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Effect of Structural Changes of Lignocelluloses Material Upon Pre-Treatment using Green Solvents

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Abstract. The Malaysia Biomass strategy 2020 stated that the key step of biofuel production from biomass lies on the pretreatment process. Conventional 'pre-treatment' methods are 'non-green" and costly. The recent green and cost-effective biomass pretreatment is using new generation of Ionic Liquids also known as Deep Eutectic Solvents (DESs). DESs are made of renewable components are cheaper, greener and the process synthesis are easier. Thus, the present paper concerns with the preparation of various combination of DES and to study the effect of DESs pretreatment process on microcrystalline cellulose (MCC), a model substrate. The crystalline structural changes were studied using using X-ray Diffraction Methods, Fourier Transformed Infrared Spectroscopy (FTIR) and surface area and pore size analysis. Results showed reduction of crystalline structure of MCC treated with the DESs and increment of surface area and pore size of MCC after pre-treatment process. These results indicated the DES has successfully converted the lignocelluloses material in the form suitable for hydrolysis and conversion to simple sugar.

INTRODUCTION

The conversion of lignocellulosic biomass into value-added products requires pre-treatment, hydrolysis (saccharification) and the conversion of simple sugar into end products. The limiting factor of these three processes lies in the pre-treatment steps. Conventional pre-treatment methods normally use strong acids or alkali which poses environmental problems. Recently, pre-treatment using Deep Eutectic Solvents (DESs) has been considered as new green and cost efficient solvent. Lignocellulose is pre-treated to remove lignin and waxes materials to make cellulose assessible for hydrolysis then followed by hydrolysis of cellulose to fermentable sugar or known as saccharification. Finally is fermentation of simple sugar into desire products. Cellulose is a crystalline biopolymer where its main chain motion is restricted by inter- and intramolecular hydrogen bonding. The crystalline region of cellulose has lower accessibility than amorphous domains, due to the impenetrability of the tight crystalline structure [1]. During enzymatic hydrolysis, it was found that the amorphous cellulose was hydrolyzed first, followed by the hydrolysis of the more recalcitrant crystalline composition [2]. Researchers have used several tools and analysis to study the impact of pre-treatment on the lignocellulose material such as X-ray diffraction (XRD), Fourier Transformed Infrared Spectroscopy (FTIR), etc. Pre-treatments can change cellulose crystal structures by disrupting

inter- and intra- chain hydrogen bonding of cellulose fibrils. Reduction of crystalline structure and increment of amorphous region improved hydrolysis process [3].

Apart from that, another factor that affects the cellulose digestibility and hydrolysis is accessible surface area. Decrease of particle size or increase in pore volume always leads to an increase of accessible surface area[4]. In general, larger surface area and pore volume is favourable to gain higher digestibility of biomass. Thus in this paper, microcrystalline cellulose (MCC) was used as a model substrate to study the structural change of the substrate upon pre-treatment with DESs; Ethylene glycol-choline chloride based DES (EG), glycerol-choline chloride based DES (GLY) and malonic acid-choline chloride based DES (MA).

MATERIAL AND METHOD

The different DESs were prepared based on the procedure described in Gunny et al., [5]. MCC was used as a model substrate to study the structural change of the substrate upon pre-treatment with DESs. 10 % (w/v) of MCC/DES was prepared by dissolving 1.0 g of MCC in 10 ml DESs. The mixture was stirred and heated at 115˚C for 24 hours. The cellulose was precipitated and regenerated using water. The regenerated MCC from each pre-treatment was dried using vacuum oven at 60 ˚C for overnight and then all the samples ground into powder before use. Then, this was followed by the analysis structural change before and after the pre-treatment process.

Typically, hydrolysis rates for amorphous cellulose are much faster than crystalline cellulose. Therefore, the crystallinity index, CrI, of a sample is useful parameter to assess the efficiency of hydrolysis [6, 7]. This crystallinity index (CrI), is a measure of the relative degree of crystallinity, which can be determined through the use of X-ray diffraction (XRD) using the relationship as stated by Segal et al., [8] in the following equation (1):

$$CrI = (I_{TOT}/I_{AM})/I_{TOT} \qquad (1)$$

Where: $CrI=$ Crystallinity index
              $I_{TOT=}$ Intensity at about $2\theta = 22°$ (represents the crystalline and amorphous material)
              $I_{AM=}$ Intensity at the "valley" between the two peaks at about $2\theta = 18°$. (represents the
                      amorphous material)

The change in the chemical structure of untreated and pre-treated rice husk was analyzed using Spectrum 65 FT-IR spectrometer from Perkin Elmer. The samples were mixed with potassium bromide (KBr) before pressing the sample into discs. The spectrum for each sample was recorded in the range of 4000-650 cm^{-1}. Crystallinity index (CI) using FTIR was determined by the formula in equation (2) as proposed by O'Connor, DuPré and Mitcham (9] :

$$Lateral\ Order\ Index\ (LOI),= A_{1431}/A_{895}) \qquad (2)$$

where $A_{1431 =}$ absorbance ratio at peak (1431) and $A_{985 =}$ absorbance ratio at peak (895)

The surface area and pore size measurement of pre-treated MCC were carried out using Micromeritics® ASAP 2020 accelerated surface area and porosimetry analyser.

RESULTS AND DISCUSSION

Crystallinity of lignocellulose material is one of the important features usually affecting enzymatic hydrolysis. Crystallinity index (CrI) is usually employed to describe the crystalline degree of lignocellulose materials [4]. Table 1 showed the crystalline index of MCC subjected with different DESs pre-treatment. Untreated MCC was found to be highly crystalline (77.1 CrI). After DES pre-treatment, CrI index of MCC was decreased to 68.4CrI under GLY pre-treated sample, 71.4 CrI for MA pre-treated sample and for EG pre-treated sample was slightly decreased to 74.2 CrI. For lignocellulose material, decreasing crystallinity can relatively increased amorphous area and this will improve initial hydrolysis rate and reduce the hydrolysis time or the enzyme loading for attaining high digestibility [4].

Apart from that, the chemical structure of untreated and treated MCC was analysed using FTIR. As shown in Figure 1, the spectra generated by samples treated with DESs show small difference as compared to that of untreated MCC at a wavelength around 1430cm^{-1}. At this wavelength, crystalline regions showed more intense for untreated MCC as compared to untreated samples. The peak is strong for crystalline cellulose and weak in amorphous cellulose [10]. Highest intensity of crystalline peak was found in an untreated sample while the lowest intensity of the crystalline peak was found in MCC treated with GLY. The treatments have changed the cellulose crystalline structure by probably disrupting the inter/intra hydrogen bonding of cellulose chains [11].

The total crystalline indexed calculated using lateral order index (LOI) formula (as stated in Equation 1.0) of FTIR spectra is shown in Table 1. The results showed that the untreated sample has the highest LOI indicating highest crystalline indexed as compare to DESs-treated sample. Thus, these observations indicated reduction in crystalline structure for DESs treated sample as compared to untreated sample.

TABLE 1. Results of XRD, FTIR and TGA analysis for DES-treated and untreated sample.

Sample	Cr Index (XRD)%	LOI,$_{A1431/895}$ (FTIR)
Untreated MCC	77.07	1.70
Treat with EG	74.29	1.41
Treat with GLY	68.42	1.32
Treat with MA	71.43	1.39
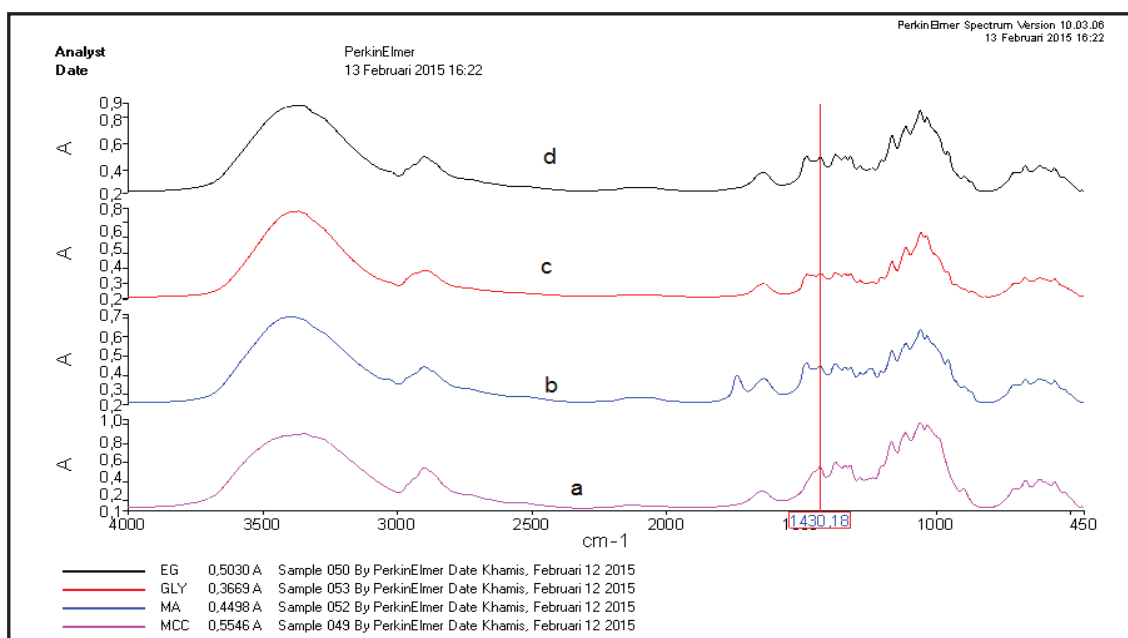
FIGURE 1. FTIR spectra of samples: 'a' represent untreated MCC while 'b', 'c' and 'd' represent the MCC treated with MA, GLY and EG respectively.

One of the criteria of cellulose hydrolysis by cellulases is the adsorption of the enzymes onto substrates where these characteristic can be evaluated by accessible surface area and pore size of the biomass [4]. MCC subjected to pre-treatment has greater surface area and pore size as compared to untreated MCC as proven in Table 2. A greater accessible area and pore size signifies an increased in the amorphous region and therefore is more susceptible to enzymatic attack [12]. This contributes most to the significant improvement in the yields of reducing sugar from pre-treated biomass [13].

TABLE 2. Result of surface area and porosity analysis for DES-treated and untreated sample.

Sample	Surface Area (m²/g)	Pore size (Å)
Untreated MCC	1.967	63.648
Treat with EG	5.353	71.773
Treat with GLY	2.115	343.578

CONCLUSION

The studies promised the DESs as green solvents for lignocelluloses pretreatment. However, the studies demonstrate the mild effects of morphological change of lignocelluloses' crystalline structure upon pretreatment with DESs. Hence, future works on the optimization of lignocelluloses material pre-treatment using DESs need to be performed in order to improve the reduction of crystalline structure and increment of MCC's pore size and surface area upon the pre-treatment.

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