The Effect of Combining Electron Beam Irradiation and Ionic Liquid Soaked (ILS) Pretreatment on Lignocellulosic of Oil Palm Frond (OPF)

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***Abstract*— Oil Palm Frond (OPF) is used as lignocellulosic biomass (LCB) as potential raw material for bioethanol production. This research was conducted to study the effect of combining electron beam irradiation and ionic liquid soaked (ILS) on lignocellulosic of OPF. LCB are soaked with 50% of 1-ethyl-3-methylimidazolium acetate, [EMIM]Ac for ionic liquid pretreatment and then irradiated with different doses which was 100-1000 kGy using electron beam under cooperation with *Agensi Nuklear Malaysia*. The characterization of treated OPF was conducted by using Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD). The combination of ionic liquid soaked and electron beam irradiation on OPF was demonstrated to be more effective by the significant reduction of Lateral Order Index (LOI) (FTIR) and reduction of Crystallinity Index (CrI) (XRD). The value of LOI of ILS OPF decreased from 0.77 (untreated OPF) to 0.64 at 800 kGy doses of irradiation and the CrI value of ILS OPF also decreased from 63.99% (untreated OPF) to 55.87% at 1000 kGy doses of irradiation.**

Keywords*— Lignocellulosic Biomass, Oil Palm Frond (OPF), Ethyl-3-Methylimidazolium Acetate, Electron Beam Irradiation

I. INTRODUCTION

The energy demand for fossil fuels are increasing due to the growing industrialization and motorization of the world. The burning fossil fuels has contributed to the increasing of CO_2 level of in the atmosphere which is directly associated with global warming and also contribution of greenhouse gasses emission.

Lignocellulosic biomass (LCB) could help to reduce or minimizing the fossil fuel burning and CO_2 level in the atmosphere and thus decrease the global warming. In another word, LCB can lower the net greenhouse gasses emission than first generation production, thereby reducing environmental pollution.

In United States, bioethanol is mostly produced from corn starch feedstocks while in Brazil biofuel is generally produced for 89% of the current global bioethanol production [1]. Although corn-based and sugar based-ethanol are favourable substitutes to gasoline production especially in the transportation sector, but they are not sufficient to replace a considerable portion of the one trillion gallons of fossil fuel presently consumed worldwide each year [1]. Furthermore, the ethical concerns about the use of food as fuel are materials have encouraged research effort to be more focused on the possible of inedible feedstock alternatives [1].

LCB materials create a considerable renewable substrate for bioethanol production which do no longer compete with food production and animal feed. LCB materials also contribute to environmental sustainability. Moreover, LCB can be supplied on a large-scale basis from different low-cost materials such as municipal and industrial waste, wood and agricultural residues.

LCB is a complex composite mainly consisting of cellulose, hemicellulose and lignin. Different approaches can be used to convert LCB into bioethanol such as thermochemical conversion. These approaches involve degradation of the recalcitrant cell wall structure of lignocellulose into fragments of lignin, hemicellulose and cellulose. Each polysaccharide is hydrolyzed into sugars and being converted into bioethanol subsequent followed by a purification [1].

Suitable pretreatment is required to separate the components of LCB, reducing the crystallinity of the material, making the cellulose accessible and the removal of lignin and hemicellulose. There are four type of pretreatment methods which are physical, physiochemical, chemical and biological pretreatment. Irradiation technology (electron beam irradiation) is used for changing the properties of polymers.

Physical pretreatment of irradiation introduces a chain-cleavage mechanism by depolymerizing the polymeric material [2]. Electron beam irradiation (EBI) pretreatment is environmentally friendly, which produces less inhibitory byproducts than the conventional thermochemical methods, it uses a linear electron beam accelerator, and is subsequently evaluated with various analytical methods [3].

Chemical pretreatment of ionic liquid is known to be effective solvents for lignin, cellulose, hemicellulose and even intact wood. Ionic liquids are molten salts, typically ion pairs containing one or more organic acid counter ions. Ionic liquids are recognized to facilitate more green applications in reactions and separations due to their unique beneficial properties, such as negligible vapour pressure, and high thermal stability [4]. It's very low vapour pressure reduces the risk of exposure that is a clear advantage over the use of the classical volatile solvents [5].

The degree of crystallinity is used to monitor the level of degradation structure of the material. The pretreated LCB can be investigated by using various methods such as Fourier Transform Infrared Spectroscopy (FTIR) or X-Ray Diffraction (XRD). FTIR analysis is applied to determine the functional group of LCB while XRD is used to determine the crystallinity of the biomass. The aim of this research is to study the effect of combining electron beam irradiation and ionic liquid soaked (ILS) pretreatment on lignocellulosic of OPF and cellulose by analyzing the structure and crystallinity of material by using FTIR and XRD.

II. METHODOLOGY

Materials and method

Preparation of LCB of OPF

OPF was grinded by grinder machine and then grinded OPF was sieving by using sieve shaker to obtain particle size of LCB less than 250 µm. The moisture content of OPF was measured to be less than 10% and placed into an oven at 105ºC for 24 hours before the pretreatment process.

The moisture content was calculated by using equation:

$$\text{Moisture content} = \frac{(W_w - W_d)}{W_w} \quad \text{(Eqn 1)}$$

Where:

W_w = Weight of wet sample
W_d = Weight of dry sample

Preparation of 50% of [EMIM]Ac solution

For the chemical pretreatment, 50% of [EMIM]Ac solution was needed to pretreat the LCBs. About 263mL of [EMIM]Ac stock was mixed with 500 mL of deionized water in volumetric flask (MV of [EMIM]Ac is 170.212 g/mol and density is 1.027g/cm^3 at 25°C).

The volume for [EMIM]Ac is calculated by equation 2:

$$C_1V_1 = C_2V_2 \quad \text{(Eqn 2)}$$

Where:

C_1 = Initial concentration of 95% [EMIM]Ac solution
V_1 = Volume of [EMIM]Ac needed to make 50% wt solution
C_2 = Final Concentration [EMIM]Ac solution
V_2 = Volume of final solution

Ionic liquid pretreatment

Ionic liquid pretreatement was performed to determine the effect of pretreatment on crystallinity of LCBs. 0.25g of LCBs was mixed with 5mL of 50% of [EMIM]Ac in 15mL tube. Then, the tubes that contain the LCBs were heated at 99°C for 4 hours with continuous shaking at 800 rpm by using Bioshake IQ.

Electron Beam Irradiation Pretreatment

For physical pretreatment, the sample of LCBs were vacuum sealed by vacuum sealer. Then, the samples were placed on the conveyer trolley and taped in to avoid any disruption inside the irradiation room. The samples were irradiated at varying dose by using electron beam accelerator with electron voltage of 2 MeV (Nissin EPS3000, Japan). Irradiation dose was set to 50 kGy for each round, thus the samples underwent a few round to achieve the required doses.

Table 1: Parameters for electron beam irradiation pretreatment.

Parameter	Range of parameter
Irradiation dose	100, 200, 400, 600, 800 and 1000 kGy
Irradiation dose per pass inside the accelerator	50 kGy
Voltage accelarator	2 MeV
Current flow	5mA

Washing Process

Next, all pretreated LCBs in tube were washed by adding 5mL of distilled water into the tube to be 20mL for washing process and placed in centrifugal at 10000 rpm, 3°C for 10 mins. After that, supernatant in the tube was discarded. Then, distilled water was added into tube until 20mL and placed in centifugal again and repeated the washing process until the clear supernatant was obtained. After that, the supernatant was dried in oven at 5°C and the solid LCB in the tube was placed into desiccator for one day. Then, the pretreated LBs were analysed using FTIR and XRD.

Analysis of Fourier Transform Infrared Spectroscopy (FTIR)

The pretreated LCBs were analysed by using FTIR to identify the presence of certain functional group in a pretreated LCBs molecules. Firstly, top plate of FTIR was cleaned with acetone. The solid pretreated LCBs was inserted into hole and then purged it until range 59-60 scan. The pretreated LCBs was scanned carefully and all the result obtained was recorded.

Latent Order Intensity (LOI) can be calculated by equation 3:

$$LOI = \frac{A_{1430}}{A_{898}} \quad \text{(Eqn 3)}$$

Where $A = 2 - log_{10}(\%T)$

%T = transmittance (%)

Analysis of X-Ray and Diffraction (XRD)

Determination of crystallinity index of treated LCBs was done by using XRD. The solid pretreated LCBs was placed on the glass plate and flatten the surface. Then, the glass plate was placed inside the XRD equipment and set the condition in Rigaku software via computer connected.

Table 2: Parameter of XRD process

Parameter	Value
Voltage	30kV
Current	20mA
Angle	Start :10° Stop : 50°
Speed angle	5°/min

The crystallinity index can be calculated by equation 4:

$$C.I = \frac{I_{200} - I_{am}}{I_{200}} \times 100\% \quad \text{(Eqn 4)}$$

Where:

I_{200} = The maximum intensity of the (200) lattice diffraction.

I_{am} = The intensity diffraction of the amorphous band.

III. RESULTS AND DISCUSSION

A. FTIR analysis

The effectiveness of [EMIM]Ac on OPF has demonstrated by reduction of LOI from FTIR and reduction of CI based on XRD [6]. The combination of ILS and electron beam irradiation pretreatment has better result of depolymerisation of cellulose. Interaction of high energy electron beam causes depolymerisation of cellulose as a result of chain scission. Irradiation induces a chain-cleavage mechanism by depolymerizing the polymeric material [7].

The structure of constituent and chemical changes of OPF occurred after pretreatment can be observed whether doses of irradiation has an effect on the LOI value of LCB. Figure 1 shows the FTIR spectra of ILS OPF irradiated at different doses. The pattern of the spectrum were similar but different on the transmittance percentage of some bands.

Increasing of doses irradiation, the O-H band was less intense due to the breakage of hydrogen bond between O-H links where causes the disruption of crystalline cellulose. In another word, it is a result of the effect of the scission of the intramolecular and intermolecular hydrogen bond.

Figure 2 shows FTIR spectra of ILS Cellulose irradiated at different doses and the pattern of spectrum of ILS Cellulose was similar to ILS OPF. Only slightly different with treated ILS OPF on the transmittance percentage of some bands. The O-H bond in

ILS Cellulose also is less intense by increasing of doses irradiation from 100-600 kGy but decreasing from 800-1000 kGy. This might be due to improper washing step and contamination on the FTIR machine that leads to opposite result prediction.

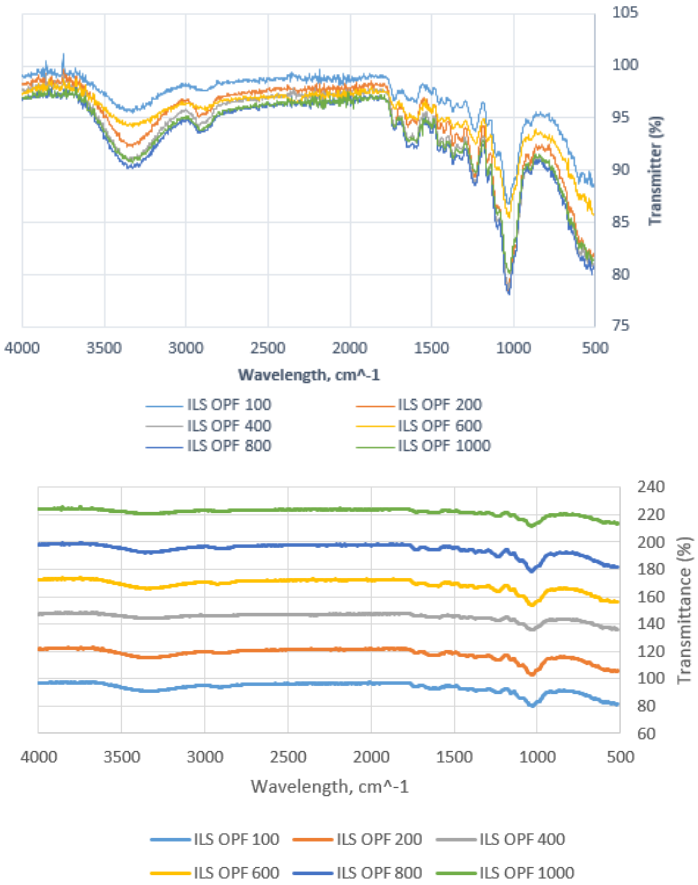

Figure 1: FTIR analysis of ILS OPF at different doses of irradiation.

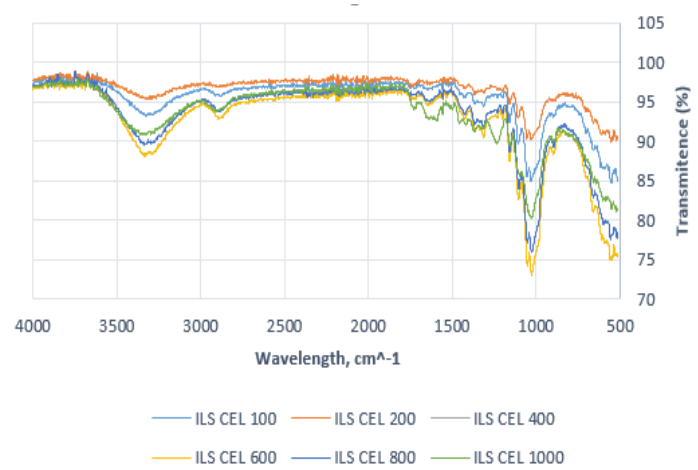

Figure 2: FTIR analysis of ILS Cellulose at different doses of irradiation.

Figure 3 shows the comparison of the band occurred in ILS OPF and ILS Cellulose at 800 kGy doses of irradiation. The FTIR spectrum of ILS Cellulose and ILS OPF were similar, maybe due to the similar functional group present in the sample. However, there are slightly difference was observed in the region of the intermolecular hydrogen bonding. Absorbance band of stretching vibration of O-H group of ILS Cellulose was observed at wavelength of 3323 cm^{-1} which is lower than ILS OPF at 3352 cm^{-1} at 800 kGy doses of irradiation. The band of ILS OPF was appeared broader than ILS Cellulose. It shows that MCC is more crystalline than OPF. This is might be due to cellulose chain polymer of MCC is much longer than OPF.

The C-H stretching vibration is assigned as alkane functional group that occurred at around 2840-2690 cm^{-1}. The result shows that the FTIR spectrum of both ILS OPF and ILS Cellulose were flatten and slightly increased in transmittance percentage. The CH_4 group in OPF is more disrupted after the combination pretreatment of ionic liquid soaked and electron beam irradiation.

The band at wavelength of 1710 cm^{-1} (HO-C=O carboxylic acid) were disappeared after the pretreatment on ILS OPF at 100-1000 kGy but only occurred at 800 kGy of irradiation. This happened might be due to improper washing sample where ionic liquid still in the sample. The disappearance of peak indicates the significant removal of hemicellulose. At wavelength of 1695-1630 cm^{-1}(C=0, C=C) shows a slight difference for both sample where peak of this band occurred at 1646 cm^{-1} in ILS OPF which is slightly higher than ILS Cellulose at 1627 cm^{-1}. Aromatic ring at 1500 cm^{-1} was not appeared in both samples which indicated the removal of lignin at 800 kGy doses irradiation. However, it can be observed in ILS OPF at 100-600 kGy at wavelength around 1590-1594 cm^{-1}. This might be due to less energy electron beam which was not enough to disrupt lignin of OPF. Next, C-O stretch was observed in all sample of ILS OPF at wavelength of 1231-1234 cm^{-1} which indicated the lignin content.

Other significant peak is C-O-C stretching (1160 cm^{-1}) which was observed in ILS Cellulose at 100,600 and 800 kGy. At wavelength of 1030 cm^{-1} that indicated C-O vibration in cellulose and hemicellulose appeared in all sample of ILS OPF and ILS Cellulose. A sharp peak was observed when doses of irradiation increased. Next, the peak at 897 cm^{-1} indicated that the sample became more amorphous. Based on hypothesis of this study, increasing doses of irradiation, the peaks decreased as the significant of the disruption of lignin, hemicellulose and cellulose.

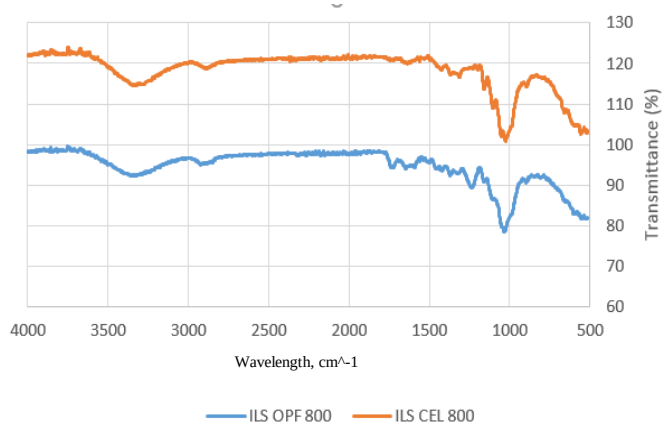

Figure 3: Comparison FTIR spectrum of ILS OPF and ILS Cellulose were irradiated at 800 kGy.

Table 1: FTIR absorbance bands of LCB

Wavelength (cm^{-1})	Assignment/functional group	Polymer
875	Glycosidic linkage	Hemicellulose [8]
930	Glycosidic linkage	Cellulose, hemicellulose [8]
990	C-O valence vibration	Cellulose [9]
1035	C-O, C=C, and C-C-O stretching	Cellulose, hemicellulose, lignin [8]
1160	C-O-C asymmetrical stretching	Cellulose, hemicellulose [8]
1200	O-H bending	Cellulose, hemicellulose [8]
1215	C-C + C-O stretch	Lignin (wood) [10]
1270	Aromatic ring vibration	Guaicyl lignin [8]

1280	C-H bending	Crystalline cellulose [8]
1310	CH_2 wagging	Cellulose, hemicellulose [8]
1327	C-O of syringyl ring	Lignin (wood) [10]
1335	C-H vibration, O-H in-plane bending	Cellulose, hemicellulose, lignin [8]
1380	O-H bending	Cellulose, hemicellulose, lignin [8]
1425	C-H in-plane deformation	Lignin (wood) [10]
1440	O-H in-plane bending	Cellulose, hemicellulose, lignin [8]
1465	C-H deformation	Lignin [8]
1500	Aromatic ring vibration	Lignin [8]
1595	Aromatic ring vibration + C=O stretch	Lignin [8]
1682	C=O stretching (unconjugated)	Lignin (wood) [10]
1730	Ketone/ aldehyde C=O stretch	Hemicellulose [8]
1750	Free ester	Hemicellulose [8]
2840, 2937	C-H stretching	Lignin (wood) [10]
3421	O-H stretching	Lignin (wood) [10]

The band at 1430 cm^{-1} is associated with the amount of the crystalline structure of the cellulose, while the band at 898 cm^{-1} is assigned to the amorphous region in cellulose. The ratio between two bands was defined as a lateral order index (LOI) which is empirical crystallinity index and it also sensitive to the amount of crystalline versus amorphous regions in the cellulose, and its lower value reflects a more disordered structure [11].

Based on Table 1, the LOI value of ILS OPF decreased by increasing doses of irradiation. Reduction of LOI value on ILS OPF was shown at 800 kGy doses of irradiation which is 0.6446 as compared to untreated irradiation ILS OPF of 0.7700.

Reduction of LOI value on ILS Cellulose was show at 600 kGy but other studies have shown a LOI reduction at 100 kGy. This may be due to the relatively high crystallinity of microcrystalline that was used in this research study. Radiation cleaves the amorphous of the cellulose more easily than the crystalline region [12]. The crystallinity of cellulose decreased with increasing irradiation doses.

Increasing doses of irradiation causes a significant changes in the structural features of the ILS OPF and ILS Cellulose as shown in FTIR analyses. The treated ILS OPF had lower crystallinity as compared to untreated OPF. The lower crystallinity of cellulose makes it more accessible to chemical reagents, and thus easier to hydrolyze to sugars [13]. This combination pretreatment has lowering the LOI value of treated OPF and MCC.

Table 2: Lateral Order Index (LOI) value for the effect of combining EBE and ILS pretreatment on lignocellulosic of OPF and Cellulose at different doses of irradiation.

Irradiation Dose (kGy)	ILS OPF		ILS CELULLOSE	
	$\frac{A_{1430}}{A_{898}}$	LOI	$\frac{A_{1430}}{A_{898}}$	LOI
100	$\frac{91.8823}{89.7055}$	0.7792	$\frac{95.5858}{93.0585}$	0.6275
200	$\frac{92.4655}{90.1186}$	0.7529	$\frac{96.8540}{995.0755}$	0.6329
400	$\frac{94.8096}{92.8394}$	0.7173	$\frac{96.5889}{94.8410}$	0.6552
600	$\frac{92.7070}{89.7698}$	0.7016	$\frac{92.8793}{88.3984}$	0.5990
800	$\frac{93.7627}{90.4926}$	0.6446	$\frac{93.5388}{89.3634}$	0.5939
1000	$\frac{96.5320}{94.3680}$	0.6088	$\frac{92.4655}{90.1186}$	0.7529

Table 3: LOI value of untreated LCB

Sample	LOI
Raw OPF	0.7700
Raw Cellulose	0.6800

B. XRD analysis

The X-ray diffractograms of the ILS OPF and ILS Cellulose at difference doses of irradiation are studied as show in Figure 4, 5, respectively. In order to determine the crystallinity index, the diffractograms are studied based on its peak and distribution. Hypothesis of this analysis is the increasing doses of irradiation is contributed to peak broadening. The peak intensities and peak broadening differ according to irradiation dosage.

Figure 4 shows the result of the XRD analysis of ILS OPF at different doses of irradiation. All the sample of ILS OPF presented the same diffraction pattern and the maximum intensity (200) repsenting the crystalline cellulose region . However, the diffraction pattern of ILS CEL in Figure 5 was different at 600-1000 kGy doses of irradiation. This might be due to some errors during the XRD analyses.

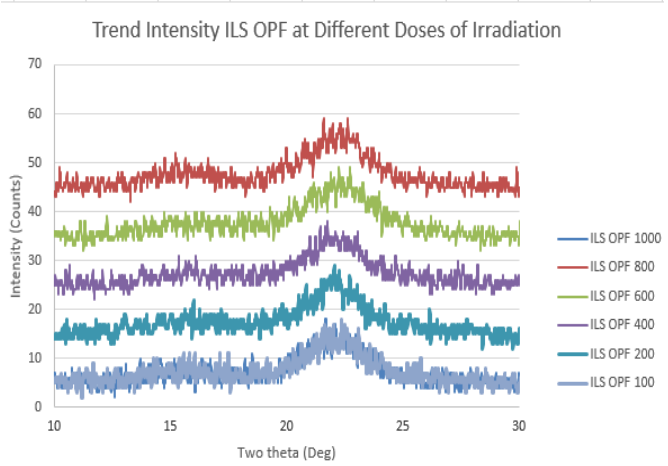

Figure 4: Graph of trend intensity ILS OPF at different doses of irradiation.

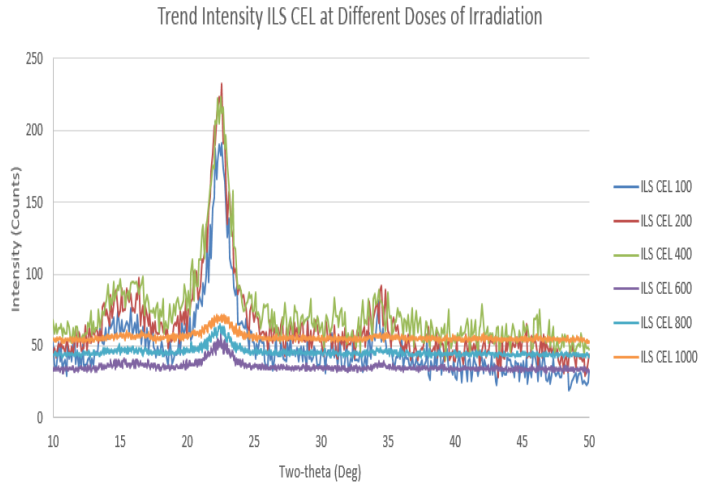

Figure 5: Graph of trend intensity ILS Cellulose at different doses of irradiation

Based on Table 3, the CrI value of ILS OPF was decreased from 63.99% for untreated OPF to 63.28% at 400 kGy doses of irradiation. Reduction of CrI was obtained at 400-1000 kGy, might be due to breakage of O-H bond by electron beam that reduced crystallinity of cellulose. However, the CrI value of ILS OPF was increased from untreated OPF at 100, 200 kGy respectively. This is might be due to disturbance of the power of the X-Ray Diffractometer that affected the interference patterns that reflecting lattice structures of sample.

The CrI value of ILS Cellulose was decreased from untreated Cellulose of 84.15% to 80.48% at 100kGy. Decreasing value of CrI of ILS Cellulose from the untreated Celullose was obtained at 100,200,400, and 1000 kGy doses of irradiation. However, at 600 and 800 kGy doses of irradiation, the CrI value obtained is higher than untreated Cellulose. This might be due to the X-ray diffractometer problem occurred during the XRD analyses.
The CrI value of ILS Cellulose obtained was 80.48% which is higher than CrI value of ILS OPF (72.22%) at 100 kGy doses of irradiation. This might be due MCC that used in this study more crystalline than OPF. These results show that the ILS OPF has lower CrI value compared to ILS OPF by combining the pretreatment of ionic liquid and electron beam irradiation.

Table 3: Crystallinity index intensity (CrI) value for the effect of combining EBE and ILS pretreatment on lignocellulosic of OPF and Cellulose at different doses of irradiation.

Irradiation doses (kGy)	ILS OPF			ILS CEL		
	I_{002}	I_{am}	CrI (%)	I_{002}	I_{am}	CrI (%)
100	18.00	5	72.22	189.58	37	80.48
200	19.00	6	68.42	219.05	39	82.20
400	19.12	7	63.39	206.52	39	81.12
600	19.07	7	63.29	28.95	3	89.64
800	19.23	8	58.40	25.00	3	88.00
1000	18.13	8	55.87	22.00	4	81.82

Table 4: CI value of untreated LCB

Sample	CrI(%)
Raw OPF	63.99
Raw Cellulose	84.15

IV. Conclusion

The LOI value of ILS OPF decreased with increasing doses of irradiation was obtained from FTIR analysis. Reduction of LOI value from untreated OPF obtained at 800 and 1000 kGy. Reduction of LOI value from untreated Cellulose obtained at 100-800 kGy. XRD analysis shows reduction of CrI value by increasing doses of irradiation in ILS OPF and has lower CrI value from untreated OPF obtained at 1000 kGy. While lower CrI value ILS Cellulose from untreated Cellulose obtained at 100, 200, 400 and 1000 kGy doses of irradiation. The crystallinity of cellulose should be decreasing with increasing doses of irradiation. However, this research does not fully achieve the hypothesis due to some error in X-Ray Diffractometer and improper washing step that affected the result. For the recommendation, ensure that the sample are washed thoroughly till the supernatant is clearly to avoid remaining of ionic liquid. Next, ensure that the sample are completely dry before the analysis to prevent the moisture that affected the sample. Lastly, make sure the equipment of analysis are completely stable to operate in order to provide the result accurately.

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