Optimization of Electron Beam Irradiation and Ionic Liquid Pretreatment on Oil Palm Trunk

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Abstract— **Oil palm trunk (OPT) waste from the oil palm plantation is one of the lignocellulosic biomass feedstock to produce biofuel. Pretreatment is an important process to break the rigid structure of the lignocellulose and make it accessible for hydrolysis. In this project, the OPT was pretreated by using electron beam irradiation and ionic liquid. The effectiveness of the pretreatment process was investigated by analyzing the crystallinity index (CrI) of the pretreated OPT by using X-Ray Diffractometer (XRD). The optimal conditions for the pretreatment process were determined by response surface methodology with Box-Behnken Design for the experimental design. The result shows that the optimal conditions for the pretreatment process can be obtained at 346.5 kGy of irradiation dose, 686.9 rpm of shaking frequency and 3 hours of dissolution time. The predicted CrI value at the optimal conditions is 32.82%.**

Keywords— **Optimization, Response Surface Methodology, ionic liquid pretreatment, electron beam irradiation, oil palm trunk biomass.**

I. INTRODUCTION

Malaysia is one of the largest producer of palm oil in the world with the planted area of oil palm reaching 5.81 million hectares in 2017 [1]. From the plantation and milling activities, the abundance of oil palm biomass such as oil palm fronds (OPF), oil palm trunks (OPT) and empty fruit bunches (EFB) was generated. These waste can be reduced by turning it into energy or value added products. The oil palm biomass is a lignocellulosic biomass composed of three chemical constituents which are cellulose, hemicellulose, and lignin. Lignocellulosic biomass has been seen as a potential feedstock for the substitution of non-renewable energy sources [2]. The pretreatment process is a necessary preliminary step in refining biomass as it will reduce the crystalline structure of the cellulose, increase porosity which makes it more accessible for hydrolysis and enhance the sugar production [3], [4].

Ionic liquid pretreatment is a chemical pretreatment method which has a potential as a green technology since it is able to break down the biomass at low temperatures, easy to recover and reuse, and nontoxic to enzymatic and microbial fermentation [5]. Electron beam irradiation is a type of physical pretreatment which is able to improve the biomass biodegradability, increase the pore size and reduce the crystalline structure of the cellulose [6]. In order to achieve an efficient bioconversion, instead of applying single pretreatment, these two pretreatment methods can be combined.

In this research work, the crystallinity index (CrI) from the combination of electron beam irradiation and ionic liquid pretreatment on the OPT biomass was investigated. Response surface methodology (RSM) by using Box-Behnken Design (BBD) was employed for the experimental design and the optimization of the pretreatment parameters. Irradiation dose, shaking frequency and time were optimized in order to achieve higher bioconversion.

II. METHODOLOGY

A. Materials

The shredded OPT was obtained from available Malaysia's oil palm plantation. It was ground and sieved to obtain particle size of less than 250 µm. The sample was placed in an oven at 105 ºC for 24 hours and the moisture content of the sample was measured to be below 10% by using equation (1).

$$\text{Moisture content} = \frac{(W_w - W_d)}{W_w} \times 100\% \qquad (1)$$

B. Electron beam irradiation pretreatment

Electron beam irradiation pretreatment process was done at Agensi Nuklear Malaysia. The samples were vacuum sealed in polypropylene bags by using vacuum sealer then irradiated at a varying dose of 100, 300 and 500 kGy using electron beam accelerator (Nissin EPS3000, Japan) with electron voltage of 2 MeV, current of 10 mA and 50 kGy per pass.

C. Ionic liquid pretreatment

After the electron beam irradiation pretreatment process was done, the irradiated samples were further pretreated by using the ionic liquid. 0.25g of irradiated samples were mixed with 5 mL of 50% 1-ethyl-3-methylimidazolium acetate

([EMIM]Ac) in a 15 mL Eppendorf tube. The mixtures were shaken by using Bioshake iQ (Quantifoil Instrument, Germany) at 400, 600 and 800 rpm shaking frequency for 1, 2.5 and 4 hours at a constant temperature of 99 ºC. After the pretreatment process was done, for washing purpose, 5 mL of distilled water was added and the mixture was centrifuged by using refrigerated centrifuge (Sartorius Stedim, Germany) and the supernatant was removed. The washing and centrifugation steps were repeated a few times until a colourless supernatant was obtained. The pretreated OPT was collected and oven-dried at 60 ºC for 24 hours for the next analysis.

D. XRD analysis

The crystallinity index (CrI) of the pretreated OPT was analyzed by using X-Ray Diffractometer (Multi-Purpose X-Ray Diffractometer, Ultima IV, Rigaku, USA) with Cu Kα at 45 kV and 40mA. The samples were scanned over a scattering angle (2θ) from 10º to 90º at a rate of 2θ per min. Segal's Equation in equation (2) was employed for the determination of CrI [7]. I_{am} is the intensity diffraction of the amorphous band taken around 18.5º and I_{200} is the maximum intensity of the (200) lattice diffraction taken around 22.5º.

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \text{ x } 100\% \qquad (2)$$

E. Response surface methodology (RSM)

RSM with Box-Behnken Design (BBD) was chosen to design the experiment by using Minitab 17 software. By inserting the low and high values for three variable factors of the experiment which are irradiation dose, shaking frequency and time as tabulated in Table 1, 15 sets of experiment were suggested by BBD as shown in Table 2. Equation (3) is the second order polynomial equation which shows the mathematical relationship of the response on the variables.

$$Y=\beta_0+\beta_1x_1+\beta_2x_2+\beta_3x_3+\beta_{12}x_1x_2+\beta_{13}x_1x_3+\beta_{23}x_2x_3+\beta_{11}x_1^2+\beta_{22}x_2^2+\beta_{33}x_3^2 \qquad (3)$$

Where Y is the dependent variable (CrI), x_1 is the irradiation dose (kGy), x_2 is the shaking frequency (rpm) and x_3 is the dissolution time (h). β_0 is the regression coefficient at the center point, β_1, β_2, and β_3 are linear coefficients while β_{12}, β_{13} and β_{23} are quadratic coefficients [8].

Table1: Low and high values of the variable factor for experimental design

Factor	**Low**	**High**
Irradiation dose (kGy)	100	500
Shaking frequency (rpm)	400	800
Time (h)	1	4

The relationship of independent variables on the response was analyzed based on the three-dimensional response surface and two-dimensional contour plot. By applying response optimizer, the response was optimized to the minimum to obtain the optimal conditions of the pretreatment process for the optimum response.

III. RESULTS AND DISCUSSION

A. Optimization of electron beam irradiation and ionic liquid pretreatment parameter

Response surface methodology (RSM) with a Box-Behnken design (BBD) was conducted to examine the effect of irradiation dose, shaking frequency and time on the crystallinity index (CrI). The experimental design and results of BBD are tabulated in Table 2. Equation (4) explain the CrI of the pretreated OPT as a function of irradiation dose, shaking frequency and time.

$$Y = 65.01 - 0.0613x_1 - 0.0412x_2 - 5.00x_3 + 0.000095x_1^2 + 0.000029x_2^2 + 0.786x_3^2 - 0.00004x_1x_2 + 0.00068x_1x_3 + 0.00078x_2x_3 \qquad (4)$$

Table 2: Experimental design and results of the Box-Behnken Design for the Crystallinity Index of the pretreated OPT.

Run order	Irradiation dose (kGy)	Shaking frequency (rpm)	Time (h)	CrI (%)
1	300	400	4.0	36.75
2	500	600	4.0	35.62
3	500	400	2.5	37.55
4	100	600	4.0	38.92
5	500	600	1.0	39.49
6	100	400	2.5	40.78
7	500	800	2.5	35.74
8	300	400	1.0	38.62
9	300	800	1.0	35.51
10	300	600	2.5	34.12
11	100	800	2.5	39.54
12	300	600	2.5	33.60
13	300	800	4.0	34.57
14	300	600	2.5	32.55
15	100	600	1.0	41.97

Figure 1 to 3 show the three-dimensional response surface and contour plots for the CrI which explained the relative effects of two variables on CrI with the third variable maintain constant. Figure 1 shows that the CrI decreases with the increasing of shaking frequency and time. Figure 2 and 3 show that the CrI decreases when the irradiation dose increases. This might be due to the cross-linking which may occur in the irradiation process, disruption of lignocellulosic component and the removal of the crystalline fraction [9], [10]. Figure 1 and 2 show that the lowest value of CrI was at the moderate value of dissolution time. Since the ionic liquid pretreatment has undergone mild temperature at 99 ºC, moderate dissolution time is needed to minimize the loss of the major extracts with the minimal structural alteration and avoid the generation of furfural and HMF which can inhibit the process [11], [12]. All figures explain that the variables which are shaking frequency, irradiation does, and time do play a role in the effectiveness of the pretreatment process. The higher the value of the variables, the lower the CrI values which indicates the higher effectiveness of the pretreatment process. The optimization of irradiation dose, shaking frequency and time for an effective electron beam irradiation and ionic liquid pretreatment were determined at 346.5 kGy, 686.9 rpm and 3 h, respectively. The predicted optimum CrI from the model was 32.82%.

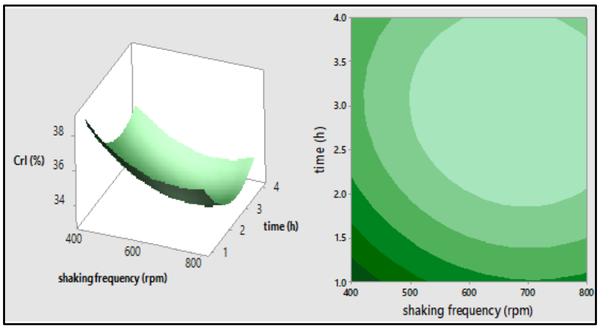

Figure 1: Response surface and contour plot for crystallinity index (CrI) based on time (h) and shaking frequency (rpm)

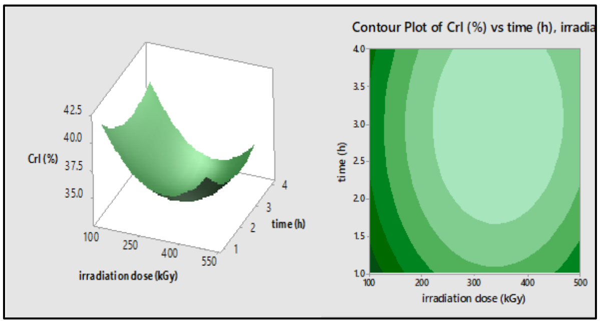

Figure 2: Response surface and contour plot for crystallinity index (CrI) based on time (h) and irradiation dose (kGy)

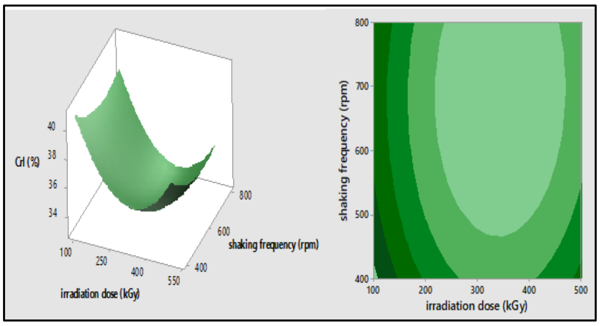

Figure 3: Response surface and contour plot for crystallinity index (CrI) based on shaking frequency (rpm) and irradiation dose (kGy)

B. Effectiveness of the pretreatment method

The Crystallinity Index (CrI) is one way to measure the effectiveness of the pretreatment. XRD was used to identify the CrI of the untreated and pretreated OPT. It was found out that the CrI of the untreated OPT is 51.12%. Based on the result in Table 2, all the pretreated OPT show the decrement in CrI which might be caused by the swelling of the cellulose in ionic liquid ([EMIM]Ac) and destruction of the crystalline structure during the irradiation [13], [6]. The predicted optimum CrI is 32.82% which has decrement of 35.80% from the untreated OPT. The decrement in CrI value indicates that the pretreatment method is effective. Thus, it is suggested that the combination of electron beam irradiation and ionic liquid pretreatment is efficient to reduce the crystallinity of cellulose in OPT for more accessible enzyme hydrolysis and enhance sugar yield.

IV. Conclusion

The experiment has been well performed using response surface methodology with a three-level design of Box-Behnken design. The combination of electron beam irradiation and ionic liquid pretreatment on the OPT is an effective method since it shows a reduction in the crystallinity index (CrI) from the untreated OPT. From the optimization of the pretreatment parameters, the lowest value of CrI was obtained at the optimal conditions thus, higher bioconversion and can be expected.

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