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Continuous Water Absorption - Regeneration using Microbubble Technology for CO_2 Removal in Biogas Upgrading System

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Abstract – *In this work, a system for upgrading biogas to biomethane was developed consisting of a continuous water absorption - regeneration using microbubble technology. The biogas upgrading system was tested using a 30% CO_2–N_2 simulated biogas. Microbubbles in the water absorbent were generated using a 0.5-inch venturi ejector before introducing into a gas separation unit. Various flow rates of the simulated biogas between 2 and 10 L/min were tested, at a constant water flow rate of 15 L/min, operating at pressure of 7 bar and their CO_2 removal efficiency was monitored. The bubble bottle was initially tested the absorbent regeneration by distributing air into CO_2 rich liquid to make CO_2 desorption. The regeneration unit was designed to create a counter current between air and used water with air flow rates of 5–30 L/min. The optimum absorption conditions were found to be a liquid/gas ratio of 7.5 achieved with a simulated biogas flow rate of 2 L/min and 15 L/min water. An optimum air flow rate of 30 L/min in the regeneration unit produced a CO_2 removal efficiency from the simulated biomethane of over 90%.*

Keywords – *biomethane, CO_2 removal, microbubbles, regeneration, water absorption.*

1. INTRODUCTION

Biogas is a versatile renewable energy source produced by the anaerobic digestion of agricultural manure wastes, sewage sludge, and food wastes. It has properties similar to those of natural gas because it consists mainly of methane (CH_4). However, biogas contains some impurities such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), water vapor, and other volatile compounds. When CO_2 is present during the combustion process it causes a decrease in the heating value of the biogas. Therefore, the removal of CO_2 is required to upgrade biogas into biomethane, which can be used directly for heating and electricity generation or as a substitute for fossil fuels.

Previous research has investigated more efficient and cost effective methods of purification and different technologies have been developed for the effective removal of CO_2 from biogas [1], which are mainly based on absorption using water or an amine solution as the solvent. One of the simplest and most common techniques for CO_2 removal is absorption by transferring a component of CO_2 from biogas into liquid water [2]. The solubility of the main components of biogas, CO_2 and CH_4, in water are 340 and 13.2 mmol $kg^{-1} \cdot MPa^{-1}$, respectively, at 25°C with the gas at a partial pressure of 0.1 MPa [3], [4]. An alternative method is to allow the CO_2 to be absorbed by reacting with the water to form the bicarbonate ion, HCO^{-3}. The water absorption process is usually operated at high pressure and low temperature to increase the CO_2 solubility and to allow the selective absorption of the CO_2 from the biogas [5]. Superior physical and chemical absorption can be achieved using the microbubble technique, in particular, in a process where the bubble diameters are less than approximately 50 μm. Mass transfer enhancement caused by the self-compression and shrinking of these microbubbles leads to their collapse and complete gas dissolution [6], [7].

Since the regeneration of the absorbent system plays a major role in the performance of the CO_2 capture process, the used water has to be regenerated by contact with air so that most of the bicarbonate ions react with the O_2 in the air. The CO_2 in the water can be released by a counter-current created by an air flow that acts as a sweeping gas [8]. The regenerated liquid phase has a very small CO_2 molar fraction and can be reused to start a new cycle of absorption [9]. Therefore, this regeneration method can lead to higher CO_2 absorption capacities with very low energy requirements and absorbent consumption [9].

This paper reports on biogas to biomethane upgrading by absorption using microbubble technology and absorbent regeneration system. The absorption process was carried out using a venturi ejector for microbubble generator. The treated gas was separated from absorbent in separation column to achieve an upgraded gaseous stream with a low CO_2 concentration. The regeneration system employed a counter current for the spent water absorbent and air flow for removing CO_2 from the water which was then recycled back to the absorption stage. This paper focuses on the absorption and regeneration behavior, including the absorption rates, regeneration efficiency, and solvent stability.

2. METHODOLOGY

The biogas to biomethane upgrading process consisted of two main parts, the absorption and regeneration system, which are described below.

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2.1 Simulated Biogas Generation

The experiments investigated the effect of gas and water flow rate on CO_2 removal from biogas in a CO_2 absorption system. To evaluate the performance of the proposed method, sets of experiments were performed with a simulated biogas with a 30% CO_2 content. Pure CO_2 and N_2 gases from gas cylinders were well-mixed in a gas mixing tank to produce the simulated biogas. Gas samples were taken using a sampling bag and analyzed for their gas concentrations by gas chromatography with a TCD detector and a Porapak Q packed column.

2.2 CO_2 Absorption System

The CO_2 absorption system comprised a microbubble generator and a gas separation column, with 100 L water storage tanks and a water pump as detailed below.

2.2.1 Microbubble generator unit

Figure 1 illustrates the two parts of the CO_2 absorption and gas separation system, the microbubble generator system, and the gas separation columns. In this research, microbubbles were generated by injecting the simulated biogas into a -0.5inch venturi ejector, at a flow rate of 2–10 L/min and operating at pressure of 7 bar. A venturi ejector is a black plastic cylinder with three sections, an inlet, the suction throat, and the outlet. In the system developed the water used as an absorbent medium was injected through the inlet with a flow rate of 15 L/min. The inlet tapers to its minimum diameter at the suction throat and a low-pressure zone is created with the gas being sucked in at the same point. Increasing the liquid velocity in the venturi ejector enhances the suction of the gas into the liquid to form microbubbles, which are spherical bubbles with a diameter of less than or equal to 50 μm [10]. The turbulent flow, shear flow, and pressure wave inside the venturi tube result in the breakup of the microbubbles [11] resulting in an increase in the gas to liquid mass transfer surface area. In this research, the bubble size was determined by a MATLAB image segmentation program, and the data was analyzed using Microsoft Excel [12].

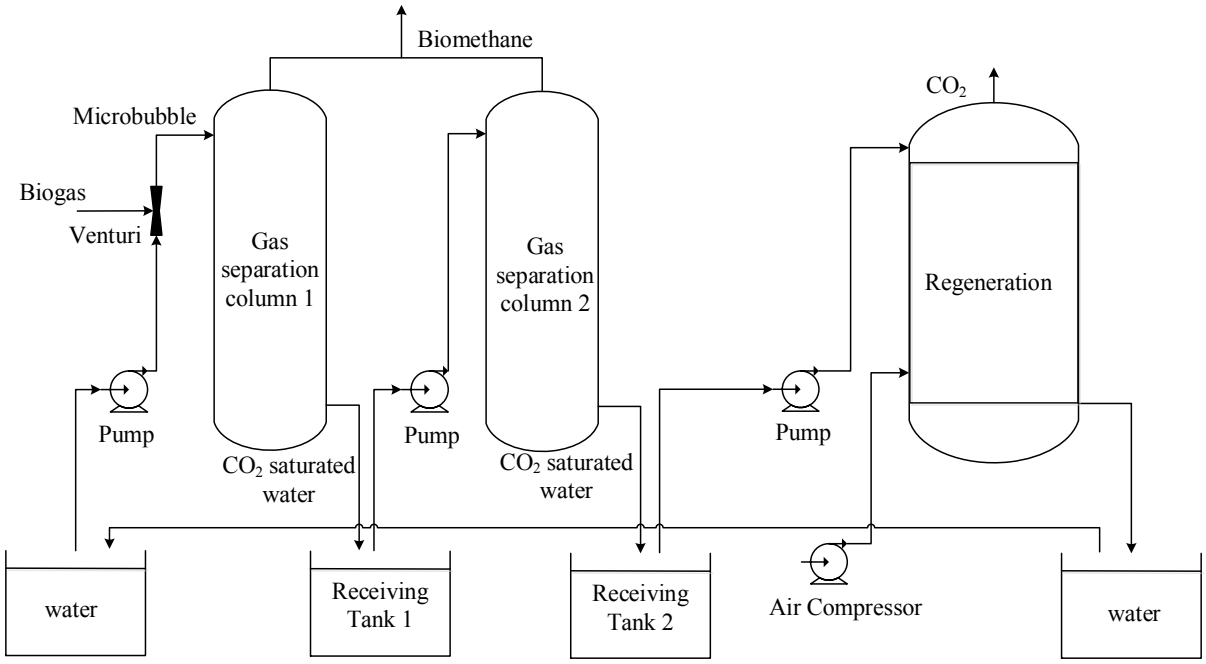

Fig. 1. Flow diagram of the CO_2 absorption, gas separation system and the regeneration system.

2.2.2 Gas separation column unit

This system used gas separation columns to separate the gas bubbles from the liquid absorbent. Two gas separation columns with a diameter of 0.3 m and a height of 1.8 m were used in the experiment to separate the treated biomethane gas from the CO_2 which was removed with water. Spiral spray nozzles at a spray angle of 120°C were installed inside the columns to spray the water in order to release the N_2 and CH_4 gases, which, not being absorbed in the water, were released from the top of the columns at pressure of 1 bar. The water in the columns was then recycled into the microbubble generator described above through a regeneration system described below. Experimental trials were conducted for 120 minutes at a flow rate of 2–10 L/minutes using the simulated biogas, and repeated three times to improve the quality of the biomethane produced by the water absorption system.

2.3 CO_2-Saturated Water Regeneration

2.3.1 CO_2 desorption tests

In order to design the absorbent regeneration system, desorption tests were performed in a laboratory. Pure CO_2 gas was introduced at 4 L/min into 200 ml tap water in a gas bubbling bottle until the pH value of the water was stable. Then air was fed into the bubbling bottle at a rate of 4 L/min for 10 minutes to monitor the CO_2 desorption from the CO_2-saturated water. The CO_2

concentrations in the gas released from the water were measured at the commencement of the test and after 5 and 10 min, and the test was repeated three times.

2.3.2 Absorbent regeneration system

This system was used to separate the CO_2 from the water absorbent to allow the water to be recycled and reused in the absorption system. The saturated absorbent was introduced into the top of a 25 L vertical absorption column (height 1 m and diameter 0.18 m) with air being injected at the bottom of the column to create a counter current flow. The water entering the column passed through a full-cone spiral nozzle in order to spray it into tiny drops, and the CO_2 was desorbed from the water by the O_2 in the air. Experiments were conducted on the effect of air-flow rates in a range of 5–30 L/min in the regeneration system. The pH of the water after passing through the regeneration system was also determined. The water regeneration system is illustrated in Figure 1.

2.4 CO_2-Saturated Water Regeneration

Gas samples were collected in 1 L gas sampling bags. The concentration of simulated biogas at the point of entering the system and in the treated gas stream were analyzed by gas chromatography using a model 14A gas chromatograph (Shimadzu, Japan) with a thermal conductivity detector column (Porapak Q, Shimadzu) using helium as the carrier gas. The injector, column and detector temperatures were 60ºC and the current, 60 mA. The concentrations of the gases sampled were calculated by analyzing the calibration curve in order to reduce the influence of fluctuations in extraneous factors or conditions. The peak areas detected were then compared to the calibration peak areas in order to calculate the concentrations of the components in the gases sampled. The CO_2 removal efficiency of the system was calculated by the following Equation 1.

$$\eta_{CO2} = \frac{CO_{2\,Inlet} - CO_{2\,Outlet}}{CO_{2\,Inlet}} \times 100 \quad (1)$$

where η_{CO_2} is the CO_2 removal efficiency, $CO_{2,\,Inlet}$ is the concentration of CO_2, and $CO_{2,Outlet}$ is the outlet concentration of CO_2.

All the determinations were conducted in triplicate and the results presented on a dry basis as the mean ± standard deviation (SD). Data analysis was performed with the SPSS program, using ANOVA, followed by Duncan's Multiple Range test. Differences were accepted as being statistically significant where $p < 0.05$.

3. RESULTS AND DISCUSSION

3.1 Absorption by Microbubble Technology

3.1.1 Microbubble generation result

The size of the microbubbles generated by feeding the simulated biogas and liquid water into the venturi ejector was tested at a water flow rate of 15 L/min was determined using the MATLAB image segmentation program. The result showed that with a range of gas flow rates from 2 to 8 L/min, microbubbles in a size range of 20.38-27.81 μm were generated.

3.1.2 Effect of L/G ratio on CO_2 removal

The removal of CO_2 by water absorption with microbubbles was conducted at various liquid to gas (L/G) ratios in a range of 1.87–7.50 simulating gas flow rates of 2, 4, 6 and 8 L/min. The water flow rate was kept at a constant 15 L/min for all the experiments, which were conducted at ambient pressure and room temperature. The highest CO_2 removal efficiency of around 95% was obtained at an L/G ratio of 7.50 as shown in Figure 3. The CO_2 concentration in the outlet gas stream was found to be below 5%, and this system was therefore capable of upgrading biogas to biomethane.

It can be seen from Figure 2 that at higher L/G ratios, better CO_2 absorption was obtained with only a slight increase in the time needed for absorption equilibrium to be achieved, which occurred after around 30 min. Decreasing the L/G ratio increased the amount of CO_2 in the gas phase while the bulk of the liquid phase was constant, indicating that the absorption of CO_2 by the water was less [13]. This result agrees with that from the studies of [5], in which higher L/G ratios were found to result in a relatively faster CO_2 absorption and slightly improved CO_2 removal efficiency. Increases in the L/G ratio from 1.87 to 7.50 resulted in an increase in CO_2 removal efficiency from 73.43 to 86.61% but increasing the L/G ratio from 3.75 to 7.50 had only a small effect on the efficiency of the system. Therefore, the L/G ratio of 3.75 was chosen for all the experiments that followed.

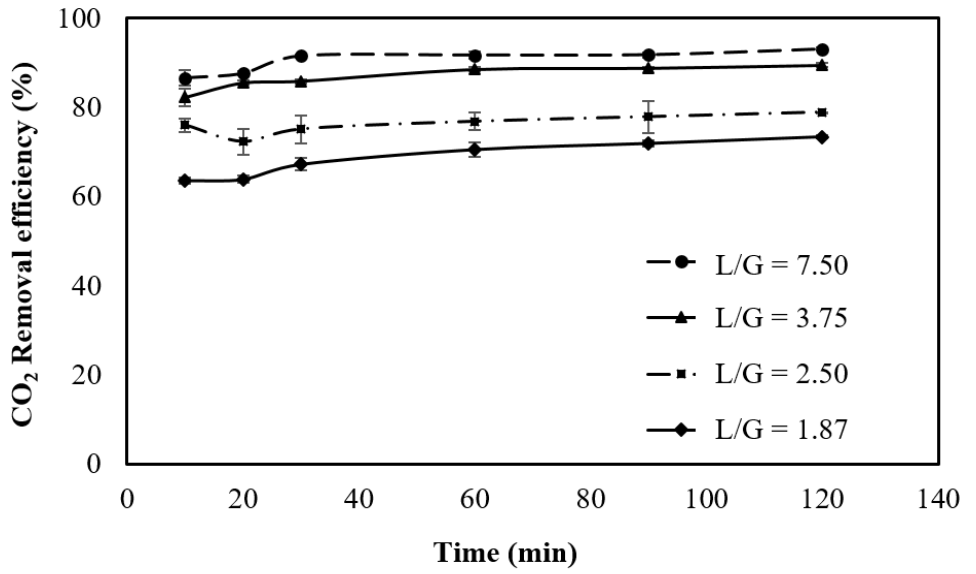

Fig. 2. Effect of L/G ratio on CO_2 removal efficiency at a constant water flow rate at 15 L/min.

3.2 Absorption by Microbubble Technology

3.2.1 CO_2 desorption test result

The desorption tests were conducted by generating CO_2-saturated water in a gas bubbling bottle. Pure CO_2 gas was introduced to the bottle until the pH value of the water (5.5) was unchanged. When air at a rate of 4 L/min was introduced into the CO_2 -rich water in the bubbling bottle, the CO_2 was released from the water and was detected in the gas outlet stream within the first 1-5 minutes with the water pH being found to increase to 6.8. Thus, the CO_2 was able to be desorbed and released from the water by air bubbling as shown in Equation 2:

$$CO_{2(aq)} + H_2O_{(1)} \leftrightarrow H_2CO_{3(aq)} \leftrightarrow H + {}^{+}HCO^{3-} \quad (2)$$

This technique was therefore able to be used in the regeneration in order to recirculate the absorbent water into the absorption process.

3.2.2 Effect of air flow rate on the regeneration unit

Experiments were conducted to investigate the effect of various air flow rates in the regeneration system on the overall CO_2 removal efficiency of the system. Air flow rates of between 5 and 30 L/min were introduced into the regeneration column with the water being recycled back to the venturi ejector of the absorption system. The experiments were all carried out using a simulated biogas flow rate of 2 L/min, a CO_2 concentration of 30%, and a water-flow rate of 15 L/min, with each experiment occupying 120 min.

The results are shown in Figure 3 and indicated that with air flow rates of 5-20 L/min, the same average CO_2 removal efficiency of 90.22 was achieved. However, the CO_2 removal efficiency was significantly increased to 94.21% at the higher air flow rate of 30 L/min. The continuous absorption – regeneration with the air flow rate combined with a simulated biogas L/G ratio of 7.5 providing the optimum desorption of CO_2 from the absorbent water. Contact between O_2 in the air and CO_2 -rich water can therefore effectively separate the CO_2 gas from the absorbent water was previously noted by [14]. The counter current of air and the CO_2-rich water together result in carbonic acid (H_2CO_3) and HCO^{3-} being broken down to form CO_2 gas, and the increased air-flow rate entailed a larger amount of O_2 coming into contact with the H_2CO_3 from the CO_2 saturated water. Hence, the H_2CO_3 transformed into CO_2 gas and water and allowed the gaseous CO_2 to be released from the water which was then able to be re-circulated into the process.

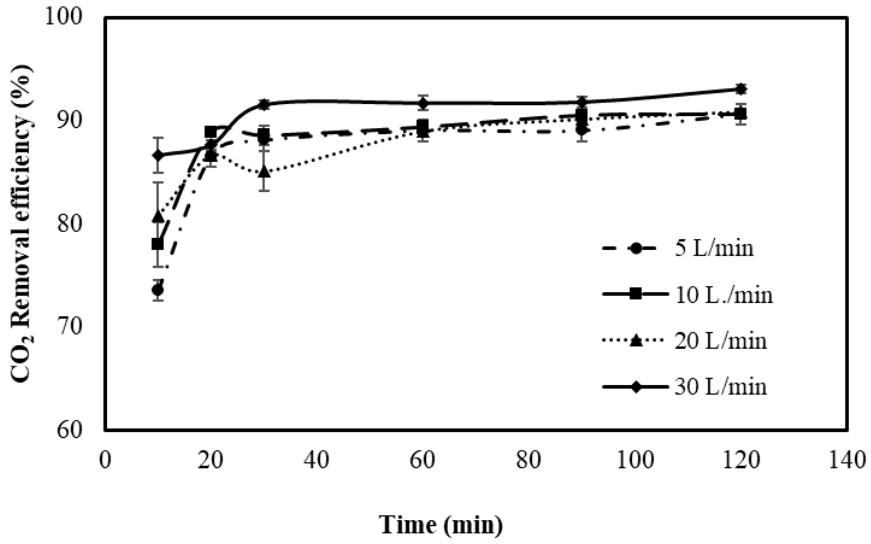

Fig. 3. Effect of air-flow rate into the regeneration unit on CO_2 removal efficiency of the prototype absorption system.

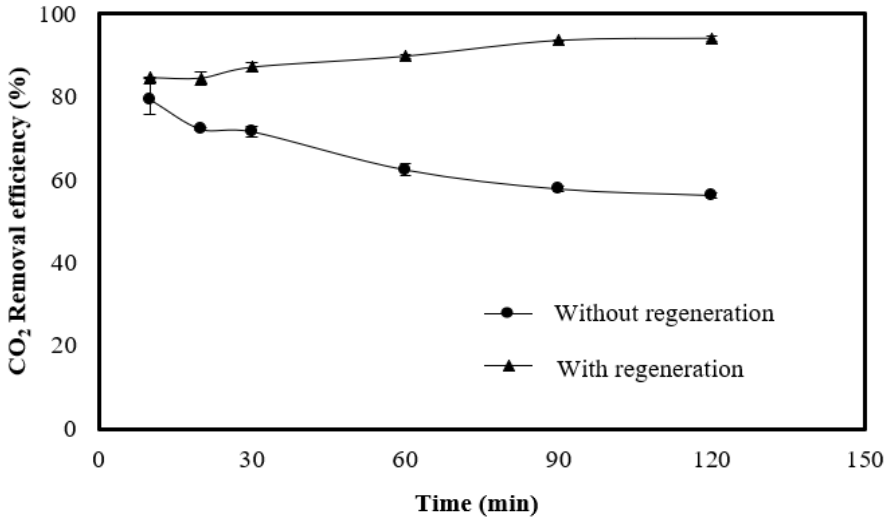

Fig. 4. CO_2 removal efficiency by water absorption unit with and without regeneration of CO_2-rich absorbent.

3.2.3 Comparison result of CO_2 absorption with and without regeneration

The efficiency of the CO_2 removal by the absorption unit was determined by re-circulating the absorbent both with and without the regeneration. The regeneration unit was applied to remove CO_2 from the CO_2-saturated water and the water was continuously recycled back into the absorption system. The air flow rate 30 L/min was used according to the most efficient to create a counter current flow in the regeneration column with the absorbent liquid being sprayed to create water droplets. The system was operated for 120 minutes and the efficiency recorded as shown in Figure 4. The results show that the CO_2 removal efficiency with the regeneration increased from 84.61 to 94.01% whereas without the regeneration the efficiency decreased from 79.42 to 56.21%. This was because recycling the absorbent without the regeneration caused the water to become saturated with CO_2. Thus CO_2 absorption was reduced by continuously re-circulating the saturated water and the CO_2 removal efficiency of the system was decreased.

3.2.4 pH of absorbent water during the regeneration

The comparison of the pH of the water at the inlet and outlet of the regeneration unit over time is presented in Figure 5. The pH of the CO_2 saturated water from the absorption unit was found to be around 6.5 while the pH of the regenerated water was around 6.9 after passing through the regeneration unit for an operation time of 120 min. The level of CO_2 is closely related to the pH of the absorbent water with the pH increasing as the CO_2 content decreases. Therefore, the increase in pH suggests that the regeneration process was successful in removing CO_2 from the water.

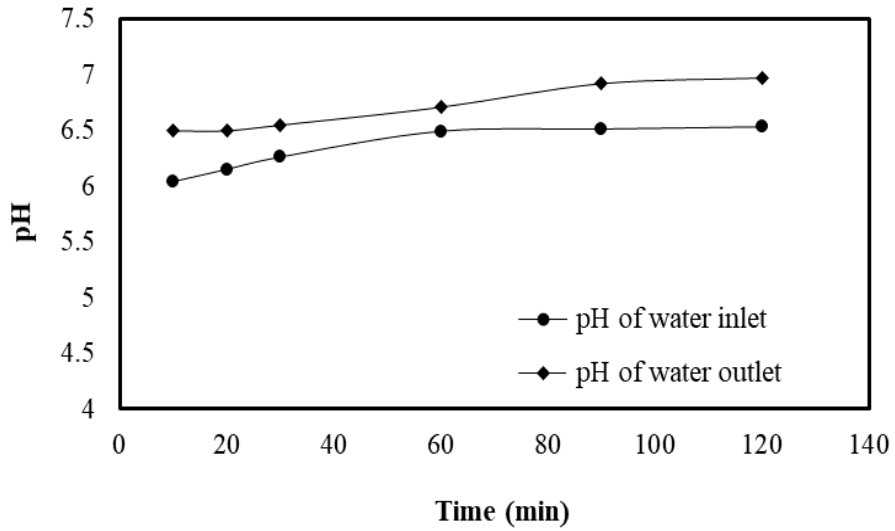

Fig. 5. Comparison between pH of water at inlet and outlet of the regeneration unit.

4. CONCLUSION

This work demonstrated that biomethane can be effectively upgraded by continuous water absorption - regeneration using microbubble technology. A 0.50-inch venturi ejector successfully generated microbubbles in mixture of water and a simulated biogas with an average bubble size of 24.23 µm which enhanced the CO_2 absorption in the water. Gas separation columns with spiral nozzles were used for spraying the absorbing water to separate the treated gas out. It was found that a higher L/G ratio in the absorption system produced better CO_2 absorption. The highest CO_2 removal efficiency of around 95% was achieved at an L/G ratio of 7.50 in the absorption unit. The regeneration unit was found to be most efficient with an air flow rate of 30 L/min, which, when combined with absorption unit at L/G ratio of 7.5, produced the optimum CO_2 removal efficiency. Moreover, the method proposed here for upgrading biogas was able to re-circulate the absorbent water into the absorption process thus maximizing its energy efficiency and reducing both the environmental impact and the cost.

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