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Enrichment Process of Biogas Using Simultaneous Absorption - Adsorption Methods

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Abstract. Removal of CO_2 in biogas is an essential methods to the purification and upgrading of biogas. Natural Clinoptilolite zeolites were evaluated as sorbents for purification of biogas that produced from palm oil mill effluent (POME) by anerobic-digestion method. The absorption and adsorption experiments were conducted in a fixed-bed two column adsorption unit by simultaneous absorption-adsorption method. The $Ca(OH)_2$ solution with concentration of 0.062 M was used as absorption method. Sorbent for removal of CO_2 in biogas have been prepared by modifying of Clinoptilolite zeolites with an acid (HCl, 2M) and alkaline (NaOH, 2M), calcined at 450°C and then coated using chitosan (0.5 w/v%) in order to increase their adsorption capacity. The removal of CO_2 in biogas was achieved about ~83% using 2.5 g of sorbent zeolite (2M)/chitosan dosage for each column, breakthrough time of 30 min, and flow rate of 100 mL/min. Clinoptilolite zeolites with modifications of an acid-alkaline and chitosan (zeolite (2M)/chitosan) are promising sorbents due to the amine groups from chitosan and high surface-volume ratio are one of important factors in a simultaneous absorption-adsorption method.

INTRODUCTION

Biogas is the mixture of methane (CH_4) and carbon dioxide (CO_2) which produced by bacterial conversion of organic compounds by anaerobic technique. In general, biogas that produced from palm oil mill effluent (POME) by anaerobic (oxygen free) condition, containing CH_4 as the main gas (~40 - 75 %), carbon dioxide (CO_2,~ 15-60 %) and other impurities in small quantities such as water (H_2O, ~5-10 %), hydrogen sulfide (H_2S , ~0.005 - 2 %), siloxanes (0 - 0.02 %), oxygen (O_2 , ~0 - 1 %), carbon monoxide (CO , < 0.6 %) and nitrogen (0 - 2 %) [1].

Enrichment method of biogas is the process of removing unwanted gases (CO_2, H_2S, and water vapor) from biogas to increase the calorific value, so it is more economical to compress and transport to longer distribution or move to other area [2]. The CO_2 and H_2S removal can increase the percentage of biomethane in biogas. Some methods for biogas enrichment process or purification of biogas have been reported [3]. On the other hand, purification of biogas using $Ca(OH)_2$ solution, thus CO_2 would be reacted with $Ca(OH)_2$ solution to form the precipitate of $CaCO_3$ also has been reported [4]. Among adsorbents such as activated carbon, silica gel, clay, alumina, and zeolite has been reported for gas purification [5]. Natural Clinoptilolite zeolite has been reported for purification of gas because it has a small pore size and uniform structure [6].

Chitosan is the secondly most abundant polymer in nature. This can be extracted from prawns, crabs, fungi and insects [7]. Chitosan has the reactive hydroxyl and amine groups, so chitosan can be used as active modifier to remove some pollutants. Chitosan having amine groups that can interact with H_2S and CO_2 to form carbamate compounds [8].

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In the paper, we study the enrichment process of biogas using the modified clinoptilolite zeolite as adsorbent. This zeolite (2M)/chitosan was modified with chemically process using acid-base and chitosan. Both chemical absorption and adsorption methods were combined to remove the CO_2 in biogas.

METHODOLOGY

Materials

POME was obtained from three ponds of POME processing facilities belonging to PT. Perkebunan Nusantara VIII Kertajaya located in Malimping, Banten. Natural clinoptilolite zeolites with moderate sizes (1 - 2 mm) were obtained from Lampung, Indonesia. All chemicals used were analytical grade.

Modification of clinoptilolite zeolites (zeolite (2M)/chitosan)

The preparation of sorbent is according the method that reported by Kusrini et al [9] with some modification in concentration of acid and base. The adsorbent based on the natural clinoptilolite zeolite was modified by 2M HCl and 2 M NaOH for 2 h, respectively. Then the sorbents were washed by distilate water until it reached the pH is neutral. After that, zeolite was calcined with temperature at 450^{o}C for 2 h. The surface of activated natural zeolite was modified with chemically treatment using acidic chitosan solution with concentration of 0.5 % (w/v). Chitosan solution was made by dissolving chitosan solution with acetic acid 1 % (v/v). The coating process was conducted by immersing the activated natural zeolite in 0.5% (w/v) chitosan solution and kept for 2 h. After that, the zeolite (2M)/chitosan was dried in oven with temperature at 110^{o}C for 3 h.

Purification of Biogas in a fixed-bed column

The production of biogas by anaerobic digestion as according to the method that reported previously by Kusrini et al. [9]. A fixed-bed column adsorption with length of 15 cm and diameter 0.8 cm that used for purification of biogas. The schematic diagram for purification of biogas using simultaneously of absorption and adsorption processes with modified zeolites produced as an adsorbent for removal of CO_2 in biogas is shown in Figure 1. We used the best dosage of adsorbent was 2.5 g [9]. The volume of biogas is 2 dm^3 and flow rate of the adsorption process was 100 mL/min. The chamber contained a solution of $Ca(OH)_2$ with concentration of 0.062 M through the pipe bubble using a peristaltic pump with a flow rate of biogas of 100 mL/min. The CO_2 concentration was measured every five (5) min as the breakthrough time. Before and after the subsequent purification of biogas was analyzed by GC. The difference concentrations between the initial CO_2 before purification and final CO_2 after purification was calculated with the equation 1 as follows:

$$\% \, Efficiency = \frac{(C_0 - C_1)}{C_0} \, x \, 100\% \quad (1)$$

Where, C_0 is CO_2 before purification, C_1 is CO_2 after purification, and Efficiency (%) is Effectiveness CO_2 absorption

Characterization

Nitrogen sorption is a key to obtain the specific area of porous solid materials. This measurement was conducted at 77.2 K (-195.8°C) using ASAP 2020 V4.02-unit gas adsorption analyzer and equilibration interval of 5 second with sample mass from 0.28 – 0.30 g. Surface area of adsorbent were determined using the Brunauer, Emmet and Teller (BET) equation. The pore size distribution was calculated according to the Barrett, Joyner and Halenda (BJH) model. The surface morphology and elemental composition was determined by field emission scanning electron microscopy-energy dispersive X-ray (FESEM-EDX).

Biogas was analyzed by gas chromatography (GC Bruker, USA) with TCD (thermal conductivity detector) and dimethyl polysiloxane as a column with BR-Q-PLOT type, length and internal diameter are 30 m and 0.53 mm, respectively with helium gas as a carrier gas.

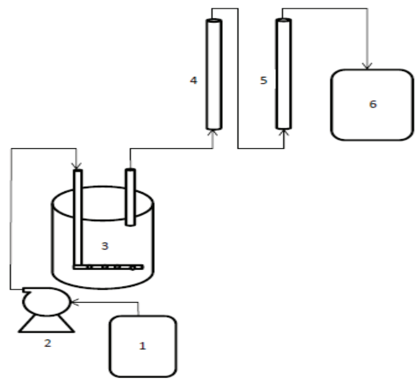

FIGURE 1. Schematic process for purification of biogas using combining absorption-adsorption process with (1). Gas holder, (2) Chamber containing $Ca(OH)_2$ solution, (3) peristaltic pump, (4) adsorption column 1, (5) adsorption column 2, (6) gas holder after purification.

RESULTS AND DISCUSION

Physical and chemical properties of adsorbent

Fig. 2(a-d) shows the SEM images of zeolite and after activation with acid-base and coated chitosan. It can be seen that zeolite surface is very heterogeneous and consists of crystalline and amorphous phases. From the SEM images, it is clearly observed that the main component in natural zeolite from Lampung (Indonesia) is clinoptilolite. The results showed a lot of rods and they were clearly observed after activation with acid and base (see Fig 2(b)). The evident that chitosan coating resulted in a rougher surface morphology on the clinoptilolite zeolite and chitosan is relatively amorphous and non-uniform. Most of chitosan are encapsulated and covered into the cavities of clinoptilolite zeolite. The results showed that chitosan was coated successfully onto the clinoptilolite zeolite (see Fig. 2(c)). Chitosan does not have pores on their surface and just like amorphous powder (see Fig.2(d)).

Elemental analysis was done by EDX which is summarized in Table 1. The general formula of zeolite is $M_{x/n}[(AlO_2)_x(SiO_2)_y]mH_2O$, where M is alkali and alkaline earth metallic cation. The clinoptilolite zeolite having chemical formula of $(Na_4K_4)(Al_8Si_{40}O_{96}).24H_2O$. The Si/Al ratio obtained is 4.18, 4.51 and 4.31 for zeolite before modification, after activation and after coated with chitosan, respectively. As mentioned in the literature, the Si/Al ratio for clinoptilolite zeolite is in the range from 4.0 to 5.2 [6]. The presence of some impurities such as Fe was observed for all sorbents. After modification with acid-base is slightly increased that indicated the dealumination occurred.

The surface area of zeolite before modification is about 47.12 m^2/g. After modification with acid-base and also coated with chitosan, the surface area is reduced to be 39.06 and 8.25 m^2/g, respectively. The chitosan coated on surface of zeolite, so some pores are covered and filled with chitosan [8]. Even though the adsorption average pore width of zeolite (8.5 nm) is increased after modification with acid-base (10.31 nm) and coated with chitosan (13.0 nm). The volume of pores for zeolite before and after activation with acid-base are similar (0.1 cm^3/g). After chemically modified with chitosan, the volume of pore is reduced to be 0.03 cm^3/g.

Enrichment process of biogas

From the results of qualitative analysis using GC-MS, the H_2S gas was not detected in biogas from POME. The results showed that methane (CH_4) of ~93% and NH_3 of ~7%. The presence of ammonia in biogas because of the C/N ratio on substrate is low, thus we need to add the cow dung as starter and to increase the C/N ratio. Usually the biogas which is produced by anaerobic digestion method has NH_3 with concentration is less than 100 ppm [10]. From the qualitative analysis of H_2S gas was also conducted by flowing biogas into the lead acetate solution (0.1 M), and no a black precipitate form was observed. This indicated that H_2S is not present in biogas.

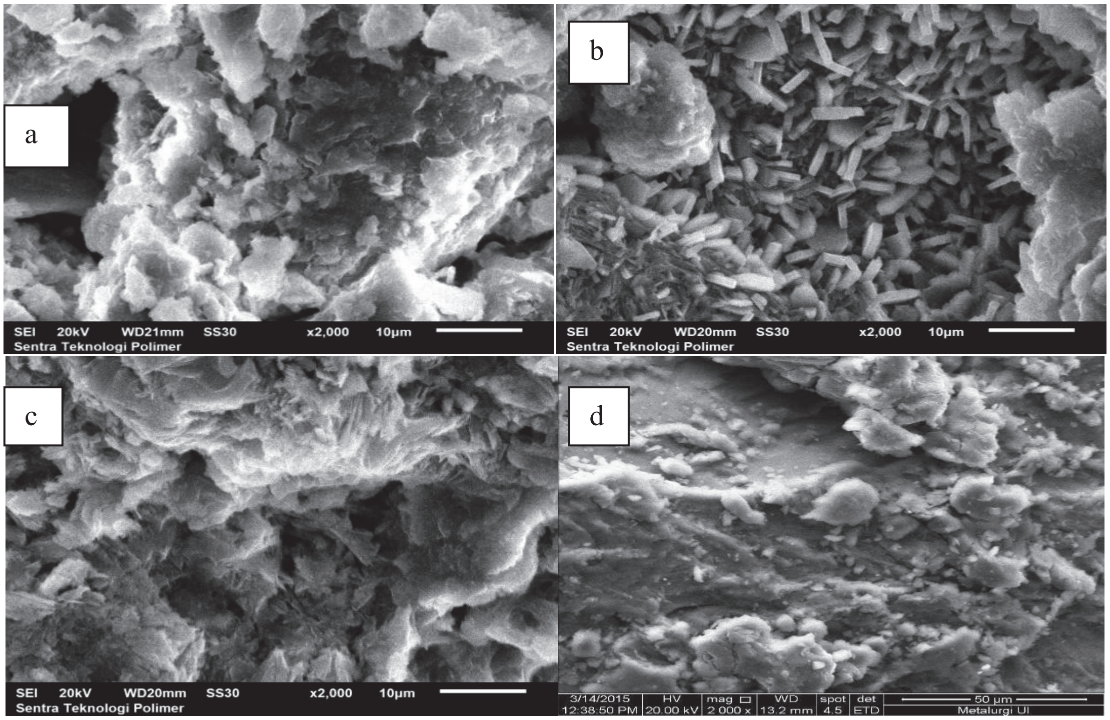

FIGURE 2. SEM images of zeolite (a), after activation (b), zeolite (2M)/chitosan (c), and chitosan (d)

TABLE 1. Comparison of elemental analysis of zeolite/chitosan and chitosan

Element	(%weight composition)			
	Zeolite before modification	Activation of zeolite by acid-base	zeolite (2M)/chitosan	Chitosan
C	3.69	3.67	4.23	36.41
O	52.3	51.97	50.68	-
Na	-	1.88	2.41	1.40
Al	7.20	6.84	6.93	-
Si	31.19	31.99	30.94	-
K	2.10	1.88	1.85	-
Ca	1.47	0.94	1.24	-
Fe	2.03	0.84	1.71	-
N	-	-	-	62.23
P	-	-	-	7.48
Si/Al Ratio	**4.18**	**4.51**	**4.31**	**-**

In this study, biogas enrichment process has been conducted using a fixed-bed two column adsorption unit by simultaneous absorption-adsorption. It was observed that the removal of CO_2 using simultaneous absorption-adsorption with two columns and zeolite (2M)/chitosan as adsorbent achieved ~83% CO_2 adsorption (see Fig. 3). This indicated that the percentage of methane in biogas could be increase by absorbing more carbon dioxide (CO_2) gas. The results showed that the amine groups of chitosan were successfully bonded with CO_2 in biogas. For comparison, the efficiency removal of CO_2 in biogas using chemical absorption with the $Ca(OH)_2$ solution is ~49% and by simultaneous absorption-adsorption method with one column using activated clinoptilolite is ~61%, while with simultaneous absorption-adsorption method with one column using clinoptilolite zeolite modified with chitosan, the removal of CO_2 in biogas is ~70% [11]. The highest CO_2 removal was achieved by simultaneous absorption-adsorption with two columns and zeolite (2M)/chitosan and the lowest CO_2 removal in biogas by using chemical absorption with $Ca(OH)_2$ solution.

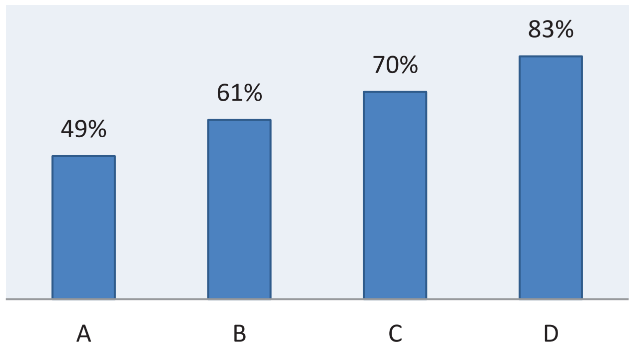

FIGURE 3. The removal of CO_2 in biogas enrichment process by chemical absorption with $Ca(OH)_2$ solution (a), simultaneous absorption-adsorption method with one column using activated zeolite (b), simultaneous absorption-adsorption method with one column using zeolite/chitosan (c) and simultaneous absorption-adsorption method with two columns using zeolite/chitosan.

CONCLUSION

Natural clinoptilolite zeolite was chemically modified by using a strong acid (HCl 2M), strong bases (NaOH 2M), calcination at a temperature of 450°C and coating with chitosan 0.5 % (w/v). The performance of zeolite/chitosan as sorbent for removal of CO_2 in biogas was achieved ~83% using simultaneous absorption-adsorption method with two columns. The zeolite (2M)/chitosan is a promising sorbent for removal of CO_2 in biogas from POME.

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