RESEARCH ARTICLE

Bubble column application on purification of biogas and production of nano-calcium carbonate in continuous process

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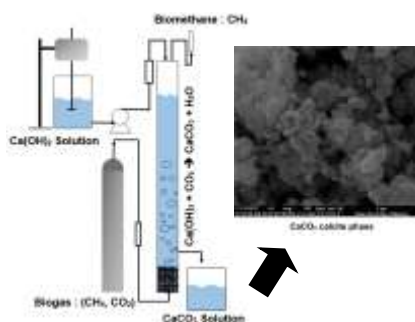
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Graphical abstract

Abstract

Purification of biogas by removing carbon dioxide content has been developed to increase its calorific value. The CO_2 contained in biogas was absorbed by contacting $Ca(OH)_2$ solution and CO_2 in the bubble column to produce high purity of biogas and generated precipitated calcium carbonate (PCC) simultaneously. Two sources of CO_2 were used in this work, which were CO_2 contained in biogas and pure CO_2. Pure CO_2 was used as a benchmark in this study to show the effect of the presence of methane contained in biogas on the absorption process. The investigation was done in a continuous process. The results showed that the highest absorption of CO_2 was obtained in biogas at 79.34 %. PCC with calcite phases was successfully formed in 225−270 nm. Rhombohedral calcite phase was formed by the use of pure CO_2 and biogas as a source of CO_2. The use of CO_2 contained in biogas and pure CO_2 in the absorption process did not have an effect on the crystalline phase and morphology of calcite formed. Several factors that significantly affected the absorption of CO_2 were gas flow rate, absorbent flow rate, CO_2 concentration in the gas inlet, and the initial liquid level in the bubble column.

Keywords: Biogas, absorption, precipitated calcium carbonate

INTRODUCTION

Biogas is one of the promising alternative energies to reduce dependency on fossil fuels. Typically, biogas consists of methane (CH_4, 50–70 %), carbon dioxide (CO_2, 30–40 %), hydrogen (H_2, 5–10 %), nitrogen (N_2, 1–2 %), water (H_2O, 0.3 %), and hydrogen sulfide (H_2S) (Mamun *et al*., 2015). The presence of a high concentration of CO_2 in biogas causes corrosion of the reactor due to the formation of carbonic acid. In addition, it can reduce the heating value of the biogas. Therefore, upgrading biogas into biomethane by CO_2 absorption is important to increase biogas quality and heating value. Water scrubbing is a proven, simple, and universal technology for CO_2 removal in various flow rates. This technology can also reduce H_2S in high quantities, but this process consumes large amounts of water. Chemical and physical absorption is preferably used for medium or large-scale process, so it is more suitable applied in industry or pilot scale biogas reactor installations in rural areas (Niesner *et al.,* 2013). Chemical absorption with amine-based absorbents such as monoethanolamine (MEA) and diethanolamine (DEA) has been developed for 70 years as an absorbent for acidic gases such as H_2S and CO_2 (Han *et al.,* 2011). This process consists of three stageswhich are absorbing CO_2 gas in the absorbent, releasing CO_2 trapped in absorbent, and CO_2 liquefaction which is a costly stage. All processes mentioned above only focusing on CO_2 capturing and storing. Converting CO_2 into a valuable product can be an alternative process. This process is more economical than other CO_2 absorption because it does not require additional CO_2 liquefaction costs.

Process of CO_2 absorption with $Ca(OH)_2$ solution followed by the formation of precipitated calcium carbonate (PCC) is an advantages alternative process. PCC is known as a product that has many uses in industry. Previous work has investigated the possibility of PCC production with high purity and narrow particle distribution size by reacting CO_2 and calcium extracted from blast furnace (slag). However, this process needs more pretreatment to extract calcium from slag and results in co-precipitation of magnesium carbonate more than PCC (De Crom *et al.,* 2015). From this method, it is possible to produce PCC and purify biogas simultaneously by reacting carbon dioxide contained in biogas and $Ca(OH)_2$ solution. Even though this process is a classic method, it may be adopted and modified for application in a small scale of biogas production. There is rare literature available in small-scale of biogas upgrading systems. Some advantages of using this process include CaO as an inexpensive raw material, a simple reaction process, and precipitated calcium carbonate which is the result of the process can add a commercial value of the biogas purification process. In addition, regeneration and disposing of a residual solution are friendly to the environment if it is carried out in the long term. Although this process has limitations of raw materials derived from nature, a lot of research on CaO regeneration of $CaCO_3$ has developed by thermal dissociation process commonly referred to as Ca-Looping (Han *et al*., 2011).

In the previous work (Ihsana *et al*., 2017), the biogas absorption process in semi-batch using a bubble column has been successfully

used to purify biogas and synthesize nanoparticle precipitated calcium carbonate simultaneously. $CaCO_3$ has been successfully formed in calcite phase. Previously, the use of absorbent concentration is based on its solubility. $Ca(OH)_2$ solution is fed in the bubble column until it fully reacts. From this semi-batch process, it has been found that the use of a perforated plate with a hole diameter of 0.5 mm gives greater absorption compared to that with 1 mm diameter hole. This work was carried out in continuous absorption to determine the maximum performance of CO_2 absorption on different operating conditions. The effect of absorbent concentration, gas flow rate, solution level, and absorbent flow rate on CO_2 absorption were investigated. In addition, the optimum conditions for CO_2 capture were reported.

EXPERIMENTAL

Materials

Materials used in this work consisted of QUALI-TECH CHEM technical grade $Ca(OH)_2$ 99 % Pure, CO_2 99.9 % (v/v), and aquadest. Biogas used in this research was from the installation of the reactor pilot plant in the rural area. Cow manure was used as a substrate to produce biogas. This biogas contained 67.8 % of methane (CH_4), 32.2 % of carbon dioxide (CO_2), and other components such as hydrogen sulfide (H_2S), and water (H_2O) after desulfurization using zeolite and dehydration using water trap. As shown in Fig. 1, the bubble column used in biogas purification was made from acrylic. It has an inside diameter of 7 cm with a thickness of 0.5 cm and a height of 100 cm. The biogas from the gas cylinder was supplied through a distributor consisting of a perforated plate and glass beads. This perforated plate has a hole diameter of 0.5 mm with an active area of 0.332 cm^2. This perforated plate was used to produce bubbles which were contacted with $Ca(OH)_2$ solution. At the bottom of the bubble column, there were glass beads that had an average diameter of 0.3 cm. $Ca(OH)_2$ solution was fed countercurrent into the bubble column. Before entering the bubble column, $Ca(OH)_2$ solution was stirred in a feed tank using a stirrer. Biogas flow was controlled by the flowmeter. The exit gas would be collected using the Tedlar bag for analyzing biogas content using the gas chromatograph.
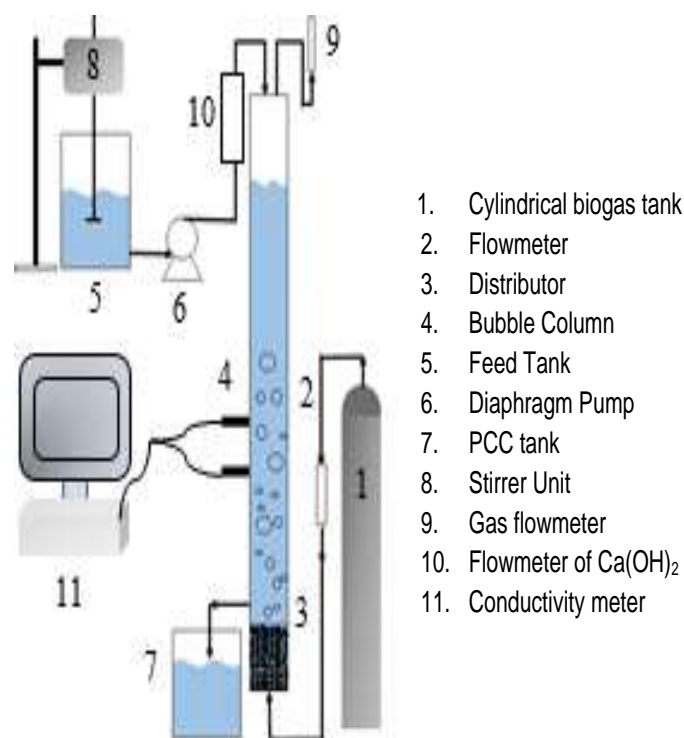

Fig. 1 Schematic purification experiment apparatus in a continuous process

1. Cylindrical biogas tank
2. Flowmeter
3. Distributor
4. Bubble Column
5. Feed Tank
6. Diaphragm Pump
7. PCC tank
8. Stirrer Unit
9. Gas flowmeter
10. Flowmeter of $Ca(OH)_2$
11. Conductivity meter

Synthesis of Precipitated Calcium Carbonate (PCC)

The absorbent concentration used in this process was varied of 1.5, 2, and 2.5 times of $Ca(OH)_2$ solubility at 30 ºC. This concentration was varied at 2.38, 3.068, and 3.82 gram/liter, respectively. Gas flow rates used were 0.5, 0.6, 0.7, 0.8, and 0.9 liter/min. The total volume of $Ca(OH)_2$ solution used in this study was 10 liters. The $Ca(OH)_2$ flow rate used was varied at 200, 250, 300, 350, and 400 mL/min. The initial liquid level was varied at 50, 65, and 80 cm to determine the performance of CO_2 absorption in a solution of $Ca(OH)_2$ at a certain height. Two conductometer probes were installed at a certain height to find out the reaction runs at a different liquid level. In this absorption process, two sources of CO_2 were used. They were pure CO_2 and biogas. Pure CO_2 was used to know the influence of other gases contained in biogas on the absorption process.

The solution of $Ca(OH)_2$ was prepared by dissolving 23.8 grams of $Ca(OH)_2$ in 1 liter of water. This solution was stirred using a magnetic stirrer at a constant speed of 450 rpm with the solution temperature of 60 °C. $Ca(OH)_2$ solution was fed into the feed tank with an addition of 9 liters of water and then was flowed by diaphragm pump into the bubble column to a certain height. The flow rates of inlet and outlet solutions were kept constant. At the same time, biogas was fed at the bottom bubble column. The determination of CO_2 absorbed was done by different treatment between pure CO_2 and biogas. In pure CO_2, the absorption was determined by changes in the flow rate of the outgoing gas while the biogas absorption was determined from the exit gas sampling which was analyzed by gas chromatography. Gas sampling was done when gas hold up was constant. The gas flow rate was stopped when the solution in the feed tank had run out completely. Then, the sample from the reactor was collected, filtered, and cooled for 12 hours. Calcium carbonate was dried at 60 °C for 12 hours before calculating its weight and performing its characterization. The content of CH_4 and CO_2 in biogas was analyzed using gas chromatography (Shimadzu GC-2010 Plus Kyoto, Japan) with Thermal conductivity detector (TCD). The type of $CaCO_3$ crystals, morphology phase, and purity of Ca were analyzed using X-ray powder diffraction (XRD), SEM (Scanning Electron Microscopy), and XRF (X-ray fluorescence), respectively. The average diameter of 300 $CaCO_3$ particles was calculated using image analysis software.

RESULTS AND DISCUSSION

Effect of Gas Flow Rate on Absorption

Effect of gas flow rate on absorption has been observed at concentration, $Ca(OH)_2$ flow rate, and the initial liquid level of 3.06 gram/liter, 200 mL/minute, and 50 cm, respectively. In general, Fig. 2 shows the reduction in absorption of CO_2 in biogas and pure CO_2 when the gas flow rate is increased. The greater gas flow rate, the faster the pH required to go to neutral. The pH changes in the carbonation solution have been studied in previous work and report that the greater gas flow rate used make the pH change to neutral faster. The neutral pH will decrease the performance of the absorbent to absorb CO_2. When pH value is more than 10, more PCC is converted. This is because carbonate ions are dominant at this high pH. Conversely, when the pH is low, precipitation will be decreased with the presence of H_2CO_3 in the absence of bicarbonate and carbonate ions. At neutral pH, bicarbonate ions are formed and it is difficult to form carbonates with divalent ions. Hence, it is difficult to form precipitation of $CaCO_3$ (Bang et al., 2011).

Compared to the absorption of biogas, the absorption of pure CO_2 is not as significant as in biogas. Based on film theory, increasing the inlet concentration of CO_2 allows more CO_2 molecules to travel the bulk gas to the gas-liquid interface, resulting in higher absorption efficiency. However, gas with the hight content of CO_2 in pure CO_2 at the same flow rate, the absorbent mole ratio to carbon dioxide decreased, leading to a reduction in efficiency of absorption (Yincheng et al., 2011). This is also seen in Table 1. The use of pure CO_2 is not worthy if the ratio of $Ca(OH)_2/CO_2$ is smaller than 1. This could have a significant effect if the concentration of $Ca(OH)_2$ is large.
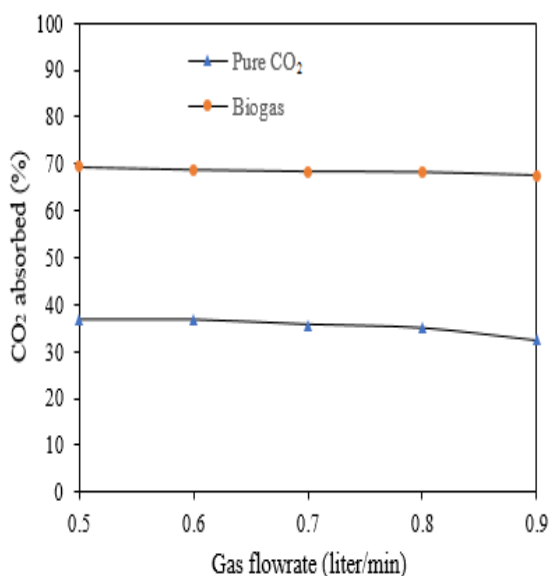
Fig. 2 Effect of gas flow rate on CO_2 absorption.

Based on Table 1, the highest CO_2 absorption is obtained from the lowest gas flow rate in both biogas and pure CO_2. However, the mole ratio of Ca $(OH)_2/CO_2$ in biogas is higher than pure CO_2. It causes higher CO_2 absorption in biogas. Based on stoichiometry, every 1 mole of $Ca(OH)_2$ requires 1 mole of CO_2 to react completely. At least, to obtain maximum absorption, $Ca(OH)_2$ must be greater than CO_2 entering with a mole ratio of $Ca(OH)_2/CO_2$ greater than 1 but it depends on the efficiency of the column design and operating condition. There are several studies that have found that to get CO_2 absorption of around 90%, the mole ratio of absorbent and CO_2 used should be equal to 4.43. It was based on research conducted using a spray column using NaOH as an absorbent and it was contacted with 15% CO_2 inlet content (Yincheng et al., 2011). Table 1 presents the mole ratio of $Ca(OH)_2/CO_2$ on CO_2 absorption.

Table 1 Mole ratio of $Ca(OH)_2/CO_2$ on CO_2 absorption.

Gas flow rate (liter/minute)	*Mole ratio $Ca(OH)_2/CO_2$	*CO_2 absorbed (%)	Mole ratio $Ca(OH)_2/CO_2$	CO_2 absorbed (%)
0.5	0.37	36.37	1.15	69.35
0.6	0.31	36.66	0.96	68.74
0.7	0.26	35.72	0.82	68.36
0.8	0.23	35	0.72	68.21
0.9	0.21	32.54	0.64	67.43

*Pure CO_2

Effect of $Ca(OH)_2$ Flow Rate on Absorption

As shown in Fig. 3, to determine the effect of $Ca(OH)_2$ flow rate, it is varied by 200, 250, 300, 350, and 400 mL/min. Meanwhile, the concentration of $Ca(OH)_2$, gas flow rate, and the level of the solution were kept constant at 3.06 gram/liter, 0.7 liters/min, and 50 cm, respectively. The absorption process in pure CO_2 and biogas shows that in the presence of an increased $Ca(OH)_2$, flow rate will increase the amount of CO_2 absorbed. In a study that has been done by Liu et al. (2015), CO_2 absorption will increase when the $Ca(OH)_2$ flow rate is increased. By increasing the flow rate of $Ca(OH)_2$, this will increase interface friction phase and decrease the resistance to the liquid film, thus causing diffusion of CO_2 and the reaction rate to increase. The highest CO_2 absorption is produced at the absorbent flow rate of 400 mL/min
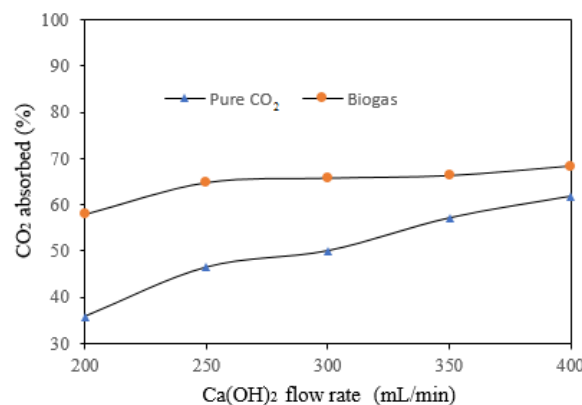

Fig. 3 Effect of $Ca(OH)_2$ flow rate on CO_2 absorption.

As seen in Table 2, the absorption of CO_2 and the mole ratio of $Ca(OH)_2/CO_2$ at 400 mL/min in pure CO_2 are 61.85% and 0.52, respectively. With the same concentration of $Ca(OH)_2$, the increased absorbent flow rate gives a greater mole ratio. The absorbent requirement will be greater if the gas inlet has lower CO_2 content. Based on the study of CO_2 absorption in the spray column and NaOH as absorbent, to get absorption efficiency around 90%, the mole ratio of absorbent and CO_2 used should be at 4.43 (Yincheng et al., 2011). This is due to the CO_2 content of the inlet used that is equal to 15%. Increasing CO_2 absorption by increasing the absorbent flow rate is considered to be an efficient option to avoid using high absorbent concentrations (Tippayawong et al., 2010). This is be useful for reducing the regeneration load of the absorbents used and reducing the use of CaO as raw materials. The presence of CH_4 as an inert in biogas followed by increasing absorbent flow rate provide a large mole ratio of $Ca(OH)_2/CO_2$. In biogas, at a $Ca(OH)_2$ flow rate of 400 mL/minute has a mole ratio of 1.64 with the CO_2 absorption of 68.35 %. The mole ratio of $Ca(OH)_2/CO_2$ will be greater if the gas inlet has a lower CO_2 content. While in the gas inlet with high CO_2 content as in pure CO_2 has a smaller ratio with smaller absorption. This means that in a gas that has a high inlet concentration, the mole ratio of $Ca(OH)_2/CO_2$ needed to get the same output with the absorption of biogas must be greater. This is also in accordance with research conducted by Guido et al. (2017). The minimum ratio of liquid/gas (L/G) needed to get the same output at the same flow rate will be greater when the gas concentration increases. In a continuous process with a low absorbent flow rate of 200 mL/min, the mole ratio $Ca(OH)_2/CO_2$ are 0.26 and 0.82 in pure CO_2 and biogas with the CO_2 absorption of 35.71%, and 68.36 %, respectively. On the other hand, at $Ca(OH)_2$ flow rate of 400 mL/minute, the absorption is not noteworthy where the absorptions are 61.86 % and 79.34 % in pure CO_2 and biogas, respectively. Noted that at the same flow rate of 400 mL/minute, the mole ratio of $Ca(OH)_2$ and CO_2 in biogas are almost 2 times that of pure CO_2. This means that in the absorption process with a low CO_2 inlet gas content, it must have a larger mole ratio $Ca(OH)_2/CO_2$ by increasing the absorbent flow rate to obtain higher absorption.

Table 2 The mole ratio of $Ca(OH)_2/CO_2$ on pure CO_2 and biogas absorption in a continuous process.

Absorbent flow rate (mL/minute)	*Mole ratio $Ca(OH)_2/CO_2$	*CO_2 absorbed (%)	Mole ratio $Ca(OH)_2/CO_2$	CO_2 absorbed (%)
200	0.26	35.71	0.82	68.36
250	0.33	46.42	1.02	70.23
300	0.39	50	1.23	74.04
350	0.46	57.14	1.43	76.15
400	0.52	61.86	1.64	

* Pure CO_2

Effect of Ca(OH)₂ concentration on CO₂ absorption

Fig. 4 shows that CO_2 absorption increases when $Ca(OH)_2$ concentration increases. However, the absorption of CO_2 in the biogas is greater than that of the pure carbon dioxide absorption. It is apparent that the use of absorbents above the solubility shows greater absorption. However, the trend of increasing CO_2 absorption is not obvious with an increase in concentration. The reaction occurring between $Ca(OH)_2$ and CO_2 is an instant reaction type, with gas resistance as a control. $Ca(OH)_2$ concentration must be excessive to obtain high absorption. When the concentration of the absorbent solution used is low, the reaction occurs in the liquid body. Whereas, if the absorbent concentration is high, the reaction will move from the liquid body to the interface between the liquid and the gas. So, it will increase the gas absorption because the gas resistance becomes small. However, the reaction will tend to remain at the interface when the absorbent concentration is constantly raised (Hayashi et al., 1975). At certain concentration limits, the absorption does not occur noticeably due to the increase in the concentration of the solution. Increasing CO_2 absorption by increasing absorbent flow rate becomes a more efficient option than using high absorbent concentrations. This will be useful for reducing the regeneration load of the absorbents used.
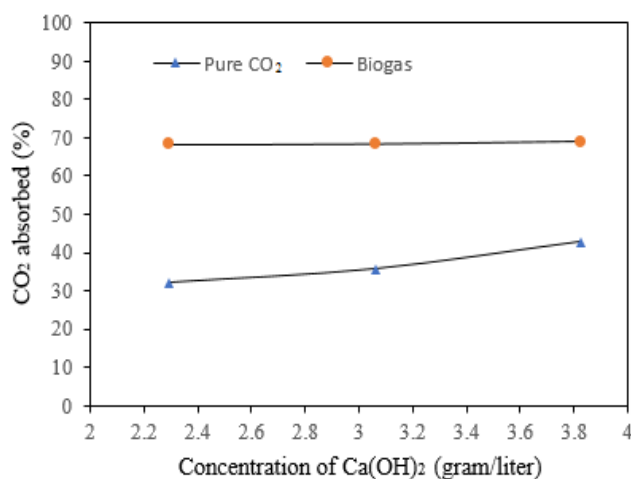

Fig. 4 Effect of Ca(OH)₂ concentration on CO₂ absorption.

Effect of initial Ca(OH)₂ solution level on CO₂ absorption

As shown in Fig. 5, the initial level of $Ca(OH)_2$ solution is varied, i.e. 50, 65, and 80 cm. The figure shows that the higher absorption is obtained on the higher initial liquid level. This trend is due to the higher initial liquid level in the bubble column resulting in longer residence time and increased interfacial area. The greater the interfacial area, the more gas that contacts to the liquid so that absorption occurs maximally. The highest CO_2 absorption is produced at 80 cm solution level in the continuous biogas system. In this study, the percentage of CO_2 absorbed in biogas were twice of pure CO_2. This is due to the presence of other gas mixtures in biogas such as CH_4 and H_2S. The other gas mixture in biogas serves as an inert. The large content and solubility of methane (0.00175 grams gas in 1 gram of water) inhibit the CO_2 to react with $Ca(OH)_2$ solution. Even though methane does not react and affect the carbonation process, it affects the absorption time. In addition, CO_2 is an acidic gas and polar so the chemical reaction will occur with $Ca(OH)_2$ solution. Conversely, the structure of tetrahedral-shaped methane gas makes methane gas non-polar so it cannot react with $Ca(OH)_2$ (Rashed et al., 2015). Other study also reported that the presence of inert can increase the hold-up gas in $Ca(OH)_2$ solution so that the gas contact time in the solution is longer (Van Baten et al., 2004). Increasing gas hold up causes more gas to be trapped in the solution so that it will increase the contact time between liquid and gas.
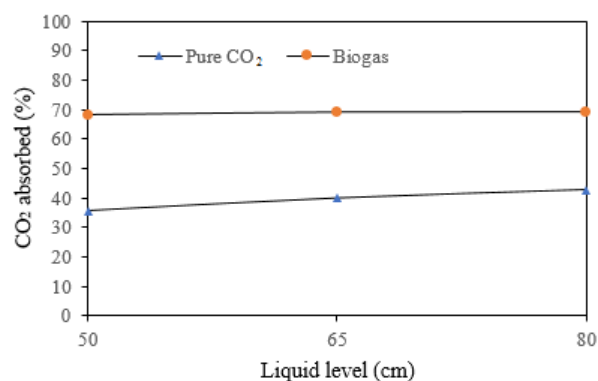

Fig. 5 Effect of initial Ca(OH)₂ solution level on CO₂ absorption.

To study of the performance of a reaction that runs in a bubble column at a certain liquid level, conductivity measurements are carried out at two points as seen in Fig. 6 The first point is located at a height of 25 cm, while the second point at the liquid level of 50 cm, 65 cm, and 80 cm is located at a height of 45 cm, 60 cm, and 75 cm, respectively. As seen in Fig. 6, there are two stages of the mechanism in the process of forming PCC. The first stage runs for about 20 minutes where there is still high conductivity. While the second stage is characterized by a decrease in conductivity to a constant. In the first stage, the pH is still around the range 12–10, while in the second stage, the pH is ranged from <10 to neutral. According to Bang et al.(2011), CO_2 in certain pH variations has different forms, namely CO_3^{2-}, HCO_3^{-}, and H_2CO_3 at pH> 10, 6–10, and <6, respectively. At the beginning of the reaction, calcium ions from a solution of $Ca(OH)_2$ react with CO_3^{2-} forming $CaCO_3$ at a high pH because of the availability of hydroxide ions which can maintain the pH level in solution. When pH decreases, the presence of CO_3^{2-} decreases and forms HCO_3^{-}, which reduces the precipitation formation. At this stage, it is also called the hatched region (HR), which is identified by a steep pH or conductivity change. Whereas at neutral pH, bicarbonate ions are formed and it is difficult to form carbonates with divalent ions. In this situation, it is difficult to form precipitation.

Fig. 6 (a) shows observations of conductivity at the liquid level of 50 cm by installing two points or probes at a height of 25 cm and 45 cm. It can be seen that at the liquid level of 50 cm, the formation of the maximum PCC occurs approximately 20 minutes which is indicated by high conductivity. At the initial stage, at a height of 25 cm, there is still high conductivity compared to the height of 45 cm. However, at a height of 25 cm and 45 cm, it has the same tendency in the second stage where there is a decrease in conductivity to a constant.

Next,Fig. 6 (b) shows observations of conductivity at the liquid level 65 cm by installing two points or probes at a height of 25 cm and 60 cm. It can be seen that at the liquid level of 60 cm, the formation of the maximum PCC occurs a little longer than the liquid level 50 cm. Then, this is followed by the second stage which is a decrease in the value of conductivity to a constant.

In Fig. 6 (c), observations of conductivity at the liquid level 80 cm by installing two points or probes at a height of 25 cm and 75 cm are presented. At a height of 25 cm, it has the same tendency as before, which is a decrease in conductivity value after 20 minutes. At this height, pH decreases after the 20th minute which is marked by a decrease in the conductivity value. It can be seen at a liquid level of 80 cm, the formation of the maximum PCC occurs longer at a height of 75 cm compared to the previous one which is more than 20 minutes. In the second stage, we can see a decrease in the value of conductivity to a constant, indicating thatthe higher the level of liquid, the more maximum the PCC is formed but at a certain high limit. Maintaining pH>10 is the most important key to ensure that the process of absorption and formation of precipitation runs optimally. By increasing the initial level of liquid at the liquid level limit, the time needed to form PCC in the first stage is much longer to allow the CO_2 absorption process to run maximally.
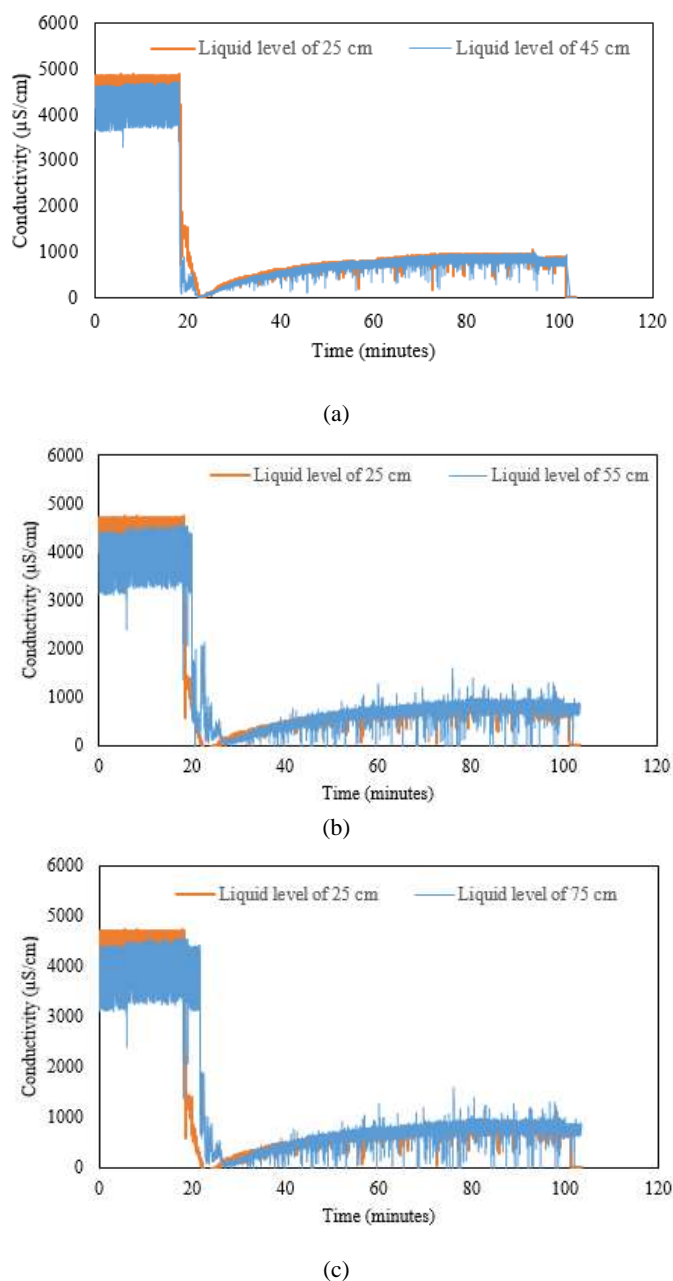
(a)

(b)

(c)

Fig. 6 Conductivity at different levels of liquid (a) 50 cm (b) 65 cm and (c) 80 cm.

Characteristic of Particle

As shown in Fig. 7, from several PCC samples, characterization of crystallinity with X-ray or XRD (Xray Diffraction) was performed. XRD pattern in Fig. 7 shows the presence of peaks at $2\Theta = 23.1, 29.4, 34.2, 36, 39.5, 43.2, 47.6, 48.6, 57.6, 60.9,$ and 64.9. The peaks show the calcite phase in calcium carbonate formed in the carbonate process.

Data on X-ray fluorescence were taken on a precipitated calcium carbonate (PCC) sample obtained from the reaction between a solution of $Ca(OH)_2$ with pure CO_2. The composition of calcium carbonate produced in this process is shown in Table 3.
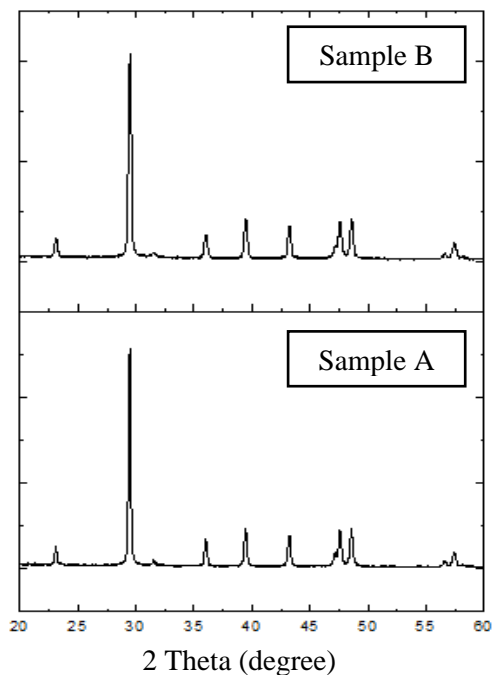

2 Theta (degree)

Figure 7 Results of PCC XRD analysis (Sample A: calcite phase with the use of biogas; Sample B: calcite phase with the use of pure CO_2).

***Table* 3** Composition elements in PCC using (*X-ray fluorescence*).

Elements	Composition (%)
Ca	99.43
Fe	0.36
Cu	0.09
Zn	0.02
Sr	0.05
Mo	0.02
Ra	0.04
Total	100

Based on the results of the morphological analysis using SEM as illustrated in Fig. 8, it shows that the calcite phase which is rhombohedral or cube is dominantly formed. The PCC size obtained from the image analysis software is between 225–270 nm.

The use of CO_2 contained in biogas and pure CO_2 in the absorption process has no effect on the crystalline phase and morphology of calcite formed. In another study, it was stated that the morphology of calcite was strongly influenced by the absorbent concentration used. Calcite with the seed-like prismatic and scalenohedron form is dominantly formed by the presence of high absorbent concentrations (Jimoh et al., 2017). Changing the properties of CO_2 sources using biogas will affect the density and viscosity of the gas. Biogas has a higher density than pure CO_2. The higher the density of the gas will change the properties of bubbles such as bubble size. This smaller bubble size will cause a greater gas hold up (Bang et al., 2015). The bigger the gas hold up the more gas is trapped in the solution so that it will increase the solubility of the gas. The use of biogas as a source of CO_2 will only affect the increase in solubility of

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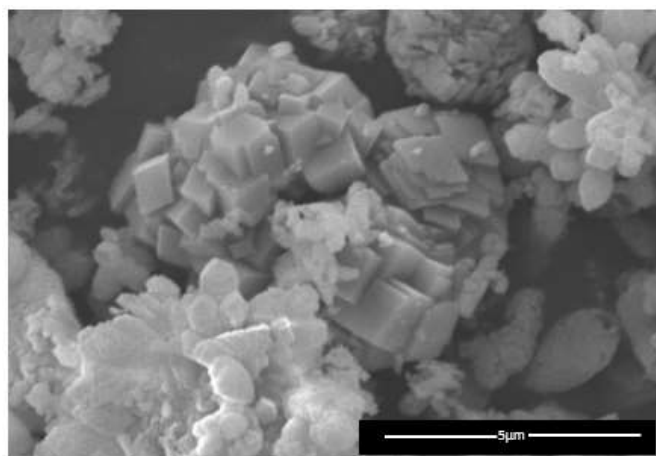
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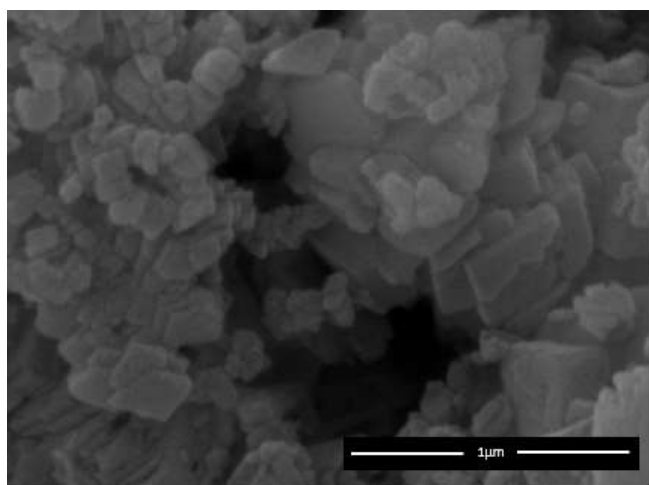
(b)

Figure 8. (a) SEM image of PCC generated from biogas (b) SEM image of PCC generated from pure of CO_2

CONCLUSION

The carbonation process using a bubble column was successfully performed to purify biogas and synthesize $CaCO_3$ nanoparticles simultaneously. The absorption of CO_2 increases as the absorbent flow rate fluctuates and the gas flow rate increases. The use of absorbent above the solubility shown in the continuous process shows higher absorption of CO_2. However, the upward trend of CO_2 absorption is not noteworthy with increasing concentration. The highest absorption of CO_2 obtained in the continuous process is 79.34 %. Overall, the crystalline phase formed in this study is calcite with rhombohedral shape and has a particle size between 225–270 nm. The use of CO_2 contained in biogas and pure CO_2 in the absorption process has no effect on the crystalline phase and morphology of calcite formed.

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