Effectiveness of Modified Natural Zeolite through Acid Activation as A Catalyst on Cellulose Conversion into Glucose from Cotton Assisted by Ultrasonic

Sumari*, Ni’matus Sholihah, Mahrullina Mahirotul Aisiyah, Intan Oktaviani, Natasha Khilmi, Yana Fajar Prakasa

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia

*Corresponding author’s email: sumari.fmipa@um.ac.id

Abstract. This study aimed to convert cotton cellulose into glucose using the catalyst of activated natural zeolite assisted by ultrasonic. The catalyst of hydrolysis of cellulose into glucose used acid-activated natural zeolite. Preparation and activation of natural zeolite used HCl solution 1M, 2M, and 3M. This activated natural zeolite was characterized using Freundlich adsorption isotherms, XRD, and XRF. Hydrolysis of cotton cellulose assisted by ultrasonic waves was conducted for 1, 2, and 4 hours. Identification of the degradation product used Fehling test and Nelson-Somogyi test. Based on the Freundlich adsorption isotherm analysis, the natural zeolite activated by 1M HCl solution had the largest surface area of 120 m²/g. The XRD diffractogram showed that zeolite before and after the activation process had a similar type structure that is mordenite. Meanwhile, the XRF test showed a decrease in the relative percentage of impurities followed by the increase in Si and Al percentage on activated natural zeolite with Si/Al ratio of 7.13. Based on the Fehling and Nelson-Somogyi test, the highest yield of glucose of 4.51% was obtained when using a catalyst natural zeolite activated with HCl 1 M for 4 hours sonication time.

Keywords: Cellulose, activated natural zeolite, glucose, catalyst, ultrasonic

1. Introduction

Cellulose is an organic compound of a polysaccharide as the main content of plant cell wall. Based on the statistical data, the biomass waste production in Indonesia reaches 147.6 million ton every year. The content of cellulose within the biomass waste is approximately 30 – 50%. Therefore, cellulose obtained from the biomass waste cultivation in Indonesia reaches about 59 million ton every year [1]. One of the biomass wastes is cotton that also causes environmental water pollution. The abundant cellulose has a significant potential to be used as a renewable energy source.

Cellulose can be hydrolyzed to be glucose by the enzyme of an acid catalyst [2]. Glucose is needed by human as the main energy source of their body [3]. Besides, glucose is a raw material of vitamin C synthesis through the Reichstein process, sorbitol, and bioethanol as a renew able energy fuel [4]. Nevertheless, this poly-glucose compound has a complex and strong structure so that it is difficult to be hydrolyzed into glucose. One of the research methods that have been developed for cellulose hydrolysis is hydrolysis method by using 2% of acid catalyst yielding the glucose of 5.0675% [5].
However, the direct use of acid is not environmentally friendly since acid is corrosive and toxic. Another research was conducted that doing cellulose hydrolysis become glucose using high temperature-ultra and the explosion of vapor pressure and it resulted in glucose of 67.7% (60 atm, 1 minute) [6]. Cellulose hydrolysis becoming glucose by using hydrothermal at the high pressure and temperature (250 atm, 300 °C) was also done, and it yielded 63.8% of glucose [7]. Another research by applying base pre-treatment method at the temperature of 121 °C continued with fermentation by cellulose enzyme yielded the high glucose of 45.69% [8]. However, those methods mentioned before were done at the high temperature and pressure so that they were less practical and safe. Moreover, the cellulose enzyme is relatively high-cost. Cellulose hydrolysis using the catalyst of activated natural zeolite (calcination) that was impregnated by Ni. This process resulted in glucose with a percent yield of 0.967 % wt [9]. This process was basically environmentally friendly, but the percent yield was still low, and thus the catalyst modification is needed to make the process more efficient.

In this research, the cellulose hydrolysis process was by using natural zeolite activated by acid (HCl) helped by ultrasonic wave. Zeolite activated by acid was expected would be filled by H⁺ ion of an acid. The existence of H⁺ ion and ultrasonic wave helped to break the glycosidic bond easily in the cellulose so that it resulted in glucose and the other much more reducer sugar.

The study of cellulose hydrolysis by using this H-zeolite catalyst was fascinating since it fulfilled the principle of green chemistry; energy is more efficient since it is done at the room temperature and pressure. The glucose production that can be from biomass waste is beneficial since it does not compete with the food need. Besides, the glucose product can be fermented easily into bioethanol as the renewable energy source as the solution to face the crisis of energy with the raw material of fossil that is getting lower.

2. Materials and Methods

2.1. Equipment
Beaker glass of 200 mL and 50 mL, crucible, 100 mL Erlenmeyer, filter paper of Whatmann 42, stirrer, Buchner funnel, mortar and pestle, oven, 100 mesh strainer, wrap plastic, spatula, drop pipette, 100 mL measuring cylinder, furnace, burette, autoclave, fume hood, ultrasonic, spectronic-20, digital analytical balance, conical funnel, magnetic stirrer, magnetic stirrer, 200 mL and 50 mL volumetric flash, watch glass, evaporation bowl, three legs, static and clamp, filler, 10 mL graduated pipette, 10 mL volume pipette, rubbing alcohol burner, netting wire, shaker, XRF PANalytical with the type of MiniPal 4, and XRD PANalytical with the type of type E’xpert Pro.

2.2. Materials
Cellulose of cotton, distilled water, natural zeolite from Malang regency, the solution of 3 M HCl, glucose, Nelson-Somogyi reagent, Fehling reagent, NaOH (s), H₂C₂O₄·2H₂O (s), pp indicator.

2.3. Procedures

2.3.1. Natural Zeolite Activation
Zeolite was pounded became powder, and it was sieved with a measurement of 100 mesh. After that, it was soaked in the solution of 1 M, 2 M, and 3 M of HCl for 24 hours. The result then was heated at the temperature of 500 °C for four hours. The active zeolite was then characterized by using Freundlich adsorption isotherm, XRF, and XRD.

2.3.2. Freundlich Adsorption Isotherm Analysis
The solution of oxalate acid was prepared with the concentration of 0.05 M, 0.1 M, 0.2 M, 0.3 M, 0.4M, 0.7 M, and 1.1M. One gram of active zeolite was soaked in the oxalate acid solution. It then was shaken for 30 minutes, and it was untreated for 24 hours. After that, the filtering was done to get a
filtrate. The filtrate was titrated with 1 M NaOH solution. The following is the equation of Freundlich adsorption isotherm.

\[
x = \frac{1}{m} k c^n
\]  

(1)

where \(x/m\) is the mass adsorbed per unit mass of adsorbent, \(c\) is the concentration, and \(k\) and \(n\) are constants [10].

2.3.3. Analysis of zeolite using XRD and XRF
The zeolite before and after activation was characterized by using XRD and XRF. XRD test aimed to determine the type of mineral in the zeolite. XRF test was intended to know the metals contained in the zeolite.

2.3.4. The Process of Cellulose Conversion using Zeolite Catalyst
The cellulose of cotton and water (1:8) was put into a reactor added by active zeolite catalyst which was 3% of cellulose mass. The tools were set to reach the set point and sonication was done for one, two, and four hours. The filtrate obtained was tested by Fehling and Nelson-Somogyi tests.

![Figure 1. Hydrolysis reaction of cellulose into glucose using acid activated zeolite catalyst](image)

2.3.5. Fehling Test
Fehling test is a qualitative test to know the existence of reducer sugar like glucose. This test was done by taking a little of filtrate as the result of sonication. After that, it was added with Fehling reagent, heated and cooled. The positive test was indicated by the change of blue into sorrel.

2.3.6. Nelson-Somogyi Test
Nelson-Somogyi test is a quantitative test to know the existence of reducer sugar like glucose. This test was done by taking a little of filtrate as the result of sonication. After that, it was added with Nelson-Somogyi regen, heated and cooled. The next step was measuring the absorbance with spectronic-20 on the wavelength of 540 nm. The measurement in this test was based on the intensity of the blue color (showing the amount of glucose in the sample). In this test, the curve of the calibration of the concentration glucose standard solution versus absorbance was obtained. Such calibration curve was used to calculate the concentration of sample glucose from the absorbance data. The percentage of glucose can be calculated by using the following equation:
yield percentage of glucose = \frac{mass \ of \ glucose \ (experiment)}{mass \ of \ glucose \ (theory)} \times 100\%

3. Results and Discussion

3.1. Natural Zeolite Activation
The natural zeolite sample used as the initial material in this research was natural zeolite from Sumbermanjing, South Malang, Indonesia. The analysis results showed that HCl could reduce the polluter metal of the zeolite and increase the percentage of the main components of zeolite which were Si and Al through ion-exchange with H⁺ ion. The existence of H⁺ ion can make the breaking of the glycosidic bond (1.4’-β glycosides) among the glucose units easy. The obtained results were subsequently heated on a furnace to delete the ions as the rest of acid like CO₂ and water molecule absorbed by the zeolite pores so that its surface area increased. Physically, the appearance was the color change of natural zeolite from light green into brown.

![Figure 2](image)

**Figure 2.** The sample of non-activated natural zeolite (a) Activated natural zeolite (b)

3.2. Freundlich Isotherm Test of Activated Natural Zeolite
The followings are the surface area data as the results of the Freundlich isotherm test.

| Sample                              | Specific Surface Area (m²/g) |
|-------------------------------------|-----------------------------|
| Non-activated natural zeolite       | 85.52                       |
| Natural zeolite activated by 1 M HCl (ZATA-1M) | 120.00                  |
| Natural zeolite activated by 2 M HCl (ZATA-2M) | 60.20                    |
| Natural zeolite activated by 3 M HCl (ZATA-3M) | 45.17                     |

The research results showed the surface area of active zeolite increased by the activation but it decreased again. The largest surface area was natural zeolite activated by 1 M HCl. The surface area decreased by the increase in acid concentration. This case was possibly caused by the high acid concentration that can damage the structure and pores of the zeolite. The surface area of all these non-activated and activated natural zeolites was smaller than that of synthetic zeolite made by Selim et al. [11] that was 374 m²/g. The more concentrated of HCl, the surface of the activated natural zeolite was smaller. The surface area of the material can be affected by temperature activation, impregnation, and concentration of acid used in the activation [12].
3.3. Characterization of Activated Natural Zeolite Using XRD and XRF

3.3.1. XRD Analysis
The spectra results of X-ray diffraction of natural zeolite before and after activation using acid solution had peaks pattern at 2θ angles like to those of zeolite mordenite (MOR) according to the diffractogram of zeolite MOR listed at the data of JCPDS (Joint Committee on Powder Diffraction Standards) [13].

![Diffractogram](image)

**Figure 3.** (a) Diffractogram of non-activated natural zeolite (b) Diffractogram of natural zeolite activated by acid
Such an assumption was strengthened by the similarity of the value of $2\theta$ and d-spacing of the sample with MOR-zeolite. The comparison of the position of $2\theta$ angles at each peak of the sample non-activated natural zeolite and activated natural zeolite with zeolite MOR standard (JCPDS) diffractogram is shown in Table 2.

Based on the data at Table 2, the number of $2\theta$ angles at each peak of the natural zeolite before and after activation was relatively the same. Therefore, it can be said that the natural zeolite is mordenite (MOR). The similarity of the diffractogram pattern of the main peaks in the same $2\theta$ angles show that the structure of the materials is similar [13, 14].

Table 2. (a) Position of $2\theta$ angles of non-activation natural zeolite and MOR (standard) (b) Position of $2\theta$ angles of activated natural zeolite and the type of MOR (standard)

| Element          | Non-activated Natural Zeolite | MOR-Zeolite | Natural Zeolite Activated by Acid | MOR-Zeolite |
|------------------|-------------------------------|-------------|----------------------------------|-------------|
| $2\theta$ (deg)  | d-spacing [Å]                 | $2\theta$ (deg) | d-spacing [Å]                    | $2\theta$ (deg) | d-spacing [Å] |
| 22.3268          | 3.98195                      | 22.20       | 4.004                            | 22.3008     | 3.98653       |
| 23.2382          | 3.82780                      | 23.64       | 3.764                            | 23.6717     | 3.75868       |
| 25.6998          | 3.46648                      | 25.63       | 3.476                            | 25.6851     | 3.46843       |
| 26.3431          | 3.38327                      | 26.25       | 3.395                            | 26.3323     | 3.38464       |
| 27.7154          | 3.21879                      | 27.67       | 3.223                            | 27.6996     | 3.22059       |
| 30.9649          | 2.88802                      | 30.89       | 2.894                            | 30.9365     | 2.89061       |
| 35.1136          | 2.55572                      | 35.61       | 2.521                            | 35.6965     | 2.51532       |
| 44.3947          | 2.04061                      | 44.13       | 2.053                            | 44.3943     | 2.04062       |
| 46.6322          | 1.94778                      | 46.58       | 1.950                            | 46.5795     | 1.94986       |
| 48.4647          | 1.87677                      | 48.45       | 1.879                            | 48.4729     | 1.87648       |

3.3.2. XRF Analysis

Based on the data obtained from the XRF analysis above, we can know that there was a decrease in the relative percentage of poluter metal except for Si and Al as the main components of zeolite. The increase in Si and Al was from 43.9%, and it had not been detected in 48.8% and 6.6%. It was caused by HCl with a dilute or concentrated concentration that could dissolve the metal such as Fe, Zn, Mn, and the others (Svehla,1990). The followings are the reactions of poluter metal and acid.

Table 3. The result of XRF analysis of natural zeolite before and after activation

| Element | Si (%) | Al (%) | K (%) | Ca (%) | Ti (%) | V (%) | Cr (%) | Mn (%) | Fe (%) | Ni (%) | Cu (%) | Zn (%) | Sr (%) | Eu (%) | Re (%) |
|---------|--------|--------|-------|--------|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Before  | 43.9   | 3.32   | 13.5  | 2.23   | 0.06   | 0.088 | 0.42   | 30.2   | 3.54   | 0.53   | 0.23   | 1.4    | 0.2    | 0.3    |
| activation| 48.8   | 6.6    | 3.51  | 12.3   | 2.34   | 0.07  | 0.081  | 0.26   | 21.0   | 2.91   | 0.45   | 0.17   | 1.2    | 0.10   | 0.3    |

$\text{Fe + 2HCl} \rightarrow \text{Fe}^{2+} + 2\text{Cl}^{-} + \text{H}_2$

$\text{Zn + 2H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2$

$\text{MnO}_2 + 6\text{HCl} \rightarrow 2\text{Mn}^{2+} + \text{Cl}_2 + 4\text{Cl}^{-} + 3\text{H}_2\text{O}$

Besides, based on the data above, we can know that the ratio of Si/Al was 7.13. The higher the ratio of Si/Al, the acidity, and crystallinity of the zeolite catalyst, the catalytic character increased as well. The increase in acid strength of this natural zeolite was seen from the theory of Bronsted-Lowry [15]. The ratio of Si/Al influences the catalytic character of the catalysts like the active site and its acidity [16].
3.4. **Qualitative Test of Glucose by Using Fehling Reagent**

Qualitative test as the result of hydrolysis presented in Table 4.

| The converted cellulose by using activated natural zeolite (acid) | Fehling test of the Result of Sonication of Cotton Cellulose |
|--------------------------------------------------------------------|-------------------------------------------------------------|
|                                                                    | One Hour | Two Hours | Four hours |
| 1                                                                   | ++       | +         | ++++       |
| 2                                                                   | +        | ++        | +++        |
| 3                                                                   | +        | +++       | ++         |

Notes:

+ : the glucose formed was very little (greenish-blue)
++ : the glucose formed was little (green)
+++ : the glucose formed was much (yellow)
++++ : the glucose formed was very much (red)

![Figure 4](image1.png)

(a) One-hour sonication  (b) Two hours sonication  (c) Four hours sonication

The highest amount of glucose was apparent in four hours sonication. This case means the sonication time of four hours was the best time in cellulose hydrolysis process becoming glucose. The longer the sonication time, the glucose concentration formed will be higher as well [17]. Such a statement is suitable for the data of experiment results shown by the color formed.
3.5. Quantitative Test of Glucose Product Using Nelson-Somogyi Reagent

Nelson-Somogy test is a quantitative test to know the existence of reducer sugar (like glucose). By this test, the glucose concentration was obtained in ppm unit by using the equation of standard solution line. The yield percentage of glucose as the result of cellulose conversion of cotton is presented in Figure 5.

![Figure 5: Influence of acid concentration on activation of natural zeolite (ZATA) catalyst and sonication time to the yield % of glucose in the degradation process of cotton cellulose.](image)

Based on the data above, the highest percentage of glucose was 4.51% from the result of cellulose hydrolysis of cotton. The products were obtained when the active zeolite catalyst (ZATA-1M) was used with the sonication time of four hours. The obtained results were in line with the surface area in which ZATA with 1 M HCl had the largest surface area so that it was the most effective to hydrolyze the cellulose into glucose. This research result was not far different from the research results of Osvaldo et al. [5] getting 5.0675% of glucose by using hydrolysis method with 2% of the acid catalyst [18]. Although the yield percentage of glucose resulted from this research was lower than the result of Osvaldo et al.[5], the method that we offer is more environmentally friendly. This research result also showed that the yield percentage of glucose was five times higher than the yield percentage of glucose resulted from the research conducted by Fungky [9] that was 0.967%, where he did cellulose hydrolysis assisted by ultrasonic with natural zeolite catalyst activated physically (calcination) with or without impregnation of Ni metal. The benefit of this method compared to the other previous research is it is more environmentally friendly and the energy used is more efficient since it does not need high temperature like what had been done by Fajriutami [8] and Sumari et al.[7]. Besides, it is more environmentally friendly than the method that used acid reagent [19]. Moreover, the excellence of using natural zeolite activated by acid (ZATA) is this zeolite can be recovered easily and used repeatedly.

4. Conclusion

Natural zeolite before and after activated by HCl was confirmed in the form of mordenite type. HCl used in the activation process could reduce the impurity through ion exchange with H⁺ ion. Moreover, the natural zeolite catalyst activated by 1 M of HCl was the most effective one to hydrolyze the cellulose from the cotton into glucose with the yield percentage of 4.71%. The ultrasonic used in the hydrolysis process gave influence in converting the cellulose into glucose with the highest yield through four hours sonication to the natural zeolite activated by 1 M of HCl.
References
[1] ZREU (Zentrum für rationell Energieanwendung und Umwelt GmbH). 2000. Biomass in Indonesia. (German Energy Saving Project)
[2] Rispiandi. 2011. Jurnal Fluida: Bandung. 7 (1) :1-11
[3] Irawan MA. 2007. Metabolisme enegri. Polton Sports Science & Performance Lab.1, 06 1-5
[4] Schenck F. W. 2006, Glucose and Glucose-Containing Syrups in Ullmann's Encyclopedia of Industrial Chemistry, (Weinheim Wiley-VCH)
[5] Osvaldo Z,S., Panca Putra S., M. Faizal. 2012. Jurnal Teknik Kimia.18 (2) 52-62
[6] Sasaki, C., Keisuke S., Chikako A., Yoshitoshii N..2012..Carbohydrate Polymers Journal. 89 298-301
[7] Sumari S., Roesyadi A, Sumarno. 2013. Scientific Study & Research Chemistry & Chemical Engineering, Biotechnology, Food Industry. ISSN 1582-540X 14(4) 229-239
[8] Fajriutami, T., Widya F, Hermiti E. 2016. Jurnal Riset Industri. Bogor. 10 (3): 147-161
[9] Fungky.2016. Penggunaan Katalis Nikel-Zeolit Alam Aktif pada Hidrolisis Selulosa menjadi Glukosa dengan Bantuan Ultrasonik.(Malang: State University of Malang)
[10] Castellan. 1983. Physical Chemistry 3rd edition. University of Maryland.
[11] Selim, M.M., El-Mekkawi, D.M., Aboelenin, R.M.M., Ahmed, S.A.S., Mohamed, G.M., 2017. Journal of the Association of Arab Universities for Basic and Applied Sciences 24, 19–25
[12] Kumar A. & Jena H.M. 2016.. Results in Physics, 6, 651-658
[13] Treacy, M.M.J & Higgins, J.B. 2001. Collection of Simulated XRD Powder Patterns for Zeolites. Elsevier. Published on behalf of the StuctureCommision of the International Zeolite Association Fourth Revised Edition.
[14] Kalla, R., Sumarno, S., Mahfud, M., 2015. Bulletin of Chemical Reaction Engineering & Catalysis, 10 (3), 304-312.
[15] Budianto A., Sumari S. and Udyani K. 2015. ARPN Journal of Engineering and Applied Sciences, 10 (22):10317-10323.
[16] Bhadavra,J., Singh,B.K., Tomar,A.,& Tomar,R. 2011.. J.Chem.Pharm.Res, 3, 245-257
[17] Vityuk, A., Hristiyana A. A., Georgi N. V., Shuguo Ma, Oleg S. A., Michael D.A..2014..Physical Chemistry Journal:A-Q
[18] Anggraini, P. A., Andri R. R., Sumarno. 2014. Jurnal Teknik. 2 (1): 9 – 20.
[19] Sun, B., Gege P., Lian D., Aihua Xu, Xiaoxia Li.2015. Bioresource Technology Journal. 196, 454-458