Adsorbents Abilities to Purify Animal Manure Biogas into Biomethane

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Abstract. This research aimed to 1). perceive the abilities of various types of adsorbents towards the percentage of CH₄ (biomethane) and 2). determine the potential types of adsorbents to increase the percentage of CH₄. The first experiment was P which consisted of P0, P1, P2, P3, P4 and P5; each of them contained grit of chicken waste adsorbent (BLAR) and chicken eggshell (CTAR). Then, the second experiment was T which consisted of T0, T1, T2, T3, T4 and T5; each of them contained BLAR and hydrated lime (KP). The measured variables were (1). biogas volume (dm³), (2). filtration rate (second), (3). percentage of filtered CO₂, (4). percentage of CH₄ produced. The observation results from the first and second experiment had a highly significant effect (P <0.01) on all four variables except for the second experiment on the biogas filtration rate which had a significant effect (P <0.05). Thus, it could be concluded that (1). P1, P2, P4, and T2 were the adsorbents which were able to purify animal manure biogas into biomethane and (2). the potential adsorbent in filtering biogas was 100% BLAR or the addition of CTAR or KP up to 75%.

1. Introduction
The regulation of the Minister of Energy and Mineral Resources of the Republic of Indonesia number 36 of 2018 concerning operational guideline for the implementation of physical special allocation funds for small scale energy field has experienced significant progress. According to the Home Biogas report as of 31 August 2016, the number of biogas units in Indonesia reached 17,397 units. The relative GWP (Global Warming Potential) towards CO₂ for N₂O gas emission is 298 tons of CO₂, in which 1 ton of N₂O is equivalent to 298 tons of CO₂ [1]. Junus [2] stated that livestock waste production in Indonesia reached 375,986 tons/day or equal to 375,986 tons/day * 2.6 tons CO₂ per year = 1154.15 tons CO₂ per year. If a 10 m² volume biogas unit is built, it needs around 8 - 9.5 million biogas units in the size 10 m³. Confronting the reality of livestock waste resources and the limited availability of fossil energy, it is necessary to increase the number of biogas units and biogas production in the future [3]. The construction of biogas units at the locations of small scale livestock farms has hitherto been very successful. Every so often, people cease using biogas units due to the excessive fuel, and damage to the stove or biogas lamp. Based on this reality, it is necessary to find other available adsorbents which are able to filter biogas in order to meet SNI 8019: 2014 on high pressure biogas quality standard. This
research aimed to (1). perceive the ability of various types of adsorbents towards the percentage of biomethane (% CH₄) and (2). determine the type of potential adsorbents to filter biogas into CH₄.

2. Materials and methods
This research was carried out in: 1). Laboratory of Solar and Renewable Energy, Faculty of Engineering, Universitas Brawijaya, 2). Jatinom egg storage of Blitar chicken farmers where chicken eggshell (CTAR) obtained, 3). Sumberjo village in Bantur, Malang Regency where grit of chicken waste (BLAR) obtained, 4). Sumberjo village in Bantur, Malang Regency where hydrated lime (KP) obtained, 5). Biogas unit in chicken farm in Wonokerto Village, Malang Regency and 6). Laboratory of Chemical Engineering, Bandung Institute of Technology, for biogas content analysis.

The research equipments included: 1). plastic balloon, 2). pestle, 3). digital scale, 4). 13 m³ concrete fixed dome type biogas 5). biogas purifier and 6). gas chromatography (GC). While the materials were 1). dairy cows manure, 2). dairy cow urine, 3). well water, 4) BLAR, 5). CTAR and 6). KP (hydrated lime). There were two experiments and both of them were designed by employing Completely Randomized Design. Each experiment consisted of 6 (six) treatments and 4 replications. The first experiment (P) with treatment P0, P1, P2, P3, P4 and P5 contained different levels of BLAR and KP adsorbents with the proportion of 0%, 100%, (75+25)%, (50+50)%, (25+75)%, and 100% respectively. Then, the second experiment (T) with treatment T0, T1, T2, T3, T4 and T5 contained different levels of BLAR and KP adsorbents with the proportion of 0%, 100%, (75+25)%, (50+50)%, (25+75)% and 100% respectively. The measured variables were: 1). biogas volume (dm³) which was measured by using a flow meter 2). biogas filtration rate which was measured by using a stopwatch (second), 3). content of CO₂ and 4). CH₄ biogas which was analyzed by using GC. The analysis of variance and Duncan multiple range test were used to analyze the observation results. The CO₂ decrease and CH₄ increase were calculated by using the treatments without adsorbent relatively (P0 and T0).

3. Results and discussions
The observation results of biogas purification for both P and T adsorbent experiments had a highly significant effect (P<0.01) on the 1) filtered biogas volume, 2) biogas filtration rate, 3) % CO₂ in filtered biogas and 4). % CH₄ biogas produced. However, there was an exception of the filtration rate which was significantly different (P<0.05) in P and T adsorbent experiments. The average of P and T adsorbent experiments results are explained in Table 1.

| Table 1. The average of filtered biogas volume, biogas filtration rate, % CO₂ in filtered biogas, CO₂ relative decrease, % CH₄ biogas filtered, and CH₄ relative increase |
|-----------------|---------|----------|------------|-------------|----------|----------|
| Treatment       | Volume (dm³) | Rate (second) | CO₂ (%) | % CO₂ relative decrease on P0 (%) | CH₄ (%) | % CH₄ relative increase on P0 (%) |
| Experiment 1    |          |            |          |                          |         |                                   |
| P0              | 3.9 ± 0.04ᵃ | 16.4 ± 0.85ᵇ | 22.2 ± 0.21ᵇ | 32.5 ± 0.93ᵇ             |         |                                   |
| P1              | 1.8 ± 0.17ᵇ | 22.2 ± 0.34ᵇ | 8.4 ± 1.84ᵇ | 164.3                    | 66.0 ± 0.36ᵇ | 103.1                 |
| P2              | 2.7 ± 0.13ᵇ | 21.9 ± 1.36ᵇ | 7.7 ± 0.82ᵇ | 188.0                    | 61.8 ± 5.01ᵇ | 90.2                   |
| P3              | 1.2 ± 0.04ᵇ | 24.6 ± 1.20ᵇ | 8.1 ± 7.56ᵇ | 174.1                    | 54.7 ± 7.88ᵇ | 69.2                   |
| P4              | 1.3 ± 0.16ᵇ | 23.1 ± 0.78ᵇ | 9.1 ± 1.02ᵇ | 141.8                    | 66.1 ± 3.62ᵇ | 103.4                 |
| P5              | 3.5 ± 0.22ᵇ | 23.2 ± 3.01ᵇ | 9.5 ± 5.59ᵇ | 133.7                    | 58.3 ± 4.80ᵇ | 79.4                   |
| Experiment 2    |          |            |          |                          |         |                                   |
| T0              | 3.9 ± 0.04ᵃ | 17.9 ± 1.36ᵃ | 22.9 ± 0.29ᵇ | 32.3 ± 0.93ᵃ             |         |                                   |
| T1              | 1.8 ± 0.17ᵃ | 22.2 ± 0.34ᵇ | 2.8 ± 7.73ᵇ | 717.8                    | 66.0 ± 0.36ᵇ | 1043                  |
| T2              | 1.5 ± 0.18ᵇ | 23.6 ± 0.28ᵇ | 1.6 ± 0.32ᵇ | 1331.3                   | 85.0 ± 8.56ᵇ | 163.2                 |
| T3              | 1.2 ± 0.17ᵇ | 23.0 ± 0.43ᵇ | 1.2 ± 0.27ᵇ | 1808.3                   | 82.5 ± 1.11ᵇ | 155.4                 |
| T4              | 2.1 ± 0.13ᵇ | 22.5 ± 0.32ᵇ | 3.8 ± 0.97ᵇ | 502.0                    | 76.2 ± 1.67ᵇ | 135.9                 |
| T5              | 0.6 ± 0.22ᵃ | 22.3 ± 0.48ᵇ | 3.5 ± 7.57ᵇ | 554.3                    | 65.5 ± 5.45ᵇ | 102.8                 |
3.1. The filtered biogas volume

The adsorbents of P and T experiments as in Table 1 indicated that P0 and T0 produced the most volume due to direct biogas flow. The adsorbent ability of P experiment in P2, P3 and P4 was less powerful in adsorbing CO\textsubscript{2} compared to T experiment. However, the results of filtered gas volume from P2, P3 and P4 with T2, T3 and T4 were similar. According to Srichat, Suntivarakorn and Kamwilaisak [6], there were 51.00% methane increase and 39.96% carbon dioxide decrease in pure water, 0.1 mol of calcium hydroxide, 0.2 mol of calcium hydroxide, 0.1 mol of Mono Ethanol Amine (MEA), and 0.2 mol of Mono Ethanol Amine (MEA). While according to [4], alkanol amine, solid alkanol amine, zeolite, carbon, metal-organic framework (MOF), zeolitic imidazolate frameworks (ZIFs), and membrane are able to decrease CO\textsubscript{2} gas. Then, Yamlilha, Argo, and Nugroho (2013) stated that the adsorption process using zeolite can reduce CO\textsubscript{2} gas [5].

3.2. The biogas filtration rate

In Table 1 indicated that the first experiment of P0 (without adsorbent) was faster compared to P1, P2, P3, P4 and P5 which passed through the adsorbents. The adsorbent in P experiment affected the biogas filtration rate. While the results of T experiment revealed that T, T0, T1, T4 and T5 were faster than T2 and T3. However, all results were the same. According to Srichat, Suntivarakorn and Kamwilaisak [6], 2017, 0.2 mol of calcium hydroxide can provide a maximum ratio of methane at 89.30% at a solution flow rate of 30 l/min and a biogas flow rate of 5 l/min. Although KP adsorbent has softer texture, it is able to pass biogas flow well. Saleh, Planetto and Yulistiah [7] (2016) stated that the biogas filtration rate is related to the biomethane increase. This shows that the longer the filtration process, the more biomethane yield obtained.

3.3. The percentage of absorbed CO\textsubscript{2} biogas in the adsorbent

From experiment P indicated that P0 was different from P1, P2, P3, P4 and P5. While experiment T indicated that T0 was different from T1, T4 and T5, and T2, T3, and T4 as in Table 1. The content of adsorbed CO\textsubscript{2} biogas in the adsorbent P and T revealed that the T experiment might be stronger in absorbing CO\textsubscript{2} in which T2 and T3 were stronger than T1, T4 and T5 and the value was lower than P1 to P5. This fact implies that BLAR, CTAR and KP have the ability to absorb CO\textsubscript{2} gas from biogas. Apriandi, Kusuma and Widiyarta [8] stated that CO\textsubscript{2} gas is absorbed more quickly by the adsorbent so that CH\textsubscript{4} increases.

3.4. The relative decrease of CO\textsubscript{2} towards P0

Adsorbent in P1, P2, P3, P4 and P5 were able to decrease CO\textsubscript{2} level by 164.3%, 188.0%, 174.1%, 141.8%, and 133.7% respectively. Then, T0 without adsorbent in T1, T2, T3, T4 and P5 were able to decrease CO\textsubscript{2} level by 717.8%, 1331.3%, 1808.3%, 502.0%, and 554.3% respectively. The ability of P and T treatments to absorb CO\textsubscript{2} was quite high, at least 133.7% (P) and 502.0% (T). So the materials used in experiment T were quite potential in decreasing the % CO\textsubscript{2}. According to Satriani and Ningsih [9], the absorption of substances or elements in biogas depends on the time and gas absorbent material. Then, the result was similar to the research result from Satriani, Ningsih and Ratman [10].

3.5. The percentage of biomethane (CH\textsubscript{4}) in filtered biogas

In Table 1 indicated that P0 in the first experiment was highly significantly different from P1, P2, P3, P4 and P5. Then, T0 in the second experiment was different from T1 and T5; T2, T3 and T4. P1 and P4 had the highest ability to increase CH\textsubscript{4} and they were not different. Meanwhile, T1 was similar to T2 and T2; T3 and T4 also had greater ability to purify or increase CH\textsubscript{4} [11] (Makaruk, Miltner and Harasek, 2010). This fact implies that there is no obstacle in the biogas purification at the farm location. In contrast to the research from [12], biogas purification using NaOH and KOH apparently still costs a lot.
3.6. The relative increase of biomethane (CH₄)

Starting from P0 in P experiment was achieved by P1, P2, and P4, in which P1 and P4 had the highest ability to increase biomethane. For the second experiment, the highest percentage of biomethane increase was in T2 then followed by T3 and T4. The high percentages of biomethane through P1 (25% BLAR+75% CTAR) and P4 (75% BLAR+25% CTAR) adsorbents were the ideal ratios to be used as adsorbents. The percentage of biomethane in T2 (75% BLAR+25% KP) had the highest ability followed by T3 (50% BLAR+50% KP) and T4 (25% BLAR+75% KP). Considering this fact, it implies that grit of chicken manure, chicken eggshell, and hydrated lime can be used as materials to purify biogas into biomethane. Similar experiment was also carried out by [13], the result indicated that zeolite can be used to improve the biogas quality.

4. Conclusion and suggestion

Lastly, it could be concluded that: 1). BLAR, CTAR and KP were adsorbents that could increase the percentage of biomethane and 2). the potential adsorbent in filtering biogas was 100% BLAR or the addition of CTAR or KP up to 75%. Thus, it is recommended that the amount of BLAR, CTAR and KP adsorbent or mixture should be carried out in longer tubes.

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