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Assessment of Calorific Value of Biogas after Carbon Dioxide Adsorption Process Using Natural Zeolite and Biochar

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***Abstract*—We evaluated the adsorption of CO_2 in biogas mixtures using the combination of adsorbents: natural zeolite-natural zeolite (Z-Z), natural zeolite-chicken manure based biochar (Z-CM) and natural zeolite-biogas sludge based biochar (Z-BS). The amount of CO_2 adsorption was controlled at room temperature and under a gas pressure range of 5-7 bar. Samples of biogas before and after adsorption were analyzed by gas chromatography (GC) to determine the percentage of CH_4. The relationship between the percentage of CH_4 composition and calorific value of biogas was investigated. The results of data from GC showed that the highest CH_4 enrichment was performed by Z-CM (28.92%). The highest CH_4 enrichment increased the calorific value of biogas in comparison to biogas before adsorption. The result suggested that CO_2 adsorption using natural zeolite and chicken manure based biochar successfully increased the calorific value of biogas.**

***Index Terms*—Biogas, CO_2 adsorption, calorific value, and biochar.**

I. Introduction

Developing countries are giving more emphasis on renewable energy to reduce greenhouse emission that triggers global warming and climate changes. However, fossil fuel has been the primary energy source in developing countries and the continuous use of fossil fuel will further aggravate environmental pollution posing a major threat to human health. The mitigation of carbon dioxide (CO_2) emission from fossil fuel demands the exploration of renewable energy, such as biogas, to reduce the dependency on fossil fuel based energy [1]. Biogas is a clean energy that has been popularized as substitute for fossil fuel for the purpose of energy saving and environmental protection [2]. According to Liu et al. [3] that greenhouse gases (GHGs) emission from the utilization of biogas was much less than that of fossil fuel such as coal. This statement is also supported by Cuellar and Webber [4]. Fig. 1 showed the comparison study on GHGs emission between two scenarios: (a) business as usual, coal is burned to produce electricity and livestock manure is left in the open air and (b) the treatment of livestock manure in anaerobic digester to generate electricity which offset coal-fired power. Total emission from coal electricity and untreated livestock manure were 65.9 to 109.3 million metric tons (MMT) and 58.8 MMT to 117.9 CO_2 respectively. Replacing coal-fired power and manure GHGs emission with biogas generated fewer CO_2 emission only of 69.9-76.8 MMT.

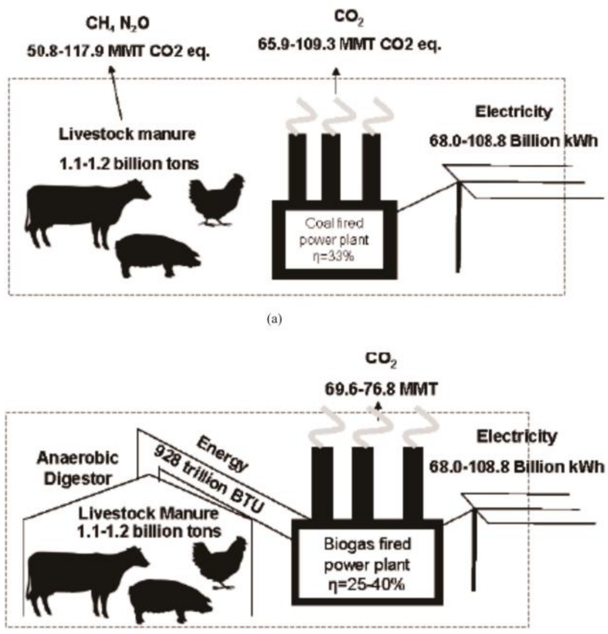

Fig. 1. Calculation of GHGs emission from coal-fired power and biogas [4].

Biogas is produced through anaerobic digestion of biomass for example from livestock waste, agriculture waste, human waste, biodegradable domestic waste, etc. Based on Ministry of Agriculture's report, the number of cattle in Indonesia is large enough, about 16 million in 2016 [5] and this number will possibly increase for next years, following the increase in human population. It will lead to the increase of livestock waste. Usually, most of cattle manure collected from outdoor are naturally decomposed. The collected manure has great potential to produced energy through anaerobic digestion. The use of manure as energy source is suitable and it becomes an efficient technology to mitigate CH_4 emission that has 21 times of global warming potential than CO_2 [6]. Reference [4] reported that replacing coal with manure would produce net potential GHGs emission reduction of 99 MMT or 3.9% of the annual GHGs emission from electricity in the US. Moreover, the use of manure has an important role in reducing livestock waste. Because of

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multiple benefits of biogas technology in mitigating GHGs emission and reducing livestock waste, the government encourages the use of new technology to enhance local biomass. The adoption of new technology is expected to raise human health and income level of small households.

Despite the concerted efforts made to promote the use of biogas in Indonesia, the rate of its uptake is lower compared to other developing countries such as India [7]. The efficiency of biogas energy depends on its calorific value [8]. Biogas contains 50-70% CH_4 and 30-40% CO_2 [9]. The anaerobic digestion process in biogas production is shown in Fig. 2. The presence of CO_2 will reduce the calorific value and increase the compression and transportation cost [10]. In order to overcome the negative impact of CO_2 in biogas, it is important to remove CO_2 from biogas mixtures.

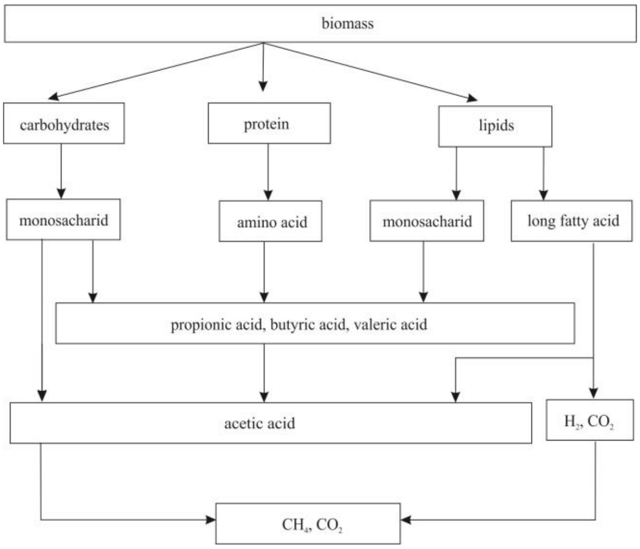

Fig. 2. Conversion pathway of biomass into biogas in anaerobic digestion [1].

A large number of technologies to remove CO_2 have been developed to date such as water scrubbing, chemical scrubbing, cryogenic separation, membrane technology and adsorption [10]-[12]. Recent technologies show that adsorption is promising for CO_2 removal since it is inexpensive and adoptable over the wide range of temperature and pressure condition [13]. Adsorption only requires low energy and capital cost compared to other technologies [14]. There are many researches on CO_2 adsorption on porous materials such as zeolite, activated carbon and biochar [13]-[16] but studies on CO_2 adsorption using chicken manure or biogas sludge based biochar in biogas mixtures are still rare. Nguyen and Lee [16] had studied pure CO_2 adsorption using chicken manure based biochar of 2.18 mmol/g and 1.53 mmol/g at the temperature of 20°C and 30°C respectively. Therefore, the objectives of this study were: (1) to assess biogas characteristics upon the application of carbon dioxide adsorption process using the combination of natural zeolite and chicken manure or biogas sludge based biochar and (2) to calculate the calorific value of biogas after CO_2 adsorption (purified biogas).

We selected chicken manure based biochar because it was abundant in livestock sector in Indonesia while we selected biogas sludge because it reduces biogas waste and lead to bio-cycle biogas production system. Bio-cycle through reuse, reduce and recycle will give optimal benefits for the communities and environment. In this study CO_2 adsorption in biogas mixtures was undertaken at room temperature and under a gas pressure of 5-7 bar.

II. Materials and Methods

A. Materials

The natural zeolite was purchased from Bratachem. Chicken manure was collected from PT Chaorend Phokpand while biogas sludge was collected from biogas production of chicken manure in Kaliurang. Biogas used in this study was supplied by the Center of Agrotechnology Innovation, Gadjah Mada University.

B. Production of Biochar

Chicken manure and biogas sludge were used as feedstock in biochar production. The dried materials were converted into biochar through pyrolysis in cylinder reactor at temperature of 500°C for 4 hours. Then the biochar was left cool at room temperature.

C. Removing CO_2 through Adsorption Technology

The adsorption was carried out by two columns that were interconnected with a gas compressor through a pipe. The columns have the diameter of 40 mm and length of 200 mm. To control and to measure the flow rate of the incoming and outgoing gas, we used flowmeter with pressure range of 0-25 liter per minute (LPM). The incoming gas was controlled at range of 10-15 LPM. The detail of adsorption system and formulation of adsorbents are shown in Fig. 3 and Table I respectively. The adsorption of CO_2 in biogas mixtures was represented by methane enrichment, shown by the analyzed data from gas chromatography (GC).

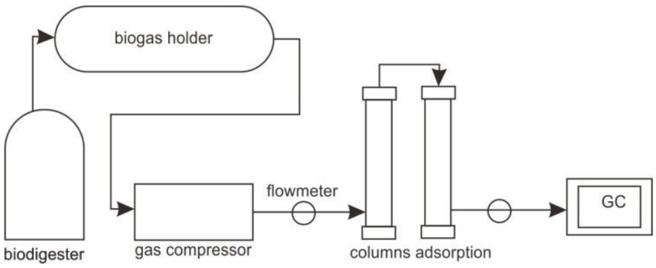

Fig. 3. System of CO_2 Adsorption

TABLE I: Formulation of the Combination of Adsorbents

Code	Column 1 (40:40 grams)	Group 2
Z-Z	Natural zeolite:natural zeolite	Natural zeolite:natural zeolite
Z-CM	Natural zeolite:chicken manure based biochar	Natural zeolite:chicken manure based biochar
Z-BS	Natural zeolite:biogas sludge based biochar	Natural zeolite:biogas sludge based biochar

D. Calculation of Calorific Value

The CO_2 removal from biogas mixtures helps to increase the calorific value. According to the law of conversation of energy, the input energy is the same as output energy. So the calorific value of biogas could be determined by calculating the calorific energy produced from heating water with biogas fuel. The detail of the formulation for to calculate the calorific energy (Q) using (1):

$$Q = mxcx\Delta T \quad (1)$$

m represents mass of heating water (kg), c is specific heat of water (kJ/kgK) and ΔT is the difference between initial and final temperature of water (K).

III. Results and Discussion

The adsorption process aims to remove CO_2 from biogas mixtures so the percentage of CH_4 can be increased. The raw and purified biogas were analyzed using GC to determine the percentage of CH_4. In this study, purified biogas samples were taken from biogas that had been through CO_2 adsorption process with 10 minutes of contact time. Fig. 4 showed the increase of CH_4 level after adsorption. This phenomenon was also found in previous studies [13]-[16]. The lowest CH_4 enrichment was performed after adsorption using Z-Z. Fig. 4 and Table II showed that the combination of natural zeolite and biochar gave higher CH_4 enrichment than pure adsorbents (Z-Z). The higher CH_4 enrichment performed by partial subtitution of natural zeolite with biochar was due to the wider specific surface area of biochar compared to the one of natural zeolite. Biochar's surface area is made of many aromatic carbons that form pore structure [17] so it implies an increase of specific surface area. The highest CH_4 enrichment was performed by natural zeolite and chicken manure based biochar (Z-CM) of 28,92% compared to raw biogas. The second highest was the biogas that had been through CO_2 adsorption using the combination of natural zeolite and biogas sludge based biochar (Z-BS) of 5,12%. Reference [18] reported that specific surface area of adsorbent had important role in CO_2 adsorption under a gas pressure range of 5-8 bar.

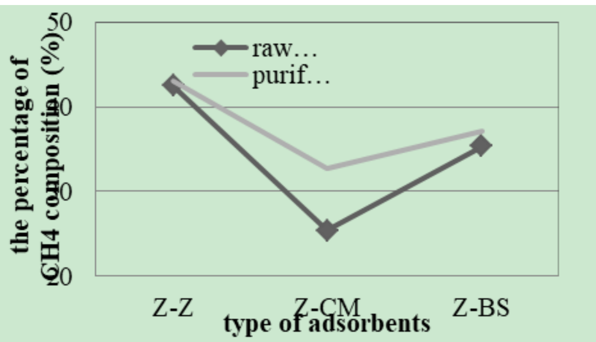

Fig. 4. The CH_4 percentages of raw and purified biogas.

TABLE II: Methane Enrichment of Biogas after CO_2 Adsorption

Biogas	Z-Z	Z-CM	Z-BS
Raw biogas	42.5	25.35	35.35
Purified biogas	43.08	32.68	37.18

The energy of biogas can be converted to energy for cooking through combustion process. The combustible component of biogas is CH_4. The raw biogas that contains CH_4 has average calorific value about 30 MJ/kg but after purification, biogas can have the calorific value of 45 MJ/kg with CH_4 level of 90% [19]. It means that the composition of biogas has influences on its calorific value [6]. In this study, we investigated the relationship between the percentage of CH_4 and calorific value. The comparison of the calorific value of biogas is shown in Fig. 5. CO_2 adsorption in biogas mixtures increased the calorific value as shown in Fig. 5. The highest increament of the calorific value was performed by the adsorption using adsorbent Z-CM of 45.06% compared to raw biogas; it was followed by Z-BS and Z-Z of 31.25% and 15.46% respectively. Besides having more pores structures, chicken manure based biochar also contains high mineral that plays important role to faciliate the capturing of CO_2 molecules [20]. The energy content of biogas as shown in Fig. 5 showed that there is a correlation between the percentage of CH_4 composition and calorific value. In other words, the increase of CH_4 improved calorific value. We also observed that the time required to heat water using purified biogas fuel was longer compared to raw biogas.

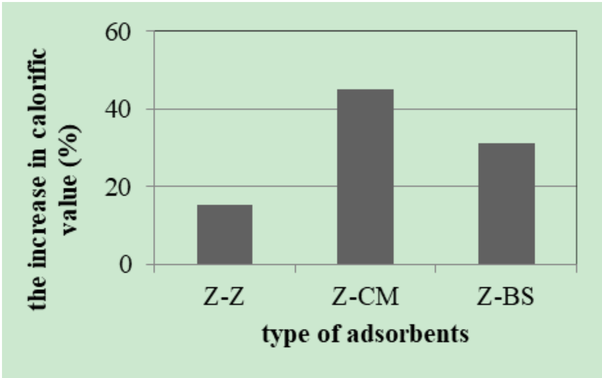

Fig. 5. The increase of calorific value in purified biogas.

IV. Conclusion

The results in this study quantified the increase of calorific value in biogas mixtures after CO_2 adsorption using Z-Z, Z-CM, and Z-BS. By capturing CO_2, the CH_4 composition in biogas increased. The highest CH_4 enrichment was performed by Z-CM. From this results, we also concluded that the highest CH_4 enrichment produced highest calorific energy than other samples. It means that the amount of energy used for heating water depended on the percentage of CH_4 composition in biogas. This study demonstrated that CO_2 adsorption using combination of natural zeolite and biochar can improve energy efficiency.

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