

CARBON DIOXIDE REMOVAL IN EMULSION LIQUID MEMBRANE CONTAINING 2-AMINO-2-METHYL-1-PROPANOL /MONOETHANOLAMINE

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Graphical abstract



Abstract

Absorption using aqueous alkanolamine is commonly used in industry to remove the carbon dioxide. However it has several weaknesses such as corrosion problem and low absorption rate. Emulsion liquid membrane is introduced as an alternatives method for CO₂ absorption because it can reduce the corrosion problem and the formation water droplets creates large interfacial area for absorption to occur. 2-amino-2-methyl-1-propanol (AMP) and monoethanolamine (MEA) present in the aqueous phase in the form of aqueous droplets, surrounded by the organic solution to form water in oil (w/o) emulsion. In this study, effects of amines ratios and amine quantities, and emulsification time and speed on the ELM stability and CO₂ absorption were investigated. The ELM was prepared by homogenizing the aqueous and the organic phases. AMP and MEA were added into sodium hydroxide (NaOH) solution to form aqueous solution, and kerosene and Span-80 were mixed to form the organic solution. The absorption study was carried out in rotating disc contactor (RDC) column. A mixture of 12 v% MEA, 4 v% AMP in 100 ml aqueous solution and 8 v% Span-80 in 100 ml organic phase has high stability and can remove 60% of CO₂. The stability of the emulsion remained high even after the absorption. This study proved that ELM has the potential to remove CO₂ by using only small amount of amines.

Keywords: Emulsion liquid membrane, carbon dioxide, removal, monoethanolamine, 2-amino-2-methyl-1-propanol.

Abstrak

Penyerapan menggunakan alkanolamin akueus selalu digunakan dalam industri untuk menyingkirkan karbon dioksida. Walau bagaimanapun ia mempunyai beberapa kelemahan antaranya masalah kakisan dan kadar penyerapan yang rendah. Membran cecair emulsi diperkenalkan sebagai kaedah alternatif untuk penyerapan CO₂ kerana ia boleh mengurangkan masalah kakisan itu dan pembentukan titisan air mewujudkan kawasan antarmuka yang luas untuk penyerapan berlaku. 2-amino-2-metil-1-propanol (AMP) dan monoetanolamina (MEA) yang hadir dalam fasa akueus dalam bentuk titisan akueus, dikelilingi oleh larutan organik membentuk emulsi titisan air dalam minyak (w/o). Dalam kajian ini, kesan nisbah amina dan kuantiti amina, dan masa dan kelajuan pengemulsian terhadap kestabilan ELM dan penyerapan CO₂ telah dikaji. ELM disediakan dengan mencampurkan larutan akueus dengan larutan organik. AMP dan MEA dicampurkan ke dalam larutan natrium hidroksida (NaOH) untuk membentuk larutan akueus, dan kerosen dan Span-80 membentuk larutan organik. Kajian penyerapan telah dijalankan dalam turus cakera penyentuh berputar (RDC). Campuran 12 % v MEA, 4 v %

AMP dalam 100 ml larutan akueus dan 8 v % Span-80 dalam 100 ml larutan organik mempunyai stabiliti yang tinggi dan boleh menyingkirkan 60% daripada CO₂. Kestabilan emulsi kekal tinggi walaupun selepas penyerapan. Kajian ini membuktikan bahawa ELM mempunyai potensi untuk menyingkirkan CO₂ dengan menggunakan sejumlah kecil amina.

Kata kunci: Membran cecair emulsi, karbon dioksida, penyingkiran, monoetanolamina, 2-amino-2-metil-1-propanol

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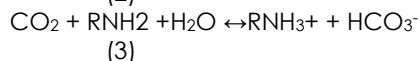
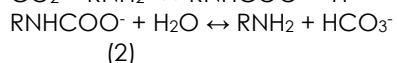
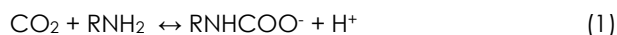
1.0 INTRODUCTION

Absorption has been widely used to treat high CO₂ concentration gases. In the existing absorption processes, alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and methyl-diethanolamine (MDEA) and their mixtures are commonly used to remove CO₂. Primary and secondary amines are known for their high reactivity meanwhile tertiary amines are known for their high absorption capacity [1]. Monoethanolamine (MEA) has gained a commercial interest in the field of acid gases removal in gas sweetening process [2]. MEA is more favorable as compared to other type of amines because the reaction rate between MEA and CO₂ is higher but the cost is lower than secondary and tertiary amines [3]. However, due to low absorption capacity and corrosion problem, researchers are looking into more efficient and economic method of CO₂ removal. Recent study shows that sterically hindered amines offer better results in term of absorption capacity, selectivity and degradation resistance for CO₂ removal processes as compared to the conventional amines [4]. It was also reported that sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) has lower corrosive nature than those primary and secondary amines [5].

Usually AMP was used together with the primary and secondary amines to increase the percentage of CO₂ removal. Primary and secondary amines are known to have higher rate of reaction with CO₂ than the tertiary and sterically hindered amines, but have lower CO₂ absorption capacity. Primary and secondary amines require 2 mol of amine to react with 1 mol of CO₂ [6]. However, sterically hindered amines such as AMP and tertiary amine such as MDEA require only 1 mol of amine to react with 1 mol of CO₂. Unstable carbamate ions is produced during reaction of the tertiary or sterically hindered amine with the

CO₂ (Eqn. (1)) [6]. The unstable carbamate ions will undergo hydrolysis to form bicarbonate ions and release free amine. Eqn. (2) shows the reformation of amine from the carbamate as given by Veawab and Aroonwilas [7]. The free amine then reacts again with the CO₂ [8]. Eqn. (3) shows the overall chemical equation of the reaction between CO₂ with AMP [9]. Bicarbonate ion (HCO₃⁻) produced in the reaction will be reduced further into hydrogen ion (H⁺) and

carbonate ion (CO₃²⁻). Eqn. (4) shows the reaction of bicarbonate to form carbonate.



where R = C(CH₃)₂CH₂OH

ELM system is capable of providing large surface areas due to the formation of small droplets, and it is applicable when the desired solute in the feed stream is low in concentrations. This is due to the presence of extractant inside the droplets that react with the solutes (CO₂) to produce other products. Therefore, the concentration of the solutes inside the droplets is always zero. And due to the concentration gradient, the solutes will continually diffuse into the droplets for the reaction to take place [10]. Bhowal and Datta has reported that if the anion (OH⁻) is predominant at internal phase while the feed gas is acidic, faster absorption takes place [11]. Other attractive features of ELM systems include simple operation, large interfacial area and suitable for continuous operation [12]. As compared to supported liquid membranes, ELM also offers other advantages; low cost and a single stage operation for both extraction and stripping. However, the ELM may also have limitations such as emulsion swelling, emulsion breakage and lack of stability [13]. Unstable emulsion or emulsion breakdown can be seen by the presence of layers that represent organic solution, emulsion and aqueous solution.

However before emulsion breakdown, three sub processes will occur; they include aggregation (flocculation), sedimentation and coalescence followed by phase separation. During aggregation or flocculation process, emulsion droplets move close to each other and start to aggregate without damage the layer of surfactant which stabilized the emulsion at the interface [14]. Then the emulsion starts to settle during sedimentation process. Emulsion settles according to the density difference between emulsion droplets and external phase under the action of gravity. Sedimentation process can be demonstrated by the formation of another layer on the top of emulsion [15].

This process also affects the removal of CO₂. Therefore, this paper presents the characteristics of emulsion and CO₂ removal using emulsion liquid membrane system.

2.0 EXPERIMENTAL

2.1 Preparation of Emulsion

Aqueous phase prepared in this study consist of a mixture of extractants (monoethanolamine (MEA) and 2-amino-2-methyl-1-propanol (AMP)) in sodium hydroxide solution. The organic phase was made of kerosene and surfactant (Span-80). Aqueous phase was prepared by dissolving the monoethanolamine (MEA) and 2-amino-2-methyl-1-propanol (AMP) in 0.1 M of sodium hydroxide (NaOH) solution. Then, the mixture was stirred and heated for 15 minutes. The stirring speed and temperature of the heating plate was fixed at 700 rpm and 30°C respectively. Several aqueous solutions with different amount of MEA and AMP were also prepared. Organic phase was prepared by mixing kerosene with 8 wt% Span-80. Then, the emulsion was prepared by adding the aqueous solution into the organic solution, and mixed using high performance Ultra Turrax 18G shaft. After that, the mixture was further homogenized at higher speed (10000 rpm) for 5 minutes. Similar sample was prepared and homogenized at different speed and time.

2.2 Absorption Study

The performance of ELM as CO₂ absorbent was measured by contacting CO₂ with the ELM in rotating disc contactor (RDC) column. Figure 1 shows the RDC column that has been used in this experiment. The RDC was filled with the emulsion and continuously stirred with the average speed of 500 rpm. CO₂ was supplied to the RDC until the pressure inside RDC reached 20 psi. This step was repeated using different emulsion formulation. The study was carried out at room temperature. After 1 min absorption, the gas was injected to gas chromatograph (GC) analyzer to analyze the concentration of CO₂ in leaving the RDC column. The percentage of CO₂ absorbed was calculated.

2.3 Characteristics of emulsion

Physical observation was conducted before and after CO₂ absorption for sedimentation or phase separation of the emulsion. The emulsion was filled in the scaled test tube and was left at room condition for 24 hours.

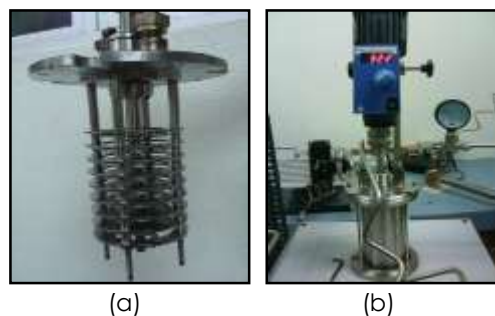


Figure 1 Rotating Disc. (b) Rotating disc Contactor (RDC) column

3.0 RESULTS AND DISCUSSION

3.1 Effect of Amines

MEA and AMP play different role in the CO₂ removal using emulsion liquid membrane. Since MEA and AMP have different viscosity and different rate of reaction rate, both affect the characteristics of the emulsion and CO₂ removal. Using 8% Span-80, no phase separation (aqueous phase and organic phase) occurred. Therefore, in this study, stability only refers to sedimentation of the emulsion droplets that result in the formation of 2 layers with different turbidity. Figure 2 shows aqueous solution (A), organic solution (B), emulsion (C) and the formation of layers (D) after absorption.



Figure 2 Aqueous solution, organic solution and emulsion

Figure 3 shows that the emulsion remains stable with minimum sedimentation. ELM containing MEA only has the highest stability (91%) and the stability decreases slightly as the quantity of AMP increases. ELM containing only AMP has the lowest stability (87.92%). This is due to different viscosity of MEA (19.75 cp) and AMP (147 cp) that affect the size of emulsion droplets. As more AMP was added, the viscosity of the aqueous solution increases, thus larger emulsion droplets may form. Using fixed speed (10000 rpm) and constant stirring time (5 minutes), the droplet formed would be larger for solution with higher viscosity. Thus, emulsion with larger droplets size would settle faster than smaller droplets (sedimentation occurs). The formation of two layers could be clearly observed. Small droplets lead to well

dispersed and stable ELM (no or negligible sedimentation).

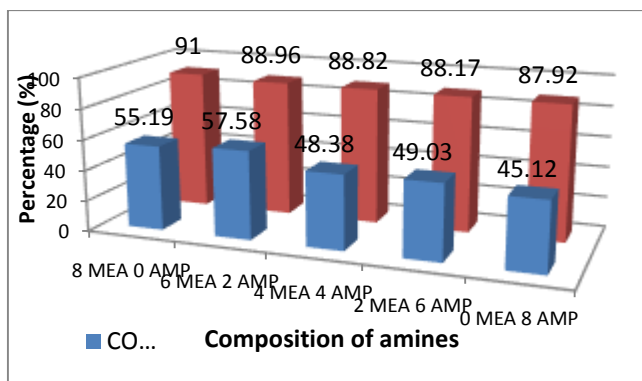


Figure 3 Stability and CO₂ removal of ELM containing different ratios of amines

Even though the same total amount of amines (8 ml) was used in each sample, the absorption capability was different. Figure 3 shows the highest CO₂ removal obtained by using ELM containing 6 ml MEA and 2 ml AMP (57.58% of CO₂ has been removed). It is higher than using only MEA (55.19% CO₂ removal) or only AMP (45.12% CO₂ removal). On the other hand, the combination of 2 ml of MEA and 6 ml of AMP was only able to remove 49 % CO₂. These results show a combination of MEA and AMP in ELM is a better formulation for CO₂ removal. It is based on the fact that MEA (the primary amine) reacts with the CO₂ faster than AMP (sterically hindered amine). In this study, 1 minute time of absorption was used and the result showed that the presence of 6 ml of MEA was able to react with more CO₂ than 6 ml of AMP that further proves MEA reacts faster than AMP. However, AMP is able to capture more CO₂ in term of the quantity but it needs longer time to react. Therefore it can be concluded that for 1 minute of absorption time, the ability of MEA capturing CO₂ is more noticeable than AMP.

This result has proved that the addition of AMP into MEA slightly reduced the stability but increased the absorption of CO₂. Moreover, as more amines were added in the formulation, more CO₂ can be removed by the ELM. Therefore, by keeping the same MEA/AMP ratio, the amount of amines was increased. Then, the stability of the ELM and the percentage of CO₂ removal were measured. Figure 4 shows the stability and CO₂ removal of ELM with different amount of amines mixture.

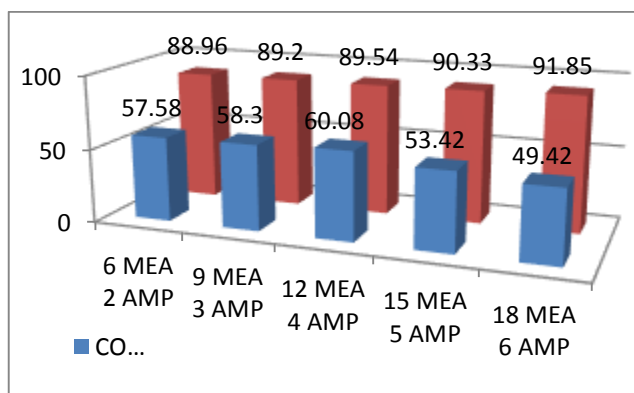


Figure 4 Stability and CO₂ removal of ELM containing different amount of amines

The stability of the emulsion remained high as the amount of amine increased. This result indicates that the amount of amine did not cause many droplets sedimentation. The percentage of CO₂ removal increases as MEA/AMP mixture increased to 12 ml MEA and 4 ml AMP. However, as the amount of amine was further increased, the percentage of CO₂ removal decreased. The main factor that contributes to the reduction of CO₂ removal is viscosity of the aqueous solution. As the amount of amines increase, the viscosity of aqueous solution increases. More energy was needed to disperse the droplets in rotating disc contactor to ensure more contacts between droplets and CO₂. In this study, the rotating speed of the disc contactor fixed at 500 rpm (RDC SPEED), whereas the viscosity increases as the amount of AMP increases. Therefore, the homogeneity of droplets in the emulsion also reduced that resulted in less contact between the droplets and CO₂. This study also revealed that 500 rpm was only sufficient to disperse the droplets of emulsion containing 12 ml MEA and 4 ml AMP mixture. The speed should be increased for larger amount of MEA/AMP.

3.2 Effect of speed and time

In the formulation of previous samples, the homogenization time and speed was fixed at 5 minutes and 10,000 rpm, respectively. However, it is also important to understand the effect of emulsification parameters such as speed and time on ELM stability and CO₂ removal. Figure 5 shows the stability and CO₂ removal of ELM prepared by using different speed of homogenizer and Figures 6 shows the effect of homogenization time on stability and CO₂ removal.

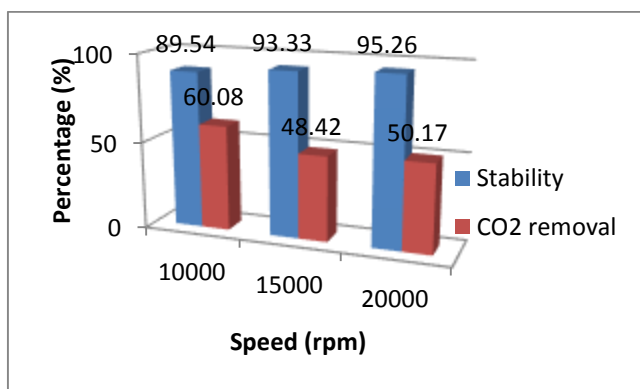


Figure 5 Stability and CO₂ removal of ELM prepared with different homogenization

From 10,000 rpm (rotation per minute) to 20,000 rpm, the stability increases from 89.54% to 95.26%. Meanwhile, as the time of emulsification increases, the stability increases from 89.54% to 94.55%. Higher speed and longer time of homogenization has provided more energy that further dispersed the ELM droplets. The smaller droplet size leads less sedimentation.

Figures 6 and 7 also show that as both stirring time and speed increases, the percentage of CO₂ removal decreases. For every 5 minutes increases of emulsification time, CO₂ removal gradually decreases from 60.08% to 52.02% and then further decrease to 45.57%. Similarly, as the stirring speed increases, percentage of CO₂ removal decreases from 60.08% to 48.42% but further increases the stirring speed to 20000 rpm, percentage of CO₂ removal is only 50.17%. Both results show that longer time and higher speed of homogenizer do not improve the percentage of CO₂ removal.

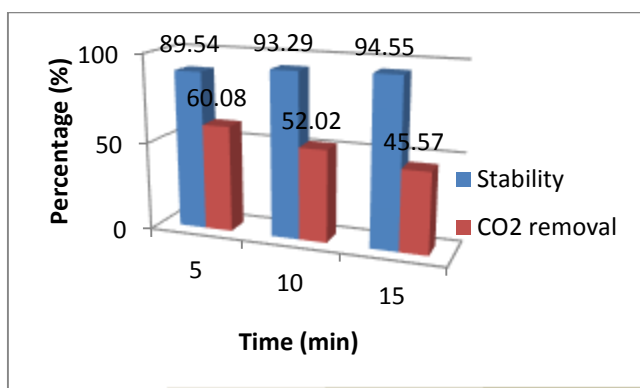


Figure 6 Stability and CO₂ removal of ELM prepared at different time of homogenization

4.0 CONCLUSION

Chemical formulation is important in the application emulsion liquid membrane for CO₂ removal. Using 8% Span-80 that acts as surfactant has produced stable emulsion. However, the amount of MEA and AMP slightly affect the stability of the emulsion. This study shows that homogenizing the solution at a speed of 10,000 rpm for 5 minutes is sufficient to produce stable

emulsion for CO₂ removal. The emulsion containing 12% MEA and 6% AMP is stable and able to remove 60% of CO₂ fed into the column.

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