Study of delignification process and crystallinity index on lignocellulose components of corn cob in different pretreatments: a combination of pretreatment (ionic choline acetate and NaOH) and NaOH pretreatment

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Abstract. This study studied the effect of combination pretreatment (ionic liquid choline acetate and NaOH) and pretreatment of NaOH in the process of delignification and lignocellulose crystallinity index. This process was carried out to obtain a good lignocellulose biomass, which has a low lignin content and a high crystallinity index to be prepared as a raw material for making bioethanol. Low lignin content and high index of crystallinity can influence the success of the enzymatic hydrolysis process and of course bioethanol production.

In the combination of pretreatment, the highest lignin removal was found from process with 5% of NaOH as much as 41.63% but the crystallinity index was found from process with 3% of NaOH as much as 46.33. While, In the NaOH pretreatment, the highest lignin removal and crystallinity index was found from process with 5% of NaOH as much as 7.63% and 3.87, respectively.

1. Introduction
Corn is a dicotyledonous plant which is a source of carbohydrates. Derivative product of corn has beneficial for health such as maize starch, maize flour, and maize oil [1]. According to ASEAN Economic Community (AEC), corn is one of strategic commodities in ASEAN that become special attention besides rice, soybeans and cassava and Indonesia is one of the largest producer of corn in ASEAN [2]. The availability of corn in large scale would generate large waste of corn such as corn cob and it becomes a problem for the environment if it is not handled properly.

Corn cob is a lignocellulosic biomass sustainable in a bioethanol production because consist of lignocellulosic material. The main component of lignocellulosic in corn are 38.8% of cellulose, 44.4% of hemicellulose, and 11.9% of lignin [3]. Based on the content, corn cob has great potential to be hydrolyzed to glucose, is a monosaccharide that can be used as a raw material for processed into various derivative products such as chemicals, pharmaceuticals, glucose, and bioethanol [4]. The large lignin content in corn cob causes small glucose yields in the hydrolysis process, so pretreatment is needed to destruct the lignin structure to improve the efficiency of the hydrolysis process [5].

In addition, by utilizing lignocellulose biomass as raw material for bioethanol, food availability will remain stable. Another advantage of using this material are its abundant presence, environmentally friendly which does not produce greenhouse gas emissions such as petroleum fuels, and sustainable energy [6].
This research was carried out at chemical pretreatment using ionic liquid which has an advantage of not having an inhibitory effect on the enzymatic process [7]. Ionic liquids are environmentally friendly solvents which are stable in temperature, not volatile and can be reused (recycle) [8]. The type of ionic liquid used in this study is choline acetate (ChOAc) which has no inhibitory properties against enzymes and microorganisms compared to 1-ethyl-3-methylimidazolium acetate (Emi-mOAc) [9]. In addition to the ionic liquid pretreatment in this study also used alkaline pretreatment (NaOH). Treatment by adding NaOH can reduce lignin and can increase the accessibility of enzymes in cellulose [10] [11]. Therefore in this study the lignin removal process on corn cobs was carried out using the ionic liquids method using choline acetate (ChOAc) in combination with alkaline NaOH. This study aims to study the pretreatment results using ionic liquid, alkali of NaOH, and a combination of ionic liquid and alkali of NaOH to lignin decreasing and the level of lignocellulose crystallinity.

2. Material and method

2.1. Material

Material used in this study was corn cob, collected from agricultural land located in Bantul and Sleman, Yogyakarta, Indonesia. Corn cob was cutted into small size (1 cm²) then dried under the sunlight for 2 days. And then it was crushed to become powder with 80 mesh of size and dried in the oven with 105°C of temperature to remove the water content bound in corn cobs powder. Ionic liquid used in this research was choline acetate (ChoAc) and for alkali method used NaOH.

2.2. Method

2.2.1. Ionic liquid method. Ten grams of corn cob powder was dissolved in 500 ml water and added with ChoAc in ratio 0,3 of IL : biomassa. The suspension was heated at 90°C, 120°C, and 150°C for 20 hours then filtered in centrifuge to separate the solid and liquid. The solid was washed by water and then separated from the liquid again. The water content was removed from sample using oven at 105°C until has constant weight.

2.2.2. Successive alkali method. Corn cob powder that has been pretreatmented by choline acetate was mixed with NaOH solution in ratio of solid : liquid = 1 : 20 (g/ml). Variation of NaOH concentration in this experiment were 1%, 3%, and 5%. The sample was heated at 90°C for 2 hours then filtered by a centrifuge to separate between solid and liquid. Solid was washed by water and separated again from the liquid and then ovened at 105°C of temperature.

2.2.3. Analysis method. In this study used two methods of pretreatment to remove lignin from corn cob powder were ionic liquid and successive alkali method. The ionic liquid used in this study was choline acetate (ChoAc) and the alkali was NaOH. Component of cellulose, hemicellulose and lignin were determined by chesson method [12] and characteristic of those were analyzed by Fourier-transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD) method. Index of cristallinity was defined using Eq. (1):

$$CrI = \left(\frac{I_{200} - I_{am}}{I_{200}}\right) \times 100\%$$

CrI = Crystallinity Index

$I_{200}$ = Crystal intensity at $2\theta$ around 22.5°

$I_{am}$ = Amorphous Intensity at $2\theta$ around 18°
3. Results And discussions

3.1. Corn cob composition
Composition of untreated corn cob powder is presented in Table 1. As known in Table 1, it consisted of 35.82% of cellulose, 37.48% of hemicellulose, and 15.59% of lignin. In this study was found higher lignin than reported by previous study that was needed to be treated [3].

Table 1. Chemical composition of untreated corn cob powder

| Component    | Concentration (%) |
|--------------|-------------------|
| Cellulose    | 35.82             |
| Hemicellulose| 37.48             |
| Lignin       | 15.59             |

3.2. Effect of temperature on corn cob composition in ionic liquid choline acetate pretreatment
Composition of corn cob treated by choline acetate in variation of temperature 90°C, 120°C, and 150°C are shown in Table 2. As indicated, choline acetate removed lignin 24.57%, 30.08%, and 36.05% in different temperature process were 90°C, 120°C, and 150°C, respectively.

Table 2. Chemical composition of corn cob after ionic liquid choline acetate pretreatment

| Pretreatment condition | Concentration (%) | Lignin removal (%) |
|------------------------|-------------------|--------------------|
|                        | Cellulose | Hemicellulose | Lignin |                |
| IL choline acetate     |           |              |        |                |
| 90°C                   | 37.00     | 36.60        | 11.76  | 24.57           |
| 120°C                  | 35.70     | 35.90        | 10.90  | 30.08           |
| 150°C                  | 33.60     | 34.00        | 9.97   | 36.05           |

As seen in Table 2, treatment at higher temperature can removed lignin in higher amount. On other hand from Table 2 known that temperature can degraded cellulose. This occurs in treatments that used temperatures of 120°C and 150°C. From this treatment the highest cellulose content was found in choline acetate treatment at 90°C of temperature that was 37.00%.

3.3. Effect of combination of ionic liquid choline acetate and NaOH alkali pretreatment
The highest cellulose content in choline acetate treatment was then subjected to NaOH treatment. The NaOH concentration used were 1%, 3%, and 5%. Comparation of removal lignin and cellulose content between combination of treatment (choline acetate and NaOH treatment) and NaOH treatment seen in Table 3.

Table 3. Chemical composition of pretreated corn cob powder

| Pretreatment condition | Concentration (%) | Lignin removal (%) | Cristallinity Index (CrI) |
|------------------------|-------------------|--------------------|---------------------------|
|                        | Cellulose | Hemicellulose | Lignin |               |               |
| IL choline acetate + NaOH |         |              |        |                |               |
| 1%                     | 37.00    | 36.50       | 11.10  | 28.80          | 35.85          |
| 3%                     | 43.29    | 35.53       | 9.52   | 33.29          | 29.85          |
| 5%                     | 53.41    | 32.35       | 6.75   | 56.68          | 31.46          |
| NaOH                   |           |              |        |                |               |
| 1%                     | 36.20    | 38.10       | 15.30  | 1.86           | 31.76          |
| 3%                     | 37.40    | 37.60       | 14.60  | 6.35           | 23.08          |
| 5%                     | 38.00    | 36.80       | 14.40  | 7.63           | 33.87          |
As seen in Table 3, combination of choline acetate and NaOH treatment removed lignin in higher amount than NaOH treatment. High concentrations of NaOH also has a higher lignin removal effect either in combination of treatment or NaOH treatment. The higher lignin removal occurred in process that used 5% of NaOH, either in combination of treatment or NaOH treatment was 56.68% and 7.63%, respectively.

Figure 1. XRD spectrum of (a) combination of pretreatment (choline acetate and 1% of NaOH) and (b) pretreatment 5% of NaOH
Cristalinity index (CrI) and XRD spectrum can be seen in Table 3 and Figure 1. Table 3 shows that the highest CrI was obtained from process used concentration of NaOH 1% in combination pretreatment while 5% of NaOH in NaOH pretreatment. In combination of pretreatment the CrI was 35.85 while in NaOH pretreatment was 33.87. In the enzymatic hydrolysis process, the character of the cell wall and the level of accessibility of lignocellulose microfibrils become a factor that determines the hydrolysis rate. And enzyme accessibility is influenced by the cristallinity and size of the cellulose particles [5]. As indicated, an increase in crystallinity can occur due to removal of amorphous parts by alkali pretreatment. This is in accordance with previous research conducted by Williams 2011 [13].

4. Conclusions

In the current research many studies have been conducted to find environmentally friendly and sustainable energy as an alternative to fossil-based energy. To solve this problem, lignocellulose biomass is a concern of researchers because it is available in abundance. Large lignin content in lignocellulose biomass can affect the enzymatic hridrolysis process so pretreatment is needed to eliminate it. From this study, combination pretreatment (ionic liquid choline acetate and NaOH) and NaOH can be considered as a method that can be used to obtain lignocellulose with a high cristallinity index and eliminate lignin. In the combination of pretreatment the highest lignin removal was found from process with 5% of NaOH as much as 56.68% but the cristallinity index was found from proces with 1% of NaOH as much as 35.85. While, In the NaOH pretreatment the highest lignin removal and cristallinity index was found from process with 5% of NaOH as much as 7.63% and 33.87, respectively.

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