



Increasing Percentage of Methane (Ch₄) from Biogas with Purification by using Zeolite Membrane

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ABSTRACT

Biogas is the one of renewable energies that is the result of fermentation of methanogenic bacteria of biomass or organic substance . The low methane content in biogas is affected by the amount of impurities in the biogas. A membrane that produced from activated zeolite as an adsorbent is used to absorb or reduce the content of impurities in the biogas in order to increase methane in the biogas . Variate of research comprise variety the composition ratio of zeolite and clay as materials for zeolite membranes are 30:70 , 50:50 , 70:30 , and the effect of flow rate on the purification were 100% open valve and 50% open the valve . Parameters to determine the quality of the purification results biogas is methane percentage were analyzed by Gas Chromatography. The percentage of methane in biogas purification before treatment was 64.86 % . The results showed that the highest percentage of methane was 72.22 % that generated by biogas purification for zeolite and clay ratio was 70:30 with 100% open valve as the flow rate.

Keywords: Biogas, zeolite, zeolite membrane, fermentation, purification, activated zeolite.

INTRODUCTION

Demand for fuel oil in Indonesia, both for the transportation industry, and households from year to year increase. Cause the fuel availability is limited or the price to soar. Indonesia has the potential to develop alternative energy, considering the number of resources that can be used. Nowadays, many developed countries increase the use of biogas generated from wastewater and solid wastes or resulting from mechanical biological treatment systems for municipal waste. In addition to treating waste potentially damaging environmental sustainability, with pure biogas that will be obtained is also one of the energy sources that are environmentally friendly. Biogas is an alternative energy that can be developed in Indonesia as well. So far, the use of livestock manure into biogas is still less known than its use as a raw material of organic fertilizer. In fact, with the utilization of biogas technology, livestock manure can be converted into usable energy to meet the energy needs of a wide range, for example; cooking, lighting, and transportation. Biogas is a mixture of gases produced by the decomposition of organic compounds in natural methanogenic biomass by anaerobic bacteria. Gases contained in the biogas are methane (CH₄), carbon dioxide (CO₂), and a little hydrogen sulfide

(H₂S). Methane gas is a fuel that can be used later, while the carbon dioxide and hydrogen sulfide is a pollutant. High levels of impurities in the biogas can reduce the calorific value of biogas and potentially pollute the environment. Purification of biogas needs to be done with the method-specific method possible before utilized directly. This research aims to reduce the levels of impurities in the biogas in a way to test the effect of zeolite membranes to obtain a high percentage of methane. High percentage of methane that would result in high fuel value.

METHODS

Materials Research

The materials used for this study is the result fermentation biogas from cow manure, zeolite, and a solution of NaOH with a concentration of 0.15 M..

Equipments

The tools used in this study were digester, and a series of purification membranes

Procedure Research

Generating Biogas

Biogas to be used is the biogas produced from the fermentation of cow manure. The fermentation process begun by inserting the raw materials of

cow dung and water into the fermenter at a ratio of 1: 1 before inserting it into the manure digester and water first stirred until homogeneous. After 7 days of biogas containing H₂S and many after 10 days will be formed methane produced by methanogenic bacteria. Cow manure is fed continuously into the digester biogas production that does not stop.

Zeolite Activation

Zeolite is a natural zeolite used in the form of rock. The size of the zeolite is reduced first to 60 mesh and then activated using NaOH solution with a concentration of 0.15%. Effect of activation of zeolite, namely zeolite can purify from impurity components, eliminating certain types of metal cations and water molecules contained in the cavity, or enlarge the pore volume, so it has a higher capacity. Therefore natural zeolite to be activated before use, to enhance workability.

Zeolite Membranes Preparation

Zeolite membranes to be made to serve media biogas purification. Biogas that has been through a zeolite membrane is expected to have a greater percentage of CH₄. Once activated, the zeolite is mixed with clay in the ratio of 70:30, 50:50, and 30:70. Clay is used as an adhesive medium zeolite membranes. With the composition mentioned above, zeolite membranes printed with a certain size that adjusts membrane housing and heated, so di dapatlah zeolite membranes. Zeolite membranes then mounted in the housing membrane.

Purification Stage

Biogas from the digester flows into the membrane housing with a certain flow rate. Before the stage of purification of biogas samples without purification treatment was taken as control. The state

of the membrane must be kept airtight to avoid contamination by air. So the gas is to be supplied in advance to overflow in advance so that no more air inside the membrane housing, known as flushing. This phase would be done every taking a sample by purification with variables. Samples that have been through the purification stages were taken with different variable flow rate. Different flow rates will

affect whether or not the contact time between the biogas by zeolite membranes so expect more of the impurities are retained. The purified sample supplied to the sampling or balloons.

Samples Analysis

Working parameters zeolite membrane as biogas purification media is increasing the percentage of methane in the biogas after

purification. The increase in the percentage of methane along with a decrease in the percentage of impurities. Biogas is purified and then analyzed using gas chromatography (GC). This tool will detect gas content contained in the biogas. Each sample is analyzed takes about 30 minutes for the content contained in the biogas can be detected.

RESULT AND DISCUSSION

Effect of zeolite membrane compositions on methane generated

From Fig. 1. could be seen that the increasing of methane (CH₄) after biogas has been through zeolite membrane. Because oxygen and nitrogen molecules were trapped in zeolite membrane pores, but methane (CH₄) can through it. So, methane percentage was increasing.

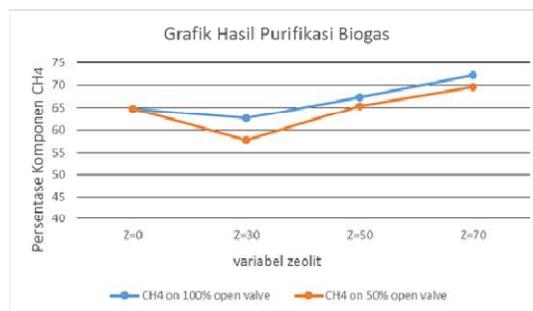


Fig. 1. Effect of zeolite membrane compositions on methane generated

In zeolites, the volume and diameter contained in a vacuum in which the crystal zeolitlahlah utilization of zeolite minerals / materials filter or molecular sieving. (Payra, 2003). Zeolite pore size also affects the zeolite adsorption capacity and rate of certain substances (Bonenfant, 2008). Zeolite is a mineral that has two types of pores, ie micropores (size up to 2 Angstroms) and macropores (size > 50 Angstroms). Macropore is the entrance to the microporous particles, and in part this is mostly microporous adsorption events occur (Ozkan, 2008). The molecules that have a smaller diameter than the inlet zeolite will be absorbed from the surface to the center of the cavity. While for molecules larger than the inlet cavity can not enter into the zeolite (Tampubolon, 1994). The activation process is carried out is expected to increase the number of micropores due to the activation process most of the micropores are formed.

Zeolite membranes in this study are made of activated zeolite with NaOH and clay as an adhesive. During the activation process with NaOH, silica dissolution process will occur, which

is one component in the zeolite framework (Jozefaciuk, 2002). Silica dissolution will lead to changes in the structure of zeolites and silica reduction in the zeolite framework, so that the Si / Al ratio decreases. The decline in this ratio will increase the adsorption capacity (Bonenfant, 2008). The ability of zeolites to absorb the material/substance based on the selectivity of the size of the center line of empty space and the selection of molecules molecules of a substance to be absorbed. Distribution of unusual charges contained in the cavity that has been dehydrated resulted in some material that has two poles (dipole) can be absorbed. If there are 2 or more molecules that can cross the line passes through the zeolite cavity, but because of the influence of the poles or the relationship between the zeolite molecular substances are absorbed, then only one substance that will be passed while others were arrested or denied. This is a trait that is only possessed by zeolite as absorbent. Water (H₂O) is a polar would be preferred by the zeolite to absorb compared with Methane (CH₄) is not polar. Molecules that berkutup more welcome than not berkutup molecules (Zussman, 1996). In this study the content contained in the biogas is nitrogen (N₂), oxygen (O₂), carbon dioxide (CO₂), and methane (CH₄) where these gases are nonpolar, so the selectivity of absorption of gases using a zeolite membrane only in large molecules. Nitrogen and oxygen can be through the channel cavity zeolite membranes, so that nitrogen and oxygen trapped in the cavities of zeolites, therefore resulting in a decrease in the percentage of nitrogen (N₂) and oxygen (O₂). The opposite occurs in methane (CH₄) and carbon dioxide (CO₂). CH₄ and CO₂ may not be able to go through the channels of zeolite cavity, so that CH₄ and CO₂ contained in the biogas when it flowed into the zeolite membrane can escape through zeolite membranes. Due to a decrease in the percentage of N₂ and O₂ in the biogas after purification with zeolite membranes, the obtained increase in the percentage of CH₄ and CO₂.

In addition to a decrease in Si / Al ratio, activation with NaOH also aims to remove certain ions from the zeolite framework and replace it with the Na⁺ ions so that the natural zeolite had closer homoionik conditions (Inglezakis, 2001). With homoionik shape, molecular pore zeolites will have relatively the same size so that, better adsorption capability. Conditions at the time of purification should be kept airtight so we drain over flow of biogas to advance in order to avoid contamination from the outside air, but it also must be installed correctly so it does not leak on the unit membrane installation. Methane(CH₄) initial percentage zeolite membranes without treatment was 64.86%. At a flow rate of 50% open valve, the percentage of

CH₄ in biogas after a zeolite membrane increased to 69.63%, while the flow rate is 100% open valve CH₄ percentage increased to 72.22%.

Effect of zeolite membrane compositions on oxygen generated

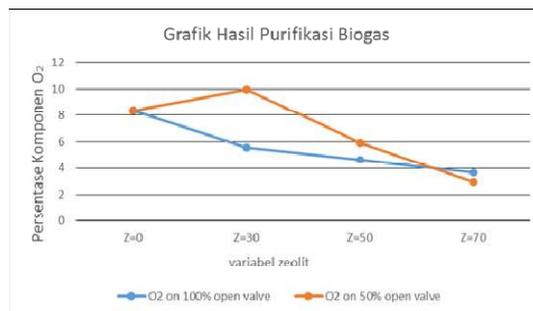


Fig. 2. Effect of zeolite membrane compositions on oxygen generated

Through fig. 2, it could be seen that there was a decreasing of oxygen (O₂) after the biogas is passed through a zeolite membrane for O₂ molecules retained in the pores of the zeolite that had been activated. Initial percentage oxygen without purification treatment zeolite membrane was 8.35%. At a flow rate of 50% open valve, O₂ percentage in the biogas after a zeolite membrane was reduced to 2.92%, while the flow rate was 100% open valve O₂ percentage was reduced to 3.64%.]

Effect of zeolite membrane compositions on nitrogen generated

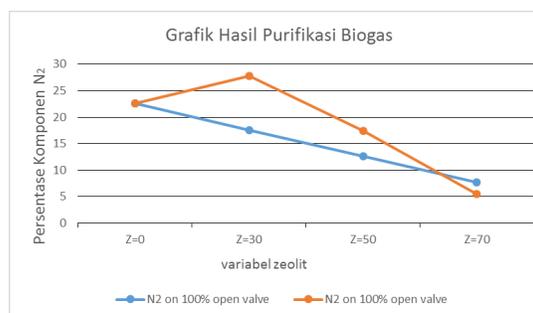


Fig. 3. Effect of zeolite membrane compositions on nitrogen generated

The open valve at a flow rate of 100% open valve due to the contact time 50% valve open longer so more restrained than O₂ at a flow rate of 100% open valve. In addition, membrane housings must be kept airtight to prevent an increase in O₂ due to contamination from the outside air. So we drain the biogas to over flow in advance so that no

more air inside the membrane housing, known as flushing.

Through fig. 3, it can be seen that there is a decrease of N₂ after the biogas is passed through a zeolite membrane because N₂ molecules retained in the pores of the zeolite that had been activated. Persentase initial N₂ without purification membrane treatment was 22.65%. At a flow rate of 50% open valve, the percentage of N₂ in the biogas after a zeolite membrane was reduced to 5.44%, while at a flow rate of 100% open valve N₂ percentage was reduced to 7.74%.

Effect of zeolite membrane compositions on carbon dioxide generated

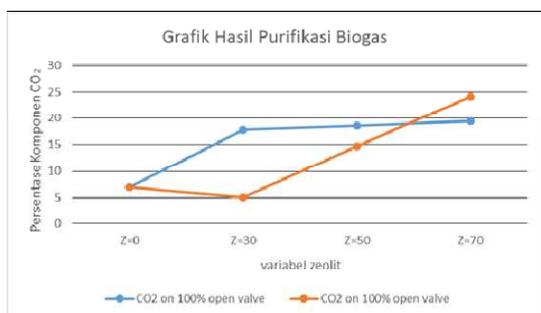


Fig. 4. Effect of zeolite membrane compositions on carbon dioxide generated

Percentage zeolite with a flow rate 50% greater than the open valve at a flow rate of 100% open valve due to the contact time 50% valve open longer so more restrained than N₂ at a flow rate of 100% open valve. In addition, membrane housings must be kept airtight to prevent an increase in N₂ due to contamination from the outside air so that we drain the biogas to overflow in advance so that no more air inside the membrane housing, known as flushing. From fig. 4, it could be seen an increase in the percentage of CO₂ after the purification of biogas by zeolite membranes. This is due to the decreased levels of N₂ and O₂ levels in the biogas. The percentage of CO₂ in the biogas without purification treatment by zeolite membrane was 6.88%. At a flow rate of 50% open valve, the percentage of CO₂ in the biogas increased to 24.1%. Meanwhile, at a flow rate of 100% open valve, the percentage of CO₂ in the get by 19.41%. From the results of biogas purification using zeolite membrane was found that only the selective absorption of N₂ and O₂. Proved by the decrease in N₂ and O₂ on every variable flow and the increase in the percentage of CH₄ and CO₂.

CONCLUSIONS

The membrane made from activated natural zeolite with NaOH solution could increase the methane percentage from biogas by adsorbing the impurities within biogas. The more composition of zeolite in zeolite membrane, more impurities could be adsorbed, so methane percentage was increasing. The best flow rate in this research for the increasing methane percentage was 100% open valve. Methane percentage in biogas before purification with zeolite membrane was 64.86%. Result in this research showed that the highest methane percentage was 72.22% which produced during biogas purification in 100% open valve and 70:30 as the ratio zeolite and clay.

REFERENCES

- [1] Abdullah, K. A. (1991). Energi dan Listrik Pertanian. JICA-DGHE/IPB Project/ADAET, JTA-9a, 132.
- [2] Abdullah, S. (2013), Purifikasi Biogas Menggunakan Zeolite dan Karbon aktif, hasil penelitian Hibah perguruan Tinggi, Fakultas Teknik, Unsri.
- [3] Astiana, S. (1991). Karakterisasi Deposit Mineral Zeolit Dalam Aspek Pemanfaatan di Bidang Pertanian jilid I, Indonesia, Vol 1. Bogor: IPB.
- [4] Baker, R. (2004). Membrane Technology and Application, 2nd Edition. John Willey & Sons, 3-6; 15-16;314.
- [5] Bonenfant, D. K. (2008). Advances in Principal Factors Influencing Carbon Dioxide Adsorption on Zeolite. Ukraina: Sci. Technol Adv.
- [6] Chengdu. (1989). The biogas Technology in china. china: Chengdu Biogas research institute.
- [7] Ditjen Pengembangan Peternakan, D. B. (2003). Integrasi Ternak dengan Areal Tanaman Hortikultura. Bogor: Departemen Pertanian.
- [8] Harjanto, S. (1983). Endapan Zeolit, Penggunaan dan sebarannya di Indonesia. Bandung: Direktorat Sumberdaya Mineral Departemen Pertambangan dan Energi.
- [9] Inglezakis, V. P. (2001). Effects of Pretreatment on Physical and Ion Exchange Properties of Natural Clinoptilolite. Environmental Technology, 75- 82.
- [10] James.D, D. (1951). Manual of Mineralogy. London: John Willey and Son., Jilid II,Edisi 17.
- [11] Jozefaciuk, G. a. (2002). Effect of Acid and Alkali Treatments on Surface Areas and Adsorption Energies of Selected Minerals. Journal Clays and Clay Minerals, 771-783.
- [12] Karki, A. (1984). Biogas field Book. Nepal: Sahayogi Press,Kathinandu.
- [13] Krauss.E.H., H. S. (1981). Mineralogy an Introduction to the Study of Minerals and Cristals. New York: The Maple Press Company.
- [14] Laeli Kurniasari, M. D. (2011, Juni). Aktivasi Zeolit alam sebagai adsorben pada alat pengeringan bersuhu rendah. Reaktor,. Vol. 13 No. 3, pp. 178-184.



- [15] Langrange, B. (1979). Biomethane2. France: Principles-Techniques Utilization. EDISVD,la Calade,13100 Aix-en-provence.
- [16] Ozkan, F. a. (2008). Diffusion Mechanism of Water Vapour in A Zeolitic Tuff Rich in Clinoptilolite. *Journal of Thermal Analysis and Calorimetry* , 699-702.
- [17] Payra, P. D. (2003). Handbook of Zeolite science and Technology. New York: Marcel Dekker.
- [18] Porterfield, W. (1993). Inorganic Chemistry 2nd Edition. New York: Prentice Hall.
- [19] Sutarti, M. R. (1994). Zeolit Tinjauan Literatur. Jakarta : Pusat Dokumentasi dan Informasi Ilmiah.Lembaga Ilmu Pengetahuan Indonesia.
- [20] Tampubolon, R. (1994). Studi Pemanfaatan Zeolit Alam Sarulla Untuk Menurunkan kadar ion NH₄⁺ dalam limbah cair rendaman dross. Medan: PT. INALUM". USU.
- [21] Teguh Wikan Widodo, A. H. (2004). Kajian Teknis Teknologi Biogas dan Potensi Pengembangannya di Indonesia. Prosiding Seminar Nasional Mekanisme Pertanian (pp. 193-198). Jawa Barat: Balai Besar Pengembangan Mekanisasi Pertanian.
- [22] United, N. (1984). Updated Guidebook on biogas Development-Energy Resources Development series. New York,USA: United Nations.
- [23] Yadava, L. a. (1981). The development and use of Biogas technology in Rural Areas of Asia. Improving Soil Fertility through Organic Recycling (p. Project field Document NO.10). ,FAD/UNDP Regional Project/75/004.
- [24] Zussman, D. (1996). An Introducing to the Rock forming Minerals. England: Longman Group Limited