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Sono-hydrolysis of banana stem midrib using HY-zeolite from natural sand-based silica as a catalyst

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ABSTRACT

Banana stem midrib has the potential as a glucose source through catalytic hydrolysis assisted by ultrasonic (sono-hydrolysis). Besides, natural sand-based silica is the potential as raw material for zeolite synthesis. The purpose of the study was to do two things: i) characterize HY-zeolite made from natural sand-based silica and ii) determine whether HY-zeolite is effective for sono-hydrolysis of banana stem midrib. There was a total of four processes that were carried out, including i) the extraction of silica, ii) the synthesis of HY zeolite, iii) the hydrolysis process, and iv) the glucose content test. The results of the study were gained two things: i) The findings of X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) on HY-zeolite are 2.3 Si/Al, obtained 2 theta and d-spacing data similarities for HY-zeolite, and formed T-O-T, O-T-O (T=Si/Al), and Si-OH groups respectively; and ii) HY-zeolite with ultrasonic was effective for hydrolyzing cellulose into glucose at maximum temperature and time, 55 °C and 6 hours.

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1. INTRODUCTION

Bioethanol is a renewable energy source as an alternative fuel [1]. Glucose can be used as the main raw material for bioethanol production [2]. So, bioethanol has been processed from various glucose sources, such as molasses, cassava, and corn [3]. These sources competed with national food security and resulted in high production costs [4]. Therefore, it is necessary to innovate the source of glucose which is used as a raw material for bioethanol production. Glucose can be effectively obtained through hydrolysis of cellulose [5]. One of celluloses is the banana (Musa parasidiaca L.) stem midrib, because it is abundant and has 63% high cellulose [6], [7].

Previous study for a cellulose hydrolysis has been developed. Cellulose hydrolysis using the hydrothermal method at 300 °C assisted by ultrasonic for 1 hour resulted in a glucose yield of 63.8% [8]. This method was impractical and unsafe. Cellulose hydrolysis can be carried out at low temperatures, but it takes a long time, so it is necessary to use a solid acid catalyst, such as H-zeolite [5]. This condition was developed by Galadima *et al.* [9] using natural zeolite catalyst which was physically activated (calcination) and was impregnated with Nickel (II) (Ni^{2+}). The hydrolysis of cellulose was carried out at room temperature and pressure, with ultrasonic assistance for 4 hours. The percentage yield of glucose was only 0.967% and the method became an uneconomical value due to impregnation with Ni. Based on the description above, natural zeolite catalyst was able to hydrolyze cellulose into glucose. However, the amount of glucose produced is still low. Therefore, there is a need for an alternative zeolite catalyst. On the other hand, using ultrasonic in the hydrolysis reaction can increase the molecular interaction and time reaction [10], so it is common to use term, sono-hydrolysis [11].

Natural zeolite had a lot of impurities, so the alternative catalyst with fewer impurities is synthetic zeolite [12]. One of the synthetic zeolites is zeolite Y which had large pores, high acid concentration, high thermal stability, and high size selectivity [13]. The basic material for the synthesis of zeolite was silica which can be obtained from beach sand [14]–[16]. The use of silica from beach sand is more economical than industrial silica, so it can increase the economical value [17]. The used beach sand was Bajul Mati beach sand which contained 31% Si in the previous X-ray florescence (XRF) test [15].

Therefore, the objectives of this research are i) characterize HY-zeolite made from natural sand-based silica and ii) determine whether or not HY-zeolite is effective for sono-hydrolysis of banana stem midrib. The benefits of this research are i) it can increase the economic value of Malang beach sand, ii) creating an alternative for glucose production from raw material for banana stem midrib (as source of cellulose) that is not utilized and the amount is abundant to be converted into bioethanol, and iii) referring to the use of new methods that are economical and safe in processing cellulose into glucose.

2. RESEARCH METHOD

This research was based on experimental laboratory. The zeolite synthesis method adopted from Belaabed *et al.* [18] with modified silica source from Bajul Mati sand. The used materials in this study were silica extracted from Bajul Mati beach sand (containing 31% Si), banana stem midrib from Malang, Nelson-Somogyi reagent (sigma aldrich), Fehling reagent (sigma aldrich), HCl pa (sigma aldrich), NH_4Cl 1 M, aquades, methylene blue, NaOH pa (sigma aldrich), Al $(OH)_3$ (sigma aldrich), and demineralized aqua. Meanwhile, the used tools and instruments in the research were beaker, erlenmeyer, furnace, pH indicator, reflux set, analytical balance, magnetic stirrer, winkler bottle, spectrophotometer UV-Vis GENESYS 10, ultrasonic cleaner Delta D68H, X-ray diffraction (XRD) (PANalytical type: E'xpert pro), XRF (PANalytical type Minipal 4), scanning electron microscopy (SEM) (FEI Inspect S-50-AMETEK), and fourier transform infrared (FTIR) (Shimadzu IRPrestige21).

2.1. Synthesis and characterization of HY-zeolite

First, $NaAlO_2$ solution prepared that: 6.5 g Al $(OH)_3$ dissolved in 100 mL NaOH 7M with reflux. Second, $NaSiO_3$ solution prepared that: 1.998 g of SiO_2 dissolved in 50 mL NaOH 2N and stirred for 30 minutes. Third, synthesis of zeolite NaY prepared that: both $NaAlO_2$ solution and $NaSiO_3$ solution were homogenized for 30 minutes with a magnetic stirrer, it was then stored at room temperature for 24 hours, it was then put into the reactor at 150 ℃ for 12 hours and filtered after. The filtered residue was washed with aqua demineralization. It was then dried at 150 ℃ for 12 hours. So, the product was NaY-zeolite. Furthermore, NaY-zeolite was reacted to NH_4Cl 2M at 70 ℃ for 30 minutes. After that, it was filtered, cleaned, and put into oven at 110 ºC for 6 hours. Next, the solid was calcined at 500 ºC for 5 minutes. The results of the synthesis (HY-zeolite) were characterized by XRF, XRD, FTIR, SEM, and surface area test using methylene blue adsorption method.

The procedure for surface area using methylene blue adsorption method was carried out by 0.01 g HY-Zeolite was put in 250 mL Erlenmeyer containing 100 mL methylene blue 20 ppm, the mixture was then shaken with a shaker at 100 rpm for 30 minutes and then filtration, the obtained filtrate was measured for absorbance using a UV-Vis spectrophotometer at a wavelength of 660 nm.

XRF tests give an information about mineral content. The XRD tests give an information about phase of zeolite and comparison with a reference. The SEM test observes the form of morphology of the zeolite. FTIR spectrum result the characteristic group of HY-zeolite. The surface area test was in the form of a graph that provides a relationship between the concentration of methylene blue (ppm) as the x-axis and the adsorption (A) as the y-axis.

2.2. Sono-hydrolysis of banana stem midrib

As pretreatment, banana stem midrib was dried under sunlight. It was then crushed small to be powder of banana stem midrib. Distilled water and the powder were put into 100 mL Beaker with a ratio of banana stem midrib: water of 1:20. The mixture was then added HY-zeolite of 7.5% mass of banana stem midrib. Sonication was carried out by adjusting the temperature according to the temperature variables, namely 30 ℃, 45 ℃, and 55 ℃ with sonication time according to the time variables, namely 1, 2, 4, and 6 hours. Next, qualitative test of glucose with Fehling's reagent prepared that: the product solution was added with Fehling's reagent in a test tube, it was then heated for 3-4 minutes, and the color change was then observed. The qualitative test of glucose was to observe changes and the intensity of the sample color.

3. RESULTS AND DISCUSSION

3.1. X-ray analysis of HY-zeolite

HY-zeolite was characterized by XRD. The diffractogram results were compared with the Y-zeolite diffractogram from the joint committee on powder diffraction standards (JCPDS) data which was shown in Figure 1. The synthesized HY-zeolite diffractogram was slightly like the standard HY-zeolite diffractogram with JCPDS no 38-0240. Then, XRF result of HY-zeolite was listed in Table 2.

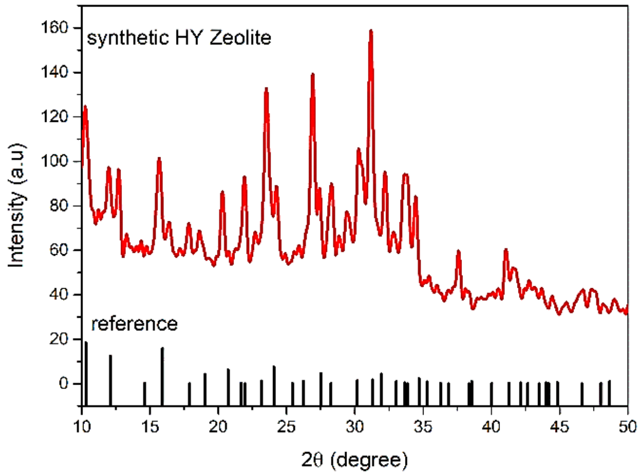


Figure 1. Comparison of diffractogram from: synthetic HY-zeolite with a reference

Table 1. XRF results of HY-zeolite

Element	Si	Al	Ca	Ti	V	Mn	Fe	Cu	Sr
Content (%)	67.5	27.9	1.6	0.47	1.5	0.17	0.13	0.56	0.16

Based on the XRF results in Table 2, it was known that Si and Al are 67.5% wt and 27.9% wt, respectively. The data can be calculated the value of the Si/Al ratio of HY-zeolite about 2.3 as a relative Si/Al ratio because of complexity of impurities. This ratio was in accordance with the Si/Al ratio range of the standard Y-zeolite of 1.5-3 [19]. This showed that the quality of the obtained HY-zeolite is relatively good, because the impurities in the synthesized HY-zeolite showed other peaks of XRD and other contents of XRF.

3.2. SEM and surface area of HY-zeolite

The SEM results for the synthesized HY-zeolite were shown in Figure 2. It was known that the rectangular morphology indicated the formation of the HY-zeolite [20]. Besides, the amorphous morphology of HY-zeolite appeared.

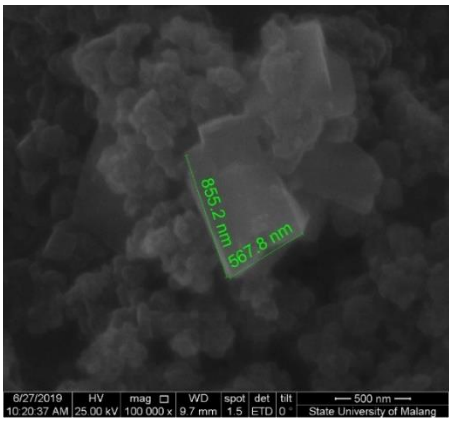


Figure 2. SEM of synthetic HY-zeolite

The result of the surface area analysis of the synthesized HY-zeolite was 73.910 m^2/g. This result was greater than the surface area obtained by Assawasangrat *et al.* [19] which was only 15.178 m^2/g. Therefore, the synthesized HY-zeolite has a potential heterogeneous catalyst, so that it is potentially easier to hydrolyze cellulose from banana midrib into glucose.

3.3. FTIR result of HY-zeolite

FTIR Result for the synthesized HY-zeolite (Figure 3) showed the absorption wavenumbers of the typical zeolite functional groups, namely: 500-420 cm^{-1} correspond to Si-O bending vibration of Si-O-Si or Al-O of Al-O-Al, 820-650 cm^{-1} correspond to asymmetric stretching vibrations of Si-O from O-Si-O or Al-O from Al-O-Al, 1250-950 cm^{-1} correspond to O-Al-O asymmetric stretching vibration, 1650-1645 cm^{-1} correspond to bending vibration of Si-OH, 3200-3600 cm^{-1} correspond to O-H stretching vibration of Si-OH . Therefore, the analysis of typical zeolite functional groups can be said that the synthesized sample was HY-zeolite [19].

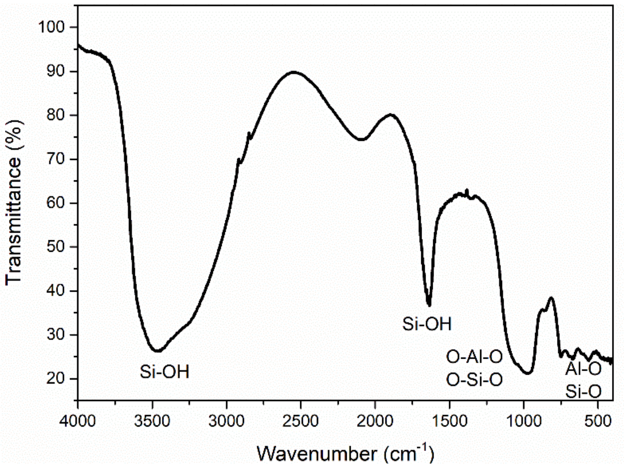


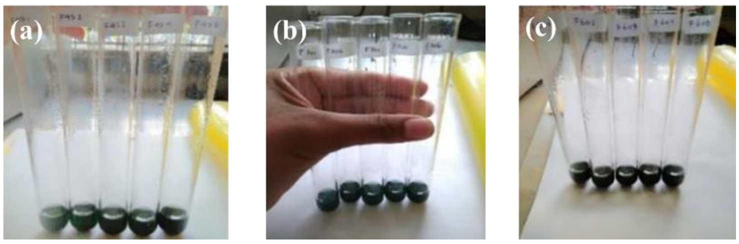
Figure 3. FTIR result of the synthesized HY-zeolite

3.4. Qualitative test of glucose with Fehling reagent

Fehling's test showed the presence of glucose based on the color change from blue to green, yellow or brick red according to glucose levels [21]. Fehling test results are seen in Table 2 and Figure 4. The details of Fehling test result shown in Figures 4(a)-4(c). Description: +: very little glucose is produced (blue-green color), ++: glucose produced a little (very bright green color), +++: sufficient glucose is produced (green color), and ++++: glucose produced a lot (dark green color).

Table 2. Fehling's test results on glucose hydrolyzed banana stem midrib

	1 hours	2 hours	4 hours	6 hours
30 ºC	+	+	++	+++
45 ºC	++	++	+++	+++
55 ºC	++	+++	+++	++++



(a) (b) (c)

Figure 4. Qualitative test results with Fehling's reagent at (a) 30 °C, (b) 45 °C, and (c) 55 °C

The results of the test showed that the highest levels of glucose were produced in the hydrolysis process with a temperature and sonication time of 55 ℃ and 6 hours, respectively. On the other hand, it can be seen that HY-zeolite has catalytical activity rather than no catalysis in sono-hydrolysis [22]. So, future study needs to develop the hydrolysis reactor.

4. CONCLUSION

The conclusions of the study were i) The results of the characterization of XRF, XRD, SEM, FTIR Zeolite Y, respectively, namely: 2.3 Si/Al, obtained the similarity of 2 theta and d-spacing data for HY-zeolite, amorphous rectangular-shaped, and formed TOT group, OTO (T=Si/Al), and Si-OH; and ii) Zeolite HY catalyst assisted by ultrasonic can hydrolyze banana stem midrib into glucose with the best reaction at 55 ℃ for 6 hours.

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