PURIFICATION OF BIOGAS FROM TOFU WASTE USING ZEOLITE AND ACTIVATED CARBON (AC) AS ADSORBENT

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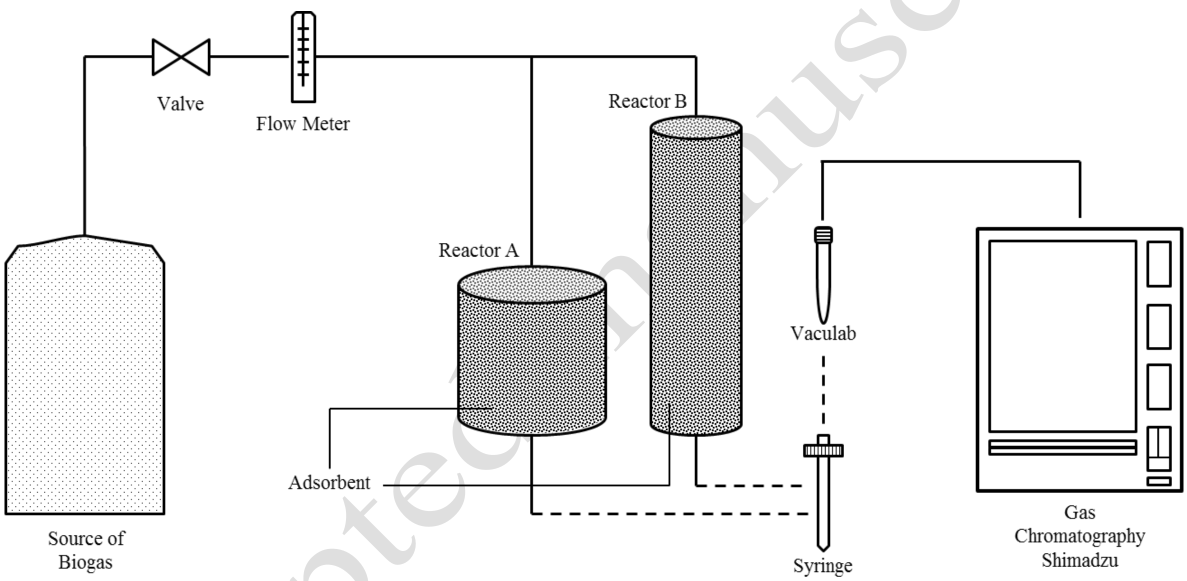
GRAPHICAL ABSTRACT



Abstract:

Substitution of fossil fuel into alternative energy sources, such as biogas, needs to be applied to prevent various problems in the environment. Biogas purification can be an alternative technology to improve the quality of biogas, which increases the heat value by reducing CO_2. Purification can be carried out by the adsorption method using solid adsorbents, for example natural zeolite and activated carbon. This study used 12 reactors from PVC, with 2 different diameters, 3 different mesh size (20,50,80) and was given both zeolite (A1-A3; B1-B3) and activated carbon (A4-A6; B4-B6). Biogas purification with the addition of zeolite has an optimal compound content in reactor A3 which has an increase in CH_4 (63.63%) and decrease in CO_2 composition (25.07%), which is better than other reactors. Meanwhile, the results of measurements of gas content on the addition of activated carbon showed optimal

performance in reactor A6, which was increased to 76.86% for CH_4 levels and CO_2 levels dropped to 19.79%.

Keywords: adsorption, activated carbon, biogas composition, biogas purification, zeolite

1. Introduction

The increase in CO_2 gas emissions in 1970-2004 was recorded at 80%, with the amount of CO_2 emitted by 35.65 million metric tons in 2011 (Stern and Stern, 2007; Boden et al., 2015)). The steps to reduce CO_2 emissions are very important to reduce the risk of global warming. Governments from various countries have taken concrete steps to achieve these goals, including the creation of the Kyoto Protocol at the 2012 and 2015 COP 21 Conference in Paris (Ferella et al., 2017; Townsend, 2013)). On the other hand, a lot of research has been done as an effort to mitigate global warming and safeguard the availability of fossil fuels, one of which is the use of biogas as an alternative to fossil fuels (Meyer-Aurich et al., 2012; Shen et al., 2018; Yousef et al., 2018)).

Biogas is a product generated by anaerobic digestion from a variety of biodegradable materials, such as agricultural waste, animal waste, waste in human activities, and industrial waste (Aghbashlo et al., 2019; Zain et al., 2018)). One of the industrial wastes that have the potential to produce biogas is the waste from the tofu industry. The tofu industry in Indonesia produces waste in the form of solid and liquid waste, which is 1.024 million m^3 per year (solid waste) and 20 million m^3 per year (liquid waste) (Faisal et al., 2016)). The number of organic compounds contained in it can produce biogas which can be recovered due to its anaerobic treatment. Biogas that is produced by 1 kg of tofu waste contains (Lay et al., 2013).

Biogas usually has a CH_4 content of 55-65%; CO_2 of 35-45%; and a small portion of traces consisting of ammonia (NH_3), nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), and hydrogen sulfide (H_2S), with concentrations of less than 1% (Remy et al., 2014; Belaissaoui et al., 2018; Abdeshahian et al., 2016)). Biogas can be used as fuel for vehicles and sources to produce heat and electricity, with the advantage of being a versatile, clean, and inexpensive fuel (Aghbashlo et al., 2019; Tabatabaei et al., 2019)). However, the CO_2 contained in biogas becomes a contaminant that can reduce the value of heat, is corrosive, and damages the pipeline from biogas (Ahmad et al., 2017; Duran et al., 2018; Jiang et al., 2018a)). Therefore, removal of these contaminants is needed to obtain greater methane content in biogas, where the heating value of biogas with 60% (v/v) methane content reaches 5,000-6,000 kcal/N.m^3, while higher methane content (96-97%) can increase the heating value up to 8,000 kcal/n.m^3 (Ryckebosch et al., 2011)).

Various methods of CO_2 removal contained in biogas from different activities are available. Adsorption, absorption, membrane separation, and cryogenic distillation are the most common method (Petersson and WeLLInGer, 2009; Songolzadeh et al., 2014; Rufford et al., 2012)). Adsorption is a technology that has advantages in economic aspects, both cost and energy use, but has high efficiency (Zhou et al., 2017; Duran et al., 2018)). Zeolites, activated carbons, and metal-organic framework (MOF) are microporous materials that are often used in the adsorption process because of their ability to remove CO_2 (Hedin et al., 2013; Möller et al., 2017; Li et al., 2013)). Zeolites are three-dimensional crystalline aluminum silicates, derived from alkali and alkaline earth cations (Turan and Ergun, 2009)). Zeolites widely used as adsorbants because of their removal ability for various chemicals, high thermal and chemical stability, and their uniqueness in carrying out molecular sifting (Zhou et al., 2017; Ferella et al., 2017; Loureiro and Kartel, 2006)). Zeolites can increase removal of CO_2 because of their higher selectivity than CH_4. However, zeolite's affinity for water is very high, where the water contained in biogas reaches 6% of its volume (Ferella et al., 2017; Bacsik et al., 2016)). Therefore, it is recommended to reduce the water content that will pass through the adsorban to improve the CO_2 removal performance.

In addition to zeolite, activated carbon is also widely used in CO_2 removal due to the high adsorption capacity of ambient air, low regeneration cost, long-term stability, and fast kinetic. The material needed to produce activated carbon has an economical price and is relatively easy to obtain because it generally comes from the rest of agriculture and forests. This material is usually found in the form of wood, starch, coconut shells, or empty fruit bunch (EFB) (Lee et al., 2013; Li et al., 2018; Vilella et al., 2017)). Activation of these materials can be done both physically and chemically. In contrast to zeolites, activated carbon has a better tolerance to water because it has low affinity and it is a hydrophilic material so that it is able to maintain its adsorption capacity in high humidity (González et al., 2013)). However, activated also has a disadvantage because it has a low CO_2 selectivity compared to CH_4 (Bacsik et al., 2016)).

The main objective of this study is to determine the trend of using filters with zeolites and activated carbons to purify biogas, eliminate contaminants in the form of CO_2, and obtain more CH_4 content from the tofu waste treatment. In addition, according to Ogunwande (2017), the reactor surface area is significantly affected by biogas production, so this study used two-reactor with different surface areas to determine the relationship between reactor dimensions and biogas purification performance.

2. Materials & Methods

2.1. Material Characteristics

Biogas generated from waste treatment of tofu industry was used in this study. The biogas was obtained from waste processing of Wismilak Tofu Industry, Mangkang, Semarang City. Before the study began, a preliminary test of raw biogas generation was conducted using 2 PVC pipe with 2-inch and 4-inch diameter. The test determined the initial composition of methane (CH_4) and carbon dioxide (CO_2) from the raw biogas, which are shown in Table 1. Biogas purification was carried out by the adsorption method using adsorbents (solids), which are natural zeolite and activated carbon. Purification process of biogas from tofu waste using both adsorbents then started to investigate the optimum condition that can improve the biogas quality.

Table 1 Composition of Biogas (%v/v) CH_4 and CO_2

Reactor	CH_4 (%v/v)					CO_2 (%v/v)				
	0 min	30 min	60 min	90 min	120 min	0 min	30 min	60 min	90 min	120 min
A0	0	43.90	43.90	43.90	43.90	0	37.30	43.90	43.90	43.90
B0	0	44.60	136,587	142,977	148,720	0	44.60	136,587	142,977	148,720

In this study, natural zeolite is used because in addition to being easily obtained, the market price is quite cheap, and natural zeolite is reactive to CO_2. Natural zeolite serves to increase CH_4 levels and eliminate CO_2 levels in the biogas purification process (Jiang et al., 2018b)). The use of natural zeolite as an adsorbent requires an activation process to enhance the special nature of zeolite and remove impurities. Activation of natural zeolite can be carried out by chemical and physical methods with the aim of cleaning pore surfaces, removing impurities and rearranging the exchanged atoms. Chemical activation is carried out through immersion using a NaOH solution with a concentration of 5% for 24 hours, previously it is necessary to wash zeolite using distilled water (Nikolov et al., 2017)). Afterwards, zeolite is washed with distilled water until it is neutral and then dried. After drying, natural zeolite is physically activated by heating at 250°C for 2 hours in a furnace (Wibowo et al., 2017)).

In addition to natural zeolite, activated carbon can also be used to carry out biogas purification. Activated carbon is a material with high porosity that has a large adsorption capacity and is widely used as an adsorbent for purification (Kim and Pui, 2015)). Activated carbon can adsorb certain gases and chemical compounds where the adsorption properties depend on the size or volume of pores and surface area (Sethia and Sayari, 2015)). The detailed adsorbent properties is shown in Table 2.

Table 2 Adsorbents Properties

Reactor	Dimension	Adsorbent (mesh)	
		Zeolite	Activated Carbon
A1	2 inch 80 cm	20	-
A2		50	-
A3		80	-
A4	2 inch 80 cm	-	20
A5		-	50
A6		-	80
B1	4 inch 40 cm	20	-
B2		50	-
B3		80	-
B4	4 inch 40 cm	-	20
B5		-	50
B6		-	80

2.2. Biogas Purification Reactor

There were 12 reactors that were made from PVC pipes with 2 variations in size, which were 2-inch tubes with 80 cm height (A1-A6) and 4-inch tubes with 40 cm height (B1-B6). All of these reactors were planned to have the same volume with a different diameter that determined from the results of preliminary study. Fig. 1 illustrates the series of measurement tools and test positional schemes in this study. Both zeolite and activated carbon will be inserted in the reactor with 3 different mesh (20, 50, and 80), with the weight of 300 grams. The mesh size was specified to obtain the most suitable dimension of adsorbent during the biogas purification process. The higher the mesh size the smaller the screen opening and the smaller the particle that will pass through.

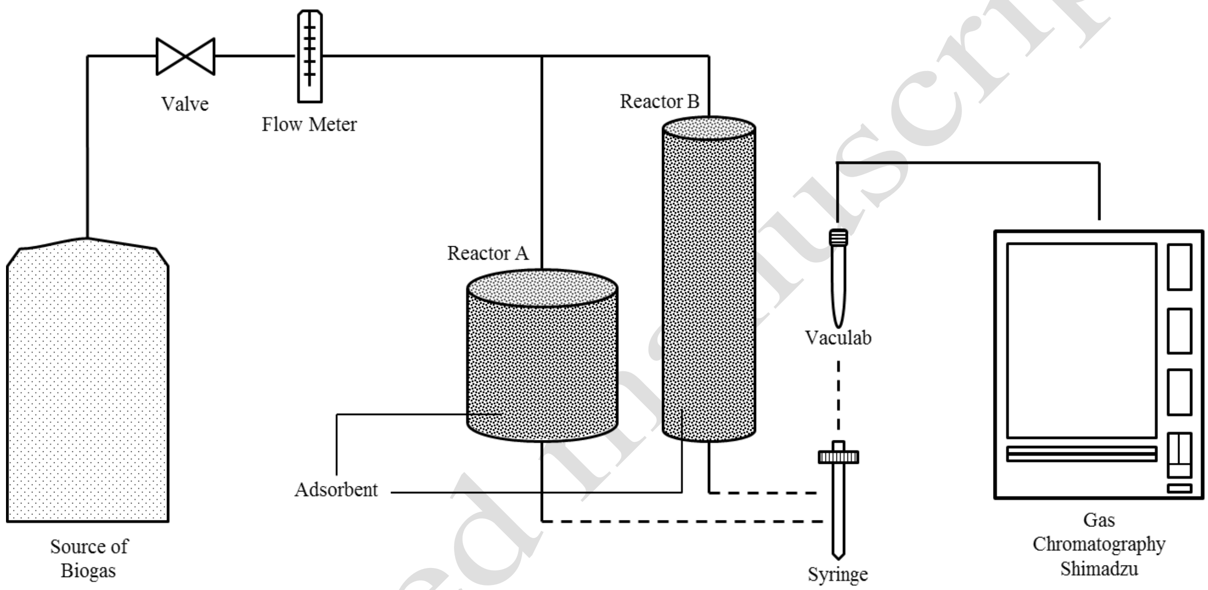


Fig. 1 Scheme of Biogas Purification

2.3. Measurement Test

On biogas purification test, the collected gas flowed from the source into the reactor using a hose and tap with flow meter installed to control the biogas flow rate. The flow rate was maintained in 10 liter/min, which adjusted from the flow of gas generation at tofu waste treatment. The addition of adsorbent, zeolite and activated carbon, was carried out by inserting it into the biogas purification tube of tofu waste through the reactor insulator for the adsorption process to the outlet. The time spent on each purification variation was 3 hours each. Samples of biogas from all reactors were collected every 30 minutes using an injection (syringe) and stored in a vaculab or vacuum tube. The measurement of CH_4 and CO_2 contents was conducted using Gas Chromatography Shimadzu-14 A (Liu et al., 2015b)), which is able to detect gaseous components in the form of methane, carbon dioxide and nitrogen based on ASTM D1945-14 (International, 2014)), at Pati and Research Center Laboratory of Pati Regency.

3. Results

3.1. CO_2 Reduction

CO_2 content in the biogas decreases until the end of the study. Fig. 2a showed the reduction of CO2 in reactor A. Reactor A1 had the highest CO^2 content of 32.00% in the 30th minute, while A3 had the lowest CO_2 content of 29.90%. Significant reduction occurred in the A3 reactor with final content of 25.07% in the 120th minute. This was lower than the other two reactors, A1 and A2, which are at 27.08% and 26.37% respectively. Meanwhile, in the activated carbon reactor (A4), CO_2 content decreased gradually from 24.37% to 21.61% in the end of the study. Reactor A5 experienced a fall until 120th minute, which decreased from 23.91% to 20,38%. Reactor A6 also decreased significantly starting from 60 minutes with 19.79% in the final composition, which also showed that it has the lowest CO_2 composition in the end of the study.

CO_2 composition in reactor B (Fig. 2b) shows the same pattern with those in reactor A. Reactor B1 had the highest CO_2 content of zeolite reactor in the 120th minute with 29.75% while reactor B3 had the lowest CO_2 value of 27.69%. In reactor B4, CO_2 was eliminated from 28.96% in the first 30 minutes into 24.64% in the final content of biogas. On the other hand, Reactor B6 showed the most decrease compared to other activated carbon reactors, which fell from 26.67% to 22.19%. These results showed that activated carbon could decrease carbon dioxide composition of biogas more than zeolite in both reactor A and B. All of reactors that added with adsorbent had significant improvement of CO_2 composition, which was reduced until less than 30% v/v.

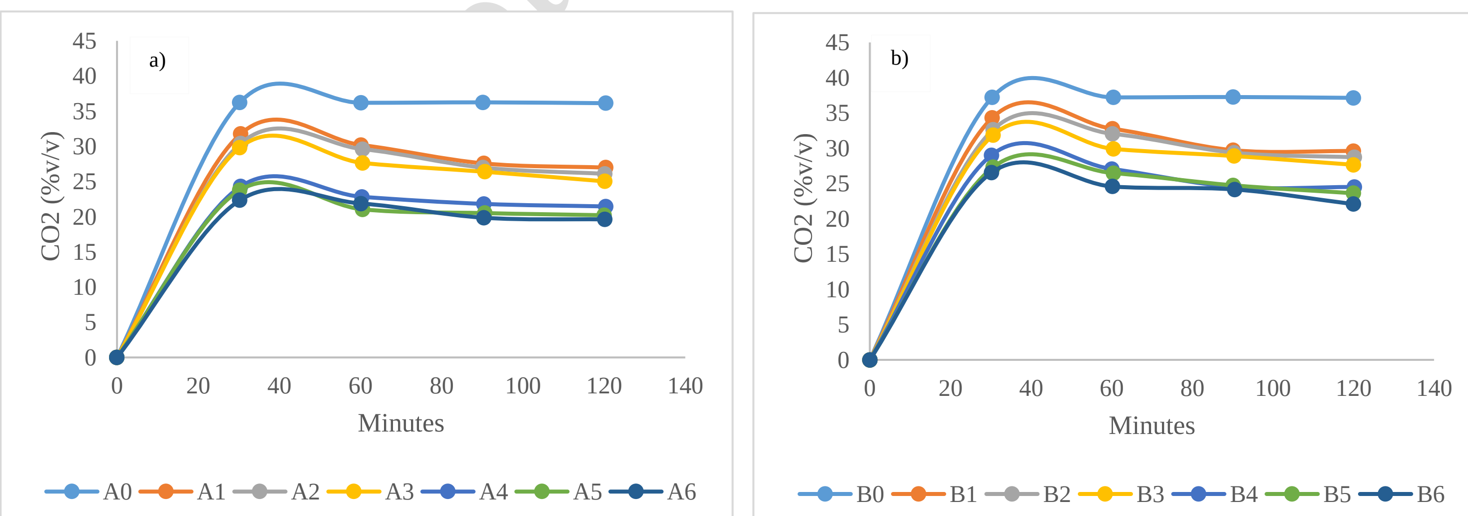


Fig. 2 a) Changes of Carbon Dioxide in Reactor A, b) Changes of Carbon Dioxide in Reactor B

3.2. CH_4 Generation

In this biogas purification test, it is known that the composition of CH_4 gases subsequently increased until it reached the highest content in the 120th minute. Fig. 3a and 3b shows the level of CH_4 in reactor A and B during the study. The final composition of CH_4 in A1 – A3 was ranged between 61% – 64%. The early CH_4 value in A1 reactor is the lowest, which was 55.70% in the 30th minute, while the CH_4 content in A3 reactor is the highest value (58.90%). Reactor A3 produced the highest methane after 2 hours generation, which was 63.63% and the lowest was reactor A1 with CH_4 content of 61.30%.

On the other hand, CH_4 in reactor A4 – A6 was ranged from 71% to 77%. Reactor A6 increased significantly compared to A4 and A5, which reached 76.86% methane content in the 120th minutes, which was also higher than A3. Meanwhile, A4 had the lowest methane content with 73.86% methane in the end of the study.

Reactor B3 had the highest CH_4 level in the 30th minute of 57.61% while the reactor B1 is the lowest with a value of 54.51%. The CH_4 level in the 120th minute on the reactor B3 became the highest with a value of 61.96% and B1 is the lowest with a value of 59.72%. Reactor B using activated carbon had higher CH_4 content compared to zeolite. Reactor B6 experienced greater increment than the other activated carbon reactor with the final methane content of 71.27% while B4 had about 5% less methane content, which is the least amount in the other two.

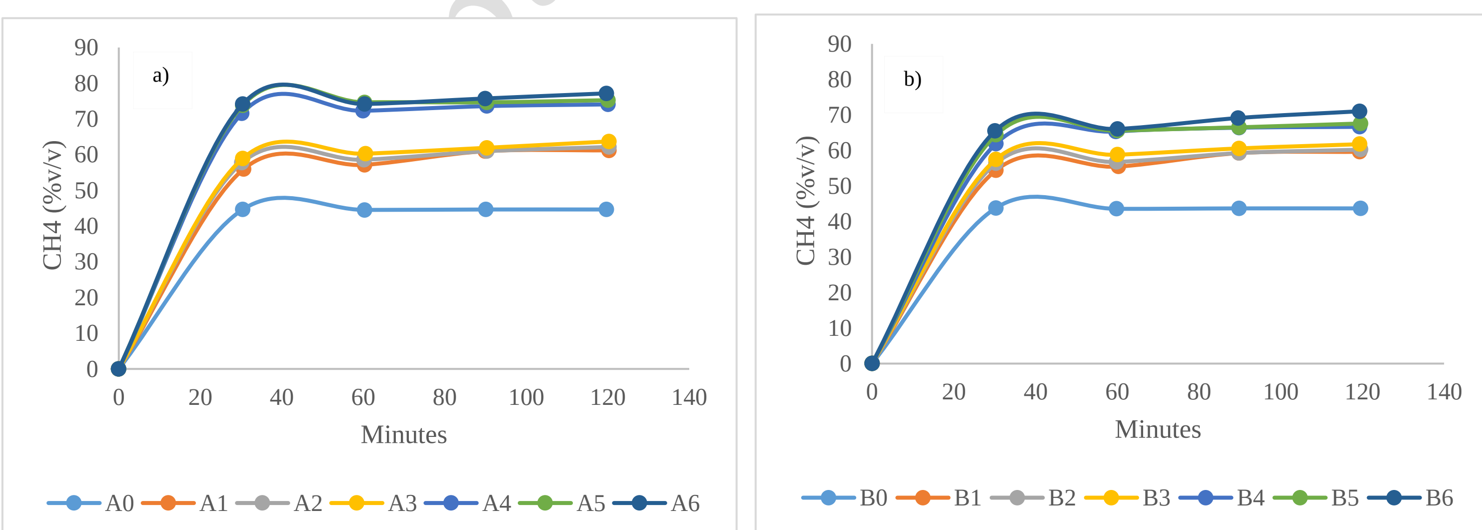


Fig. 3 a) Changes of Methane Gas in Reactor A, b) Changes of Methane Gas in Reactor B

4. Discussion

Compared to the preliminary study results, both zeolite and activated carbon reactor had better biogas composition. This means the addition of both adsorbents increases CH_4 and reduces CO_2 content. Although zeolite has higher CO_2-CH_4 selectivity, activated carbon improved the biogas composition better than zeolite, which was shown in higher methane and lower carbon dioxide.

CH_4 is an inert material towards the adsorption on activated carbon (Liu et al., 2015a)). Inactosite methane molecules are completely neutral (neither acidic nor basic). Methane has a regular tetrahedral structure, which favors incompletely non-polar structure. In contrary, CO_2 is acidic and polar, which makes chemical reactions in basic interaction with activated carbon. Based on Mamun (Al Mamun et al., 2016)), activated carbon, which has high porosity, is able to adsorb carbon dioxide and separate it from a certain gas mixture. The use of activated carbon is more beneficial because it can in generation while zeolite does. (Hauchhum and Mahanta, 2014). CO_2 can form a permanent polarity because there are transformations of CO_2 molecules that perform stretching motion of asymmetric bond at normal pressure and temperature. The van der Waals force in CO_2 molecule and the framework of carbon determine the adsorption of CO_2 takes place, which is between single or multilayer of activated carbon. Moreover, the adsorption of CO_2 performed differently based on the level of interaction between quadrupole of CO_2, which is higher than CH_4, and gradient of electric field. This interaction is determined by the ratio of Si/Al in the adsorbent (Jiang et al., 2018a; Li et al., 2013)).

Fernández (Juárez et al., 2018)) has conducted a research about purification of biogas using biomass ash. The purified methane gas increased significantly more than crude CH_4. It also applied on purified CO_2 and crude CO_2. The reaction of CO_2 occurred rapidly because of high alkalinity and the ash humidity. CO_2 broke through the filter in several hours after most of alkaline mineral and reactive hydroxides were consumed. Durán et al. (Duran et al., 2018)), who used activated carbon from pine sawdust, stated that CH_4 broke faster than CO_2 but CH_4 will be replaced later because of roll-up effect. The gas mixture affected the adsorptive performance of the activated carbon due to the decrease of partial pressure when mixing components.

Besides the type of adsorbent, the mesh size also affects the performance of the biogas purification process. It can be seen that the reactor with the size of 80 mesh has the lowest CO_2 content compared to other mesh sizes. This is because the smallest adsorbent size is at 80 mesh size, which causes a larger contact area and increases the adsorption rate. The finer adsorbent can absorb more CO_2 than the coarser one because of the smaller fraction size, thus increasing the adsorption process. (Jafari et al., 2017; Mastalerz et al., 2017). Furthermore, gas adsorption capacity is strongly related to the specific surface area and micropore volume (Lee and Park, 2011). Usually, gas molecules in the gas-solid interaction (adsorption) potential are driven by strong van der Waals forces. In particular, the gas adsorption potential is highest in the sub-nanometer pores as they begin to overlap with decreasing pore size, leading to much higher binding energy come from the creation of deep potential wells (Romanos et al., 2011). Therefore, it is crucial to maximizing the number of sub-nanometer pores by increasing the specific surface area.

In this study, reactors A and B have the same volume but have different results. The composition of biogas in reactor A showed a better improvement than reactor B. Reactor A produced less CO_2 and more CH_4 content than reactor B. It happens because the diameter/surface area in reactor A is wider than in reactor B. According to Ogunwande (2017) study, the reactor surface area is significantly affected by biogas production. Biogas yield increases when the surface area increases. Furthermore, specific surface area, porosity, surface roughness, pore size, and orientation of the packing material were found to play an important role in anaerobic reactor performance (Singh and Prerna, 2009).

5. Conclusion

This study discusses the effect of adding size variations of adsorbents-zeolite and activated carbon-on biogas purification. Both of these materials have a variety of advantages, such as high adsorption that can increase CH_4 levels and eliminate CO_2 levels in the biogas purification process. Measurement tests carried out on the level of CH_4 increase and CO_2 adsorption using the Gas Chromatography Shimadzu-14 A.

In conclusion, choosing activated carbon as an adsorbent is more appropriate than zeolite. This is due to activated carbon could eliminate the most CO_2 contaminants and obtain the most CH_4 content. Furthermore, using the smallest adsorbent size and reactor with largest surface area has been identified to be able to increase the CH_4 content and reduce the CO_2 gas content. There are still interesting things to do to improve the performance of biogas purification. Measuring the capacity of two adsorbents and measuring the purification process using a mixture of two ingredients can be an alternative research in the future.

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