

CO₂ Measurement of Synthetic Biogas by Passing It Through Dilute NaOH Solution

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ABSTRACT: *The feasibility of measuring CO₂ content in biogas was evaluated in this research. Firstly, Curtipot pH simulator was used to visualize the titration behaviors of various percentages of dissolved CO₂ in a wide range of concentration of NaOH solution. As a general output of those simulations, it was shown that when the titration curves of different CO₂ content samples are separated enough, titration can provide precise information about the value of dissolved CO₂. In addition, when the ratio of molar concentration of NaOH to the molar concentration of CO₂ is in the range of 1 to 2 (equivalent to stoichiometric ratio of bi-carbonate and carbonate), the separability of the curves is enough satisfactory to be used for precise determination of CO₂; Outside this range, the accuracy of data segregation by titration diminishes. Moreover, when the ratio of molar concentration of NaOH to CO₂ is between 1 and 2, by only a one-time probing, it is possible to determine the concentration of CO₂ in standard NaOH solution. In this case, titration over a wide range of pH, does not provide more reliable and accurate information. The effects of temperature on CO₂ measurement shows that a difference of even 10 °C can only cause less than 1% decrease in CO₂ estimation. Finally, a comparison between gas chromatography and pH measurement was performed and the experimental results showed closeness the results of our proposed method with that of GC (less than 0.05% relative error). This method can be used in designing a non-expensive measuring method that would pave down the road for developing countries.*

KEYWORDS *Biogas; Anaerobic processes; Biogas measurement content; Titration; Gas absorption; Curtipot software*

INTRODUCTION

According to the statistical review of world energy in 2017, the primary energy consumption has increased by 265% from 1965 to 2017 [1]. Meanwhile, world population has more than doubled [2]. These trends have led to an increasing demand for all sources of energy,

including oil, gas, coal, biofuels, and other renewable sources. The only exception is nuclear energy, which has experienced a decline in production [1]. Aside from the energy crisis, the rapid increase in the world's population and consumption has resulted in the generation of more

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waste. In the year 2012, the world's cities produced 1.3 billion tons of solid waste, equal to a footprint of 1.2 kilograms per person per day. With rapid population growth and more urbanization, municipal waste generation is expected to rise to 2.2 billion tons by 2025 [3]. To compound the above-mentioned catastrophic problems, the underscored issue of the depletion of phosphorus resources and the need for the recycling of this element indicate the importance of using and developing renewable processes such as anaerobic digestion all around the world as a way to recirculate elements in short supply and to generate clean energy [4].

Anaerobic digestion consists of a series of biochemical reactions in which biodegradable compounds are converted to methane and carbon dioxide in the absence of oxygen. Anaerobic digestion processes bring several advantages, such as the generation of biogas, lower sludge production, and the capability to treat a wide range of biodegradable organic wastes with different strengths [5]. Despite the considerable pros of anaerobic digestion, due to the high vulnerability of methanogenic microorganisms to reactor operating conditions (such as abrupt changes in pH or temperature, excessive accumulation of - volatile fatty acids) [6], it is essential to monitor key parameters continuously. To obtain the best results, the pH, alkalinity, temperature, rate of biogas production, organic loading rate, oxidation reduction potential, and VFAs should be monitored. Shifts in gas production and composition can be signs of process failure because the decrease or cessation of methane production shows that methanogenic species are no longer working properly. In the case of high alkalinity, pH reduction might not be fast and hence, it might be too late to restore the population of methanogens [7]. Therefore, in operation of biogas plants, it is of prime importance to have the trend of amount of produced biogas and its composition. depending on the source of untreated biogas (swage plant, biogas plant, landfill), it consists of methane (45-70%), carbon dioxide (20-55%), Nitrogen (less than 15%) and other gases (Hydrogen Sulfide, Ammoniac, Hydrogen, etc.) [8,9]. Since more than 90% of this gas consists of methane and CO₂, it could be concluded that the subtraction of CO₂ percentage gives methane content. Thereupon, proposing a simple and inexpensive method of CO₂ measuring decrease the risk of reactor failure. Titrimetric methods has been used for assessing the stability of the anaerobic digesters. Assessment of VFA Content [10-12],

Alkalinity and total CO₂ [13,14], Ammonia nitrogen content [15], or a combination of phosphate, VFAs and more [16,17] shows that using this cost-effective method in assessing the slurry phase condition of bioreactor is well-established. In this article, we are going to propose a single addition method to obtain the CO₂ content of biogas.

The collection of generated gas is the first and most crucial step in the measurement of the gas composition. Volumetric and monometric methods are being used to measure the volume of produced gas [18]. Errors that are commonly made in the quantification of biogas were well discussed in Walker et al. investigation [19]. The collection methods, regardless of further content measurement method, could also be a cause of error in biogas composition measurement. Specially on the laboratory scale, in liquid displacement method, when liquid and gas phases contact, CO₂ can be dissolved into barrier liquid and therefore, the measured CH₄ percentage would be higher than its real value. This could be addressed as the first source of errors in biogas content determination.

There are generally two methods of biogas composition measurement: absorption in a basic solvent (using Orsat) and using GC (Gas Chromatography) [20]. In the first method, CO₂, O₂ and H₂ are absorbed in KOH, alkaline pyrogallol and a CuO column, respectively. This method is relatively simple and there is no need for calibration. However, it is time-consuming and might not be appropriate for daily operation. On the contrary, the main advantage of GC is its fast implementation. Some other advantages of this method are that there is no need for a collecting system and it can be applied to small samples. However, this method requires a certified gas mixture for calibration and high capital investment, which can make it unaffordable for low and medium-size digesters.

Also based on *Parajuli* study, even using GC as a rather costly measurement method, does not guaranty higher accuracy. In addition to errors caused by infusion of air into biogas sample and absorption of CO₂ into barrier liquid, some other sources of error in GC measurement are difference of calibration and gas sample temperature, as well as the presence of some interfering compounds like water in gas sample which are discussed thoroughly in his Thesis [21]. Considering the above-mentioned sources of errors, it is reasonable to introduce a new measurement approach. Since pH meters are cheap devices and because

working with them doesn't require special trainings, using them as a simple tool to measure the CO₂ content of biogas could come in handy in undeveloped countries. In this study, we first investigated the titrimetric simulated behavior of varied concentrations of a CO₂-CH₄ mixture in a range of NaOH solutions in order to visualize the optimum molar concentration of basic absorbent solutions. Then, based upon the developed method through experimental practice, the results were compared from accuracy viewpoint with the reliability of GC.

EXPERIMENTAL SECTION

Principles of measurement

The absorption of carbon dioxide or any acid gas in

NaOH basic solvent is a chemical process. In this process, the CO₂ first reacts with water to form carbonic acid, subsequently reacting with the hydroxides to form soluble salts of sodium carbonate. By-products include both heat and water.

To simulate the titration of H₂CO₃ and NaOH, we used Curtipot which is a titration simulator in Excel Microsoft software [22]. The simulator uses the following equations to calculate H⁺ or OH⁻. Since NaOH was used to absorb CO₂, the solution contains the following ions: Na⁺, OH⁻, H₃O⁺, HCO₃⁻, CO₃²⁻ and H₂CO₃. Since H₂CO₃ is a deprotonated acid, simultaneous solving of mass and charge equilibrium equations without neglecting activity coefficients can give us the pH:

$H_2CO_3 = \frac{f_{H_3O^+}^2 \cdot f_{HCO_3^-} \cdot [H_3O^+]^2 \cdot f_{CO_3^{2-}}}{f_{H_3O^+}^2 \cdot f_{HCO_3^-} \cdot [H_3O^+]^2 \cdot f_{CO_3^{2-}} + K_{a1} \cdot f_{H_2CO_3} \cdot f_{H_3O^+} [H_3O^+] \cdot f_{CO_3^{2-}} + K_{a1} K_{a2} \cdot f_{H_2CO_3}} C_T$	(1)
$[HCO_3^-] = \frac{K_{a1} \cdot f_{H_2CO_3} \cdot f_{H_3O^+} [H_3O^+] \cdot f_{CO_3^{2-}}}{f_{H_3O^+}^2 \cdot f_{HCO_3^-} \cdot [H_3O^+]^2 \cdot f_{CO_3^{2-}} + K_{a1} \cdot f_{H_2CO_3} \cdot f_{H_3O^+} [H_3O^+] \cdot f_{CO_3^{2-}} + K_{a1} K_{a2} \cdot f_{H_2CO_3}} C_T$	(2)
$[CO_3^{2-}] = \frac{K_{a1} K_{a2} f_{H_2CO_3}}{f_{H_3O^+}^2 \cdot f_{HCO_3^-} \cdot [H_3O^+]^2 \cdot f_{CO_3^{2-}} + K_{a1} \cdot f_{H_2CO_3} \cdot f_{H_3O^+} [H_3O^+] \cdot f_{CO_3^{2-}} + K_{a1} K_{a2} f_{H_2CO_3}} C_T$	(3)
$[H^+] + [Na^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$	(4)

$$[H^+] + [Na^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (4)$$

In equations 1-4 C_T is the total molar concentrations of all species of CO₂ present in water (dissolved CO₂-undissociated H₂CO₃-HCO₃⁻ and CO₃²⁻), f is the activity coefficient of species, Ka1 is the dissociation constant of H₂CO₃ and Ka2 is its second dissociation constant.

Table 1 depicts the titration chart that was simulated.

The effect of temperature

Anaerobic processes can operate in a wide range of temperatures (from 5 to 65 °C) [6] since adjusting the environment temperature at 25 °C for conducting the test might not be always possible, We also investigated the effect of temperature on the final estimation of CO₂ content.

The acidic equilibrium constant is a thermodynamic quantity which is influenced by temperature. The basic absorbent solution could be considered an ideal solution

because of its low ionic strength, so the Hernald's equation can be used to calculate the pK of carbonic acid [23]

$$pK1 = \frac{3404.71}{T} + 0.032786T - 14.8435 \quad (5)$$

$$pK2 = \frac{2902.39}{T} + 0.02379T - 6.4980 \quad (6)$$

To observe the effect of the temperature deviation from 25 °C both in the biogas mixture and biogas-NaOH solvent, a set of simulations was also performed as shown in Table 2.

CO₂ measurement procedure

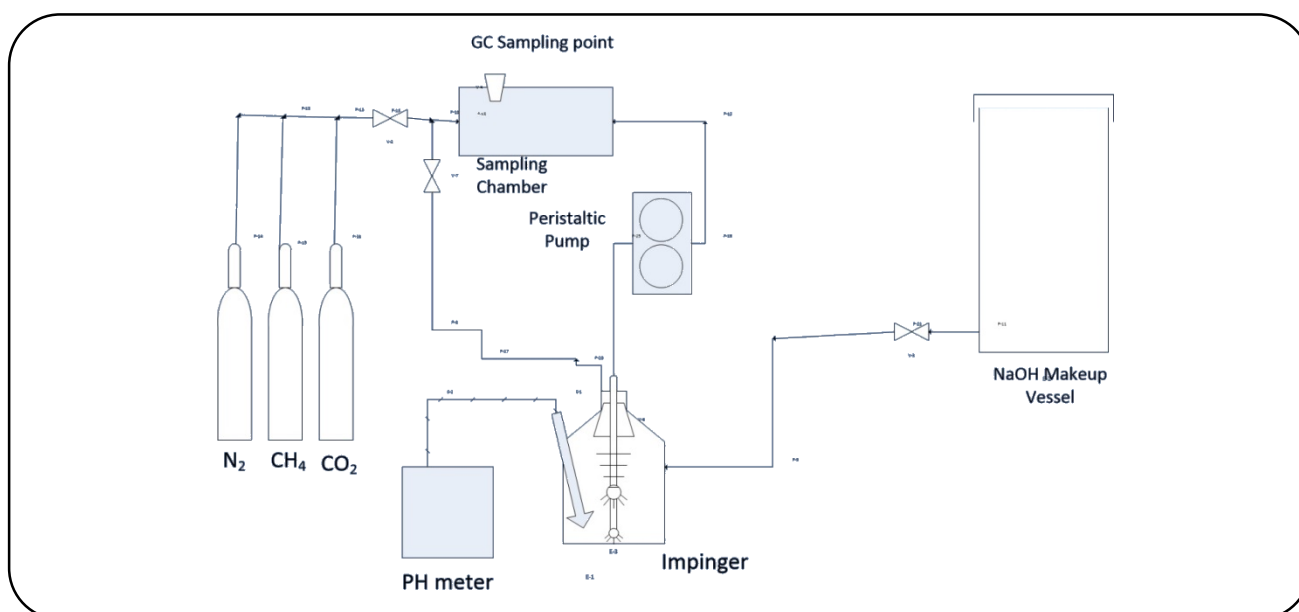
To confirm the plausibility of our proposed method, a set of experiments was performed in order to compare the obtained results from GC. Fig. 1 shows the experimental setup that used to compare the results of two methods. To create an arbitrary mixture, the chamber was first purged by N₂. The CH₄ and CO₂ valves were then adjusted. The pH

Table 1: Concentration of CO₂ and NaOH and acidic titrant used in simulated titration.

Row	NaOH molar concentration (mol/L)	Range of CO ₂ percentage in biogas (%)	Equivalent molar concentration of CO ₂ in solution	Molar concentration of Titrant(mol/L)	Resulted Curve
1	0.0025	25-60	0.0102-0.0245	0.0025	Fig 2a
2	0.01	25-60	0.0102-0.0245	0.0025	Fig 2b
3	0.025	25-60	0.0102-0.0245	0.0025	Fig 2c
4	0.1	25-60	0.0102-0.0245	0.0025	Fig 2d
5	0.0025	25-60	0.0102-0.0245	0.01	Fig 3a
6	0.01	25-60	0.0102-0.0245	0.01	Fig 3b
7	0.025	25-60	0.0102-0.0245	0.01	Fig 3c
8	0.1	25-60	0.0102-0.0245	0.01	Fig 3d

Table 2: Simulated condition to obtain temperature effect.

Phase	CO ₂ range (%)	NaOH (mol/L)	Temperature (°C)
Gas sample	20-60	0.025	20-25-30
Solution	20-60	0.025	20-25-30-35-40-45-50

**Fig. 1: Experimental pilot plant utilized in this study.**

of the CO₂-NaOH solution was measured with a pH meter (SCHOTT-CG 825) and the composition of the mixture (CH₄ and CO₂) was analyzed by a gas chromatograph (PERICHROM-PR2100) equipped with a thermal conductivity detector. To ensure accurate results, the preparation of the samples was performed scrupulously. Ten experiments were conducted by considering the following measures: The basic solution was tried

to be prepared absolutely free of carbon dioxide. Since basic solvents are prone to absorb CO₂ from the atmosphere, it was pivotal to keep them in a fully sealed container. The NaOH solution was made according to Standard Method 2310.b [20]. The pH meter was calibrated with its calibration buffer solution before use. The gas sample was circulated for 3 minutes to ensure complete absorption. In order to get desirable result, it was tried to perform all

experiments exactly in 25 °C (for both gas sample and absorbent liquid) and the NaOH solvent has a normality of 0.025 mole/L.

RESULTS AND DISCUSSION

To visualize the optimum initial concentration of the NaOH solution, the titration curves for CO₂ and NaOH were presented (Figs. 2 and 3). In order to compare the curves separability of different scenarios properly, the range of vertical ordinates of all figures were equalized to six pH units. One liter of biogas in sampling chamber with a volumetric percentage between 20 to 60% of CO₂, has 0.00817 to 0.00245 mole CO₂. Accordingly, the NaOH solutions with molar concentrations of 0.0025 to 0.25 was considered to be absorbent in order to examine the titration behavior. Two different concentration of HCl (0.0025-0.01 mol/L) as titrant was used to investigate the behavior of NaOH-H₂CO₃ curve in pH range of 13.5 to 4. Figs. 2 and 3 represents curves based on Table 1. The obvious result of these simulations shows that when curves are separated enough, titration can provide precise information about amount of dissolved CO₂ (Figs. 2c and 3c illustrate this fact). Besides, Figs. 2c and 3c make it clear that when the ratio of molar concentration of NaOH to CO₂ is between 1 and 2, the separability of datum allows to determine CO₂ content with 1% precision. In other words, the pH measurements are made with a precision of 0.01 pH for each solution, allowing to determine the CO₂ concentration within 1%. Outside this ratio the ability of titration to segregate data diminishes. As can be seen in Figs. 2a, 3a, 2d and 3d, because of slight change in pH, it is hard to find corresponding CO₂ concentration. Figs. 2c and 3c also show that when the ratio of NaOH to H₂CO₃ is near its stoichiometric value, a pH meter can be used to determine the concentration of CO₂ by a one-time probing. In this case, titration by acid does not provide more information. After carbon dioxide dissolves into an aqueous environment, the problem will reduce to obtaining total carbon dioxide in aqueous phase. In this case many convenient methods are available to measure the dissolved CO₂ in aqueous environment. *Liat Brinkhat* [14] listed the different methods of measuring H₂CO₃ in his article. Based on his classification, the method used in this article could be best classified under Single Addition Technique (SAT). In SAT first introduced by *Anderson* in 1946, a known volume of strong acid is added to a known

volume of water. Assuming no CO₂ stripped from the sample (constant CO₂) the amount of H₂CO₃ alkalinity is obtained from final pH [24]. Some advantages of this method are its simplicity and low cost, and ability to provide data with high time resolution. Drawbacks of this methods are that it requires precise laboratory work and it is dependent on pH measurement. However in pervious works, the measurement was based on addition of a strong acid to a sample with unknown ions, however in measuring H₂CO₃ from absorption of CO₂ in a prepared NaOH solvent, all variables except H₂CO₃ is known. So errors associated to the interferences of other weak acid-base conjugates (like VFAs, silicate, phosphates and ammonium) will not affect the final result. Moreover, error associated with loss of CO₂ due to pH drop will not be present in our method because the pH of the solvent even after adsorption will be above 8 (NaOH concentration=0.025 and H₂CO₃=0.025), where H₂CO₃ is around 500 times less than HCO₃⁻ and so the risk of CO₂ escape is negligible.

Figs. 4a and 4b show the change in pH by one-percent change in CO₂ concentration when the basic solutions are 0.025 and 0.01 mol.L⁻¹ NaOH respectively. As it can be seen, in range of 20 to 70% CO₂, the corresponding pH change is more than 0.05 pH unit. Accordingly, a change of 1% in the concentration of CO₂ is equivalent to at least a change of 0.05 in the pH value of the solution and this change in pH allow us to associate pH to CO₂ concentration. Between pH=7.5 to 11.5. There are two maximum in ΔpH-CO₂ curves. For both figures these are the points in which the first and second equalization reaction completed (carbonate to bicarbonate and bicarbonate to carbonic acid). The key for more accuracy in this method is sensibility of pH due to change in CO₂ and this happens when H₂CO₃-NaOH system has low buffer capacity. Aquatic solution of high (or low) pH are resistant to pH changes, so cannot be used for determination of CO₂. Comparison of Figs. 4a and 4b also indicates that despite higher sensibility of more dilute solutions (Fig. 4b), they do not cover a smaller range of CO₂ concentration for a one-liter sample. So in case of using smaller biogas samples one should consider that the average molar ratio of H₂CO₃-NaOH remains in range of carbonate and bicarbonate equilibrium point.

Fig. 5 shows the effect of temperature deviation of gas samples from 25 °C. From Boyle's law it is known that

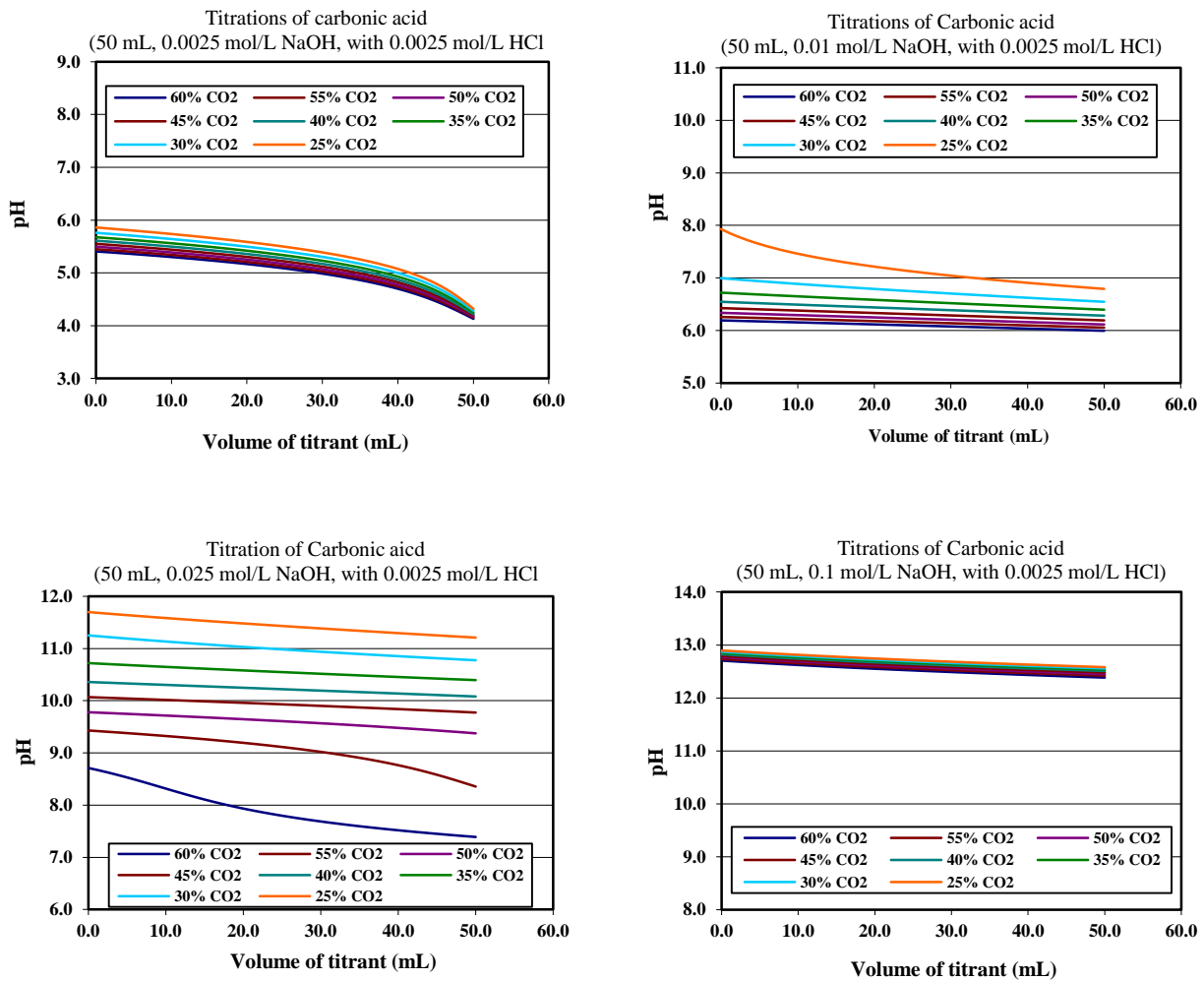


Fig. 2: Titration curves of different CO₂ and NaOH concentration with 0.0025 mol/L HCl.

by increasing the temperature in a rigid chamber (resembling constant volume), molar amount of gas decreases. As a result, there would be less CO₂ to be solved in solvent, therefore, the pH deviation increases slightly as CO₂ percentage decreases. However, even in a 60% CO₂ sample, a difference of 10 °C causes no more than 2% error. Table 2 shows calculated pH in three different gas temperatures. To fix this problem, the true percentage can be calculated as Equation (10) and after that the obtained results can be used to determine CO₂ percentage in STP condition.

$$\%pH_{\text{real}} = \%pH_{\text{measured}} \times \frac{T_{\text{measured}}}{T_{298}} \quad (7)$$

Fig. 6 shows the deviation of the solution temperature from 25°C. Since anaerobic digesters operates at a wide range of temperature and the environment in which pH

measurement conducted might not be fixed, it is important to see how NaOH-H₂CO₃ solvent temperature deviation from 25°C insert error in estimated CO₂ percentage. It is obvious that by increasing the solution temperature the obtained pH was decreased. However, this shift is not uniform in the whole range. When CO₂ percentage is less than 29, the difference in pH is negligible (less than 0.05 unit of pH) but this deviation enhances as CO₂ percentage increases. The curves cluster again converge from 55%. It is worth noting that even a change of 10 °C would not cause a major difference in final results. For instance, when pH is 10, its corresponding CO₂ percentage for a 25 degree-one-liter chamber is 43% in a 20 °C solution and 41.5% in a 30 °C. This difference reaches to 3.5% if the obtained value for a 20 °C solution compared with a 50 °C solution

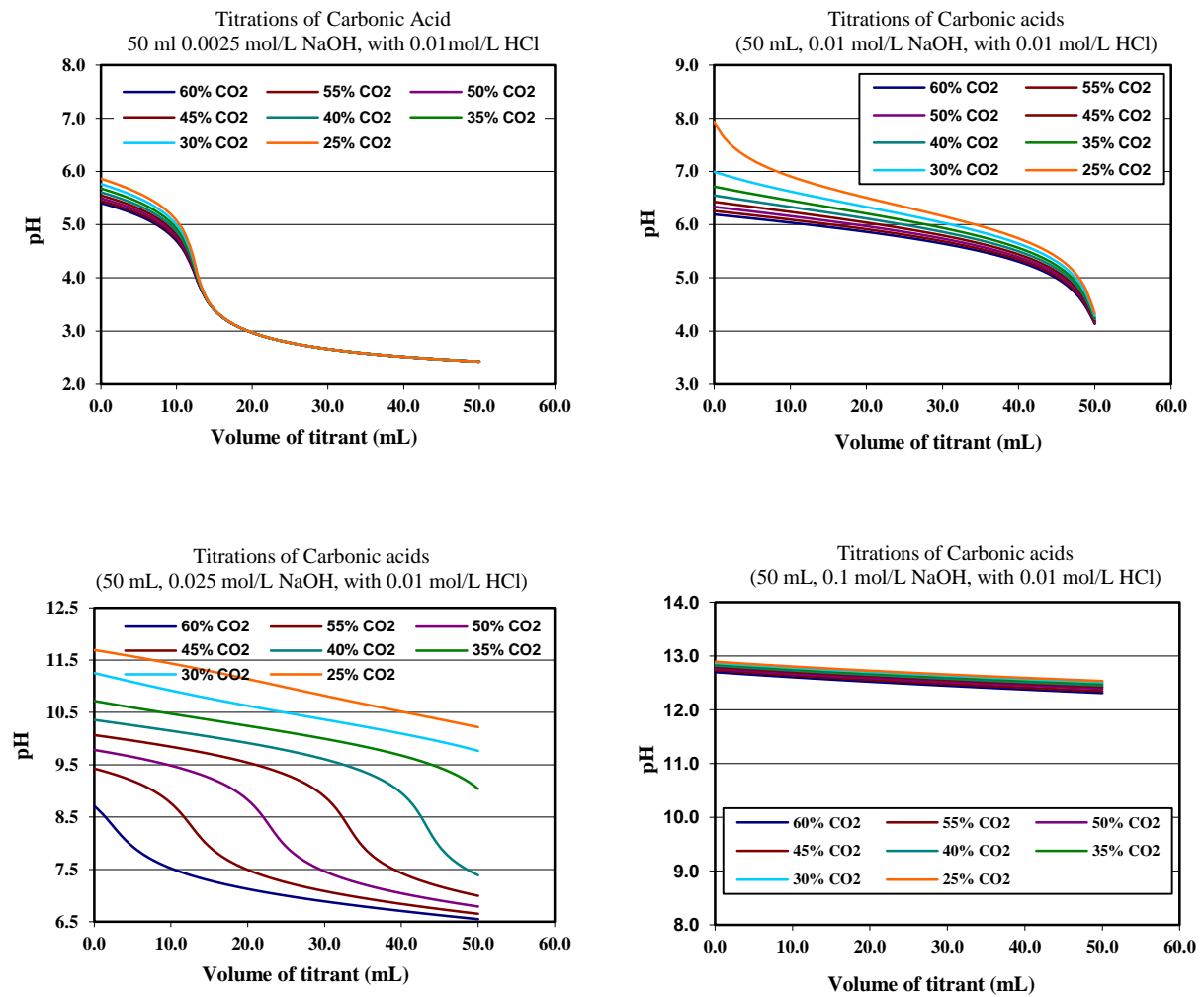


Fig. 3: Titration curves of different CO₂ and NaOH concentration with 0.01 mol.L⁻¹ HCl.

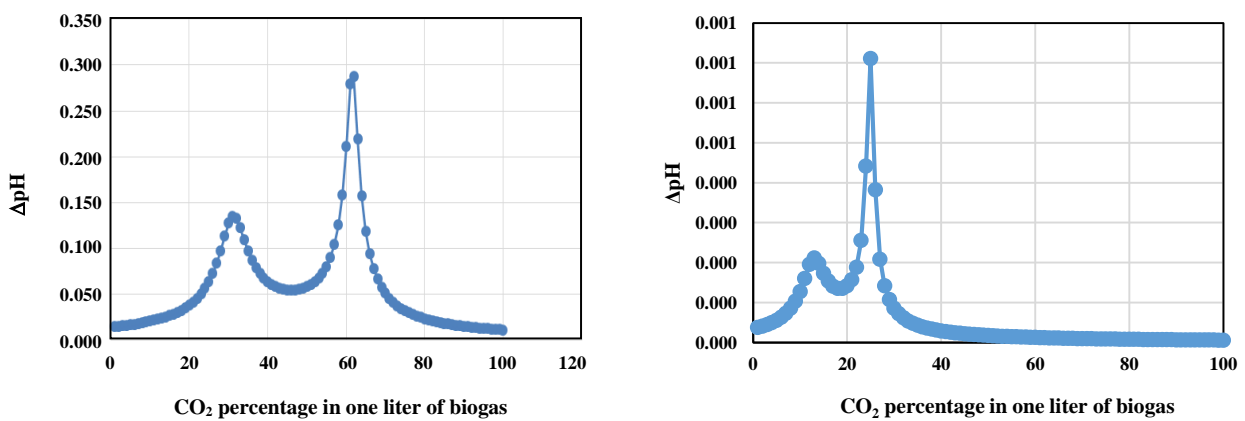
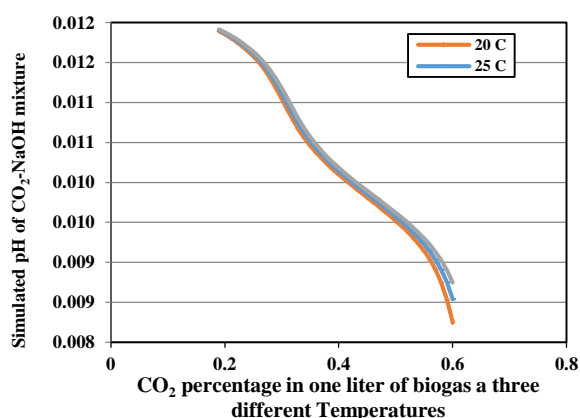


Fig. 4: Sensibility of change in pH by one-percent change in CO₂ percentage.

Table 3: result obtained by GC and pH measurement method.

pH measurement	Results by interpolation	GC results	Absolute error
8.55	0.60	0.603	0.003
8.92	0.58	0.580	0.000
9.33	0.54	0.535	-0.005
9.65	0.49	0.491	0.001
9.80	0.46	0.460	0.000
9.97	0.43	0.429	-0.001
10.15	0.40	0.401	0.001
10.43	0.36	0.363	0.003
10.85	0.32	0.319	-0.001

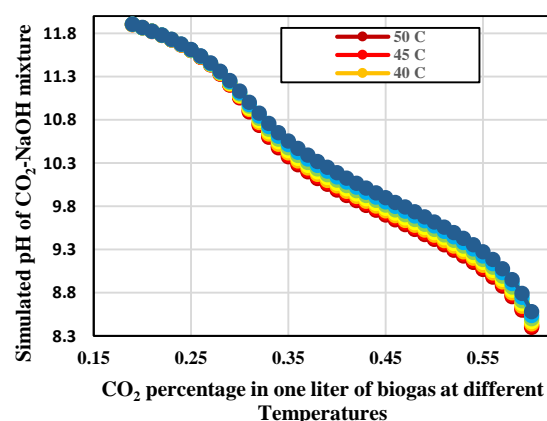
Fig. 5: Calculated pH of 20-60% CO₂ at three different temperature of gas sample.

(39.5% vs. 43%). So it is recommended to conduct the experiment when the solution temperature is near 25 °C or to use curves in Figs. 2c and 3c.

Table 3 compared result obtained by GC and pH measurement method within specified CO₂ range. In all cases the obtained results from pH measurement method was in accordance with GC. The upper and lower absolute errors within range of 25-60% CO₂ were less than 0.005% CO₂. Watanabe et al reported a precision of 2 μmol/L by their automatic flow-through analyzer developed for determination of sea water alkalinity provided that appropriate standard solutions are used [25]. As a result our proposed method can be used to measure CO₂ content of biogas with precision comparable with GC.

CONCLUSIONS

In this research CO₂ absorption by a basic solution and the measuring of the pH used to determine the CO₂

Fig. 6: Calculated pH of 20-60% CO₂ at three different temperature of absorbent solvent.

percentage in biogas with an acceptable degree of precision and accuracy. It is important to be scrupulous while preparing and storing of NaOH solution. The operator must be trained to read and interpret the CO₂-NaOH tables. The low cost of the equipment used in this method would make it possible to be employed in small and medium sized digesters especially in less developed countries. It was shown that when the stoichiometric ratio of Nbase/NCO₂ is around 2, the separability of the data is the greatest. It was also shown that this method is not very sensitive to temperature and in the case of deviations from 25°C (a lab standard temperature), the error can be compensated for by a simple proportion. Some other errors that might influence the final results are the infiltration of air into the digester and the release of too much NH₃. However, these errors can also affect other measurement methods, like GC and Orsat if they are not correctly calibrated.

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