Potential of 2-Amino-2-Methyl-1-Propanol Solution as Absorbent for CO₂ Absorption from Biogas

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Abstract. Biogas is a source of clean energy that mainly consists of methane (CH₄) and carbon dioxide (CO₂). However, the presence of CO₂ in biogas limits the heating value of the gas. Thus, biogas upgrading is a crucial process for reducing the CO₂ content in raw biogas for purified biomethane production. Chemical absorption is a matured technology for CO₂ removal process. The selection of chemical solvent with desirable characteristics is a substantial consideration for the effectiveness of the process. In this work, a potential solvent, 2-amino-2-methyl-1-propanol (AMP) was tested for the removal of CO₂ from simulated biogas. The absorption process was conducted at different gas flow rates (22.1 kmol/m².hr and 26.5 kmol/m².hr) in a packed column at an operating pressure of 2 bars. The performance was evaluated in terms of percentage of CO₂ removal along the column. It was found that the CO₂ removal performance decreased by about 15 % at higher gas flow rates. Besides, the absorption efficiency of AMP was also compared with a well-established solvent, monoethanolamine (MEA). The experiment substantiated that 30 wt.% MEA effectively captured CO₂ with 100 % removal as compared to 30 wt.% and 40 wt.% AMP with only 69 % and 87 % removal. In order to achieve high reaction rate for efficient CO₂ removal, the addition of activator to form a blended amine solution with AMP was suggested to accelerate the CO₂ absorption performance.

1. Introduction

In this era, world energy demand has increased rapidly due to the annual growth of population with 88 % of the energy supported by fossil fuels [1]. However, intensive combustion of fossil fuel emits large amounts of greenhouse gases (GHG) to the atmosphere, consequently leading to several environmental problems [2]. Due to this reason, numerous studies are being conducted in finding an alternative energy source to balance human needs and environmental health. Therefore, special attentions have been centered on the development of renewable energy. Biogas is one of the environmental friendly methane resources produced by the conversion of organic matters via biological processes. The constituents of raw biogas are mainly methane (CH₄) (40 % – 85 %) and carbon dioxide (CO₂) (15 % – 60 %) with other trace amounts of impurities such as hydrogen sulphide (H₂S), nitrogen, oxygen and vapour [3]. Energy from biogas can be utilized in many applications, including power generation, transportation,
residential and industrial with low environmental impact. However, the presence of noncombustible gases (i.e. CO₂, nitrogen, moisture and oxygen) limits the energy efficiency of the biogas [4]. Since CO₂ is the major component in biogas, it plays a significant role in reducing the heating value, flame velocity, ignition limit and causing equipment corrosion [5], [6]. Hence, CO₂ reduction in the gas is an essential process to improve the quality of the biogas and meet the standard for marketability (upgraded biogas with > 95% CH₄).

Several biogas upgrading technologies have been implemented, for instance the process of adsorption, absorption and membrane separation. Among these technologies, chemical absorption is the most mature technology for CO₂ removal in gas streams due to high selectivity of CO₂ (higher purity), fast absorption rate, and lower CH₄ losses [7], [8]. The basic principle of chemical absorption is as described by the two-film theory, of which it explains the mechanism of CO₂ molecules that diffuse through the gas and liquid films to react with chemical solvent in forming covalent bonds [9]. Additionally, CO₂ is absorbed to the solvent from the up flowing gas and the captured CO₂ is then released upon heating in the subsequent regeneration process.

Alkanolamine-based solvents are remarkable for CO₂ capturing process such as monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), methyldiethanolamine (MDEA) and diisopropanolamine (DIPA). These solvents can be further classified into primary, secondary and tertiary group of amines according to their chemical structures. Each solvent behaves differently and their reaction mechanism with CO₂ is unique based on their chemical properties [10]. For instance, MEA, a primary amine, has received the most attention and is widely used in industry due to its higher rate of reaction and cost-effectiveness [11]. However, the maximum CO₂ absorption capacity in MEA is limited by stoichiometry to 0.5 mol CO₂/mol MEA. Besides, MEA also suffers from the corrosiveness of the solvent as well as higher degradation rate [12]. Hence, an alternative solvent with good characteristics is currently being investigated by researchers to replace MEA.

Other than alkanolamines, sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) was proven to have the ability to capture CO₂ from flue gas. AMP is one of the commercially attractive solvents due to its higher absorption capacity with 1 mol CO₂/mol AMP, lower degradation rate and lower corrosivity as compared to MEA [12], [10]. It has been tested for CO₂ removal from flue gas at low CO₂ concentrations in the range of 4 % – 18 % [13], [14], [15], [16], [17], [18]. Despite the chemical properties, process parameters such as gas flow rate and amine concentration also need to be considered for a promising removal performance. In Kasikamphaiboon et al. [19] experimental studies, the CO₂ absorption process was conducted using MEA solvent at various gas flow rates, which found that the CO₂ removal efficiency decreased with increased gas flow rate. Moreover, numbers of studies have reported the CO₂ absorption performance to increase linearly with increased amine concentration [20], [13], [21].

In this work, the potential of AMP solution as absorbent for CO₂ removal from biogas was tested in a designated packed absorption column at 2 bars operation. Process screening was conducted on the effects of gas flow rate and amine concentration. Besides, a comparative study on the CO₂ removal percentage was also presented by comparing the absorption performance of AMP (30 wt.% and 40 wt.%) and established MEA solution (30 wt.%). Absorption efficiency profile was reported in terms of CO₂ removal percentage (%) along the height of the column.

2. Materials and methods

2.1. Chemical and gases

The chemicals used in this study were MEA (99 % purity) and AMP (95 % purity), purchased from Merck, Germany. The CO₂ and natural gas (NG) with 97 % CH₄, 2 % CO₂ and 1 % heavier hydrocarbon were bought from Air Product Malaysia Sdn. Bhd. and PETRONAS Dagangan Sdn. Bhd., respectively. No further purification of chemicals and gases were performed for the purpose of experimental work.
2.2. Equipment and procedures
A packed absorption cylindrical column fabricated from 316 stainless steel was used for all experiments. The packed column was designed with a packing height of 2.04 m and internal diameter of 0.046 m. For sampling purposes, six sampling points with equally spaced interval of 0.34 m were tapped along the column. The packing section was packed with Sulzer metal gauze packing (Sulzer Chemtech Pte Ltd., Winterthur, Switzerland) as shown in Figure 1 and had a surface area of approximately 500 m²/m³.

Figure 1. Sulzer metal gauze packing [22].

Figure 2 shows a schematic diagram of the experimental setup to evaluate the CO₂ absorption performance. The desired composition of simulated biogas was prepared by setting the mass flow controllers for the inflow gasses (NG and CO₂) independently. The gas mixture was pressurized by a compressor and retained in a gas vessel at 30 bars. The gas mixture was introduced at the bottom of the column and flowing in a bottom-top motion. Simultaneously, the liquid solvent was introduced at the top of the column and flowing in a top-bottom motion, to create a counter-current flow configuration between gas and liquid with the respective flow rates. The CO₂ absorption experiments were expected to reach steady state conditions upon operation for 30 minutes. CO₂ concentrations in the gas phase were sampled along the column using an online CO₂–CH₄ Infrared (IR) Gas Analyzer (Fuji Electric Instrument, Japan). The treated gas and CO₂-rich solvent exited the column from the opposite directions of entry for both gas and liquid.

The simulated biogas containing 40 vol.% of CO₂ in the NG was used for all CO₂ absorption experiments. The operating pressure was maintained at 2 bars in the column. The effect of gas flow rate on CO₂ removal efficiency was conducted using 30 wt.% AMP solution. The gas flow rate was controlled at 22.1 kmol/m².hr and 26.5 kmol/m².hr while the inlet liquid flow rate was fixed at 3.61 m³/m².hr. Meanwhile, the comparative studies on the CO₂ removal efficiency between AMP and MEA were conducted using 30 wt.% and 40 wt.% AMP solutions and were compared with 30 wt.% MEA solution.

The CO₂ concentration in the gas phase was recorded at each sampling point along the column. Based on the data collected, the absorption performances were analyzed in terms of CO₂ removal percentage along the column, calculated using Equation 1 where \( y_1 \) and \( y_0 \) represent the CO₂ mole fraction at the inlet and outlet of the column, respectively.

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\text{CO}_2 \text{ removal (\%)} = \frac{y_1 - y_2}{y_1} \times 100 \%
\] (1)
3. Results and discussion

3.1. The influence of gas flow rate on CO₂ removal efficiency using AMP solution

Figure 3 shows the CO₂ absorption performance using 30 wt.% AMP at two different gas flow rates (22.1 kmol/m².hr and 26.5 kmol/m².hr). The graph shows that CO₂ removal steadily increased along the column height for both gas flow rates. However, further increase of gas flow rate from 22.1 kmol/m².hr to 26.5 kmol/m².hr resulted in decrease of absorption efficiency from 69 % to 54 %, as recorded at 2.04 m height. One possible reason of this behavior is due to insufficiency of active amines to react with excess CO₂ molecules in the gas phase. At higher gas flow rates, the amount of CO₂ molecules entering the column increased while the amine molecules in the liquid remained the same due to constant liquid flow rate. The up flowing gas consisting of CO₂ was continuously absorbed into the down flowing liquid along the column, consequently increasing CO₂ loading in the liquid. This concomitantly decreased the number of free amine molecules in the liquid phase which resulted in limitations on reaction for CO₂ absorption process. Moreover, the increase of gas flow rate further limits the residence time of gas in the absorption column and lowers the chances of reaction to occur between CO₂ and amine molecules. The same observation was also demonstrated by Zeng et al. [23] and Kasikamphaiboon et al. [19].

Figure 2. The experimental set up for the CO₂ absorption process.
3.2. The performance evaluation for MEA and AMP on the CO₂ removal efficiency

Figure 3. Effect of gas flow rate on CO₂ removal using AMP solution. (Liquid flow rate = 3.61 m³/m².hr; [AMP] = 30 wt.%; [CO₂] = 40 % in NG; operating pressure = 2 bars).

Figure 4 shows the performance of MEA and AMP in terms of CO₂ removal percentage along the column. Differences in the increasing trends along the column between both solutions can be further elaborated based on each amine solvents' characteristic. Referring to the trend line of MEA solution, the rapid increase of 77 % of CO₂ removal occurred within the height of 0 to 0.68 m due to its fast reaction rate characteristic. Then, the rate of CO₂ uptake increased slowly beyond the column height of 0.68 m and reached a maximum removal (100 %) at 1.70 m. On the other hand, the CO₂ removal of AMP solution steadily increased from 0 to 2.04 m of the column height without reaching a plateau. This observation proved the fact that AMP has a slower reaction rate as compared to MEA, as it takes noticeably longer time to reach saturation. Hence, due to slower reaction rate, it is predicted that further increases of the column height would allow AMP to take up more CO₂ due to higher CO₂ loading capacity.

Figure 4. The CO₂ absorption performance using MEA and AMP solutions. (Gas flow rate = 22.1 kmol/m².hr; liquid flow rate = 3.61 m³/m².hr; [CO₂] = 40 % in NG; operating pressure = 2 bars).
At 2.04 m, the 30 wt.% and 40 wt.% AMP solution both demonstrated the ability to remove 69 % and 87 % of CO₂, respectively. Nevertheless, both are still comparatively to lesser degrees as compared to that of 30 wt.% MEA. As stated previously, MEA is a primary amine which offered a higher rate of absorption characteristic as compared to AMP. Thus the higher reactivity of MEA has resulted in the higher absorption efficiency [24]. In this case, it was proven that MEA was superior for CO₂ absorption and the same observation has been reported for flue gas treatment in Choi et al. [20] and Khan et al. [13] research work.

Besides that, the influence of AMP concentration can be discussed by comparing the CO₂ absorption performance at 30 wt.% to 40 wt.%. It can be observed that the CO₂ removal percentage was increased by 18 % as the AMP concentration increased from 30 wt.% to 40 wt.%. At higher concentrations, more active amine molecules are introduced into the packed column, thus corresponding to the higher reaction activities with CO₂ molecules [25]. Yet, increase of AMP concentration up to 40 wt.% was unable to surpass the removal performance of 30 wt.% MEA. For industrial process, increasing the AMP concentration beyond 40 wt.% is not preferable because the absorption process will suffers from the increase of solvent cost, corrosivity and degradation rate which highly impact on the operational costs [20], [26], [27], [28]. This was further substantiated by Choi et al. [20] who reported that, the optimum concentration of the amine solvent was 30 wt.%. Hence, it was proven that AMP is unsuitable as a single solvent for intensifying the absorption process for biogas application. Therefore, the addition of activator to form a blended solution is suggested to enhance the performance of AMP in CO₂ removal process. To date, there are several activators such as piperazine (PZ) [29], 2-(1-piperazinyl)-ethylamine (PZEA) [30], 2-(ethylamino)ethanol (EAE) [31] and 2-(2-Aminoethyl) amino)ethanol (AEEA) [32], which play an important role as reaction rate accelerator. Other than that, in an attempt to combine the advantages of individual amine solvents, mixing two or more amine solvents could potentially improve the process of CO₂ capture, for instance, from blended MEA + AMP [33], MEA + DMEA [34], MEA + MDEA [35] and MEA + DEEA [36].

4. Conclusion
In current studies, the performances of CO₂ absorption from simulated biogas into AMP and MEA solutions were observed in continuous operation in a packed column. Hence, the findings of the current research are concluded as follows:

1. The CO₂ removal efficiency for AMP was enhanced at a lower gas flow rate (22.1 kmol/m².hr) with maximum removal of 69 %.
2. The CO₂ removal efficiency was significantly enhanced with the increase of AMP concentration from 30 wt.% to 40 wt.%, with the highest CO₂ removal percentage was observed at 87 %.
3. The CO₂ absorption process was superior at 30 wt.% MEA as compared to 30 wt.% and 40 wt.% of AMP. Therefore, in order to commercialize the AMP in biogas industries, it is suggested to enhance the reaction rate by adding an activator or blending two or more amine solvents for CO₂ absorption.

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