THE EFFECT OF FERMENTATION TIME TO BIOGAS PRODUCTION FROM COW DUNG AND SOUR WATER

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ABSTRACT

Liquid waste can cause environmental pollution. Therefore, industrial wastewater must be treated properly so as not to exceed the quality standard limits set by the government. One type of liquid waste is sour water from Pertamina RU III. In addition to waste problems, fossil energy reserves are increasingly depleting so that they require renewable energy reserves, one of which is biogas to produce methane gas. This research will analyze the effect of fermentation time on the quality and quantity of biogas obtained. The quantity of biogas includes the volume of gas produced, while the quality of biogas includes the content of methane gas, pH, CaCO3, total solid, and volatile solid. Biogas has 4 process stages, including hydrolysis, acidogenesis, acetogenesis, and methanogenesis. From this study it was concluded that the longer the fermentation time, the gas volume, methane content, and carbon dioxide content increased, microbial activity in this study only reached its peak phase on day 50, so it had not yet reached the decline or death phase. The hydrolysis stage took place on days 0-10, the acidogenesis stage took place on days 10-20, the acetogenesis stage took place on days 20-30, and the methanogenesis stage took place on days 30-50.

Keywords: biogas, cow dung, sour water, time fermentation

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INTRODUCTION

According to Indonesian Government Regulation No. 82 of 2001, liquid waste is the residual waste from the production process or domestic activity in the form of liquid (Anon., 2016). Liquid waste can be in the form of other waste materials that are mixed (suspended) or dissolved in water which is classified into four groups, including domestic liquid waste, industrial liquid waste, seepage and overflow, and rain water (Anon., 2016).

One type of liquid waste is industrial waste. Liquid waste is a pollutant that cannot be released from industrial processes, ranging from small industries, medium industries, to large industries. The effects of the liquid waste can cause environmental pollution. Therefore, industrial wastewater must be treated properly so as not to exceed the quality standard limits set by the government.

At Pertamina RU III, there is one unit of SWS or Sour Water Stripper which functions to reduce or eliminate sulfide and ammonia gas from wastewater from the RU III refinery process. Sour water itself comes from waste water from CDU (Crude Distilling Unit), HVU II (High Vacuum Unit II), and FCCU (Fluidized Catalytic Cracking Unit) processes (Pertamina RU III, 2017). Sour water includes oil and gas industrial waste that must be treated before being disposed of so as not to pollute the environment.

Fossil energy is the energy with the largest use in every aspect of human life, such as electricity, transportation and consumption purposes. Humans need fossil energy such as coal and generator fuel to produce electricity, petroleum as fuel for various types of vehicles, and natural gas for household purposes such as cooking. The Minister of Industry stated that currently industry is still very dependent on fossil fuels, even the share of industry in national energy consumption reaches 49.4 percent (Ministry of Industry, 2019).

The need for fossil energy is increasing every year, but fossil energy reserves are dwindling. Fossil energy in the world is projected to run out by 2050 (Sukmana, 2016). According to Sukmana (2016), oil reserves in the bowels of Indonesia are predicted to run out in the next 12-15 years due to the imbalance between the declining oil production and the increasing consumption of oil every year. According to Nugraha (2016), national oil reserves as of January 1, 2014 decreased by 2.3% from the previous year, both in the form of proven reserves and potential reserves. Indonesia is estimated to run out of oil reserves in 2030 because oil reserves in Indonesia are currently only around 3.3 billion barrels, while fuel consumption continues to increase to reach 1.6 million per day (Silaban, 2019).

Therefore, the problem of the energy crisis, especially the decline in fossil fuel reserves, can be solved by producing alternative energy to replace renewable fossil energy in order to build sustainable energy security. Alternative energy produced should have several advantages, including being renewable, low in emissions, based on domestic resources to save foreign exchange, and not depending on other countries (Gapki, 2016).

One type of alternative energy is biogas, which is a type of alternative energy to replace fossil fuels in the form of natural gas. Biogas is produced from anaerobic activity that degrades organic materials, including dirt, domestic waste, or any organic waste that can be decomposed by living things under anaerobic conditions. The main constituents of biogas are methane gas (CH4) and carbon dioxide gas (CO2). Biogas is produced in a biodigester which contains organic matter. Under anaerobic conditions, methanogenic bacteria activity takes place in the organic material to form methane gas (CH4) and carbon dioxide gas (CO2). Methane gas is one component of natural gas from fossil energy that can be used for various purposes, such as cooking and turning on electricity.

RESEARCH METHODS

A. Tools and Material

Cow Manure (2.5 liters), Sour Water (2.5 liters), Salt (2.5 kg), water (5 liters), Gallon Polyethylene (10 Liters), Aquarium Aerator Hose Valve, Gas Valve (3/8”, 600 psig), Aquarium Hose (ID 6 mm, 35 gram), Aquarium Pipe (ID 16 mm, OD 17 mm, 50 gram), Aquarium L Pipe (ID 17 mm, OD 18 mm, 5 grams, Polyethylene Measuring Cup (250 ml), Statif Full Set Clamps (iron, 2.5 kg), Compressor Hose (60 cm, 150 grams), Trolley Inner Tube (rubber, 300 grams), Krusible (porcelain, 50 ml, max temperature 700^{o}C), Gravity Oven (208/240 volts, 6.8 A, 1.6 kW, 50/60 HZ, 40-260oC), Furnace (230 volts, 7.8 A, 1.8 kW, 50/60 HZ, 30-3000^{o}C), Analytical Balance (10 kg capacity, pan size 168x168 mm), Digital pH-meter (portable, 200 grams, accuracy 0.01), Electric Soldering (250 grams, 40 watts , 220-240 volts, Glue Gun (200 grams, 20 watts, 220-240 volts, 50-60 Hz), Aquarium Pipe Caps (10 grams, 2 cm diameter), Square Plastic Container (Polyethylene. 60x30 cm), Tedlar Bag Gas (1 liter capacity, polypropylene, 8.0”x6.0”), Gas Chromatography, Ecom Gas Analyzer J2KN.

B. Biodigester Assembly Process

The top left and right of the 10 meter gallon are drilled using a soldering iron. The left side of the gallon is glued to the aquarium aerator hose faucet using hot glue, then the right side of the gallon is glued to the gas valve using hot glue.

The aquarium aerator faucet is connected to a meter long aquarium hose, then tightened using aibon glue. Each aquarium pipe is cut 10 cm long by 4 pieces, then connected with 4 aquarium elbows to form the letter "U". Each aquarium pipe hubcap is given a hole using solder the size of an aquarium hose, then glued together with the letter "U" connection.

The aquarium hose connected to the aerator hose faucet is connected to the aquarium pipe hubcap, then glued using glue gun. The hubcap of the other aquarium pipe is reconnected with the aquarium hose.

The 250 ml measuring cup was perforated using a soldering iron, then connected to the gas valve and glued using hot glue. The top of the gas valve is glued to the compressor hose using aibon glue.

A 250 ml measuring cup that has been connected to the gas valve and compressor hose is supported using a stand. While the compressor hose is connected to the lorry tires as a gas reservoir.

A total of 2 kg of salt water is dissolved in 5 liters of water. The supersaturated brine is put into a square plastic container. The 250 ml measuring cup was filled with salt water, then it was erected using a stand in the saline solution to measure the volume of gas obtained. The aquarium hose is inserted into the 250 ml measuring cup which already contains salt water.

First, measure the volume of Jumputan batik liquid waste using a beacker glass. Then the jumputan batik liquid waste was examined for the value of the content contained in the waste.

C. Fermentation Time

Cow dung is diluted with water to 2.5 liters, then put into a biodigester, then tightly closed under anaerobic conditions. From day 1 to day 10, 250 ml of Pertamina RU III sour water was added.

Every 10th, 20th, 30th, 40th, and 50th day, 250 ml samples were taken from the bottom faucet of the biodigester for analysis. Then it is fed back to 250 ml of diluted cow dung through the gas valve connected to the top of the biodigester.

Every 5.00 pm, the aquarium aerator hose faucet connected to the biodigester is opened. The fermented gas will flow into the brine in the measuring cup. The decrease in water in the measuring cup is equal to the volume of fermented gas and is recorded every day. The gas valve connected to the gas sample container is opened.

FINDINGS AND DISCUSSION

The results of this study can be seen in table 1 and table 2:

Table 1. Gas Analysis Results

Days to-	Volume (liter)	%CH_4
0	0	-
10	0,770	0,037
20	1,500	3,991
30	2,730	2,192
40	1,980	8,106
50	4,555	9,578

Table 2. Slurry . Analysis Results

Days to	pH	$CaCO_3$ (mg/liter)	Total Solid (%)	Volatil Solid (%)
0	6,43	-	-	-
10	5,63	28,1	3,4304	25,0044
20	5,52	341	3,2283	50,1610
30	5,50	306	3,0420	63,5166
40	6,60	226	2,5491	29,5254
50	8,44	318	1,9260	36,1378

A. Effect of Fermentation Time to Volume and Gas Content

When the product gas valve in the biodigester is opened, the trapped gas will flow into the goose's neck which contains salt water, then flows back into the 250 ml measuring cup which already contains salt water. The water in the measuring cup will decrease according to the amount of gas flowing. When the gas stops flowing, the water drop will stop, so the gas volume can be measured. The gas valve above the measuring cup is opened, then the gas flows into the sample container. Gas volume measurements are carried out every day at 10 am.

The brine used is supersaturated brine (more than 360gr/1000gr of salt solubility), which is 2 kg of brine in 5 liters of water. This is because some gases can dissolve in plain water, whereas if you use salt water, the solubility of the gas decreases (Sun & Liang, 2020). The solubility of CO_2 and CH_4 decreases as the molality of the NaCl solution increases (Sun & Liang, 2020).

Therefore, the use of salt water is an effective measurement medium to determine the volume of gas without dissolving the gas. An illustration of the biodigester equipment can be seen in Figure 1.

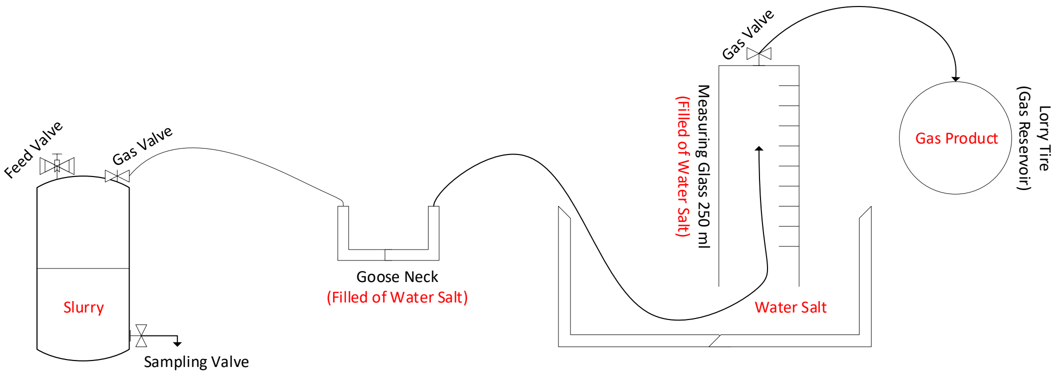

Figure 1. Biodigester Design

When gas begins to form, the slurry in the biodigester will increase. Initially, a slurry of a mixture of cow dung, sour water, and water only occupied 50% of the capacity of the biodigester. However, when the gas starts to form, the slurry occupies almost 80% of the capacity of the biodigester. In addition, bubbles are formed in the biodigester which indicates that gas has started to be produced. The fermentation time in this study was carried out for 50 days, then the slurry and gas analysis was carried out once every 10 days. In 50 days, the gas undergoes four stages of fermentation, consisting of acidogenesis, acetogenesis, and methanogenesis.

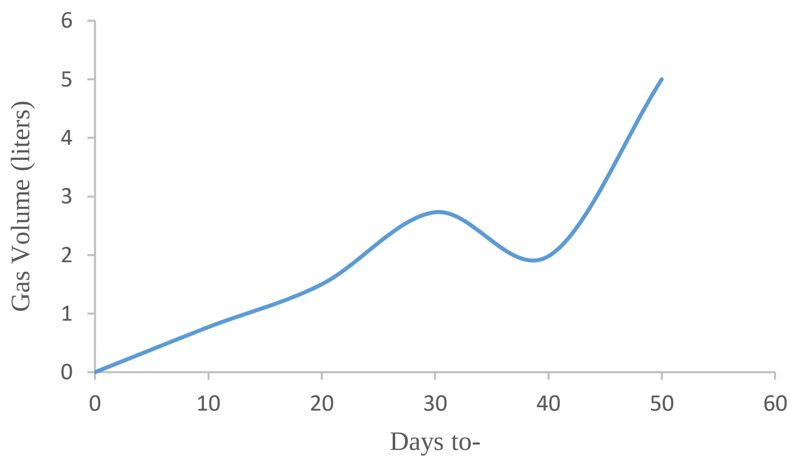

Figure 2. Effect of Fermentation Time to Volume

Figure 2 shows the effect of fermentation time on the volume of gas produced. On day 10, the volume of gas produced was 770 ml (0.77 liter). On the 20th day, the gas volume increased to 1500 ml (1.5 liters). Gas volume again increased on the 30th day by 2730 ml (2.73 liters), but decreased on the 40th day by 1980 ml (1.98 liters). On the 50th day, the volume of gas experienced a very significant increase until it reached 4555 ml (4.555 liters).

Day 0 to day 10 is the adaptation stage of bacteria to produce gas, so that only 770 ml of gas is produced. Gas production increased from the 20th day of 1500 ml to the 30th day of 2730 ml. However, on the 40th day, the gas decreased to a gas volume of 1980 ml. This decrease is due to the 30th to 40th day is the phase where the gas has started to form methane. The stage of methane formation is called the methanogenesis stage, where this stage theoretically produces methane, carbon dioxide, and water (Baredar, et al., 2020). Entering the 40th day when the methanogenesis stage took place, the reaction product was dominated by the formation of water (H_2O) so that the gas content decreased. This was also indicated by the observation that on the 40th day, the slurry content increased in the biodigester until it occupied 80% of the volume of the biodigester.

Day 50, the volume of gas experienced a very significant increase from 1980 ml to 4555 ml. On the 40th day to the 50th day, the gas has started to form methane as the main content.

Research on biogas using cow dung was also carried out by Afrian, et.al (2017). One of these variables uses 25 kg of cow dung and 25 liters of water with the highest biogas volume production on day 30, then decreases slowly until fermentation stops on day 61 with a total gas produced of 519.3 liters (Afrian, et al. al., 2017).

Nikiema, et.al (2017) conducted a study using cow dung and wastewater with inoculum in the form of activated sludge with a total feed volume of 100 ml with a 25-day study. The optimal total volume is obtained at 50% cow dung and 50% wastewater, which is 880 ml (Nikièma, et al., 2017). The optimal independent variables in this study are the same as the fixed variables in this study, namely wastewater and cow dung used in a 1:1 ratio.

A similar study was also conducted by Chibueze, et al (2017) with the independent variable being 150 gr of cow dung without a mixture, with cow dung mixed with food waste (corn cobs and plantain skin) in a 1:1 ratio and 150 gr of slurry. The optimal volume obtained when cow dung is mixed with food waste is 30.58 ml, compared to biogas production using unmixed cow dung, which is 19.20 ml (Chibueze, et al., 2017).

By combining cow dung and rosewater which has been pre-treated with 2% NaOH, Nong, et al (2020) conducted a study by combining the two materials with 3 mixing ratios for 45 days with a feed volume of 700 ml. The optimal mixing ratio is 2:1 (rosewater:cow dung) with a total biogas volume of 8610 mL (Nong, et al., 2020).

B. Effect of Fermentation Time to Methane Content

On the 10th day, the CH_4 content in the gas was only 0.037%, then increased to 3.991% on the 20th day. On the 30th day, CH4 levels decreased to 2.192%. This decrease was due to hydrogen (H_2) as the raw material for the formation of dominant methane out as gas. This is indicated by the increase in the number of gas products on the 30th day by 2.73 liters, where the most dominant content is hydrogen. A decrease in the availability of hydrogen in the rumen can reduce the formation of methane (Lopez, et al., 2017). Khiaosa-ard et.al (2015) stated that the amount of methane decreased in grape seed fermentation due to a decrease in the number of Faciens Ruminococcus flave, total fungi, and total protozoa. The decrease in the number of microbes is due to the tannin in the grape seeds which limits the supply of hydrogen to form methane. The 40th and 50th days are the phase of the formation of methane gas. Where, CH_4 gas increased significantly to 8.106% on the 40th day and 9.578% on the 50th day.

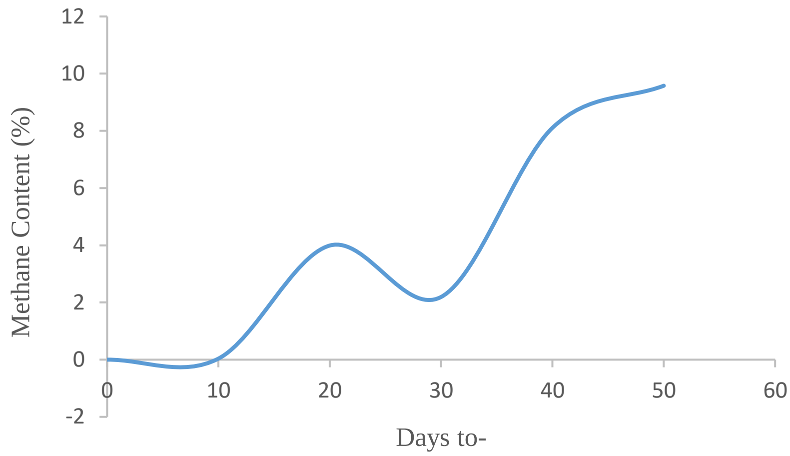

Figure 3. Effect of Fermentation Time to Methane Content

The CH_4 level in this study is still far from the ideal biogas composition theory. In general, biogas products contain 50-75% methane gas, 25-50% carbon dioxide, and 2-8% other gases such as nitrogen (N_2), oxygen (O_2), hydrogen sulfide (H_2S), ammonia (NH_3) and hydrogen (H_2) (Welllinger, et al., 2013). In fact, if the methane content reaches an average of 98%, then biogas has the same physical properties as natural gas (Wellinger, et al., 2013). Methane content in biogas is influenced by residence time and dilution rate, so the longer residence time with high dilution, the greater the methane content produced (Afrian, et al., 2017).

In this study, the methane produced tends to be low or even less than 10%. One of the contributing factors is that the C:N analysis was not carried out on the raw materials first. Good raw materials contain a C:N (carbon:nitrogen) ratio of 25:1 (Wellinger, et al., 2013). In addition, this study uses process wastewater before entering the sour water stripper which was obtained on Monday, 7 June 2021 at 15.20 at Pertamina RU III with the following composition:

Table 3. Sour Water Composition

Parameters	**Composition (ppm)**
H_2S	342
Ammonia	740
Oil Content	335
Phenol	728

The content above states that in this study there were three inhibitors of methane gas production from sour water waste, namely H_2S, ammonia, and phenol. Some of the influences of these three factors include (Wellinger, et al., 2013).

- NH_3 (ammonia) is able to inhibit components in biogas fermentation that contain a lot of nitrogen. The concentration of NH_3 is affected by temperature and pH. In order for the anaerobic process to be stable in ammonia-rich conditions, the microbes must have good adaptability and low H_2S concentrations.
- Similar to ammonia, H_2S acts as an inhibitor. In addition, S_2^- precipitates a lot of metal ions which adversely affect the anaerobic process. The H_2S content is a problem even at low concentrations because it is able to combine with other inhibitory components, one of which is ammonia.
- Antibiotics and disinfectants are able to inhibit or even kill microbes so that they have a negative effect on anaerobic processes. In this study, phenol is a type of disinfectant.
- The presence of NH_3, H_2S, and phenol is an inhibitor of the anaerobic process. However, in this study, these three materials did not kill microbes in the anaerobic process. This is because the microbes continue to produce gas until the 50th day and even reach 4,555

liters. So it can be concluded that the microbes are still doing the degradation process, but the degradation process is not perfect until the highest methane content only reaches 9.578%.

- Improper degradation process can be caused because the C:N ratio in raw materials is not ideal. In addition, the content of NH_3, H_2S, and phenol inhibits the formation of methane gas.

Besides CH_4 gas, the dominant gases are carbon dioxide (CO_2), hydrogen gas (H_2), and hydrogen sulfide (H_2S). This is because before the formation of methane, the anaerobic process produces hydrogen first.

The stages of the reaction for the formation of methane are as follows (Baredar, et al., 2020):

- Hydrolisis Stage

At this stage, the biogas feedstock reacts with water and breaks the polymer chains into monomers. The gas produced at this stage is hydrogen gas (H_2). Where hydrogen gas is ags that dominates on day 0 to day 10.

$$\text{Biogas} + H_2O \longrightarrow \text{Monomer} + H_2$$

- Acidogenesis Stage

This stage is an acidification process characterized by a decrease in pH and the formation of Volatile Fatty Acids (VFA), ketones (glycerol and acetone), and alcohol. In addition to VFA, the substances formed in this process are ammonia, CO_2 gas, and H2S. This process takes place on day 10 to day 30.

$$C_6H_{12}O_6 + 2H_2 \longrightarrow 2CH_3CH_2COOH + 2H_2O$$
$$C_6H_{12}O_6 \longrightarrow 2CH_3CH_2OH + 2CO_2$$

- Acetogenesis Stage

At this stage, the acid molecules formed in the acidogenesis stage are converted to acetic acid by several bacteria, including Syntrophobacter wolinii, propionate decomposer Syntrophomonas wolfei, butyrate decomposer Clostridium spp., peptococcus anaerobes, lactobacillus, and actinomyces. This stage takes place on day 10 to day 30 and produces CO_2 and H_2 gases.

$$CH_3CH_2COO^- + 3H_2O \longrightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2$$
$$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 2CO_2 + 4H_2$$
$$CH_3CH_2OH + 2H_2O \longrightarrow CH_3COO^- + 2H_2 + H^+$$
$$2HCO_3^- + 4H_2 + H^+ \longrightarrow CH_3COO^- 1+ 4H_2O$$

- Methanogenesis Stage

At this stage, acetic acid is converted to methane gas, carbon dioxide, and water. In addition to these three components, this reaction also produces ammonia and H_2S gas. This methanogenesis stage takes place on the 40^{th} day to the 50^{th} day.

$$2CH_3CH_2OH + CO_2 \longrightarrow 2CH_3COOH + CH_4$$
$$CH_3COOH \longrightarrow CH_4 + CO_2$$
$$CH_3OH \longrightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$
$$CH_3COO^- + SO_4^{2-}2 + H^+ \longrightarrow 2HCO_3 + H_2S$$
$$CH_3COO^- + NO^- + H_2O + H^+ \longrightarrow 2HCO_3 + NH_4^+$$

In the methanogenesis stage, two groups of microorganisms work together to degrade acetic acid, namely acetate oxidizers and methanogens that work together via interspecies hydrogen transfer (IHT) (Su & Yang, 2020).

The low CH_4 content in this study was due to the gas being dominated by H_2 at the hydrolysis, acidogenesis, and acetogenesis stages on the 10th to the 30^{th} day. At the methanogenesis stage on the 40^{th} day to the 50^{th} day, more acetic acid was converted to H_2S gas. This is because the sour water used is rich in H_2S, which is 342 ppm. In addition, theoretically biogas from animal waste contains higher H_2S than biogas from plants (Wellinger, et al., 2013).

By using 25 kg of cow dung diluted with 25 liters of water, a study from Afrian et al (2017) stated that the largest methane content occurred on day 60, namely 53.88%. T3-B. A similar study was conducted by Nong, et al (2020) by producing 68.20% methane percentage in samples with a 2:1 ratio (rose water:cow dung) and pre-treatment using 2% NaOH for 2 weeks.

C. Effect of Fermentation Time to Acidity (pH)

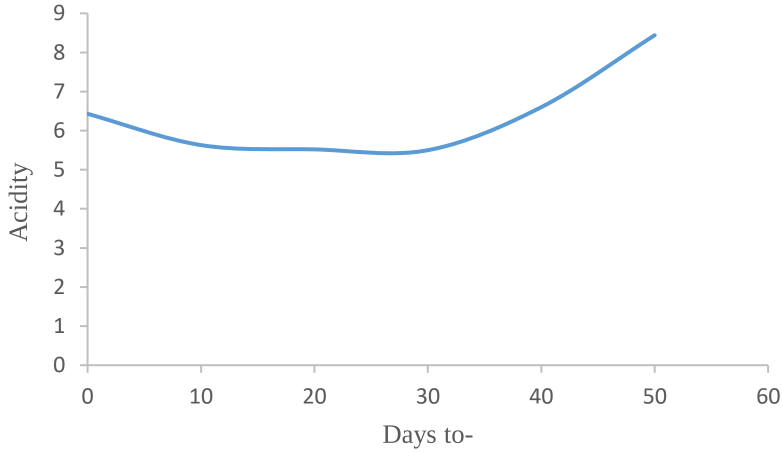

Figure 4. Effect of Fermentation Time to Acidity (pH)

Theoretically, cow dung has a pH of 7.1-7.4, while the raw material for biogas in this study has a pH of 6.43. This is because the raw materials have been mixed with sour water waste which has acidic properties.

On the 10th, 20th, and 30th days, the pH continued to decrease which was not too significant, including 5.63; 5.52; and 5;50. This is because on day 0 to day 30 is the stage of acidogenesis and acetogenesis. Where the acidogenesis stage produces Volatile Fatty Acid (VFA) such as propionate, butyrate, and alcohol as the main product and the acetogenesis stage converts VFA into acetic acid as the main product (Wellinger, et al., 2013). Therefore, in the stages of acidogenesis and acetogenesis the pH will tend to be low below the neutral limit.

On the 40th day, the pH returned to near neutral, namely 6.60 because the methanogenesis stage began to occur. Methane levels began to increase significantly from 2.192% to 8.106%. Methanogenic bacteria were inhibited when the slurry pH was below 6.60 and acidogenic bacteria resumed their activities when the pH decreased to 4.5-5.0 (Wellinger, et al., 2013).

pH increased to 8.44 on day 50. This is due to the high ammonia content in the slurry. In addition, one of the side reactions in the methanogenesis stage produces NH_4^+ ions (Baredar, et al., 2020).

$$CH_3COO^- + NO^- + H_2O + H^+ \longrightarrow 2HCO_3 + NH_4^+$$

Microorganisms degrade protein and produce ammonia, then ammonia reacts with water and produces hydroxide ions (Wellinger, et al., 2013).

The production of NH_4OH is suspected to be the cause of the pH to become alkaline on the 50th day. pH is one of the important factors in the formation of methane gas. Even though it is too high, this pH value falls into the pH range of the theoretical methanogenesis process, which is 6.8 – 8.5 (Baredar, et al., 2020)

On the 70th day, a mixture of 25 kg of cow dung and 25 liters of water in the study of Afrian et.al (2017) resulted in a pH of 7.30. This value is included in the theoretical pH limit of the methanogenesis process, which is 6.8-8.5. Research from Abubakar & Ismail (2012) with a range of 7.2-7.4. In both studies, the pH value was in the normal range for the methanogenesis process because there was no base formation.

However, in a study by Nikièma et al (2017), 100% fermentation of wastewater produces a pH in the range of 8-9, while 100% fermentation of cow dung produces a low pH in the range of 3-4. A pH value that is close to neutral (pH=7) occurs in a mixture of 30% cow dung and 70% wastewater, as well as 10% cow dung and 90% wastewater (Nikièma, et al., 2017).

D. Effect of Fermentation Time to Calcium Carbonate ($CaCO_3$) Content

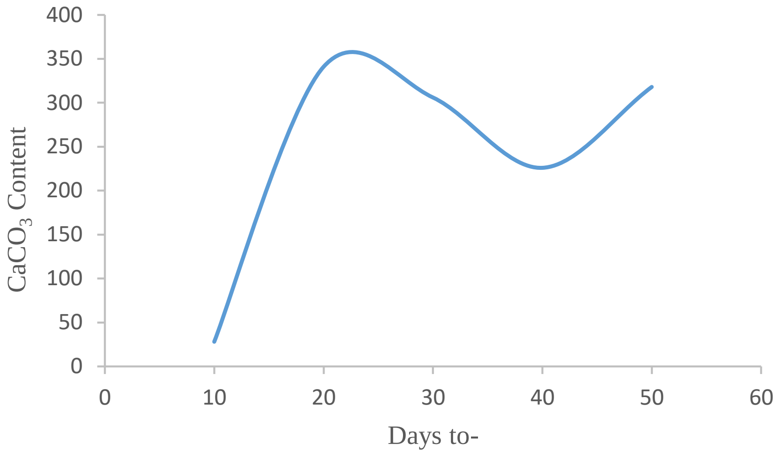

Figure 5. Effect of Fermentation Time to Calcium Carbonate ($CaCO_3$) Content

On the 10th day, the $CaCO_3$ content in the biodigester was 28.1 mg/liter. On the 20th day, the $CaCO_3$ content increased significantly to 341 mg/liter. On the 30th and 40th days, the $CaCO_3$ content decreased again to 306 mg/liter and 226 mg/liter. The increase again occurred on the 50th day, which was 318 mg/liter.

The carbonate ion (CO_3^-) in calcium carbonate ($CaCO_3$) in the biodigester acts as a buffer to maintain the pH value. The buffer capacity depends on the concentration of CO_2 in the gas phase, ammonia in the liquid phase, and water content (Wellinger et al., 2013). The content of $CaCO_3$ in this study was analyzed using the method of determining total hardness. $CaCO_3$ levels in this study tend to fluctuate. This is because $CaCO_3$ is a parameter that shows the solubility of CO_2 in slurry water in an effort to maintain pH by forming a buffer solution.

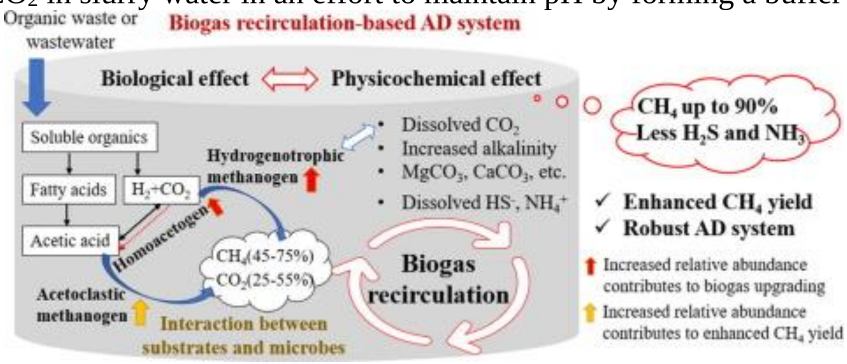

Figure 6. Biogas Recirculation (Yuan, et al., 2021)

The 20th day was the highest peak of the amount of $CaCO_3$ in the slurry. Apart from the amount of CO_2 absorbed in the slurry as shown in Figure 6, the factor that causes the increase in alkalinity in the slurry is the pH value above 7.9 (Yuan, et al., 2021). However, day 20 was the stage of acetogenesis with a pH below neutral, namely 5.52. The increase in carbonate deposition below neutral pH can be caused by an increase in soluble inorganic carbon (Yuan, et al., 2021). Soluble inorganic carbon decreased with anaerobic digestion activity on day 30 and day 40. On the 50th day, alkalinity rose again due to the pH value touching 8.44. Where, when the pH exceeds 7.9, the carbonate deposition increases (Yuan, et al., 2021).

CO_2 produced from anaerobic processes partly forms a gas phase, partly dissolves in water (Wellinger, et al., 2013). If the slurry is under acidic conditions, CO_2 forms gas and participates in biogas products, in neutral conditions it forms HCO_3^-, and in alkaline conditions it forms CO_3^- ions (Wellinger, et al., 2013).

Buffer formation reaction scheme in biogas slurry (Wellinger, et al., 2013)

$$CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$$

$$H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$$

The buffer solution serves to maintain the pH value so that the anaerobic process runs properly without the need for additional external buffers. Multivalent cations such as calcium are present in wastewater (Yuan, et al., 2021). After the pH increases and the solubility of inorganic carbon is reached, there will be precipitation of Ca_2^+ ions (Su & Yang, 2020). Ca cations react with CO_3^- ions to form $CaCO_3$.

E. Effect of Fermentation Time to Total Solid and Volatile Solid

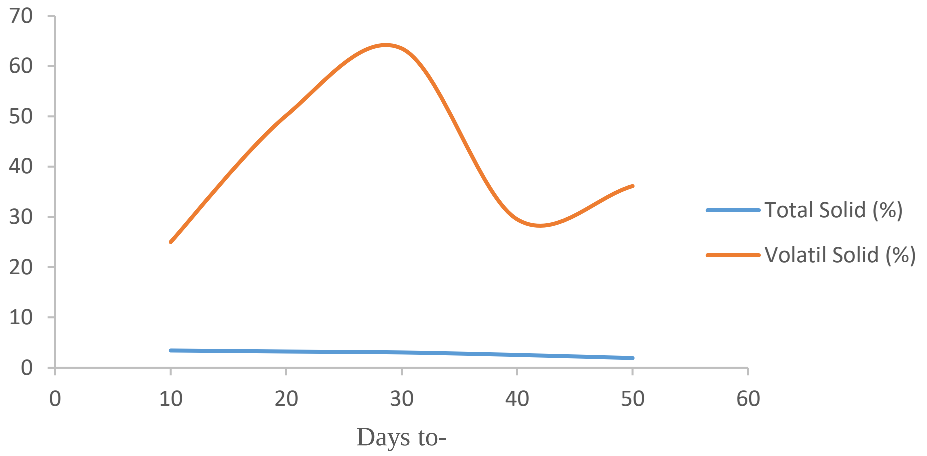

Figure 7. Effect of Fermentation Time to Total Solid and Volatile Solid

From day 10 to day 50 the total solid in this study decreased continuously. On the 10th day, the total solid contained in the slurry was 3,4304%, then decreased to 3,2283% on the 20th day and 3.0420% on the 30th day. The big decline occurred on the 40th and 50th days, namely 2,5491% and 1,9260%. The total solid analysis method was obtained in several previous studies from Wellinger, et.al (2013) and Miah., et.al (2015). This analytical method uses EN 12880 and APHA 2540 B Standards.

Total solid is the amount of solids contained in the substrate, including the nutrients needed by microbes. In this study, the total solid number decreased due to the degradation of microbes in the substrate for 50 days. The process of substrate decomposition by microbes during fermentation converts the substrate into gas and water (Afrian, et al., 2017).

When the raw material contains a very high total solid, the addition of water or other liquid is required in the biodigester so that the solid is more soluble (Wellinger, et al., 2013). In addition, the smaller the substrate surface area, the better the fermentation process (Wellinger, et al., 2013). Therefore, cow dung in this study was dissolved in water in a 1:1 ratio and then filtered. If the raw material contains too much water, the volume of the biodigester will be higher and the concentration of nutrients will be lower (Wellinger, et al., 2013). The total solid in the raw material so that microbes develop optimally is 5% (Afrian, et al., 2017).

In contrast to total solid which shows the amount of nutrients in the substrate, volatile solid is one of the parameters to determine how much organic matter in the form of Volatile Fatty Acid (VFA) is formed in the substrate. The solid volatile analysis method was obtained in several previous studies from Wellinger., et.al (2013) and Miah., et.al (2015). This analytical method uses EN 12879 and APHA 2540 E Standards.

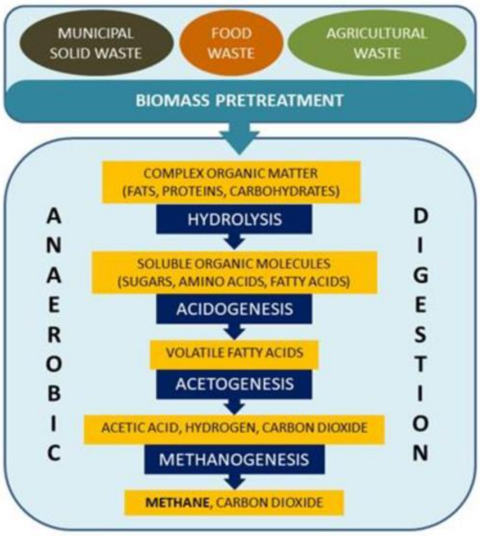

Figure 8. Anaerobic Digestion Processes

The first stages of the Anaerobic Digestion Process include (Baredar, et al., 2020):

- Hydrolysis stage: Hydrolytic enzymes break insoluble polymer chains, carbohydrates, fats, and proteins into water-soluble monomers, sugars, fatty acids, and amino acids. Hydrolysis is the stage where biogas reacts with water using ecoenzymes such as cellulosomes and proteases from bacteria, protozoa, and fungi.
- Acidogenesis stage: sugars, amino acids, fatty acids, and monomers are degraded into acetic acid, carbon dioxide, hydrogen, volatile fatty acids, and alcohol. At this stage, the main products produced are VFAs such as propionic acid, butyric acid, and so on.
- Acetogenesis stage: volatile fatty acids and alcohol are degraded into hydrogen and acetic acid.
- Methanogenesis stage: a mixture of acetic acid, formic acid, ethanol, as well as H_2 gas and CO_2 gas are converted to methane.

In this study, the volatile solid on the 10th day was 25.0044% then increased on the 20th day to 50,1610% and on the 30th day it became 63.5166%. The hydrolysis stage occurs on day 0 to day 10, and the acidogenesis stage begins on day 10. This is supported by changes in pH starting from 6.43 on day 0 and then decreasing to 5.63 on day 10. The stages of acidogenesis and acetogenesis occurred on day 10 to day 30. This statement is relevant to the production of volatile fatty acids (VFA) in the form of volatile solids of up to 63.5166%.

On the 40th day, solid volatility decreased to 29.5254%. This is because on the 40th day the substrate begins to enter the methanogenesis stage, so that the VFA is converted to methane. This is supported by the methane gas content increasing to 8.106% and pH increasing to 6.60. On day 50, solid volatility increased to 36.1378%. This is due to solid volatile substances not only in the form of Volatile Fatty Acid (VFA), but in the form of precipitation of inorganic substances which are characterized by increasing pH and alkalinity values in the slurry. Alkalinity and pH increase due to increased deposits of inorganic substances (Su & Yang, 2020).

CONCLUSION

The longer the fermentation time, the gas volume, methane content, and carbon dioxide content will increase. Microbial activity in this study only reached its peak phase on the 50th day, so it has not yet reached the decline or death phase. The stages of biogas formation process from day 0 to day 50 consist of hydrolysis stage (days 0-10) is characterized by gas volume and low methane content, neutral pH, high total solid, low solid volatile, and low $CaCO_3$, acidogenesis stage (days 10-20) is characterized by increasing gas volume, low methane content, acidic pH, decreasing total solids, increasing volatile solids, and high

$CaCO_3$, acetogenesis stage (days 20-30) is characterized by increased gas volume, low methane content, acidic pH, decreased total solids, increased volatile solids, and decreased $CaCO_3$, methanogenesis (days 30-50) stage is characterized by a significant increase in gas volume, an increase in methane content, a neutral to alkaline pH, a decrease in total solids, a decrease in volatile solids, and a decrease in $CaCO_3$.

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