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THE UTILIZATION OF BIOGAS SLUDGE BIOCHAR TO LEAD ZERO WASTE SYSTEM IN BIOGAS IMPLEMENTATION: THE EFFECT OF VOLUME ON CARBON DIOXIDE AND METHANE CONTENT

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ABSTRACT: Biogas is a solution to slow the effects of global warming by converting and trapping methane of manure into energy. To make biogas cleaner and more environmentally friendly, residue from biogas also should be treated. The strategy is to recycle biogas sludge to be an adsorbent for biogas purification because it will reduce waste generation. It means the utilization of sludge leads to a zero-waste biogas system. The study was to investigate the use of biochar from biogas sludge and find the optimal condition for biogas purification. Five treatment of biochar-based biogas sludge were be conducted, every column of adsorption filled with 100% of the volume zeolite, 50% of the volume zeolite and biochar, 25% of the volume zeolite and 75% of the volume of biochar, and the last 100% of the volume biochar. The results showed that 5 treatments of biochar reduced carbon dioxide (impurity gas in biogas) and the largest reduction of carbon dioxide presented by 100% of the volume biochar. The decrease in carbon dioxide by 100% volume of zeolite is almost the same as the decrease in carbon dioxide by 100% volume of biochar. But the system also decreased the methane content in proportion to the decrease in carbon dioxide. The reduction in carbon dioxide also affected the temperature of biogas combustion and calorific value. We agree that using 100% of the volume biochar from sludge can replace zeolite in biogas purification but further modification is also needed to increase the value of methane.

Keywords: Biochar, Biogas, Methane, Sludge, Zero Waste

1. INTRODUCTION

Biogas is one of many solutions to slow the effects of global warming by converting and trapping methane of manure into energy. The implementation of biogas technology reduces dependency on fossil fuel energies for cooking or electricity in rural or urban areas [1].

By utilization waste or manure from livestock, biogas becomes a cheap energy source. In a rural area, adopting biogas technology improves energy access, reduces the cost for purchasing firewood or fossil fuel, reduces the workload of women for looking for firewood, and diminishes manure smells [2,3]. It's more beneficial if the dissemination of biogas applies the bio-cycle system [4]. For example, biogas also generates waste, bio-slurry, that it's usually used as organic fertilizer [5-6]. Bio-cycle systems in the biogas and livestock sector can be presented in Fig. 1 [7]. Biogas generates bio-slurry that can be used as worms and mushroom media, fertilizer, and biochar for soil enrichment and biogas purification adsorbent.

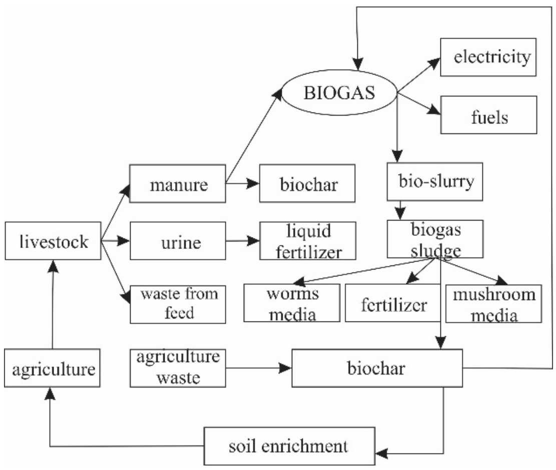

Fig.1 The scheme of zero waste implementation by re-using biogas sludge as biochar for soil enrichment and biogas upgrading [7]

Bio-cycle is the cycle through which energy and essential substances are transferred among species and between the biotic and abiotic parts of the environment. The bio-cycle system is an alternative agriculture system that harmonizes not only agriculture but also non-agriculture aspects like agro-industry, tourism, and industry [8]. In the bio-cycle system, recycling of biogas sludge as organic fertilizer gives benefits not only to reduce biogas waste but also to enhance soil productivity [9]. But utilization of biogas sludge as biochar for biogas purification in the biogas system is rare. Whereas the use of sludge generated from biogas production for biogas purification leads to zero waste management in biogas implementation. The use of biogas sludge as biochar also drives a circular economy because biochar is not only can use in biogas purification but also agriculture, energy, and waste management sectors. In a circular economy system, biogas sludge can be utilized and recycled as a valuable product in the biogas system [10]. Circular economy benefits empower the community and driving the local economy [11].

Biochar is a carbon-based material that is from agricultural residue, animal waste, or forestry waste, that has carbon content [12]. Biochar has been utilized for the removal of heavy metals from wastewater, soil enrichment, and gas separation. Many studies are reported that biochar can use for carbon dioxide adsorption in biogas purification [13-15]. It's also claimed to be comparable to other commercial porous materials like zeolite and activated carbon. Pore structures in biochar, like in zeolite or activated carbon, play an important role in carbon dioxide adsorption [16]. However, most of these commercial adsorbents are too expensive because some rural areas don't have access to the distribution of commercial adsorbents. According to Minh-Viet et al. [14], biochar has the advantages of relatively low cost, easy regeneration, and stable cyclic performance. It can be concluded that biochar is a green adsorbent. There is a need to develop local-based potential resources of biochar to minimize the cost distribution of adsorbent. Moreover, local potential sources that are came from biogas production lead to the bio-cycle system in biogas and zero-waste biogas management [15]. Mandu et al. [16] also di d a comparison study about characteristics of biochar from sugarcane bagasse and anaerobically sugarcane. Based on Fourier Transform Infrared (FTIR) analysis, the presence of an additional phenolic, C–O stretch band with high absorption intensity in BC at wave number 1090 cm1 suggests that the alkalinity of BC was lower than that of DBC because the phenolic functional group promotes acidity in the biochar. Also based on surface area analysis, biochar from anaerobically sugarcane bagasse has a higher surface area than from sugarcane bagasse (18 and 14 m^2/g respectively). The results may reflect the microbial utilization of more labile pore in-filling organic matter during digestion, leaving the refractory pore framework intact [16].

Our previous study has been investigated the capability of carbon dioxide adsorption from biogas sludge-based biochar for biogas adsorption [10]. In Ambar et al. [10] biogas sludge-based biochar was combined with zeolite in each mass of 40 grams every column. But we evaluated that utilization of each 40 grams' mass of biogas sludge-based biochar and zeolite is not to be comparable because both of them have different specific mass. So, in this study, we evaluated the utilization mass of adsorbents with volume ratio.

2. METHODOLOGY

The carbon dioxide adsorption column was made from stainless steel material and completed with two flowmeters with measurement specification in a range of 25 LPM (liter per minute) at outlet and inlet pipes, and the compressor. The inlet and outlet pipes of column adsorption were connected with a biogas holder that holding of raw biogas (biogas from biodigester) and purified biogas (biogas from column adsorption) respectively. The biochar was produced from biogas sludge that was collected from biogas production of dairy cattle manure in the Center of Agro Technology Innovation, Universitas Gadjah Mada.

2.1 Biogas Sludge-Based Biochar Synthesis

Biogas sludge-based biochar was produced by the pyrolysis process. Before the pyrolysis process, biogas sludge was dried under sunlight for four days to reduce water content. The pyrolysis process was going for four hours at the temperature of 255ºC. The heat from pyrolysis induced the oxidation of carbon and then formed stable carbon of biochar. Biochar was characterized by a surface area analyzer to identified the surface area, volume, and diameter of pores. Surface area analysis used a nitrogen adsorption method at 77 K.

2.2 Biogas Purification: Carbon Dioxide Adsorption

Carbon dioxide adsorption is conducted at room temperature. Each column adsorption contained a volume of zeolite and biochar. There were six formulations of adsorbents presented in Table 1. The first step of biogas purification is biogas filled in an adsorption column by the compressor with a pressure range of 5-7 bar. Biogas that after through the adsorption column was held in a purified biogas holder to analyze the composition. Samples of biogas before and after carbon dioxide adsorption were analyzed by Gas Chromatography (GC) to be identified the composition of methane and carbon dioxide. The scheme composition of adsorbents in the adsorption column can be presented in Fig. 2. Zeolite was filled in the bottom of the adsorption column and biochar was on zeolite.

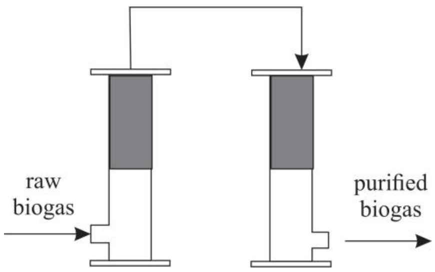

Fig.2 Scheme of adsorbents in adsorption column [15]

Table 1 Formulations of the adsorbents in a column adsorption

Biogas Samples	% volume of zeolite	% volume of biogas sludge-based biochar
P0	0	0
P1	0	100
P2	75	25
P3	50	50
P4	25	75
P5	100	0

3. RESULTS AND DISCUSSION

Synthesis of biochar from biogas sludge was processed by pyrolysis at 255ºC for 4 hours. Before doing pyrolysis, biogas sludge was dried under sunlight for 4 days. Fig. 3 was represented the raw material of biogas sludge and biochar from biogas sludge in this experiment. Conversion from 2460 grams of sludge produced 1350 grams of biochar (yield of 45.12%). This yield is higher than biogas sludge-based biochar from that produced by Magdalena and Patryk [17] with a biochar yield of 18%.

Mass reduction in yield can be due to loss of chemically bound moisture, decomposition of organic substances, dehydration of hydroxyl groups, and degradation of the thermal cellulose structure, whereas at higher temperatures it can also be caused by the formation of aromatic structures with the loss of large amounts of CO_2, CO, H_2O, and H_2.

(a)

(b)

Fig.3 Raw material of biogas sludge (a) and biochar from biogas sludge (b)

Biogas composition was analyzed and calculated by gas chromatography. The relation of the capability of carbon dioxide adsorption and surface area was investigated in this study. Before and after carbon adsorption, biogas samples are analyzed its composition, especially methane and carbon dioxide because it's the largest composition in biogas.

3.1 Surface Area Analysis

The feature of carbon-based material is having many pores on its surface like biochar and zeolite. The porous structure of biochar and zeolite was determined from a nitrogen adsorption-desorption isotherm method at low temperature (77 K). Pore volume, pore size, and specific surface area were evaluated and showed in Table 2.

Table 2 Specific surface area, volume, and pore size of natural zeolite and biogas sludge-based biochar

Sample	S_A	d	V_{tot}	V_{mi}	V_{me}
	(m^2/g)	(nm)		(cc/g)	
Z	47.66	47.41	0.11	0.017	0.093
B	34.06	39.15	0.067	0.013	0.054

*Note: Z (zeolite), B (biochar), S_A (specific surface are), d (mean pore size), V_{tot} (total pore volume),

V_{mi} (micro-pore volume), V_{me} (Meso-pore volume)

These results showed that zeolite has a higher specific surface area, pore-volume, dan size compared to biochar. Both zeolite and biogas sludge biochar-based biochar have a dominant pore size in the mesopore zone (pore size range of 2 - 50 nm) according to the International Union of Pure and Applied Chemistry (IUPAC). These results were also strengthened by the bigger mesopore volume of zeolite and biochar compared to micropore volume. The relation between pore characteristics and the capability to absorb carbon dioxide was investigated in this study.

3.2 Carbon Dioxide Composition

Carbon dioxide is the main impurity gas in biogas, which ranges from 20-40% [18]. These results of carbon dioxide analysis raw and purified biogas are shown in Table 3. The capability of zeolite and biochar to adsorb carbon dioxide has been proven. The results showed that all formulations of adsorbents capable to reduce carbon dioxide composition in biogas. The use of 100% volume of biochar reduced 26.54% carbon dioxide. The carbon dioxide reduction performed by 100% volume of zeolite was 26.65%. These results indicated that biogas sludge-based biochar has the same capability in carbon dioxide capturing as zeolite. The features in pore structure and mineral contents such as K, Na, Ca, Mg in biochar facilitate carbon dioxide adsorption. The existence of mineral content can increase alkalinity conditions on biochar's surface and has implication to increase adsorbent affinity to carbon dioxide that plays as acidic molecules [19]. In line with Magdalena and Patryk's research [17], biogas sludge-based biochar has more mineral content than non-biogas sludge-based biochar. Although these results show the ability of zeolite for capturing carbon dioxide is not significant compared to the 100% volume of biogas sludge-based biochar.

Table 3 The carbon dioxide reduction (%) after biogas purification

Sample	P1	P2	P3	P4	P5
1st	36.61	0.07	16.99	1.04	26.39
2nd	29.48	30.79	20.10	3.25	24.40
3rd	11.00	20.86	22.66	10.40	29.16
Average	25.70	17.24	19.92	4.89	26.65

3.3 Methane Composition

Methane is the main component in biogas that produces energy for cooking or electricity. By carbon dioxide adsorption, methane in biogas should be increase. But the study showed different results. After biogas purification, methane composition in biogas went down. The reduction of methane was presented in Table 4.

Table 4 The methane reduction (%) after biogas purification

Sample	P1	P2	P3	P4	P5
1st	25.67	6.53	16.90	14.22	25.65
2nd	20.10	15.44	17.86	17.58	23.67
3rd	30.08	2.67	19.14	12.28	29.45
Average	25.70	8.43	17.97	14.69	26.26

The decrease in methane composition looked directly proportional to the decrease in carbon dioxide composition. The highest methane reduction performed by 100% volume of zeolite, the same as with carbon dioxide reduction (Fig. 4).

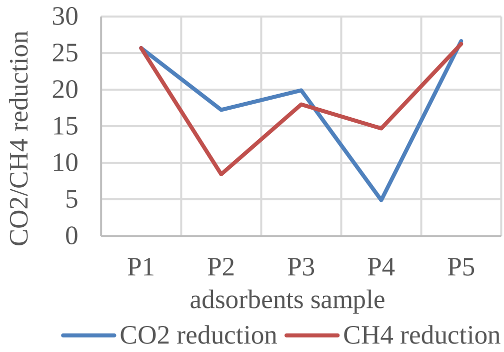

Fig.4 Carbon dioxide and methane reduction after biogas purification

These results can be explained. The physical characteristic of adsorbents that are represented by specific surface area contributes to the capability to carbon dioxide adsorption [20]. The greater specific surface area resulted not only in the greater capability in carbon dioxide adsorption but also in the methane reduction in biogas. It can be explained that dominant pores in biochar and zeolite, mesopore (see Table 2), played an important role in methane adsorption. It's happened due to methane molecules are easier adsorbed in mesopore areas than micropore areas [22].

Based on surface area analysis, either zeolite or biochar was included in mesopore-based material [23]. Mesopore size is capable to adsorb large size molecule effectively like methane molecules [22]. Mesopore volume of zeolite or biochar can adsorb not only carbon dioxide but also carbon dioxide, which has a molecule size of 0.32 and 0.4 nm respectively. Although there is methane reduction, the value is still smaller than carbon dioxide reduction because carbon dioxide molecules are more reactive to interact with pore structures in biochar. To increase the micropore area, biochar needs to be activated. Akram et al. [24] revealed that with activation process makes the presence of abundant pores and the porosity of carbon consists mainly of micropores and a few mesopores.

4. CONCLUSION

From these results, we concluded that biogas sludge-based biochar can be an alternative adsorbent of natural zeolite in biogas purification. Further research is required to improve the carbon dioxide adsorption and methane enrichment capabilities. Activation of adsorbent is recommended to enhance micropore size in adsorbents so that increasing carbon dioxide adsorption in biogas.

The use of biogas sludge biochar also minimizes adsorbent cost because it uses the residual of biogas process to upgrade quality of biogas. The use of biogas sludge biochar also implements zero waste in biogas technology.

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