Pretreatment of Water Soaked Oil Palm Frond (OPF) by Electron Beam Irradiation and Ionic Liquid

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***Abstract*—Various methods such as physical, chemical, physicochemical and biology have been done for the pretreatment process of biomass to produce biofuel. This research is conducted to investigate the effect of combining the electron beam irradiation and ionic liquid pretreatment and to determine the composition of lignin, cellulose and hemicellulose. The method used in this research was referred to the Kappa number and Tappi method. For the lignin degradation, when the dose of the irradiation increases, the value of lignin degradation also increases. For the alpha cellulose, when the irradiation dose increases, the percentages of alpha cellulose also increases. It can be concluded that this research achieve the findings.**

Keywords— Oil Palm Frond (OPF); Ionic Liquids (ILs); Electron Beam Irradiation (EBI); Lignin; Fourier Transform Infrared (FTIR) Spectroscopy

I. INTRODUCTION

Various methods such as physical, chemical, physicochemical and biology have been done for the pretreatment process of biomass to produce biofuel. Due to the highly energy intensive and industrially inapplicable, the outcome of irradiation method for the pretreatment process is not satisfying. It had been proven that the physical method can be more precise and accurate than the physical method itself by combining it with either biological or chemical method. In the previous study, usually the dissolution of lignocellulosic is conducted by using pure ionic liquid only. To improve the efficiency of the process, irradiation method is added.

For this research, the scopes focus more on the combination of pretreament of Oil Palm Frond (OPF) between ionic liquid and the electron beam irradiation. Electron beam irradiation were conducted at Agensi Nuklear Malaysia and usually electron beam irradiation was used to pretreat lignocellulosic biomass. The ionic liquid pretreatment is chosen because of its great potential as compared to the other pretreatment methods.

Ionic liquid (IL) is usually an ionic salt in the liquid state. Ionic liquids are also considered as molten salt with low melting point (below 100°C). IL is constituted solely by a large asymmetric organic cation and a polyatomic organic or inorganic counterion (André *et al.*, 2013). IL has high thermal stability, high electrical conductivity and wide electrochemical window, negligible the vapour pressure and low flammability (Zhang, Hu and Lee, 2017).

There are two types of ILs which are IL (Ionic Liquids) and RTIL (Room Temperature Ionic Liquids). RTIL is more convenient and economical to be kept and can be used in the industrial process.

Electron beam irradiation (EBI) is a process to treat a substances with variety processes by involving beta radiation. Electron beam irradiation will decrease the crystallinity and the molecular weight of the cellulose but increase the surface area. EBI has many other advantages such as short treatment time, mild temperature and less undesirable inhibitor byproduct (Xiang, 2017). Electron beam irradiation offers enhanced and efficient large scale processing (Balaji, 2017).

The purposes of this study are to investigate lignocellulosic biomass pretreatment under the presence of ionic liquid with and without electron beam irradiation and to determine the composition of lignin, cellulose and hemicellulose in Oil Palm Frond.

II. METHODOLOGY

A. Preparation of lignocellulosic biomass and parameter

The OPF was ground by using grinder machine and sieving by using siever to obtain size particles less than 250 μm**.** The moisture content of the OPF was measured and needed to be below 10% before proceed with pretreatment. The moisture content was determined by placing the sample into oven at 105°C for 24 hours. It was measured by using equation 1:

$$\text{Moisture content} = \frac{(W_w - W_d)}{W_w} \qquad \text{Eq.1}$$

Where;
Ww = weight of wet sample
Wd = weight of dry sample

B. Electron Beam Irradiation Pretreatment

For the physic-chemical pretreatment, the sample of OPF was sealed by using vacuum sealed before irradiated at varying dose. It was placed in the conveyer trolley. The irradiation dose was set at 50 kGy for each round and for every 200 kGy, the container of the samples were changed and vacuum sealed to avoid contamination. The details parameter was shown in Table 1.

Table 1: Parameters for electron beam irradiation

Parameter	Range of parameter
Irradiation dose	100, 200, 400, 600, 800 and 1000 kGy
Irradiation dose per pass inside the accelerator	50 kGy
Voltage accelerator	3 MeV
Current flow	5 mA

C. Ionic Liquid Pretreatment

For the chemical pretreatment, Ionic liquids (IL) used was [EMIM]Ac solution. 5 ml of diluted ILs and 0.25g of OPF (<250 μm) were mixed for 4 hours, heat it with continuous shaking at 800

rpm. Then, 5 ml of distilled water was added to wash the ILs and proceed with washing process by using centrifuge machine. The mixture was centrifuged at 10000 rpm for 10 minutes at 3 °C. the washing and centrifuging were repeated for several times until a colorless supernatant was obtained. The colorless indicated that there was no more IL in the pretreated OPF.

The preated OPF was collected and oven-dried at 60 °C for 24 hours. The details parameter was shown in Table 2.

Table 2: Parameter details for pretreatment

Parameter	Range of parameter
Concentration of [EMIM]Ac solution	50%
Temperature for continuous shaking	99 °C
Mass loading of OPF	0.25g
Speed for Bio-shake IQ	800 rpm
Time of pretreatment	4 hours

D. Preparation of 0.5M of [EMIM]Ac solution

[EMIM]Ac solution was prepared by mixing [EMIM]Ac with deionized water in 500 ml of volumetric flask with 50% v/v concentration. 263 ml of [EMIM]Ac was measured by using measuring cylinder and then it was poured into volumetric flask. Next, 237 ml of deionized water was added. The volume for [EMIM]Ac solution can be calculated by using this equation 2:

$$C_1V_1 = C_2V_2 \quad \text{Eq. 2}$$

Where;
C1 = initial concentration of 95% of [EMIM]Ac solution
V1 = volume of [EMIM]Ac needed to make 50% wt solution
C2 = final concentration of [EMIM]Ac solution
V2 = volume of final solution

E. Lignin Degradation

Lignin degradation was determined by using Kappa number and calibrated with Klason lignin method. 0.05 g of pretreated OPF was mixed with 20 ml of H_2SO_4 (2 M) and 5 mL of 0.02 M $KMnO_4$. The mixture was stirred at 200 rpm for 5 minutes and then filtered. The filtrate was analyzed by using UV-vis at 546 nm.

For the controller, the mixtures of H_2SO_4 (2 M) and 0.02 M $KMnO_4$ was used as the blank sample. The lignin degradation was calculated by using equation 3 and 4 below:

$$\text{Kappa number, K} = 100\ \frac{(A_o - A_{CT})}{A_o} \quad \text{Eq.3}$$

$$\text{Lignin degradation (wt\%)} = \frac{Ao - A_{CT}/A_{UT}}{Ao}\ x\ 100 \quad \text{Eq.4}$$

Where;
A_o = absorbance of blank sample
A_{UT} = absorbance reading of treated
A_{CT} = absorbance reading of untreated
Lignin content = 0.15K

F. Cellulose and Hemicellulose Determination

Preparation of Filtrate

The test specimen was placed in 300 ml of tall beaker and 75.0 mL of 17.5% NaOH reagent was added. The pulp was stirred until it completely dispersed. Then, the stirrer was rinsed with 25.0 mL of 17.5% NaOH reagent, adding it to the beaker, so that exactly 100.0 mL of the reagent had been added to the pulp. The pulp suspension was stirred with a rod and placed it in a bath at 25 °C. After 30 minutes, 10 ml of distilled water was added to the pulp and continued with stirred it. The beaker was left in the bath for another 30 minutes. Then, the pulp suspension was stirred with a rod and transferred to the filtering funnel. The first 10 or 20 ml of filtrate was discarded and then collected about 100 ml of filtrate.

Alpha-Cellulose Determination

25.0 mL of the filtrate and 10.0 mL of 0.5*N* potassium dichromate solution was pipetted into a 250-mL flask. While swirling the flask, 50 mL of concentrated H_2SO_4 was added cautiously. The solution was allowed to remain hot for 15 min, and then added 50 mL of water and let it cooled to the room temperature. 2 to 4 drops of Ferroin indicator is added and titrated with 0.11*N* ferrous ammonium sulphate until it changed to purple colour.

Beta-Cellulose and Gamma-Cellulose Determination

50.0 mL of the pulp filtrate was pipetted into a 100-mL graduated cylinder having a ground glass stopper. 50.0 mL of 3*N* H_2SO_4 was added and mixed thoroughly by inverting. The cylinder submerged is heated in a hot water bath at 70°- 90°C for a few minutes to let the beta-cellulose to coagulate. The precipitate was allowed to settle for several hours to obtain a clear solution. 50.0 mL of the clear solution and 10.0 mL of 0.5N $K_2Cr_2O_7$ was pipetted into 300 mL of flask and 90 mL of concentrated H_2SO_4 was added. The solution was allowed to remain hot for 15 min, and then added 50 mL of water and let it cooled to room temperature. 2 to 4 drops of Ferroin indicator is added and titrated with 0.11*N* ferrous ammonium sulphate until it changed to purple colour.

G. Analysis of Fourier Transform Infrared (FTIR) Spectroscopy

To identify the functional group in the pretreated and unpretreated OPF, it was analyzed by using the FTIR. The top plate of FTIR machine was cleaned by using acetone. The pretreated OPF sample was inserted into a hole and pressed it with gauge with the range 60-70. The result were collected and observed the pattern of the sample.

III. RESULTS AND DISCUSSION

A. Lignin Degradation (in progress)

Lignin degradation was used to determine the amount of lignin left after the pretreatment process. The lignin degradation was calculated and tabulated in the table 3 below.

Table 3: Analysis of lignin degradation

Irradiation dose (kGy)	Lignin degradation (%)	
	Cellulose	OPF
100	87.434	19.730
200	89.365	19.912
400	91.791	20.088
600	94.508	20.193
800	96.319	20.764
1000	98.406	20.835

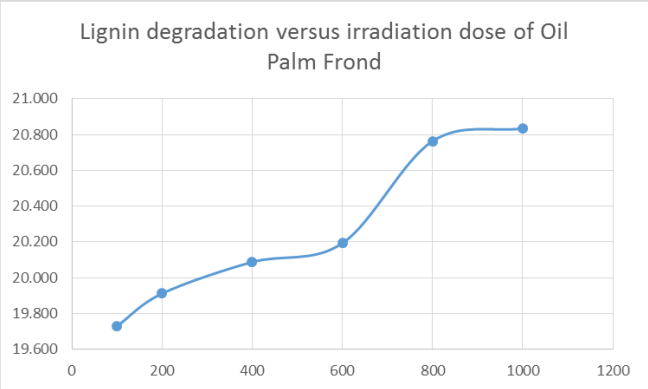

Figure 1: Graph of lignin degradation for OPF

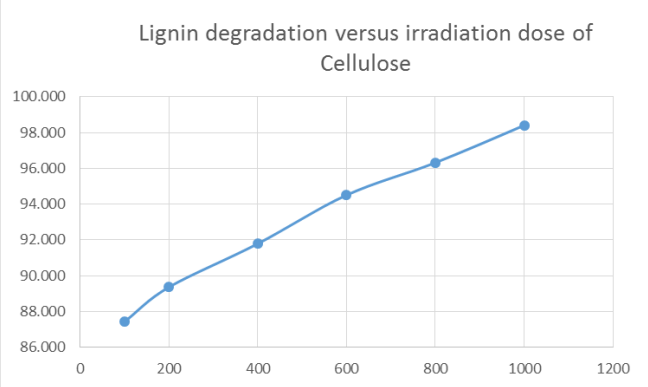

Figure 2: Graph of lignin degradation of cellulose

The percentage of the lignin degradation should increase when the dose of irradiation increase (Talebnia, Karakashev and Angelidaki, 2010). Table 3 shows the analysis of lignin degradation on OPF and cellulose. The value of lignin degradation of cellulose was taken as reference. Both sample were water-soaked and treated with electron beam irradiation and ionic liquid pretreatment. From the table above, when the irradiation dose was 1000 kGy, the value for the lignin degradation was 20.835 while when irradiation dose was 100 kGy, the value for the lignin degradation was 19.730. The lignin degradation increase when the dose of irradiation increase.

B. Alpha-Cellulose Determination

Table 4: Alpha cellulose percentages of OPF

Dose	X (ml)	Alpha-cellulose, %
Untreated	11.2	80.75
100	23.3	85.17
200	27.6	86.74
400	32.4	88.49
600	40.1	91.31
800	43.8	92.66
1000	48.5	94.37

From table 4, it shows that the increasing of dose will increase the alpha cellulose. The alpha cellulose untreated is 80.75% and for the highest dose, 1000 kGy, the value is 94.37.

C. Beta-Cellulose and Gamma-Cellulose Determination (in progress)

Table 5: Gamma cellulose percentage for OPF

Dose	V_3(ml)	Gamma cellulose, %
Untreated	21	8.77
100	23.8	7.75
200	27.4	6.43
400	39.6	1.97
600	41.2	1.39
800	42.4	0.95
1000	43	0.73

Table 6: Beta cellulose percentages for OPF

Dose	Beta cellulose, %
Untreated	10.49
100	7.09
200	6.83
400	9.54
600	7.31
800	6.39
1000	4.90

Gamma and beta cellulose also known as hemicellulose. Percentages of gamma and beta cellulose were calculated and tabulated in the table 5 and 6.

From the table, the highest value for the samples with irradiation dose was when the dose 100 kGy. The gamma cellulose was 7.75% compared to the untreated sample. The lowest value of gamma cellulose when the irradiation dose was 100 kGy. From table 5, the percentages of gamma cellulose decrease when the irradiation dose increase.

D. FTIR Analysis

It was used to investigate the structure of constituent and the chemical changes during the pretreatment. Table 5 shows the characteristic and the variations of wavenumber in FTIR spectre possible for cellulose.

The covalent bonds of each functional group can be stretched, vibrates, bended or twisted due to the absorption of certain amount of energy produced from the radiation. In the crystal structure, the absorbance values at ~1430 cm^{-1} and ~898 cm^{-1} are quite sensitive. Therefore, in order to determine the effect of pretreatment to the crystallinity in cellulose, the absorbance ratio which is known as crystallinity index and the lateral order index, LOI was used. The lower the value of LOI, the lower the crystallinity in the material. Table6 Shows the LOI value for the effect of pretreatment based on the radiation dose on pretreated LCBs.

Table 5: Characteristics and variation of wavenumber in FTIR

Wavenumber, cm-1	**Organic Groups**	**Related Structure**
3350	**O-H**	**Cellulose**
3175	**-OH stretching**	**Cellulose**
2918	C-H stretching	Cellulose
1730	C=O stretching of acetyl or carboxylic acid	Hemicellulose & Lignin
1627	C=C stretching of the aromatic ring	Lignin
1598	C=C	Lignin
1510	C=C stretching of the aromatic ring	Lignin
1465	Asymmetric bending in C-H3	Lignin
1410	C-H stretching of aromatic ring	Cellulose
1423	C-H2 symmetric bending	Cellulose
1430	C-H2 bending	Cellulose
1375	C-H bending	Cellulose
1315	C-H2 wagging	Cellulose
1200	C-O and C=O stretching	Lignin
1270	C=C stretching of the aromatic ring	Lignin
1158	C-O-C asymmetric stretching	Cellulose
850	β-glycosidic bonds between sugars	Cellulose

Table 6: LOI value for the effect of pretreatment based on the radiation dose

Irradiation dose (kGy)	Lateral Order Index	
	Cellulose	OPF
Untreated	0.6792	0.7700
100	0.9066	0.6184
200	0.5907	0.5953
400	0.6150	0.6111
600	0.6763	0.6121
800	0.9970	0.5724
1000	0.9449	0.6139

IV. Conclusion

For the lignin degradation, the percentages of lignin degradation increase when irradiation dose increase. The highest irradiation dose was 1000 kGy with 20.835% of lignin degradation. For the alpha cellulose determination, when the irradiation dose increase, the alpha cellulose also increase. This research fulfill the hypothesis to determine the composition of lignin, cellulose and hemicellulose and also the effect of combining the electron beam irradiation and ionic liquid method.

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