International Journal of Technology (2016) 4: 625-634
ISSN 2086-9614

BIOGAS FROM PALM OIL MILL EFFLUENT: CHARACTERIZATION AND REMOVAL OF CO_2 USING MODIFIED CLINOPTILOLITE ZEOLITES IN A FIXED-BED COLUMN

Eny Kusrini[1*], Maya Lukita[1], Misri Gozan[1], Bambang Heru Susanto[1], Teguh Wikan Widodo[2], Dedy Alharis Nasution[2], Shella Wu[1], Arif Rahman[3], Yusraini Dian Inayati Siregar[4]

[1] *Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia*
[2] *Center for Development of Agricultural Engineering, Agricultural Research and Development Agency, Ministry of Agriculture, Tangerang, Indonesia*
[3] *Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Jakarta, Indonesia*
[4] *Department of Chemistry, Faculty of Science and Technology, UIN Sharif Hidayatualloh, Ciputat, Indonesia*

(Received: October 2015 / Revised: January 2016 / Accepted: April 2016)

ABSTRACT

The main focus of this article was to investigate the potential of natural zeolite adsorbent for the removal of CO_2 and H_2S in biogas produced from palm oil mill effluent (POME) in fixed-bed column adsorption. The effects of the flowrates and dosage of the adsorbent on the CO_2 adsorption were also studied. The surface area of the adsorbent was determined using the Brunauer, Emmett, and Teller (BET) model, while the pore size distribution was calculated according to the Barrett, Joyner, and Halenda (BJH) model. The morphology of the adsorbent was determined by field emission scanning electron microscopy and energy dispersive x-ray (FESEM-EDX) analysis. Before and after purification, the biogas was analyzed by gas chromatography with a thermal conductivity detector and polydimethylsiloxane as a column. Biogas from the POME, via the anaerobic digestion process, produced 89% CH_4 and 11% CO_2. The surface and structure of the clinoptilolite zeolites was modified by a strong acid (1M HCl), strong base (1M NaOH), and calcination at 450°C, and the surface area of the natural zeolites was reduced up to 16%. The working capability of CO_2 adsorption by the modified zeolites decreased with increasing flow rates (100, 200, and 300 mL/min) of the biogas, with levels of CO_2 at 106,906, 112,237, and 115,256 mg/L. The removal of the CO_2 in the biogas by using adsorbent dosages of 1.5, 2.0, and 2.5 g was 97,878, 97,404 and 93,855 mg/L, respectively. The optimum purification of the biogas occurred under the flow rate of 100 mL/min and adsorbent dosage of 2.5 g. The high working capability of the modified zeolites for the removal of CO_2 in the biogas was a key factor, and the most important characteristic for the adsorbent. The results indicate that clinoptilolite zeolites are promising adsorbent materials for both the purification and upgrading of biogas.

Keywords: Biogas; Clinoptilolite zeolite; Fixed-bed column adsorption; Palm oil mill effluent; Purification

*Corresponding author's email: ekusrini@che.ui.ac.id, Tel. +62-21-7863516 ext.204, Fax. +62-21-7863515
Permalink/DOI: http://dx.doi.org/10.14716/ijtech.v7i4.2207

1. INTRODUCTION

Biogas is produced from the anaerobic digestion of organic wastes, such as palm oil mill effluent (POME), which contain carbohydrates, fats, and protein, and are commonly used as feedstocks. These feedstocks are available at a low cost, thus making biogas production economically favorable. POME containing 60% wastewater, 36% sterilizer condensate, and 4% hydrocyclone water can be produced from several processes in the palm oil industry (Ahmed et al., 2015; Poh & Chong, 2009). One of parameters used to evaluate how much biogas can be produced from the POME bioprocess is the chemical oxygen demand (COD) value. Because the COD value is indicative of the amount of organic materials that are contained in the effluent, the COD can be a useful measure of potential biogas production. For example, there is a high level of COD in POME, so it is suitable for biogas production. Bioprocesses utilizing anaerobic bacteria mainly produce biogases with CH_4, CO_2, and small amounts of H_2O, N_2, H_2S, and siloxane (Ahmed et al., 2015). Biogas production via anaerobic digestion is comprised of four main biochemical processes: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Lam & Lee, 2011; Yang et al., 2014).

Usually, biogas consists of CH_4, CO_2, and other impurities, like H_2S and water vapor (Ji et al., 2013; Ahmed et al., 2015). The high concentration of CO_2 in biogas results in a low calorific value of the biomethane (CH_4) gas. Thus, further purification of the resulting biogas is required to remove the CO_2. Moreover, some of the impurities must be removed before the utilization of biogas, to ensure better performance and to prevent the environmental pollution of toxic gas emissions (Liu al., 2015). The removal of CO_2 and H_2S from biogas via adsorption is a very simple method, with good results, and the simultaneous and competitive separation of impurities to upgrade the quality of biogas and increase CH_4 via the adsorption method have been reported (Sigot et al., 2014; Gil et al., 2015; Bacsik et al., 2016).

Here, we have employed modified mesoporous zeolite, namely clinoptilolite, as an adsorbent. Zeolites are microcrystalline aluminum silicates that are used for the separation, purification, and/or upgrading of biogas (Bacsik et al., 2016). Clinoptilolite is the most common natural zeolite, with a general chemical formula of $(Na,K,Ca)_4Al_6Si_{30}O_{72}\cdot 24H_2O$. The Si/Al ratio of clinoptilolite zeolites varies from 4.0 to 5.3, with high thermal stability (600–800°C) (Kowalczyk et al., 2006), and such a natural zeolite is highly rigid under dehydration or other aggressive surroundings. In order to increase the adsorption capacity of natural clinoptilolite zeolite, and to make its pore size suitable for the CO_2 molecule, we modified the surface and structure of the natural zeolites by using a strong acid-base and calcination process. Via the dealumination and desilicalization processes, the pore structures, pore volume, and surface area of the modified zeolites are different, compared to the pristine zeolites. It is known that the physicochemical properties of clinoptilolite zeolites can be managed by the thermal and chemical treatment (Kowalczyk et al., 2006), making them potential adsorbents for the separation of CO_2 from CH_4 in biogas (Bacsik et al., 2016).

The purification of biogas in fixed-bed column adsorption, with modified clinoptilolite zeolite as an adsorbent, is highly attractive. In this study, we employed anaerobic bacteria to digest organic materials from POME by adding 10% cow feces to stimulate the biogas production. The purpose of this article was to present our investigation of potential of natural zeolites as adsorbents for the removal of CO_2 and H_2S in biogas produced from POME. Prior to the application, the clinoptilolite zeolites were activated by acid-base and calcination treatments to dispose of previously adsorbed gases and soluble impurities, which may contain CO_2 and H_2S in the zeolite active sites (Alonso-Vicario et al., 2010). The effects of the flowrate and dosage of the adsorbent on the CO_2 adsorption were also studied. This research shows the importance

of the selection of the optimal activation method for clinoptilolite zeolites as adsorbents, and the flowrate and dosage responsible for the removal of CO_2 to increase the CH_4 level.

2. MATERIALS AND METHODS

2.1. Materials

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

2.2. Characterization

Nitrogen adsorption is the key to obtaining the specific area of porous solid materials, and this measurement was conducted at 77.2 K (-195.8°C), using an ASAP 2020 V4.02 unit gas adsorption analyzer, at an equilibration interval of 5 seconds, with a sample mass from 0.28 to 0.30 g. The surface area of the adsorbent was determined using the Brunauer, Emmet, and Teller (BET) equation, and the micropore volume of the adsorbent was measured using the t-plot method. The pore size distribution was calculated according to the Barrett, Joyner, and Halenda (BJH) model, and the surface morphology was determined by field emission scanning electron microscopy and energy dispersive x-ray (FESEM-EDX) analysis.

The resulting biogas was analyzed by gas chromatography (GC Bruker, USA), using a thermal conductivity detector (TCD) and polydimethylsiloxane as a column (BR-Q-PLOT type), with a length and internal diameter of 30 m and 0.53 mm, respectively, and helium as a carrier gas.

2.3. Production of Biogas by Anaerobic Digestion

The POME and cow feces (10%) were thoroughly mixed; then, the pH of the mixture was adjusted to 7 by adding a $Ca(OH)_2$ solution to the optimized biogas production. A schematic diagram of biogas production by the digesting anaerobic method is shown in Figure 1. A tank digester (50 dm^3) was used for continuous biogas production, and the POME-cow feces mixture was inserted into the inlet periodically. The residue of the bioprocess was removed through an outlet, and the biogas produced from the anaerobic digestion process flowed into the gas holder. A manometer was used to monitor the progress of the biogas process.

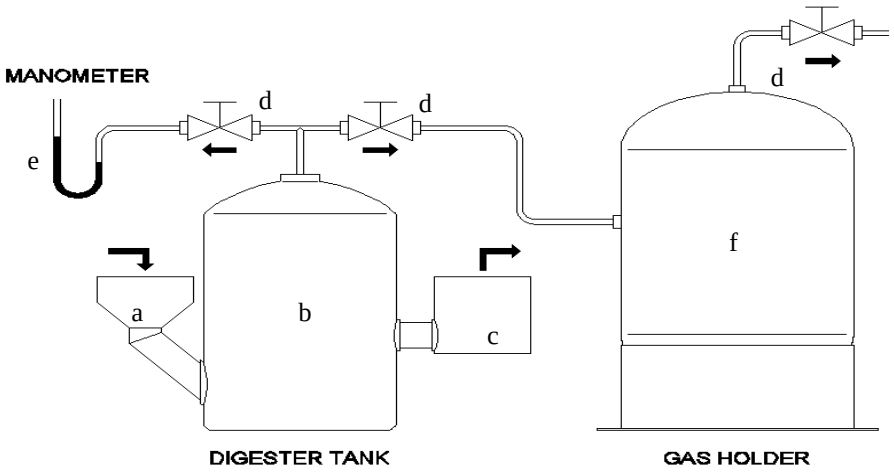


Figure 1 Schematic diagram of biogas production: (a) tank inlet; (b) digester tank; (c) tank outlet; (d) valve; (e) manometer; and (f) biogas storage

2.4. Modification of Clinoptilolite Zeolites

A natural clinoptilolite zeolite (100 g) was immersed and stirred for 2 h in a 1M hydrochloride acid (HCl) solution at a 1:2 (zeolite:acid) mass-to-volume ratio. Then, the mixture was filtered and washed by demineralized water to remove any remaining impurities. For the dealumination process, the mixture was then neutralized with a 1M sodium hydroxide (NaOH) solution in a 1:2 (zeolite:base) mass-to-volume ratio. Finally, the mixture was filtered and washed in the same manner as in the activation by HCl. The precipitate leftover was calcined at 450°C for 2 h.

2.5. Purification of Biogas in a Fixed-Bed Column

Fixed-bed column adsorption with a length of 15 cm and diameter of 0.8 cm was used for the biogas purification. In this purification process, we only used the modified zeolites (after acid-base treatment) as an adsorbent for the removal of the CO_2 in the biogas. The adsorbent dosage varied (1.5, 2.0, and 2.5 g), the volume of the biogas was 2 dm^3, and the flow rate of the adsorption process varied (100, 200, and 300 mL/min).

3. RESULTS AND DISCUSSION

3.1. Physical and Chemical Properties of POME and the Production of Biogas

The physical and chemical properties of POME are summarized in Table 1. In general, the chemical properties (BOD_5 and COD) of POME are suitable for the production of biogas. Moreover, POME is acidic, with a pH of 4.75, so we needed to adjust the pH to 7 to optimize the biogas production. The ratio of C/N in the POME was observed at only 0.44, which is much lower than the C/N ratio for biogas production (in the range of 20-30); therefore, cow feces (10%) were added as a bacterial starter to increase the C/N ratio (Mujdalipah et al., 2014). To control the C/N ratio and to enhance the microbial utilization of Ca^{2+}/Mg^{2+}, 10% clinoptilolite zeolite was added to the anaerobic digestion (Wang et al., 2015). The latter was also used to improve the biogas production through the inhibition of NH_3-N/NO_3-N formation (Wang et al., 2015).

The biogas processing of the POME-cow feces mixture via anaerobic digestion using a digester tank produced 89% CH_4 and 11% CO_2. Overall, the addition of cow feces and adjustment of the pH were found to increase the C/N ratio (Mahajoeno et al., 2008).

Table 1 The physical and chemical properties of POME

No	Analysis	Results	Unit	Method
1	Total Volatiles Suspended (TVS)	6,620	mg/L	Gravimetry
2	Total Suspended Solids (TSS)	7,048	mg/L	US EPA 160.2-1983
3	pH	4.75	-	APHA 4500-H+B-2012
4	Biochemical Oxygen Demand (BOD5)	6,616	mg/L	APHA 5210 B-2012
5	Chemical Oxygen Demand (COD)	22,038	mg/L	SNI 6989.2-2009
6	Oil and grease	17.2	mg/L	SNI 6989.2-2011
7	Ratio C/N	0.44	-	Spectrophotometry and SNI-06-6989.30-2005

3.2. Modification of Clinoptilolite Zeolites

In this study, we used zeolites of moderate size (1–2 mm) to prevent floating (if they are too small; nanosized), and avoid reductions in the porosity and surface area (if they are bulky). The

adsorption characterization method used nitrogen gas at 77.2 K to measure the textural properties of the porous solids, namely, the specific surface area, pore volume, and pore size distribution (De Lange et al., 2014). The pore volume and specific surface area were determined using the Brunauer, Emmet, and Teller (BET) equation, and the pore size distribution was calculated according to the Barrett, Joyner, and Halenda (BJH) equation; both equations are based on the sorption isotherm. The BET equation is an extension of the Langmuir sorption isotherm model for multilayer adsorption formation (Gongda et al., 2014).

The physicochemical properties, including the BET surface area, micropore volume, and pore sizes of the natural zeolites before and after modification, are summarized in Table 2. The adsorption average pore diameter via the BET was smaller than the BJH adsorption average pore diameter for all of the samples. The differences in the average pore diameters from both equations were based on the 4V/A equation, where V = volume and A = area. The volumes used in these calculations of the average pore diameter were different. For the BET equation, the V was a single point volume, which is the total volume less the greatest relative pressure (P/P_0). For the BJH equation, the V represents a volume at a range of pore diameters or relative pressures (P/P_0), with the assumption that the pore is cylindrical. The area (A) is given by the BET equation.

The results of the BET surface area calculations of the adsorbents suggest that the zeolite modified by a strong acid (1M HCl), strong base (1M NaOH), and calcination (450°C) had a reduced surface area (up to 16%). The highest BET surface area was obtained when the zeolite was not treated with the acid, base and calcination. We assume that the BET surface area was reduced due to the increasing nanoparticle sizes of the adsorbent after the acid-base-calcination treatments (Table 2). However, there was no effect from the acid-base-calcination on the surface area of the zeolite. Modification by a strong base, in particular, can dissolve SiO_2 (one of the constituents of natural zeolites), so that it forms new pores in the natural zeolite, resulting in an increase in surface area (Hamidi et al., 2011). Moreover, calcination can remove the water and volatile compounds. In this study, the BET surface area for the zeolite after the acid-base-calcination treatment was similar to that of the zeolite after a calcination treatment. Overall, we observed that the strong acid and strong base treatments did not have significant effects on the BET surface area. This translates to no changes in the zeolite structures after these treatments.

A zeolite modified by using acid-base-calcination treatments has a unique pore structure, with a size of 9.32 Å, which allows small molecules (such as CO_2 and N_2, with sizes of 3.4 and 5.8 Å, respectively) to diffuse, but prevents the diffusion of CH_4 and other larger molecules (Ackley, 2003).

Table 2 The physicochemical properties of clinoptilolite zeolites before and after

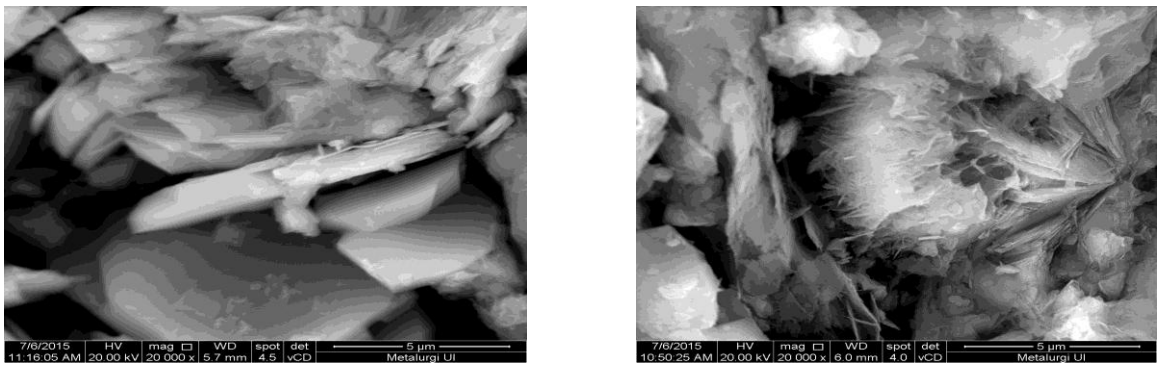
Parameter	Without treatment (pristine zeolite)	With acid-base-calcination treatments	With calcination treatment only
BET surface area (m^2/g)	47.12	39.43	39.36
BJH adsorption cumulative surface area of pores (m^2/g)	28.50	29.20	22.97
Micropore volume (cm^3/g)	8.58×10^{-3}	5.01×10^{-3}	8.17×10^{-3}
t-Plot micropore area (m^2/g)	17.22	10.22	16.31
BJH adsorption cumulative volume of pores (cm^3/g)	9.03×10^{-2}	8.6×10^{-2}	8.3×10^{-2}
Adsorption average pore (nm)	8.51	9.32	9.34
BJH adsorption average pore diameter (nm)	12.67	11.79	14.48
Average nanoparticle size (nm)	127.32	152.17	152.44

The morphology and composition properties of natural zeolites were analyzed by FESEM-EDX, and the Si/Al ratios of the natural zeolites before and after treatment are shown in Table 3. Strong acid, strong base, and calcination treatments in natural zeolites could affect their initial structure, and the Si/Al ratio in the natural clinoptilolite zeolite was modified by these treatments. As the results show, the Si/Al ratio increased from 4.00 to 5.05 after the calcination treatment, and from 4.00 to 6.10 after modification by the acid, base, and calcination treatments. In addition, eliminating the impure compounds from the pores of the zeolites leads to a cation exchange in the natural zeolite structure, in which desilication and dealumination result in a reduction in the Si/Al ratio. The treatment with the base dissolves some of the SiO_2 of the natural zeolite structure, creating more pores in the natural zeolites and increasing the surface area. The decreased Si/Al ratio means that the dealumination rate is smaller than the desilication rate. However, the acid-base treatment cannot be done in an excessive concentration of acid-base, because it can completely destroy the structure of the natural zeolite.

Table 3 Si/Al ratio of natural zeolite before and after the treatments

Modification of Natural Zeolite	Si/Al Ratio
After acid-base treatment	6.10
After calcination treatment	5.05
Before treatment	4.00

The SEM images in Figures 2a and 2b show the morphology of the surface area of natural zeolite treated with acid-base and calcinated, respectively. The morphology of the modified zeolite after acid-base-calcination resembled thick, flat layered plates, with many porosities (Figure 2a). While the morphology of the modified zeolite after calcination only was more amorphous, thin, and flat, and showed very clearly an increased number of pores (Figure 2b). It can clearly be seen that there was an increased number of pores in the natural zeolites after treatment with the acid-base, and this increase was due to the removal of the impurities. In addition, the structure of the zeolites was modified because of dealumination by the acid and the dissolving of some of the SiO_2 by the base.

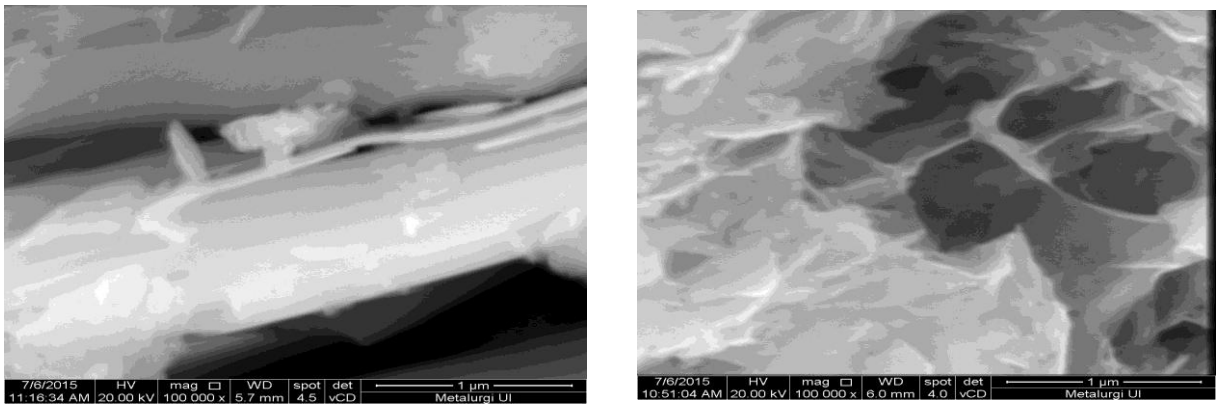


(a) (b)

Figure 2 SEM images of modified zeolites: (a) acid-base treatments; and (b) calcination treatment

The pore sizes of the modified zeolites can be seen in the SEM images shown in Figures 3a and 3b. These images also show that the pores of the modified zeolite, after the calcination process, ranged from 300 to 500 nm in size. The observed profile of the thin, flat surface after calcination showed that the finest grains are characterized by cleavage, and matched for the removal of CO_2. Based on the morphology of the modified zeolites, they can be used as

adsorbents for the removal of carbon dioxide (CO_2) in biogas. Due to the unique pore structure of modified zeolites, small molecules like CO_2 and N_2 diffuse quickly, inhibiting the diffusion of CH_4 and other larger molecules (Ackley, 2003).



(a) (b)

Figure 3 SEM images of modified zeolites: (a) after acid-base treatments; and (b) after calcination treatment

3.3. Purification of Biogas by Fixed-Bed Column Adsorption

In this study, we only used the acid-base-calcination treatment modified adsorbents for the removal of the CO_2 in the biogas. A qualitative analysis was conducted to determine the presence of H_2S by using 0.1M Pb-acetate (Moore, 2003). There was no formation of black precipitate (PbS) in the solution; thus, impurities in the H_2S gas were not found or detected in the biogas produced from the POME by anaerobic digestion.

The removal of CO_2 at a variety of flow rates in the adsorption process (100, 200, and 300 mL/min) is shown in Figures 4 and 5.

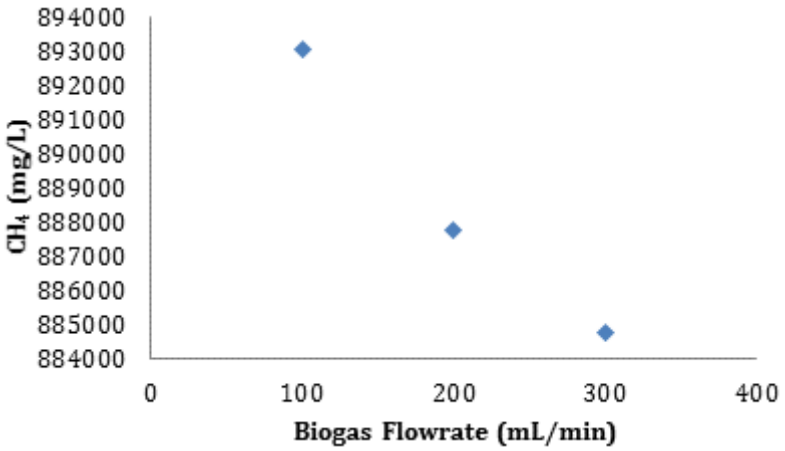


Figure 4 The effect of the flowrate on the CH_4 level in biogas

The capability for CO_2 adsorption by a modified zeolite decreases with increasing flow rates (100, 200 and 300 mL/min) of the biogas, and the levels of CO_2 were 106,906, 112,237, and 115,256 mg/L, respectively. The best purification results were obtained under the flow rate of 100 mL/min, due to the optimum contact between the biogas and the adsorbent. At a higher flow rate of biogas, the contact time becomes shorter, because the excess flow rate results in a shorter contact time of the CO_2 with the surface of the natural zeolites, so that more CO_2 can

escape. On the other hand, if the flow rate is too low, it results in a pressure drop in the adsorption column. After modification, the clinoptilolite zeolites with a high capability of increasing the removal of CO_2 are promising adsorbent materials for the purification of biogas. A high surface-volume ratio is one of the most important factors in adsorption (Ozekmekci et al., 2015).

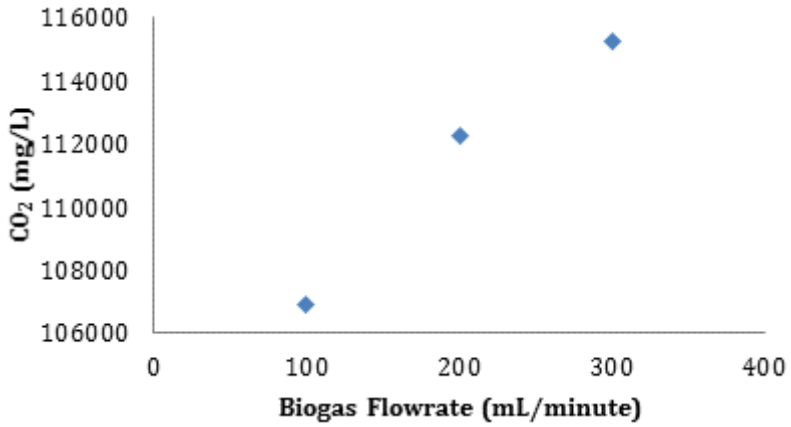


Figure 5 The effect of the flowrate on the removal of CO_2 in biogas

The effects of the adsorbent dosage on the purification and adsorption of CO_2 in biogas are shown in Figures 6 and 7. The percentage of CO_2 removal increases with an increase in the adsorbent dosage in fixed-bed column adsorption, and the increasing adsorbent mass provides more available pores and surfaces for the removal of CO_2 in biogas. The maximum removal of CO_2 occurs when the dosage of the adsorbent is 2.5 g. The adsorptions of CO_2 in the biogas determined by using adsorbent dosages of 1.5, 2.0, and 2.5 g were 97,878, 97,404, and 93,855 mg/L, respectively.

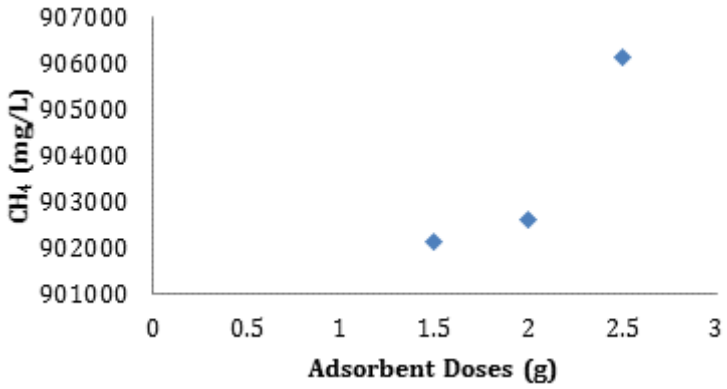


Figure 6 The effect of the adsorbent dosage on the CH_4 level in biogas

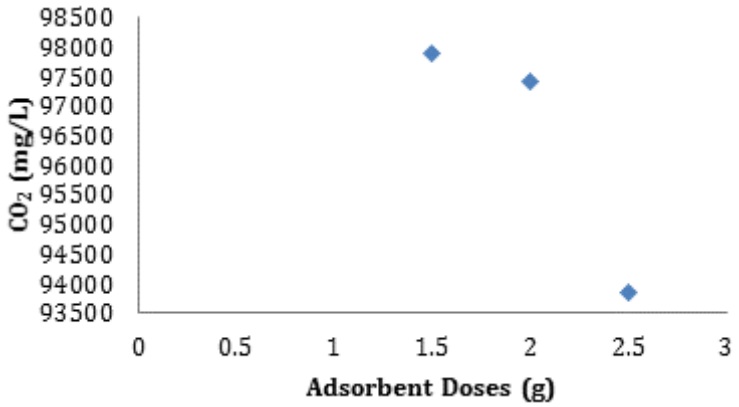


Figure 7 The effect of the adsorbent dosage on the removal of CO_2 in biogas

4. CONCLUSION

The initial characterization of the POME determines the potential biogas content; therefore, anaerobic digestion to produce biogas can be prepared and controlled by adjusting the pH to 7, with the addition of a $Ca(OH)_2$ solution. For this research, the purification of the biogas was performed with fixed-bed column adsorption. In this case, the modified clinoptilolite zeolites (using acid, base, and calcination treatments) were employed as adsorbents to obtain the best possible CO_2 removal, which was optimum at the biogas flow rate of 100 mL/min and adsorbent dosage at 2.5 g. The performance of the modified zeolites used in this research for the removal of CO_2 in the purification of biogas was affected by the acid-base-calcination treatments.

5. ACKNOWLEDGEMENT

This work was supported by *Kerjasama Kemitraan Penelitian dan Pengembangan Pertanian Nasional* (KKP3N) from the Ministry of Agriculture of Indonesia (Grant No.0589/H2.R12/HKP.00.05/2015).

6. REFERENCES

Ackley, M., 2003. Application of Natural Zeolites in the Purification and Separation of Gases. *Microporous and Mesoporous Materials*, Volume 61(1–3), pp. 25–42

Ahmed, Y., Yaakob, Z., Akhtar, P., Sopian, K., 2015. Production of Biogas and Performance Evaluation of Existing Treatment Processes in Palm Oil Mill Effluent (POME). *Renewable and Sustainable Energy Reviews*, Volume 42, pp. 1260–1278

Alonso-Vicario, A., Ochoa-Gómez, J.R., Gil-Río, S., Gómez-Jiménez-Aberasturi, O., Ramírez-López, C.A., Torrecilla-Soria, J., Domínguez, A., 2010. Purification and Upgrading of Biogas by Pressure Swing Adsorption on Synthetic and Natural Zeolites. *Microporous and Mesoporous Materials*, Volume 134(1-3), pp. 100–107

Bacsik, Z., Cheung, O., Vasiliev, P., Hedin, N., 2016. Selective Separation of CO_2 and CH_4 for Biogas Upgrading on Zeolite NaKA and SAPO-56. *Applied Energy*, Volume 162, pp. 613–621

Chin, M.J., Poh, P.E., Tey, B.T., Chan, E.S., Chin, K.L., 2013. Biogas from Palm Oil Mill Effluent (POME): Opportunities and Challenges from Malaysia's Perspective. *Renewable and Sustainable Energy Reviews*, Volume 26, pp. 717–726

De Lange, M.F., Vlugt, T.J.H, Gascon, J., Kapteijn, F., 2014. Adsorptive Characterization of Porous Solids: Error Analysis Guides the Way. *Microporous and Mesoporous Materials*, Volume 200, pp. 199–215

Fehime, C.O., Semra, U., 2005. The Effect of HCl Treatment on Water Vapor Adsorption Characteristics of Clinoptilolite Rich Natural Zeolite. *Microporous and Mesoporous Materials*, Volume 77(1), pp. 47–53

Gil, M.V., Álvarez-Gutiérrez, N., Martínez, M., Rubiera, F., Pevida, C., Morán, A., 2015. Carbon Adsorbents for CO_2 Capture from Bio-hydrogen and Biogas Streams: Breakthrough Adsorption Study. *Chemical Engineering Journal*, Volume 269, pp. 148–158

Gongda, W., Kai, W., Tingxiang, R., 2014. Improved Analytic Methods for Coal Surface Area and Pore Size Distribution Determination using 77 K Nitrogen Adsorption Experiment. *International Journal of Mining Science and Technology*, Volume 24, pp. 329–334

Kowalczyk, P., Sprynskyy, M., Terzyk, A.P., Lebedynets, M., Namieśnik, J., Buszewski, B., 2006. Porous Structure of Natural and Modified Clinoptilolites. *Journal of Colloid and Interface Science*, Volume 297, pp. 77–85

Lam, M.K., Lee, K.T., 2011. Renewable and Sustainable Bioenergies Pfrom Palm Oil Mill Effluent (POME): Win–win Strategies toward Better Environmental Protection. *Biotechnology Advances*, Volume 29, pp. 124–141

Liu, C., Zhang, R., Wei, S., Wang, J., Liu, Y., Li, M., Liu, R., 2015. Selective Removal of H_2S from Biogas using a Regenerable Hybrid TiO_2/zeolite Composite. *Fuel*, Volume 157, pp. 183–190

Mahajoeno, E., Lay, B.W., Sutjahjo, S.H., Siswanto, 2008. The Possibility of Palm Oil Mill Effluent for Biogas Production. *Biodiversitas*, Volume 9, pp. 48–52

Moore, 2003. *Qualitative Analysis of Metal Ions in Solution*, Texas: American School of Gas Measurement Technology

Mujdalipah, S., Dohong, S., Suryani, A., Fitria, A., 2014. Effects of Fermentation Time toward Biogas Production by using Two Stages Digester on Various Palm Oil-mill Effluent and Activated Sludge Concentration. *AGRITECH*, Volume 34(1), pp. 56–64 [in Bahasa, Abstract in English]

Ozekmekci, M., Salkic, G., Ferdi Fellah, M., 2015. Use of Zeolites for the Removal of H_2S: A Mini-review. *Fuel Processing Technology*, Volume 139, pp. 49–60

Poh, P.E., Chong, M.F., 2009. Development of Anaerobic Digestion Methods for Palm Oil Mill Effluent (POME) Treatment. *Bioresource Technology*, Volume 100(1), pp. 1–9

Sigot, L., Ducom, G., Benadda, B., Labouré, C., 2014. Adsorption of Octamethylcyclotetrasiloxane on Silica Gel for Biogas Purification. *Fuel*, Volume 135, pp. 205–209

Wang, X., Zhang, L., Xi, B., Sun, W., Xia, X., Zhu, C., He, X., Li, M., Yang, T., Wang, P., Zhang, Z., 2015. Biogas Production Improvement and C/N Control by Natural Clinoptilolite Addition into Anaerobic co-digestion of *Phragmites australis*, Feces and Kitchen Waste. *Bioresource Technology*, Volume 180, pp. 192–199

Yang, L., Ge, X., Wan, C., Yu, F., Li, Y., 2014. Progress and Perspectives in Converting Biogas to Transportation Fuels. *Renewable and Sustainable Energy Reviews*, Volume 40, pp. 1133–1152