Pretreatment of Cellulose By Electron Beam Irradiation Method

N A A Jusri[1,a], A Azizan[1,b*], N Ibrahim[1,c], R Mohd Salleh[1,d] and M F Abd Rahman[2]

[1] Faculty of Chemical Engineering, Universiti Teknologi MARA, Shah Alam, Malaysia
[2] Agensi Nuklear Malaysia, Bangi, Malaysia

[1,a]aiedajusri@yahoo.com, [1,b*]amizon@salam.uitm.edu.my,
[1,c]norli816@salam.uitm.edu.my, [1,d]ruzitah@salam.uitm.edu.my,
[2]faizal@nuclearmalaysia.gov.my

Abstract. Pretreatment process of lignocellulosic biomass (LCB) to produce biofuel has been conducted by using various methods including physical, chemical, physicochemical as well as biological. The conversion of bioethanol process typically involves several steps which consist of pretreatment, hydrolysis, fermentation and separation. In this project, microcrystalline cellulose (MCC) was used in replacement of LCB since cellulose has the highest content of LCB for the purpose of investigating the effectiveness of new pretreatment method using radiation technology. Irradiation with different doses (100 kGy to 1000 kGy) was conducted by using electron beam accelerator equipment at Agensi Nuklear Malaysia. Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD) analyses were studied to further understand the effect of the suggested pretreatment step to the content of MCC. Through this method namely IRR-LCB, an ideal and optimal condition for pretreatment prior to the production of biofuel by using LCB may be introduced.
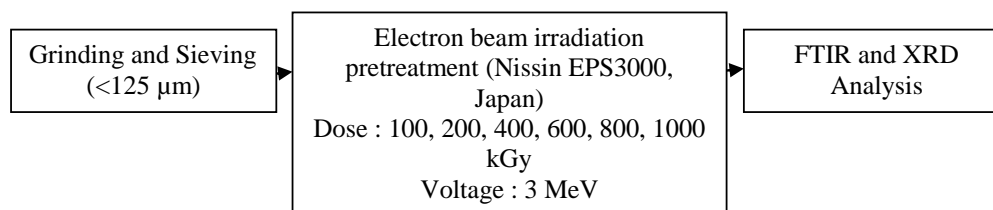
1. Introduction

The production of bioethanol through the pretreatment of LCB is one of the alternatives to produce environmental friendly and safer fuel as well as increasing the reduction of CO_2 emissions [1]. Waste that is bio-based material can be applied as the raw material for bioethanol production [2]. Biomass such as rice husk showed great potential to be one of the second generation bioethanol as it contained high MCC as well as nanocrystalline cellulose (NCC) [3]. There are several of methods that can be applied for the pretreatment of the LCB. Some of the pretreatment technologies showed impressive outcome as well as cost-effective pretreatment for LCB for the conversion to fuels and chemicals. These LCB pretreatment strategies are focusing on the reduction of lignin content and the crystalline structure of cellulose without damaging the fermentable sugar content [4]. Irradiation method for the pretreatment of LCB does not require any chemicals for the process and it reduces the crystallinity of the cellulose [5]. The conversion of sugar monomer to ethanol is obtained from the hydrolization of cellulose [6]. Cellulose is a natural polymer that can be easily obtained from LCB material such as oil palm frond and other agricultural residue [7].

Cellulose is the main structural components in the plant cells walls and located at the fibrous structure of the walls. D-glucose subunits comprised in the cellulose are linked to one another by β-(1,4) –glycosidic bond [8]. According to previous studies, the conversion yield of cellulose to glucose is increasing by 4% after 24 hours and 6% after 48 hours with 20 kGy of irradiation dose [9, 10, 11]. However, irradiation method alone is highly energy intensive and highly inapplicable. The indirect

measurements of cellulose were studied via the analyses by using various methods such as Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD).

2. Material and Method

| Grinding and Sieving (<125 µm) | → | Electron beam irradiation pretreatment (Nissin EPS3000, Japan) Dose : 100, 200, 400, 600, 800, 1000 kGy Voltage : 3 MeV | → | FTIR and XRD Analysis |

The irradiated MCC was then analyzed via FTIR and XRD for the Lateral order index (LOI) and Crystallinity Index (CrI), respectively. The LOI for FTIR sample was calculated by using the absorbance (A) ratio A_{1430}/A_{898}. From the raw data of FTIR, the transmittance (T) value was converted to absorbance by using Equation 1 from Beer's Law [12]. Crystallinity Index (CrI) of samples were measured by using a High-Resolution X-Ray Diffactrometer (Multi-Purpose X-Ray Diffactrometer, Ultima IV, Rigaku, USA) with Cu Kα at 50 kV and 300 mA. Samples were scanned over a scattering angle (2θ) from 10° to 50° at a rate of 2θ per min. The CrI was calculated by using Segal's Equation (Equation 2) in order to determine the crystalline structure of each treated samples [13] where CrI, I_{am} and I_{002} are defined as the crystallinity, the lowest intensity of the peak at 2θ =18.0$^{°}$ and the maximum intensity about 2θ = 22.6°, respectively.

$$A = 2 - log_{10}\,(\%T) \quad (1) \qquad\qquad CrI\,(\%) = \frac{I_{002} - I_{am}}{I_{002}}\,x\,100 \quad (2)$$

3. Result and Discussion

3.1 FTIR Analysis

FTIR spectroscopy was frequently used to investigate the structure of constituents and the chemical changes occurring during the pretreatment of lignocellulosic biomass [14]. Table 1 shows the characteristics and variations of wavenumber in FTIR spectra possible for MCC. The FTIR spectra of MCC samples irradiated with different doses are shown in Figure 1.

Table 1. Characteristic and variations of wavenumbers in FTIR spectra possible for MCC [15, 16, 17].

Wavenumber	Possible Functional Group	Wavenumber	Possible Functional Group
3350	O-H	1158	C-O asymmetric stretching
3175	-OH stretching	1050	C-O stretching in cellulose I and cellulose II
2918	C-H stretching	850	β-glycosidic bonds between sugar
1430	C-H$_2$ bending	550	β-glycosidic linkages
1315	C-H$_2$ wagging		

In FTIR spectra, due to the absorption of certain amount of energy produced from the radiation, the covalent bonds of each functional group are stretched, vibrated, bended, rocked or twisted [14]. According to the structure of MCC, all the wavenumbers obtained from FTIR spectra show almost similar characteristic as explained in Table 1. Functional bond of O-H is shown at the range of 3600-3200 cm^{-1} while C-H stretching as well as C-H$_2$ bending and wagging are observed at wavelength bonds between 2900-2800 cm^{-1} and 1500-1300 cm^{-1}, respectively. Other than that, C-O-C stretching and bonds between sugar are defined at the wavenumber of 1200-800 cm^{-1}. Table 2 below shows the LOI value for the effect of irradiation dose on MCC pretreatment.
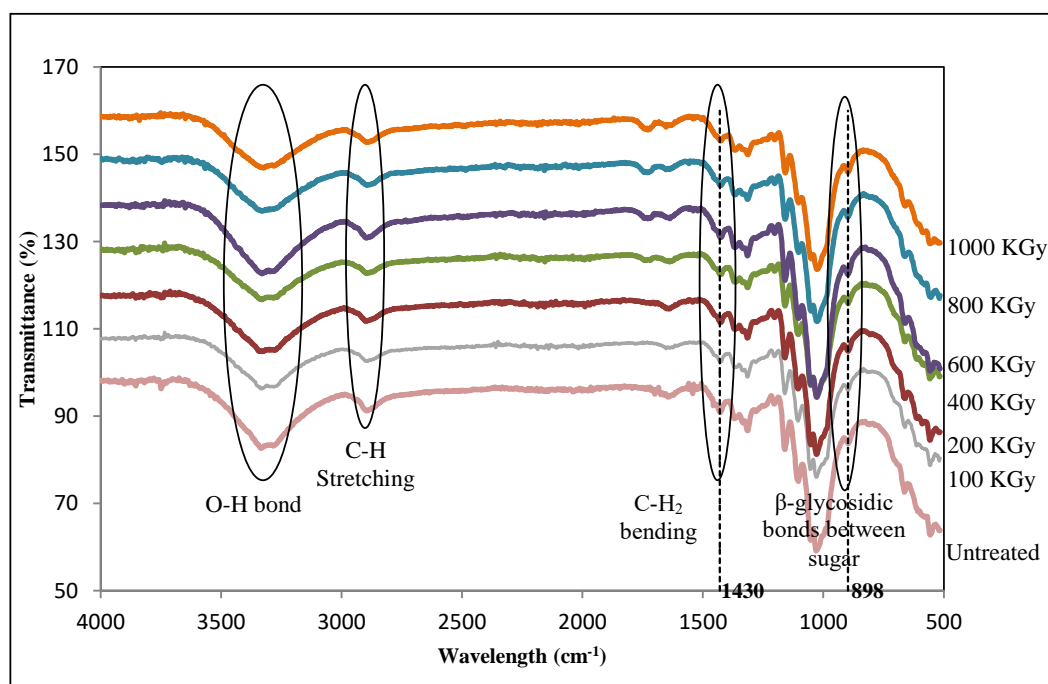
Figure 1. FTIR band for microcrystalline cellulose (MCC) with different irradiation dose (100 to 1000 kGy).

Table 2. Lateral order index (LOI) value for the effect of irradiation dose on MCC pretreatment.

Irradiation Dose (kGy)	LOI	Irradiation Dose (kGy)	LOI
Untreated	0.551	600	0.486
100	0.536	800	0.476
200	0.518	1000	0.464
400	0.508		

The absorbance values at ~1430 cm^{-1} and ~898 cm^{-1} are quite sensitive in the crystal structure of cellulose in cellulosic material [18]. Therefore, the absorbance ratio of A_{1430}/A_{898} which is known as crystallinity index known as LOI was used in determining the effect of pretreatment to the crystallinity in cellulose. The lower the value of LOI reflects that the material has a lower crystallinity. High dosage of irradiation resulted in lower LOI values indicating that the MCC structure has changed to amorphous structure. Thus, with higher amorphous structures present, it enables better hydrolysis via suitable enzyme in comparison to with the presence of ordered arrangement of crystalline structures resulting in a higher effectiveness in biofuel production. The initial investigation of irradiation opens to possible different prospective in pretreatment on Malaysian LCB without using any additional chemicals.

3.2 XRD Analysis
XRD was used to identify the crystallinity index of the MCC (after pre-treatment). From Table 3, it is shown that CrI of pretreated MCC decreases with the increment of irradiation dose. XRD pattern for untreated and irradiated MCC are shown in Figure 2. Due to cross linking which may take place in the reaction and the removal of the crystalline fraction, there was a slight decrease in the degree of

crystallinity after pretreatment by the irradiation. The untreated MCC gave the highest crystallinity index as compared to the irradiated MCC which was 85.9%. The lowest crystallinity index was shown by the irradiated MCC at 1000 kGy. Table 3 was constructed to show the effectiveness of pretreatment by crystallinity index (CrI) for each irradiation dose in percentage (%) form. The lowest CrI values represent the most efficient dose for pretreatment due to the highest value in effectiveness which is 14.32% at 1000 kGy irradiation dose as compared to the untreated one.
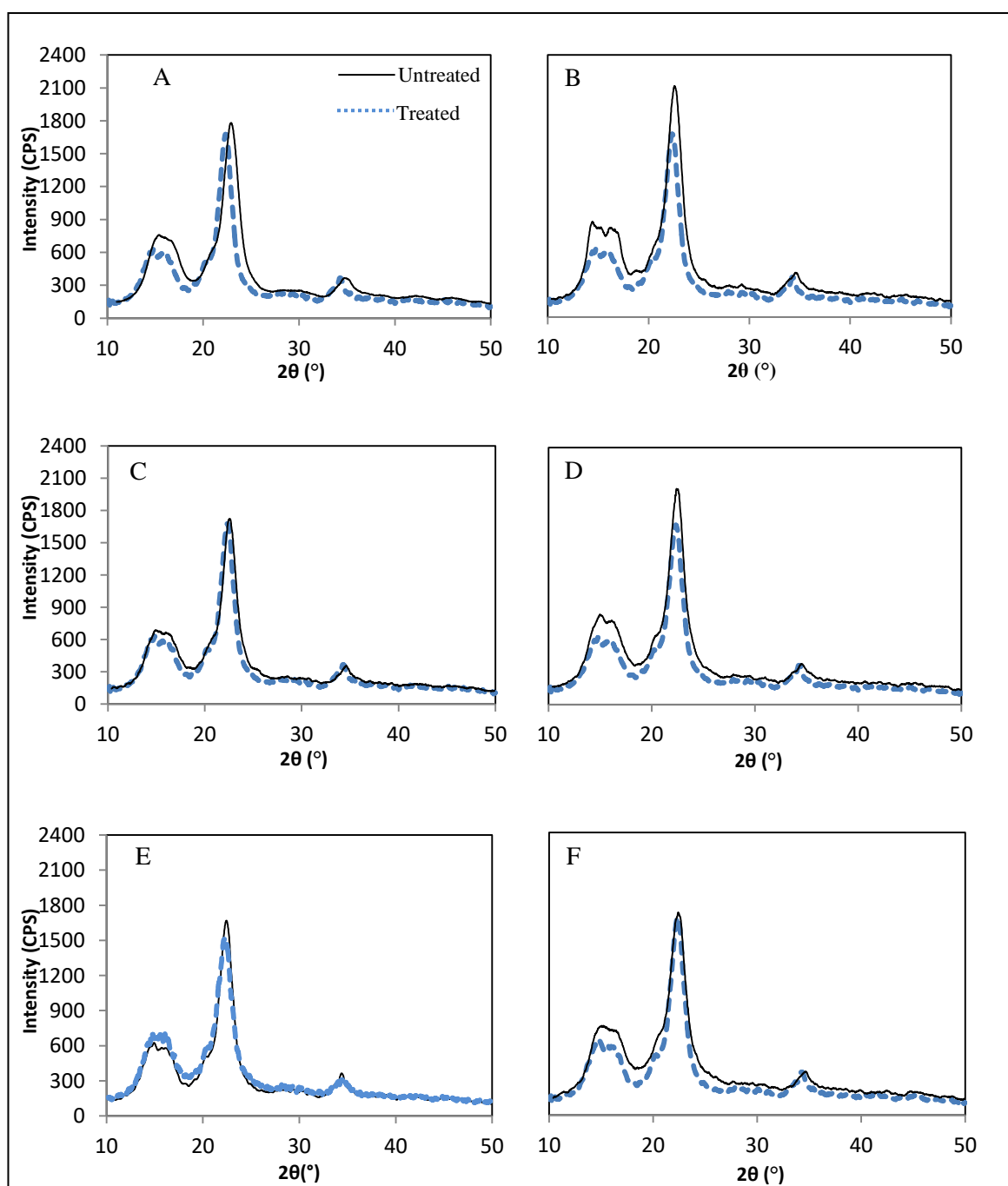

Figure 2. XRD pattern of untreated (unirradiated) and treated (irradiated) MCC
[A: 100 kGy, B: 200 kGy, C: 400 kGy, D: 600 kGy, E: 800 kGy and F: 1000 kGy].

Table 3. Values of crystallinity index and effectiveness of pretreatment.

Irradiation Dose (kGy)	Crystallinity Index (%)	Effectiveness (%)
0	85.9	-
100	84.2	1.98
200	80.9	5.82
400	80.0	6.87
600	77.4	9.90
800	76.1	11.41
1000	73.6	14.32

4. Conclusion

Microcrystalline cellulose powder which was treated by electron beam irradiation process at different dose indicates that the method is possible for further improvement From the FTIR spectra, it can be concluded that the lower transmittance at O-H bonds wavelength may indicate that higher cellulose could be recovered after pretreatment. XRD analysis also shows that as the irradiation dose increases, the crystallinity index of cellulose decreases. This indicates that the crystalline structure of cellulose may be leading towards amorphous states. If this is consistent with the lower crystallinity index it becomes with the irradiation technology introduced on MCC, a better conversion into biofuel can be expected.

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