

OPTIMIZATION STUDIES OF OIL PALM EMPTY FRUIT BUNCH LIQUEFACTION FOR CARBON CRYOGEL PRODUCTION AS CATALYST IN LEVULINIC ACID ESTERIFICATION

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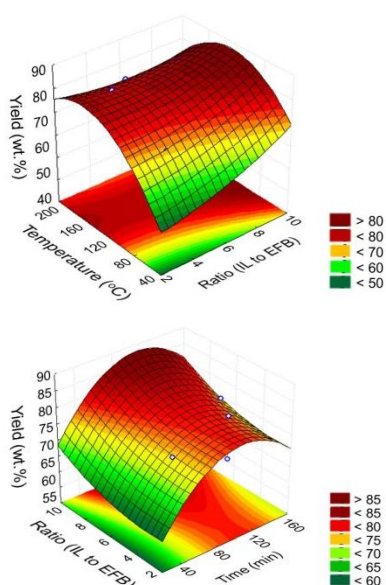
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Article history

Received
2 August 2017
Received in revised form
28 September 2017
Accepted
10 January 2018

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Graphical abstract



-3D plots of liquefied EFB yield-

Abstract

Liquefaction of oil palm empty fruit bunch (EFB) using 1-butyl-3-methylimidazolium chloride was investigated in this study. The experiments were designed based on central composite by response surface methodology (RSM). The optimum conditions for the predicted liquefied EFB yield of 80.97 wt% was obtained at the temperature of 151.9 °C, a reaction time of 112.78 min and a ratio (Ionic liquid to EFB) of 4.27. The Regression coefficient (R^2) for the model was 0.90 indicating a high correlation between observed and predicted values. The liquefied EFB mixture was used in the preparation of carbon cryogel via a sol-gel poly-condensation reaction and calcination process. The presence of sulfuric acid during the gel synthesis promoted an active site on the gel linkage and surface. The carbon cryogel prepared was tested as catalyst in an esterification reaction. The conversion of levulinic acid and yield of ethyl levulinate were reported as 58.7% and 57.2 mol%, respectively.

Keywords: Liquefaction, oil palm empty fruit bunch, biomass, carbon cryogel, ethyl levulinate, esterification

Abstrak

Pencairan tandan kelapa sawit (EFB) dengan menggunakan 1-butyl-3-metillimidazolium klorida di siasiat dalam kajian ini. Eksperimen di rangka menggunakan komposit pusat oleh kaedah permukaan tindak balas (RSM). Keadaan optimum bagi jangkaan hasil pencairan EFB ialah 80.97 wt% yang terhasil pada 151.9 °C, masa tindak balas 112.78 min dan nisbah (cecair ionik kepada EFB) 4.27. Pekali regresi (R^2) bagi model telah ditemukan kepada 0.90. Ini menunjukkan bahawa terdapat perkaitan yang tinggi diantara nilai yang di pantau dan nilai jangkaan. Campuran pencairan EFB telah digunakan bagi penyediaan karbon kriogel melalui tindak balas poli-kondensasi sol-gel dan proses pengkalsinan. Kehadiran asid sulfurik semasa penghasilan gel telah menggalakan tapak aktif pada hubungan gel dan permukaan. Karbon kriogel yang terhasil telah diuji sebagai pemangkin dalam tindak ballas pengesteran. Penukaran asid levulinik dan hasil etil levulinat yang dilaporkan masing-masing sebanyak 58.7% dan 57.2 mol%.

Kata kunci: Pencairan, tandan kelapa sawit, bio-jisim, karbon kriogel, etil levulinat, pengesteran

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1.0 INTRODUCTION

There have been increasing efforts into research and development for effective utilization of waste biomass. The utilization of waste biomass is indeed important from the energy, economic, and environmental aspects. Millions of tonnes of waste biomass by-products such as agricultural crops, wood wastes, and pulp process wastes are generated every year.

Malaysia is the largest producer of palm oil in the world and its production accounts for 40–60% of total world palm oil production [1]. Oil palm empty fruit bunch (EFB) is a waste biomass, produced by palm oil mills. The Malaysia palm oil industry generates approximately 140 million tonnes of waste biomass every year from the processing of palm oil, of which EFB comprises 20 million tonnes. EFB is used for animal feeds, organic fertilizers, allowed to decay naturally in fields, or discarded or burnt. In order to provide efficient, sustainable and green energy, it is necessary to use waste biomass resources effectively.

A thermochemical process usually works on lignocellulosic biomass in order to convert it into useful product. One possible application is liquefaction to produce bio-oil. The liquefaction has been conducted at high temperature to produce bio-oil rich in phenolic fraction. Previously, several liquefaction processes have been applied to lignocellulosic biomass such as liquefaction of EFB in alkaline hot compressed water [2], hot-compressed water for liquefaction of sawdust and cornstalk [3], and hot-compressed phenol-water in liquefying cornstalk powder [4]. The potential of lignin in lignocellulose compounds to be liquefied and also to produce lignin-derived phenolic compound has been explored. The conditions used are quite different: moderate temperature in the presence of acid catalyst and different solvent such as ionic liquids compared to production of bio-oil by liquefaction in water at high temperature that produces bio-oil. Previous studies report that liquefaction was carried out for conversion of biomass into phenolic product at medium temperature using phenol or ionic liquid in the presence of acid catalyst [5-7].

Phenol is a highly toxic chemical for the application in biomass conversion. Thus, the application of ionic liquids as solvents has been applied in liquefaction. In addition, the biomass liquefaction products have been explored in organic gel or resin production. Phenol and its derivatives are usually used with formaldehyde as the feedstocks in gel synthesis. Previously, tannin and furfural [8] and lignin and furfural [9] have been used as substitutes for phenol and formaldehyde. Use of ionic liquid as composite in the synthesis of gel has been reported [10]. Different types of gel structures are produced with different feedstocks. Therefore, the study on gel synthesis by using liquefied biomass in ionic liquid mixture with furfural has been conducted. The

synthesized gel was freeze-dried to produce cryogel and finally carbonized into carbon cryogel. Based on our previous studies, the carbon cryogel produced have potential to be applied as acid catalyst for the esterification reaction [9,11]. As for the ethyl levulinate production, many acid catalysts have been applied for the reaction between levulinic acid and ethanol to produce ethyl levulinate [12-17]. Ethyl levulinate is useful as oxygenate additive in fuels [18], diesel miscible biofuel [12] and also as flavoring agent and precursor for production of γ -valerolactone (GVL) [19].

The objective of the present study is to determine the optimum conditions for the liquefaction of EFB with ionic liquid (IL). The effects of process variables, such as temperature, reaction time and IL/EFB ratio were studied using a Central Composite Design (CCD). The solid and liquid samples in the liquefaction process were characterized with Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). In addition, the liquefied EFB was used to produce carbon cryogel as acid catalyst. The carbon cryogel was tested in the synthesis of ethyl levulinate from the catalytic esterification of levulinic acid and ethanol.

2.0 METHODOLOGY

2.1 Material

Oil palm empty fruit bunch was obtained from Malaysian Palm Oil Board (MPOB), Bandar Baru Bangi, Kajang Selangor. The EFB was dried for 24 h in air at room temperature before being further shredded and crushed in a high-speed rotary cutting mill to give a particle size in the range of 0.4-1.0 mm. Then, it was dried in an air circulated oven at 105 °C for 8 h to remove any remaining moisture. The composition of EFB is shown in Table 1 [20].

Table 1 Composition of EFB (wt%, dry-weight basis) [20]

Components	Composition (wt%)
Cellulose	45.9
Hemicellulose	14.9
Lignin	28.2
Ash	8.9
Others	2.1

The ionic liquid 1-butyl-3-methylimidazolium chloride [BMIM][Cl] and cellulose microcrystalline powder were supplied by Sigma-Aldrich, USA. Sulfuric acid (H₂SO₄), ethanol (C₂H₅OH), and furfural were purchased from Merck, Germany.

2.2 Liquefaction of EFB

0.5 g of EFB was mixed with an ionic liquid in various ratios (IL/EFB around 4 to 8), different temperatures

(between 80 and 160 °C) and holding times (between 60 and 120 min) without the presence of acid catalyst. The experimental runs were conducted based on the design of experiment (section 2.4). The EFB and [BMIM][Cl] were charged into a 500 mL three-necked round-bottom flask equipped with a Teflon-coated magnetic stirrer bar and thermometer. Then, the flask was immersed in a silicone oil bath at specific temperatures and times. Response surface methodology (RSM) was used to find optimum conditions for the liquefaction process based on design of experiment (DOE). After the heating process was completed, the mixture was washed repeatedly with water and acetone mixture (1:1) and vacuum filtered to separate the solid residue from liquefied product. The solid residue and liquid product were oven dried at 105 °C for 24 h.

2.3 Lignin Degradation

0.1 g EFB was mixed well into a 20 mL of aqueous 0.02 mol/L potassium permanganate (KMnO₄) with 5 mL of 2.0 mol/L sulfuric acid (H₂SO₄) mixtures for 3 min. Oil palm empty fruit bunch was separated from the solution by filtration using Advantec filter paper 110 mm, and the filtrate was measured using Ultraviolet (UV)-Spectrophotometer (Buck Scientific 100) at wavelength 546 nm. A one-point calibration was carried out to determine the value of Kappa number [21], as shown in Eq. (1)

$$K = \frac{a}{w} \left(1 - \frac{A_e}{A_o} \right) \quad \text{Eq. (1)}$$

where, K is Kappa number, a is the volume of KMnO₄ used in the solution, w is weight of moisture-free sample used, A_o is spectral intensity before sample addition and A_e is spectral intensity after the reaction is completed.

Lignin content of the sample was calculated from the values of Kappa number K, using Eq. (2), where the percent of lignin degradation is calculated in Eq. (3) [22].

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

$$\text{Lignin Degradation (wt\%)} = (L_i - L_a) / L_i \times 100 \quad \text{Eq. (3)}$$

where, L_i and L_a are lignin content of EFB before and after liquefied, respectively.

2.4 Design of Experiments

Optimization of processing conditions for the liquefaction of EFB was carried out using response surface methodology. The effect of reaction temperature (X₁), reaction time (X₂), IL/EFB ratio (X₃) were investigated at low, central and high levels and coded as (-α, -1, 0, +1, +α), respectively. Table 2 lists the range and levels of the variables. A central composite design for each variable at two levels was selected for the optimization, with a total of 16 runs. The experimental data were analyzed using a

STATISTICA software. The quadratic mathematical model for the yields of the liquefied products was fitted to the second-order polynomial regression model:

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad \text{Eq. (4)}$$

where y is the response variable (total percentage of liquid yield), β₀ is the constant coefficient, β₁, β₂, and β₃ are linear coefficients, β₁₁, β₂₂, and β₃₃ are quadratic coefficients, β₁₂, β₁₃, and β₂₃ are second order interaction coefficients. The details of experimental design can be found elsewhere in the literature [20].

Table 2 Experimental levels for the independent variables

Independent Variable	Symbol	Range and level				
		-α	-1	0	+1	+α
Temperature (°C)	X ₁	49.4	80	120	160	190.6
Time (min)	X ₂	37.08	60	90	120	142.92
Ratio (IL/EFB)	X ₃	2.47	4.0	6.0	8.0	9.53

-1 is low value, +1 is high value, 0 is central value, -α is low star value, +α is high star value

2.5 Characterization and Analysis

Fourier Transform Infrared by Perkin-Elmer Spectrometer equipped with KBr pellet was used to detect the chemical bonding of EFB and solid and liquid products after reaction, in the IR range of 500 to 4000 cm⁻¹. Thermogravimetric analysis was conducted using a Perkin Elmer TGA 7 instrument using ramp temperature of 10 °C/min from 30 to 900 °C under nitrogen flow. The thermogravimetric data were used to study the thermal stability of EFB and solid product. In addition, TGA also applied to differentiate the components of the solid residue through their decomposition at different temperatures. Field Emission Scanning Electron Microscopy (FESEM) by ZEISS Supra 35VP with Gemini column technology was used to observe the surface of EFB and EFB residue.

High performance liquid chromatography (HPLC) (Agilent Technology 1260 Infinity) was used to analyze and quantify the concentration of sugar reduced in the liquid product based on the standard concentration via calibration curve. A Hi-Plex H column (length, 300 mm; diameter, 7.7 mm) was used at 65 °C, with detection using refractive index (RI) detector, an auto injection volume of 20 μL and 0.6 mL/min of 5 mM H₂SO₄ as the mobile phase.

2.6 Carbon Cryogel Production

The method of gel synthesis was that referred to in a previous study [9]. However, the reaction condition between liquefied EFB mixture and furfural has been modified. The mixture in furfural was prepared in ratio

1.0 w/w in the presence of 9 M of H₂SO₄ (in water) as the acid catalyst. The distilled water/liquefied EFB in a ratio of 0.125 w/w and water/ethanol in a ratio of 1.0 v/v were used to dilute and homogenize the mixture. The gel synthesis reaction was conducted at 100 °C for 1 h. The product was then pre-frozen for 24 h and freeze dried for 24 h to form a cryogel. Finally, the carbon cryogel was prepared by calcination of the cryogel in the furnace at 400 °C for 2 h. The carbon cryogel produced was tested in the esterification levulinic acid. The surface morphology of the carbon cryogel was observed via FESEM.

2.6 Esterification of Levulinic Acid

The prepared carbon cryogel was tested in the esterification reaction of levulinic acid to observe its performances as catalyst. The esterification reaction of levulinic acid (LA) was conducted in reflux condenser at reflux temperature (~78 °C) for 4 h with 20:1 molar ratio of ethanol to LA and 30 wt% catalyst loading to produced ethyl levulinate. The parameters were selected based on the optimum condition of our previous studies and other heterogeneous catalysts for the esterification of levulinic acid in ethanol [11, 23].

Gas chromatography with flame ionization detector (GC-FID) 7820A gas chromatograph system (Agilent Technology) was used to characterize ethyl levulinate (EL) yield. The analysis was conducted using a HP-5 GC column (length, 30.0 m; diameter, 320.0 µm) with the settings injector temperature, 270 °C; column temperature was increased from 80 °C (13°C/min) to 170 °C (40 °C/min) and finally to 300 °C; carrier gas, nitrogen (1.0 mL/min). The HPLC from Agilent Technology (1260 Infinity) was used to measure the concentration of levulinic acid for the calculation of their conversion. The HPLC were the same as described above, but UV detection was used for this analysis and the column temperature was 60 °C. The yield and conversion were calculated based on the standard concentration of ethyl levulinate and levulinic acid, respectively. The equations below were used to calculate the EL yield and levulinic acid conversion.

$$\text{Yield (mol\%)} = \frac{[(C_E \times V_p) / (1000 \times m_E)]}{M_L} \times 100 \quad \text{Eq. (5)}$$

$$\text{Conv (\%)} = \frac{[M_L - (C_L \times V_p) / (1000 \times m_L)]}{M_L} \times 100 \quad \text{Eq. (6)}$$

where, C_E and C_L are the final product concentrations of ethyl levulinic and levulinic acid, respectively (mg/L), m_E and m_L are the molecular weights of ethyl levulinic and levulinic acid, respectively (g/mol), V_p is final volume of product (L), and M_L is initial mol of levulinic acid.

3.0 RESULTS AND DISCUSSION

3.1 Optimization Study of EFB Liquefaction Yield

Response surface methodology and central composite design were employed to analyze interactions between responses and the variables. Responses for liquefaction yields and lignin degradation are presented in Table 3. The yields of liquefied products were found between 57.0 and 85.0 wt% while the yields of lignin degradation were found between 41.0 and 68.0 wt%. The results in Table 3 were fitted to the second-order polynomial regression model using temperature, reaction time and IL/biomass ratio as independent variables.

$$y = 4.6526 + 0.6819X_1 + 0.4027 X_2 + 0.8534X_3 - 0.0024X_1^2 - 0.0026X_2^2 + 0.1893X_3^2 + 0.0011X_1X_2 - 0.0172X_1X_3 + 0.0013X_2X_3 \quad \text{Eq. (7)}$$

where, the liquefied EFB yield (y) is the response for the tested variables in coded units; reaction temperature (X₁), reaction time (X₂) and IL/EFB ratio (X₃).

Table 3 Experimental design and analysis results

No. Run	Temp. (°C)	Time (min)	Ratio (IL to EFB)	Y (wt%)	D (wt%)
	X ₁	X ₂	X ₃		
1	80.0	60.00	4.00	69.20	41.01
2	80.0	60.00	8.00	75.33	46.59
3	80.0	120.00	4.00	67.20	60.34
4	80.0	120.00	8.00	75.78	46.63
5	160.0	60.00	4.00	74.80	54.62
6	160.0	60.00	8.00	77.56	42.60
7	160.0	120.00	4.00	80.40	68.32
8	160.0	120.00	8.00	81.33	65.87
9	120.0	90.00	6.00	79.71	63.94
10	49.4	90.00	6.00	57.43	42.31
11	190.6	90.00	6.00	74.29	65.38
12	120.0	37.08	6.00	62.86	41.11
13	120.0	142.92	6.00	78.57	61.73
14	120.0	90.00	2.47	76.03	41.35
15	120.0	90.00	9.53	84.54	42.45
16	120.0	90.00	6.00	78.86	50.34

Y is liquid mixture yield, D is lignin degradation

Figure 1 shows the *t*-distribution values in a Pareto chart and the corresponding *p*-values of the variables in Eq. (7). The *p*-value for the factor of linear and quadratic terms of temperature, and linear terms of time and ratio are less than 0.05 (*p*<0.05) which refers to the 5% significance level. This illustrates that the linear and quadratic effect of temperature was statistically significant for yield of liquefied EFB. The linear effects of time and ratio of IL to EFB were also significantly influential on the yield of liquefied EFB.

Analysis of variances (ANOVA) was employed to check the validity of data and identify parameters that affected the yields of liquefied EFB. The *p*-value of lack of fit (0.1159, Table 4) confirms the insignificant of lack of fit relative to the pure error as the $p > 0.05$. Thus, the model indicates good predictability of data. Besides, the Fisher *F*-test shows that the *F*-value of 42.81 of liquefied EFB yield was higher than the tabulated *F*-value at 5% significance level. The model significantly provides a satisfactory fitting as indicated through the ANOVA and *F*-test.

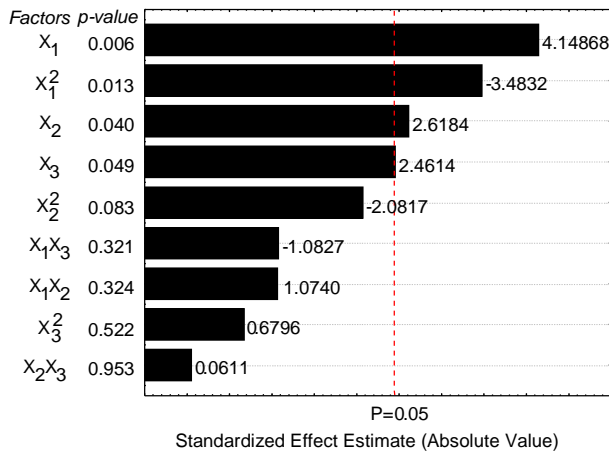


Figure 1 Pareto chart of liquefied EFB yield

Table 4 ANOVA for lack of fit testing of liquefied EFB yield

Source	SS	Df	MS	F-value	p-value
Lack of Fit	77.33	5	15.47	42.81	0.1159
Pure Error	0.36	1	0.36		
Total Error	77.69	6	12.95		

SS, sum of squares; Df, degrees of freedom; MS, mean square

The regression coefficient (R^2) for the model indicates a satisfactory fitting of experimental results due to a good correlation between observed and predicted values (Figure 2).

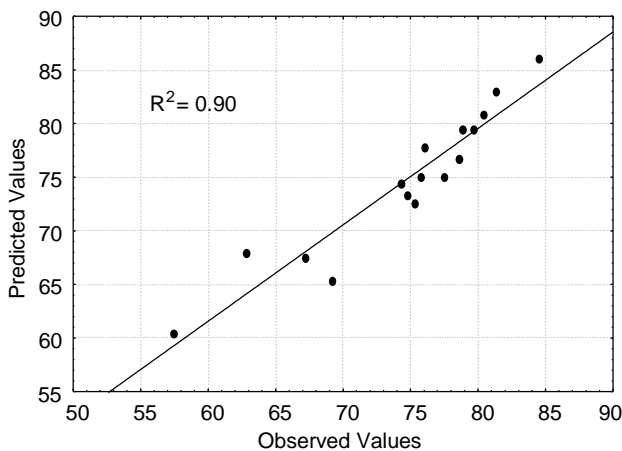


Figure 2 The regression coefficient determination based on predicted versus observed values for liquefied EFB yield

The R^2 value of 0.90 is in acceptable agreement with the adjusted R^2 value of 0.75 for response predictability. According to Haaland, (1989), if R^2 value is 0.75 or higher, the model is able to estimate the response within the experimental conditions [24]. Both R^2 and adjusted R^2 values were influenced by the variation of the insignificant factors in the model. As stated by Rahman (2009), the additional terms in the model equation that were not valuable to the model would decrease the adjusted R^2 value [25].

Figure 3 depicts the contour plots for the interaction between two of three variables. It is evident in Figure 3(a) that there is less interaction between the temperature and ratio on yields of liquefied EFB but that temperature had an important effect.

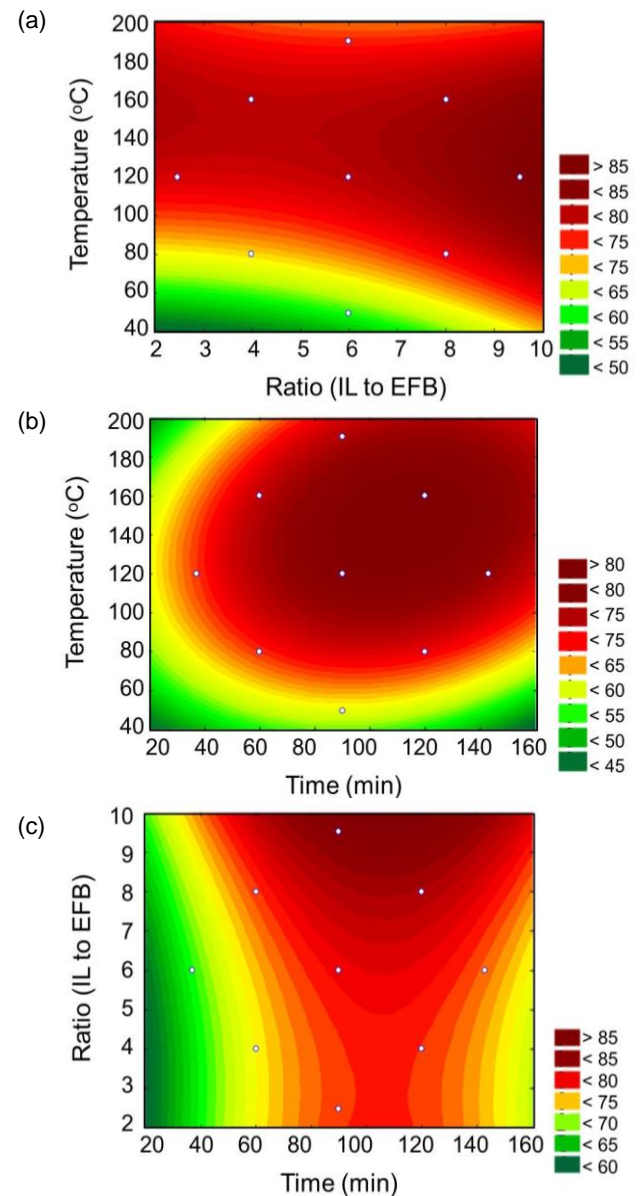


Figure 3 Contour plots of liquefied EFB yield versus (a) reaction temperature and IL/EFB ratio (b) reaction temperature and reaction time (c) IL/EFB ratio and reaction time

Liquid product yields increased with increasing temperature. At 160 °C, yields of liquefied EFB produced were the highest and the yield started to reduce above 160 °C. At temperatures above 180 °C, the reduction in liquefied EFB yield was due to slurry formation and polymerization of the slurry which reduced the liquid yield. Liquefaction of biomass in water occurred around 200 °C and 1 MPa, which turned the biomass into slurry [26]. This situation might occur in EFB-IL mixture at high temperature as the liquid product may mix with slurry produced. Thus, reduces the total amount of liquid mixture. The effect of IL / EFB ratio on the yields of liquefied EFB was prominent at low temperatures. However, there was no effect of IL / EFB ratio at high temperatures.

The interaction effects between the temperature and reaction time on the yields of liquefied EFB are shown in Figure 3(b). The liquefied EFB yields increased with increase of both temperature and reaction time until the critical point at which liquefied EFB yields was highest at the optimum temperature and reaction time. This indicates that, even if the reaction is carried out at high temperatures, liquefied EFB yields is still low when the reaction times are short. The effect of reaction time is noticeable above temperature of 120 °C. Less effect of reaction time is seen at low reaction temperature. The liquefied EFB yield slowly reduced at temperatures above 160 °C as the reaction time increased above 80 min due to prolonged reaction which possibly affected on the polymerization of the liquid mixture and solid EFB. As stated by Yokoyama and Matsumura (2008), the hydrothermal liquefaction in water formed an oily product which polymerized into char if the reaction is prolonged [26]. Thus, polymerization might occur on the product mixture, producing other products and possibly reducing the yield of liquid mixture.

The contour plot of the response surface of the IL/EFB ratio and reaction time (Figure 3(c)) reveals that there is no significant interaction between both parameters but there is a significant effect shown by the reaction time as discussed above. The yield increased with increasing time up to an optimum time and reduced when the time was further increased. The ratio shows only a small effect on yields of liquefied EFB in the range of 60 to 100 min. It can be concluded that the time has a significant effect on yields of liquefied EFB but there was no interaction between the IL/ EFB ratio although a small effect was observed in a small range of time (60 to 100 min).

The optimum conditions for the predicted liquefied EFB yield of 80.97 wt% was at a temperature of 151.9 °C, a reaction time of 112.78 min and a ratio (IL to EFB) of 4.27. Additional experiments were carried out at the optimum condition (151.9 °C, 112.78 min, ratio of 4.27) to validate the results of the optimum yield at the condition predicted by the response surface method. The experiments were repeated three times. The observed liquefied EFB yields were 79.31 wt%, 82.35 wt% and 84.72 wt% with 2.05%, 1.70% and 4.63% error, respectively.

3.2 Characterization and Analysis of Product

The surface functional group of the EFB, the solid residue and the liquid product were analyzed using FTIR analysis and the results are presented in Figure 4. The related functional group and the changes of chemical bonding affected by liquefaction process were observed. The spectra of EFB and EFB residue are shown in Figure 4(a) and 4(b), respectively. The broad frequency peak of O-H was observed around 3300–3400 cm^{-1} related to the alcohol functional group in the cellulose, hemicellulose and lignin structure of EFB. Aliphatic C-H group was detected around 2850 to 2960 cm^{-1} , and aromatic C=C of lignin was identified around 1625 and 1500 cm^{-1} . In addition, high stretching of C–O bonding structure was observed around 1000–1260 cm^{-1} related to the asymmetric stretch of C-OH around 1237 cm^{-1} and the stretching of C-O-C around 1100 cm^{-1} . After the liquefaction reaction, the EFB residue showed some changes in the pattern of spectra. The C-O peak showed some reduction due to the degradation of lignin from EFB into IL. There were new peaks existed in the bonding structure of EFB residue which is influenced by the IL structures. The IL structure possibly linked in the solid structure although the repeating wash of EFB residue was conducted to remove the IL.

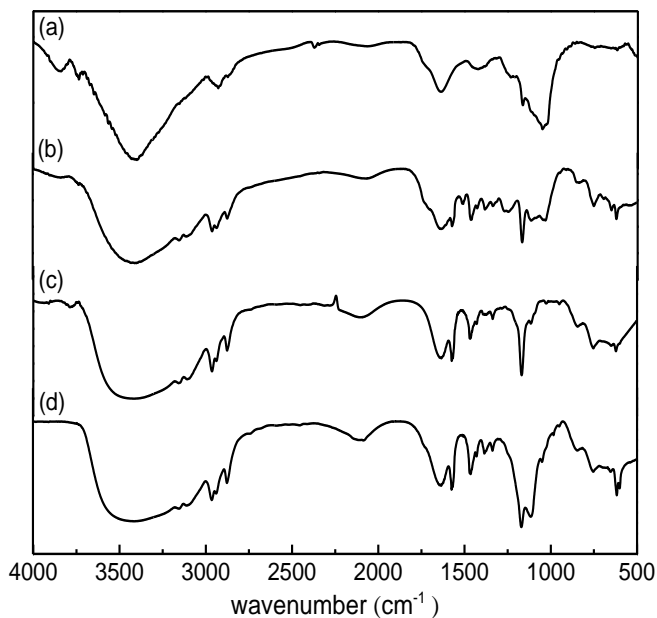


Figure 4 FTIR spectra of (a) EFB, (b) EFB residue, (c) [BMIM][Cl], and (d) liquefied EFB-IL (LEFB) mixture

Based on the IL and LEFB-IL mixture, FTIR showed the peaks related to IL which are: [BMIM][Cl] structure as the broad peak of quaternary amine salt formation between 3400 to 3600 cm^{-1} ; C=C and C=N stretchings at wavelength numbers around 1655 and 1470 cm^{-1} , respectively; stretching vibration of methyl group around 1110 to 1200 cm^{-1} ; and small peak of

C–C and C–N stretching vibration around 750 to 1000 cm^{-1} and 600 to 750 cm^{-1} , respectively. The detection was related to the imidazolium and the bonding with methyl and butyl structure in IL. The identification of peaks was observed and discussed based on spectra study by Dharaskar *et al.*, [2016] [27].

The spectra of liquid samples showed only small differences of peak structure of LEFB-IL compared to [BMIM][Cl]. The broad peak around 3400 to 3200 cm^{-1} was the relevant contribution of O–H stretching derived from lignin. The spectrum around 1000 to 1260 cm^{-1} showed the existence of a new peak related to C–O stretching in LEFB-IL related to lignin structure. Therefore, based on the FTIR result the lignin has been derived from EFB through liquefaction into IL mixture.

The TG/DTG curves in Figure 5 show the thermal stability of samples tested up to 900 °C. Besides, the curves also were used to observe the changes of chemical composition of the sample at different temperatures. The decomposition of moisture content of the samples occurs between 30 and 200 °C. For EFB and EFB residue samples, the result shows the decomposition of hemicellulose between 200 and 350 °C and cellulose between 350 and 500 °C. The mass loss above 500 °C up to 900 °C was referred to the lignin compound. Based on TG/DTG of the commercial cellulose, the result proved that cellulose was decomposed around 300 to 500 °C. As for the liquid product, the [BMIM][Cl] was thermally degraded between 200 and 350 °C, which is similar to the temperature range for decomposition of hemicellulose.

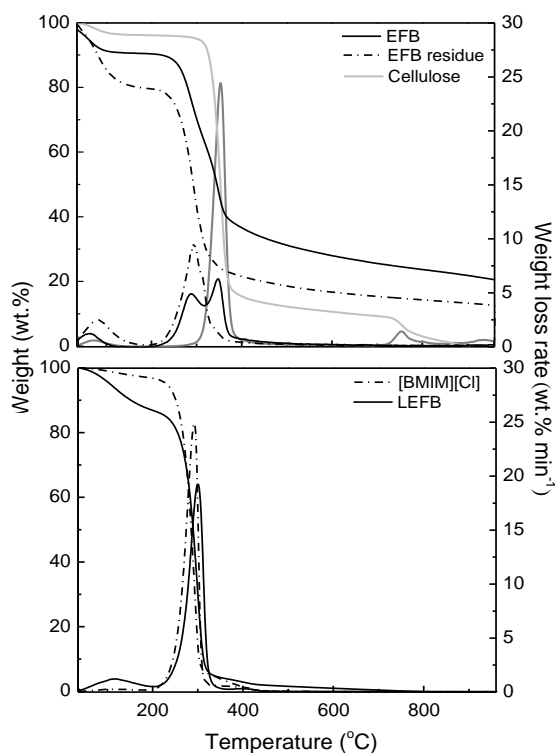


Figure 5 TG/DTG curves of EFB, EFB residue, cellulose, [BMIM][Cl] and LEFB mixture

As for EFB residue, the liquefaction showed the changes in the TG/DTG curves as the lignin composition is reduced by some of the sugar from cellulose. The thermal stability at temperatures between 500 and 900 °C was reduced due to lignin degradation into IL during the liquefaction process. The DTG peak of EFB cellulose reduced due to sugar reduction during the reaction. Besides, the DTG peak of hemicellulose increased due to high rate of loss of hemicellulose with IL in the EFB residue structure. As presented in FTIR result, the IL was possibly linked to the EFB residue during the reaction as some IL peaks were observed in EFB residue spectra. TG/DTG results of EFB residue also explained the existence of IL in EFB residue structure, as the increasing rate of loss of EFB residue was observed in the temperature range of 200 to 350 °C. The structure of IL was possibly linked with the EFB residue structure during the reaction as the IL remained in the EFB residue even though repeated washing steps were conducted after reaction. As for the liquid samples, the DTG curve of LEFB-IL mixture showed a further loss above 400 °C as compared to original [BMIM][Cl]. The losses are due to the lignin compound in the LEFB-IL mixture that was degraded into the IL during the liquefaction process. Accordingly, the lignin of EFB degrades into the [BMIM][Cl] during the liquefaction process as the result of lignin degradation is consistent with observation through the FTIR and TG/DTG results.

FESEM images (Figure 6) show the surface structure of EFB before and after the liquefaction reaction. The structure of EFB shows changes affected by the liquefaction reaction in ionic liquid as the thermochemical conversion has taken place. Through this reaction, the main composition of EFB was derived and converted into liquid product such as soluble lignin, sugar monomer, etc.

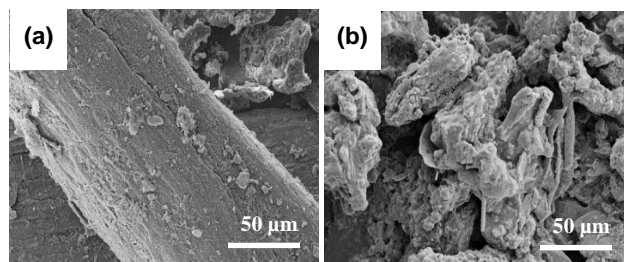


Figure 6 FESEM images of (a) EFB and (b) residual EFB at 500X

The HPLC result of LEFB mixture exhibited low sugar reduction from cellulose as low percentage of glucose reduced in the liquefaction process. The detected glucose is about 0.3 wt% of biomass weight. Other than glucose, lower sugar weight percentage from hemicellulose such as sucrose, galactose and arabinose were also detected in the LEFB mixture through HPLC. Although the [BMIM][Cl] is useful for reducing sugar due to its high solubility in biomass, but the process requires longer reaction

time. Therefore, the liquefaction product has minor contribution toward reducing sugar as the liquefaction only performed near to 2 h of reaction time at high temperature of 151.9 °C which is more favorable to the lignin degradation.

3.3 Carbon Cryogel and Catalytic Testing

The carbon cryogel has been synthesized by the reaction of LEFB-IL mixtures with furfural. Figure 7 was shown the surface structure of the carbon cryogel. Microspheres carbon cryogel was obtained from the liquefaction of EFB with furfural. Similarly, microspheres carbon gel structure using different feedstocks were also reported [9,11,28-30]. The carbon cryogel produced as a dark coloured powder and was further tested for catalytic activity.

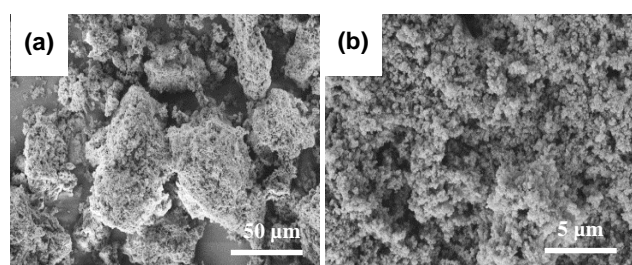


Figure 7 FESEM images of carbon cryogel at (a) 500X and (d) 5000X

The esterification reaction of levulinic acid with ethanol showed the ability of the carbon cryogel produced from the LEFB-IL mixture to catalyze the reaction, producing of ethyl levulinate in a yield of 57.2 mol% with a levulinic acid conversion of 58.7%. The used of sulfuric acid during the gel synthesis improved the surface chemistry of the carbon cryogel to function as catalyst with an acid active site.

Table 5 compares the results obtained by carbon cryogel from LEFB-IL mixture with previous studies. The HZSM-5 and desilicated HZSM-5 registered low performance (16.0 and 28.0 mol%, respectively) compared to dodecatungstophosphoric acid supported on desilicated H-ZSM-5 (DPTA/DH-ZSM-5) at moderate reaction conditions [12]. The modification by DPTA has improved the surface chemistry of desilicated HZSM-5 to obtain high yield of ethyl levulinate of 94.0 mol%. The SO_4/SnO_2 and Amberlyst-15 catalyst have obtained moderated yield by applying low catalyst loading at moderate condition [13]. However, the SO_4/SnO_2 and Amberlyst-15 could possibly obtain a higher yield of ethyl levulinate by adjusting the reaction parameters. For example, Ramli *et al.*, (2017) reported better reaction performance by using Amberlyst-15 with 71.0 mol% yield of ethyl levulinate at different condition [23]. NaOH treated HBEA zeolite, applied for the reaction, only produced ethyl levulinate yield of 39.0 mol% [14]. Moderate yield was obtained by

using low CNT-150 loading [15] and high $\text{H}_4\text{SiW}_{12}\text{O}_{40}\text{-SiO}_2$ loading [16] with ethyl levulinate yield of 54.0 and 67.0 mol%, respectively. The S-ZrSBA 15 produced 79.0 mol% of ethyl levulinate yield, but the reaction was conducted with long reaction time of 24 h [17].

Table 5 Comparative studies of heterogeneous catalysts on levulinic acid esterification

Catalyst	Reaction parameters				Y (mol%)	Ref.
	T	CL	MR	t		
HZSM-5 zeolite	78.0	20.0	6.0	4.0	16.0	[12]
Desilicated HZSM-5	78.0	20.0	6.0	4.0	28.0	[12]
DPTA/DH-HZSM-5	78.0	20.0	6.0	4.0	94.0	[12]
SO_4/SnO_2	70.0	2.5	5.0	5.0	44.0	[13]
Amberlyst-15	70.0	2.5	5.0	5.0	54.0	[13]
Amberlyst-15	78.4	30.0	20.0	5.0	71.0	[23]
NaOH treated HBEA zeolite	78.0	20.0	6.0	5.0	39.0	[14]
CNT-150	70.0	2.5	5.0	5.0	54.0	[15]
$\text{H}_4\text{SiW}_{12}\text{O}_{40}\text{-SiO}_2$	75.0	51.0	18.0	6.0	67.0	[16]
S-ZrSBA 15	70.0	5.0	10.0	24.0	79.0	[17]
Carbon cryogel (lignin)	78.0	15.0	19.0	10.0	64.5	[11]
Carbon cryogel (LEFB-IL)	78.0	30.0	20.0	4.0	57.2	This study

Y is ethyl levulinate yield, T is temperature (°C), CL is catalyst loading (wt%), MR is molar ratio of ethanol to levulinic acid, t is time (h)

Carbon cryogel from commercial lignin-furfural was applied for the esterification reaction of levulinic acid in ethanol [11]. The reaction was conducted at 78 °C, 15 wt% of carbon loading and 19.0 molar ratio of ethanol to levulinic acid for 10 h to produce 64.5 mol% ethyl levulinate. The carbon cryogel from LEFB-IL mixture also has shown potential in catalytic reaction with almost similar yield over $\text{H}_4\text{SiW}_{12}\text{O}_{40}\text{-SiO}_2$, CNT-150, Amberlyst-15 and carbon cryogel from lignin catalysts. Based on the selected conditions from the esterification study, the carbon cryogel derived from LEFB-IL mixture has shown moderate reaction yield. The selected experimental condition conducted at 78 °C, 30 wt% of catalyst loading and 20.0 molar ratio of ethanol to levulinic acid for 4 h produced 57.2 mol% ester.

4.0 CONCLUSION

Optimization studies for the pretreatment of EFB with an IL were performed using response surface methodology. The effects of experimental variables, such as temperature, reaction time and IL/ biomass ratio were studied using a Central Composite Design (CCD). The optimum conditions for the predicted liquefied EFB yield of 80.97 wt% were obtained under the following conditions: temperature, 151.9 °C; time, 112.78 min; ratio IL /EFB, 4.27. The liquefied EFB was used for production of microspheres carbon cryogel. The carbon cryogel was tested as catalyst for

esterification of levulinic acid in ethanol. Levulinic acid conversion of 58.7% and ethyl levulinate yield of 57.2 mol% were obtained.

Acknowledgement

The authors would like to thank Universiti Teknologi Malaysia (UTM) and the Ministry of Higher Education (MOHE), Malaysia for the project financial support under Research University Grant (vote 04H69), and for sponsoring one of the authors, M. M. Zainol under MyBrain15-MyPhD programme.

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