Factors Influencing Chemical Absorption of CO_2 and H_2S in Biogas Purification: A Review

O.I. Maile, H.B. Tesfagiorgis, and E. Muzenda

Abstract—**Absorption is a process in which a substance (solute) is brought into contact with a solvent normally for a purpose of separation. pH and concentration of the solvent, temperature of both the gas and the solvent, and absorbing surface area influence the absorption process. Any deviation of pH from the optimal level by adding acid or base into the system can lower the absorption rate. Concentration of carbon dioxide in the gas stream and the loading rate influence the rate of absorption. Monoethanolamine (MEA) has an optimum absorption rate at liquid temperature of 35 ˚C. Ammonia has high removal efficiency at ambient temperature and there exists a direct relationship between absorption rate and temperature. Absorption of CO_2 with sodium hydroxide is normally done at a temperature range of 1─16 ˚C (30─60 ˚F). Calcium oxide requires high temperature for absorption ranging from 300─390 ˚C, while 22─80 ˚C is used for H_2S absorption with K_2CO_3. A linear increase results from heating the CO_2 gas stream prior to absorption. The rate of absorption is influenced by the contact area between the absorbing fluid and the gas.**

Keywords—**Absorption rate, efficiency, solvent, temperature**

I. INTRODUCTION

Absorption is a process in which a substance (solute) is brought into contact with a solvent normally for a purpose of separation, which can be either physical or chemical. Physical absorption occurs when a gas is absorbed into a liquid with no reaction taking place. For instance, carbon dioxide is absorbed into water. On the contrary, a chemical reaction occurs when the gas is absorbed into the solvent for chemical absorption. An example is carbon dioxide absorption into alkanolamine solutions [1]. For gas absorption to occur, the gas is firstly contacted with the liquid through bubbling or passing it over streams of the liquid [2]. A counter current flow configuration is normally preferred in absorption mainly because a large surface area for mass transfer is needed for an effective absorption.

Factors affecting absorption include pH of the solvent and the concentrations and temperatures of both the gas and the solvent [3]. Reference [4] suggested that different solvents perform differently upon heating and that the temperature of both phases influence the reaction mechanism. Subsequently, rate of absorption involves a complex relationship between time, turbulence and temperature. Reference [3] studied the effect of temperature in the ranges of 25-75 ˚C and recorded that 75 ˚C resulted in best absorption. Therefore an opportunity to investigate temperatures above 75 ˚C exists.

NaOH is a good CO_2 absorbent, but KOH proved to be even better because when it is used for the same process, it captures 27% more CO_2 and only uses 125 kWhr/ton CO_2 energy [4]. A solvent is considered economically attractive if it has low energy requirements, can be regenerated easily, does not impose environmental impacts and cost effective.
The purpose of this work was to unpack the factors that affect absorption of CO_2 and H_2S into chemical solvent for biogas purification. With the main focus being temperature, concentration and pH of the liquid without neglecting the gas phase. This work will, however, be further studied in laboratory conditions at a later stage to validate the results with available literature.

II. FACTORS AFFECTING THE ABSORPTION

A. *pH of the solvent*

The pH of the solvent affects the absorption process and, therefore, the absorption rate. Addition of acid or base leads to low absorption rate [3]. When KOH and NaOH were used, the optimum pH was found to be 13.3 and 12.9, respectively [5]. Ammonia and amines had the best pH value of 11.5-12 [3]. In a study conducted by [6] reaction kinetics of H_2S with ferric chelates of EDTA and HEDTA were established. From a stirred cell reactor with a varying pH (4─10), it was established that pH plays an important role in oxidative absorption.

B. *Concentration of the absorbent*

Concentration plays an important role in absorption. Factors that affect the absorption include: (i) gas loading rate, (ii) increase in solution viscosity which decrease diffusion coefficient and absorption rate [7]. H_2S absorption rate is directly proportional to the concentration of K_2CO_3 in

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the solution [7]. The same authors further showed that the rate of CO_2 absorption increases initially and then decreases as the concentration solution increase. It must be taken into account that the concentration of the CO_2 in the gas stream influences the absorption rate [8] - [9]. Since the absorption of CO_2 decreases towards the end of the cycle, its concentration in the solution may increase at that stage [8]. The absorption effect increases with higher absorption rate for MEA, DEA and NH_3(aq) to the range of and mol/sec/cm^2 [3].

C. Reaction temperature

Temperature is an important parameter of any chemical, biological, and physical reactions. Chemical absorption is influenced by temperature and the different absorbents behave differently at particular temperatures. The effect it has is discussed below:

Amines

Monoethanolamine (MEA) is a primary amine commonly used as a solvent in chemical absorption. Reference [3] studied absorption of MEA at temperature range of 25─75 ˚C and 15% gas concentration at a flow rate of 2L/min together with 30% solvent. MEA proved to be a good absorbent. An absorber- desorber setup containing packed absorption column with 6 theoretical stages and packed desorption column of 10 theoretical stages was used [10] for simulation of the absorption process with MEA. A typical schematic diagram is shown in Fig. 1. Reference [10] studied the ratios of solvent to CO_2 and observed a linear and direct proportion relationship at a fixed temperature of 20 ˚C. A removal efficiency of 80% has a MEA to CO_2 ratio above 3, with a solvent concentration of 20% wt required [10]. As a comparative study between MEA and NH_3, ammonia performed better at 20 ˚C by having higher removal efficiency. Reference [11] reported that increasing the liquid temperature to 35 ˚C improved the absorption reaction rate, but a decline in the absorption rate was observed for temperatures more than 35 ˚C. An inverse relationship between temperature and absorption rate was observed by [12]-[13] as a result of the reaction zone relocation in the absorption column.

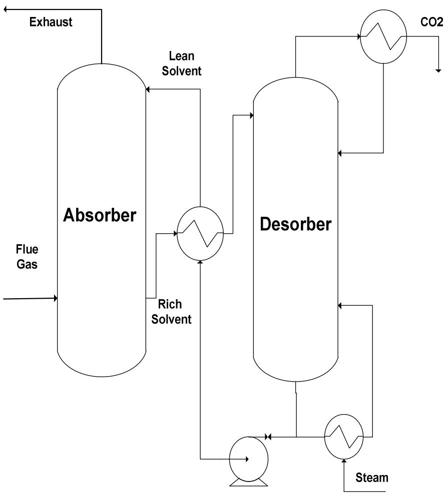

Fig. 1. Schematic diagram of absorption section for CO_2 scrubbing with MEA and DGA solutions.

Ammonia

Ammonia can be used to reduce all acid pollutants in gases with CO_2 included. Reference [3] used 3% aqueous NH_3 solvent at temperatures of 25, 50 and 75 ˚C. They observed that absorption rate is directly proportional to the temperature. It has also been reported that ammonia has a better absorption capacity and best absorbent qualities [3], [10], [14]. According to [10], the advantage of using ammonia is that it has low energy requirements for absorption. In a simulation study, using solvent concentration of 0.02─0.2 % wt, the same researchers showed that ammonia had very high removal efficiency at ambient temperature. They further mentioned that 80% removal efficiency was achieved, which means a ratio of 1.5 NH_3 to CO_2 requiring 7% wt solvent.

Sodium Hydroxide

Sodium hydroxide reacts with carbon dioxide by path shown in Eqs (1) to (3) which is first order with respect to CO_2 and OH [15].

$$CO_2 + OH^- \rightarrow HCO_3^- \quad (1)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad (2)$$

$$CO_2 + 2OH^- \rightarrow CO^{2-} + H_2O \quad (3)$$

Temperature range between -1─16 ˚C (30-60 ˚F) was used for absorption of CO_2 in sodium hydroxide. The rate of absorption increases with the increase in temperature. The relationship between the temperature and absorption cycle, demonstrated that an increase in temperature often result in a gradual decrease in the rate of CO_2 absorption at the later stages of the cycle [8]. The temperature of the absorbing fluid is also related to the absorbing system design. The rate of CO_2 absorption by sodium hydroxide decreases with absorbent utilization during the process. This is a result of the increased concentration of sodium carbonate and all of the sodium hydroxide has completely reacted to form sodium carbonate [8]. Absorbing fluid temperature also affect the formation of sodium carbonate precipitate, a higher temperature has less capacity to form precipitate when compared to lower fluid temperature [8].

Calcium Oxide and Calcium Hydroxide

When calcium oxide is used to absorb CO_2, the process is reversible and occurs according to the following reaction:

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} \quad (4)$$

Sometimes the $CaCO_3$ reacts when it is exposed to water vapour and can result in the formation of $Ca(OH)_2$ as shown in Eq. (5).

$$CaCO_{3(s)} + H_2O_{(g)} \leftrightarrow Ca(OH)_{2(s)} + CO_{2(g)} \quad (5)$$

CaO_3 is effective in absorbing CO_2 completely, but a penalty of high heat requirements has to be paid. According to a study conducted by [16], temperature range of 300─390 ˚C is required. Thus, it can be said that CO_2 absorption rate is dependent on temperature. The extent of CO_2 absorption (X_{CO_2}) by CaO and $Ca(OH)_2$ as a function of temperature.

More CO_2 is absorbed during the early stages of the absorption process and a substantial decrease occurs thereafter and X_{CO_2} increases with temperature [16]. The reaction between calcium hydroxide and carbon dioxide occurs at a faster and higher conversion degree than calcium oxide [16]. Thus, it can be said that $Ca(OH)_2$ captures more CO_2 as compared to CaO as expected and supported and by other researchers [18].

Potassium Carbonate

In a study conducted by [7], K_2CO_3 was used to simultaneously absorb H_2S and CO_2. They observed that increased temperature caused a quick increase in absorption rate of CO_2 while that of H_2S decreases slowly. CO_2 absorption is liquid-phase mass transfer coefficient and H_2S is gas-phase mass transfer. A temperature range of 22-80 ˚C was used. The use of hot solvent is an advantage as it not only increases the rate of absorption but also makes regeneration less costly as lower energy requirements exists [7].

Iron chelates

When $FeCl_2$, $FeCl_3$ or $FeSO_4$ are added to the digester, FeS forms a precipitate which is removed with the digestate because it is insoluble. Ferric chelates can also be used for H_2S absorption. The process is normally operated at a temperature range of 20-60 ºC, a pH between 4-8, with iron concentration of 1000-10000 ppm and molar ratio of 1.1-2.0 [18]-[19]. Reference [19] proved that the removal of H_2S at both low and high concentration is possible with the ferric chelate oxidative absorption process. Equations 6 and 7 shows the absorption and regeneration process of the chelate respectively. Where the

$$H_2S_{(aq)} + 2Fe^{3+}Chelant^{n-} \rightarrow S\downarrow + 2H^+ + 2Fe^{2+}Chelant^{n-} \tag{6}$$

$$O_{2(aq)} + 4Fe^{2+}Chelant^{n-} + 2H_2O \rightarrow 4Fe^{3+}Chelant^{n-} + 4OH^- \tag{7}$$

Heated CO_2

Reference [4] investigated the effect of heating the CO_2 gas stream prior to absorption at 25─55 ˚C. They observed that a 33% linear increase for 0.8 lpm liquid load. They further reported that higher liquid loads of 1.4 and 1.8 lpm reduced the heating effect as it resulted in absorption rate increase by 20% and 3% respectively. They believed that this was due to the kinetic energy attained at the reaction zone as the molecules diffuse faster. As a result of the hot CO_2, formation of carbonic acid is enhanced as heat is transferred to the mixture.

Absorbing surface area

Surface area is an important aspect of any chemical reaction. The rate of absorption is influenced by the contact area between the absorbing fluid and the gas. Consequently, surface contact area is proportional to the rate of absorption [8]. Thus, the absorption column configuration also plays an important role in absorption rate.

III. ENERGY DUTY REQUIREMENTS

Thermal energy input required for complete $CaO-CaCO_3$ thermochemical cycle is 10.6 MJmol-1 of CO_2 captured. The required thermal energy input for solvent regeneration leads to an energy penalty ranging from 4-5 GJ/t CO_2 captured in post combustion CO_2 capture using amines. This applies for the traditional absorber-desorber process [10], [20]. However, absorption process with ammonia has lower energy requirements because it does not require solvent regeneration heat and separated CO_2 compression. Subsequently, ammonia process requires a great amount of water for exhaust gas washing to prevent emissions to the atmosphere [10]. This, however, still makes the ammonia process economically attractive [21]. Energy requirements for gas scrubbing using alkali metal hydroxide solutions range between 30 to 390 kJ/mol [22].

IV. CONCLUSION

Chemical absorption has been used in biogas purification and upgrading worldwide. Effective as it is, there are some factors that can influence its efficiency. These factors include: pH of the solvent, concentration, temperature of both the gas and the solvent, effect of heated carbon dioxide and absorbing surface area. Concentration of carbon dioxide in the gas stream and the loading rate influence the rate of absorption. The rate of absorption increases with the increase in temperature. A linear increase results from heating the CO_2 gas stream prior to absorption. The rate of absorption is influenced by the contact area between the absorbing fluid and the gas.

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