LA. The choice of the optimal hydrolysis conditions is very important for maximum yield of sugars and minimal formation of unwanted sided reaction while giving high yield of desire product. The LA yield obtained from this study is comparable to previous reported studies on *M. giganteus*: 58–72 mol% of LA [17], wheat straw: 19.86% based on total weight of wheat straw [18], sugarcane baggase: 65 mol% (194 kg from 1 dry tonnes of sugarcane baggase) [19] and water hyacinth plant: 35 wt% of LA based on the total amount of C6 sugars [20]. All these were conducted at hydrolysis temperature ranging from 160 to 200 °C.

4. Conclusions

The combinations of BM pretreatment on EFB fibres have great potential use as a raw material for LA production due to its rich carbohydrates content. Moreover, no chemicals were required in this process. BM improved the acid hydrolysis process by decreasing the degree of crystallinity and particles size of the EFB fibres. BM for 12 h was chosen as the optimal parameter because longer BM time shows insignificant effect on hydrolysis process to produce LA. From the optimisation process, LA yield increased as the acid concentration, reaction temperature and reaction time increased. However, further increase of these three variables had an adverse effect on LA yield. Therefore, an optimise condition was achieved via experimental design in which acid concentration 0.57 N, reaction temperature 185.98 °C, and reaction time 195.77 min can obtained 10.77 g/L (53.93%) of LA. A linear regression model was capable of predicting the LA yield with respect to the effects of reaction temperature, acid concentration and reaction time ($R^2 = 0.9542$). It is concluded that the combination of BM pretreatment is an environment-friendly method approach to pretreatment of EFB fibres to produce LA thus improve the suitability of this abundantly available lignocellulosic material.

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