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## Dynamic Study of Carbon Dioxide Absorption Using Promoted Absorbent in Bubble Column Reactor

**Abstract**-The most common process to remove carbon dioxide from natural gas and the flue gasses is absorption into suitable solvents. Absorption of carbon dioxide are studied experimentally in this work using bubble column reactor (glass cylindrical (QVF) of 7.5 cm i.d. × 140 cm height), where different types of absorbent (30%MEA, 30%K<sub>2</sub>CO<sub>3</sub>), promoter types (organic(piperazine)and inorganic(amino acids)) and concentrations were examined over a wide range of gas flow rate cover homogeneous to transition flow regime at ambient temperature and atmospheric pressure. The results showed that the dissolved gas undergoes a pseudo-first order reaction, and the optimum superficial velocity of gas given a higher conversion and rate of reaction at  $U_g=0.025$  m/sec, at this velocity the reaction rate of monoethanolamine with carbon dioxide (94.1% conversion and  $R_A = 7.75 \times 10^{-3}$  Kmol/m<sup>3</sup>.sec) is higher than reaction rate of potassium carbonate with carbon dioxide(29.3% conversion and  $R_A = 2.73 \times 10^{-3}$  Kmol/m<sup>3</sup>.sec). Furthermore, the addition of promoters to the 30%K<sub>2</sub>CO<sub>3</sub> absorbents enhanced the reaction between potassium carbonate with carbon dioxide and increased the reaction rate when increasing the concentration of promoters to the critical concentration. The results show that the piperazine is a better promoter from other types of the amino acid promoter used was 52.1% increase in carbonate conversion with carbon dioxide.

**Keywords**- Absorption, Carbon Dioxide Capture. Promoted Potassium Carbonate, Organic Promoter, Amino Acid.

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### 1. Introduction

Carbon dioxide removal technologies are crucial in the field of purification as for natural gas and power plants that are operated using petroleum-derived fuels. The most commonly used routes for capturing the carbon dioxide gas involve oxyfuel, post-combustion and pre-combustion [1]. In the case of post-combustion, the carbon dioxide produced by combustion is removed from the combustion's flue gas. While in the case of pre-combustion, the carbon dioxide gas is required to be removed ahead of combustion as in gasification processes [2-4]. The main idea behind carbon dioxide capture processes is to achieve an industrial benefit from the carbon dioxide that is produced by power plants or that is present in natural gas, which is currently considered as a problem since a large number of the remaining natural gas reservoirs are expected to contain about 87% carbon dioxide [6]. The process of capturing carbon dioxide from natural gas or from the power plant's combustion gas is difficult and expensive due to the requirements of high pressure and temperature. Carbon dioxide

can be removed and captured through various processes which may depend on adsorption [7], absorption [8-9], membrane technology or cryogenic [10]. Chemical absorption is the most widely used approach for carbon dioxide capture due to its high absorption capacity. Removal of CO<sub>2</sub> by absorption requires the use of an amine-based solvent like MEA, which is the industrially preferred choice for its high rate of reaction [11-12]. However, this solvent is not ideal where in addition to its degradable nature, high amount of energy will be required for its regeneration thus other solvents like ammonia and K<sub>2</sub>CO<sub>3</sub> solution were used for efficient CO<sub>2</sub> capture where the K<sub>2</sub>CO<sub>3</sub> is advantageous for its lower toxicity and volatility and its resistance to degradation [8,13]. K<sub>2</sub>CO<sub>3</sub> is commonly used in a process that is operated at a temperature that exceeds 100°C using the pressure swing method [8]. Such route is expected to be more economically feasible since it will lead to preserving energy by avoiding the operation at high temperatures and pressures as in the purification of natural gas and pre-combustion CO<sub>2</sub> capture. In addition, K<sub>2</sub>CO<sub>3</sub> is

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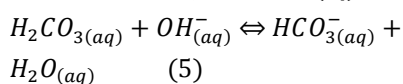
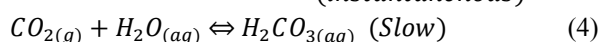
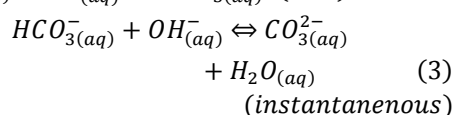
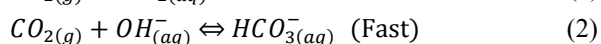
reported to have a lower heat of absorption than that of MEA, which leads to a reduction of the efficiency penalty from 20 to 30 % for MEA to about 13.1% for  $K_2CO_3$ . On the other hand, using  $K_2CO_3$  instead of MEA will render the absorption rate [8, 11-13].

## 2. Theory

### I. Reaction Mechanism

The use of  $K_2CO_3$  instead of MEA as an absorbent in  $CO_2$  capture absorption process will lead to a slower reaction kinetics, which is considered as the main obstacle, especially under post-combustion conditions: low temperature and low  $CO_2$  partial pressure.

The absorption of carbon dioxide in a potassium carbonate aqueous solution, slower reaction kinetics that is considered as the main obstacle, especially under post-combustion conditions.  $CO_2$  absorption with  $K_2CO_3$ , the reactions can be described as follows [4]:-



(instantaneous)

Studies showed that at a temperature of about 378K, an enhancement in the mass transfer of the absorption could be achieved through chemical reactions Eqs. (2) and (4). Major improvement in the absorption rate is not possible by elevating temperature alone since the chemical reactions are not fast enough at 378k. In the reaction regime Eqs. (1)–(5) for  $CO_2$  absorption into potassium carbonate solutions, Eq. (2) is fast but not fast enough to be treated as instantaneous. When the pH of the absorbent is greater than 9, Eq.(4) is negligible in comparison with Eq.(2, hence the rate-limiting step of the absorption process is Eq. (2). Since Eq. (2) is not quite fast, the absorption kinetics is slow.

### II. Rate promoters for $K_2CO_3$ solutions

$CO_2$  absorption kinetics are relatively slow in potassium carbonate solutions, in such cases higher absorption efficiencies can be achieved by increasing the length of the absorber, which will lead to an increment in the capital and operation costs thus more attention was given to the use of promoters which may be the proper solution to

the previously discussed challenges [4,14-16]. A range of promoters [8,13,15-16] has been studied in potassium carbonate absorbents for accelerating carbon dioxide absorption, including inorganic promoters such as arsenic acid [17] and boric acid [18] organic promoters such as MEA and DEA [19-23] and amino acid salts[9,24-26] and enzymatic promoters such as carbonic anhydrase[27-28] . Of these, amino acid salts have attracted the most attention as they are environmentally benign, with low evaporation and have the potential to be either rate promoters or individual absorbents [8,9,13,24-25]. A variety of amino acid salts has been studied to investigate the possibility of their use with  $K_2CO_3$  absorbent as promoters; a comparison of these results is difficult to conduct due to the variation in equipment and operation conditions from one study to another. In addition the reaction kinetic type and regime with containing those amino acids as promoters were not sufficiently studied. In this paper, recent progress on different promoters is presented and suggestions for future improvements are given, where the reaction kinetic and parameters affected on the performance of bubble column for  $CO_2$  absorption in un-promoted potassium carbonate and monoethanolamine are studied. In addition, promoters types (Alanine, Arginine, Glycine, Taurine, Lysine, Proline, Serine and Piperazine) and concentrations were examined.

## 3. Experimental work

### I. Experimental apparatus

The bubble column (glass cylindrical (QVF) of 7.5 cm i.d.  $\times$  140 cm height) apparatus used in the experiment is shown in Figure 1; this device consists of: a reactor in which the reaction between carbon dioxide and absorbent takes place sparger for gas distributor and placed between the column and distributor chamber which has a drain at the bottom and gas inlet at the side, air compressor,  $CO_2$  cylinder, air and  $CO_2$  rotameters, one way valves, gate and needle valves and degassed line. Experiments of carbon dioxide capture by absorption from gaseous mixture (10% carbon dioxide + 90% air) have been carried out by aqueous solution of un-promoted 30% monoethanolamine and 30% potassium carbonate( $K_2CO_3$ ) as absorbent promoted with various amino acid salts (AAS) over a wide range of gas flow rate, cover homogeneous to transition flow regime, promoter types and concentrations are shown in Table 1. The time used for each experiment was (5400 s), and the sample withdrawn in each run was

analyzed for each (600 s). Gas (mixture carbon dioxide + air) flow rate was computed by using two separate calibrated rotameters. In all experiments, the volume of the aqueous solution has been stabilized and equal to (1liter above the sparger) and all experiments were perforated at ambient temperature and atmospheric pressure.

### III. Physico - Chemical Properties

• Diffusion coefficient of carbon dioxide in aqueous solutions can be determined by CO<sub>2</sub>-N<sub>2</sub>O analogy and modified stokes Einsten relation [29-30] as follows:

$$D_{CO_2\text{-water}}^0 = 2.35 \times 10^{-6} \exp(-2119/T) \quad (6)$$

$$D_{N_2O\text{-water}}^0 = 5.07 \times 10^{-6} \exp(-2371/T) \quad (7)$$

$$(D_{N_2O} \cdot \eta_{\text{water}}^{0.8})_{\text{Solution}} = (D_{N_2O\text{-water}}^0 \cdot \eta_{\text{water}}^{0.8})_{\text{water}} \quad (8)$$

$$D_{CO_2} = (D_{N_2O} / D_{N_2O\text{-water}}^0) \times D_{CO_2\text{-water}}^0 \quad (9)$$

$$\eta = \mu \quad (10)$$

• The solubility of carbon dioxide in the liquid phase was calculated using Henry's law, and then the concentration of free carbon dioxide at the interface is calculated, as follows [29-30]:

$$C^* = P_{Ai} / H \quad (11)$$

$$\log (H/H^0) = K_{MEA} \times M \quad (12)$$

$$\log [H^0]^{-1} = -4.3856 + (867.4932/T) \quad (13)$$

• Liquid side mass transfer coefficient in the absence of reaction for bubble column can be calculated from [31] as follow:-

$$k_L^0 = 0.5 (D_{CO_2} / d_v) (\eta / D_{CO_2})^{0.5} (g \cdot d_v^3 / \eta^2)^{0.25} (g \cdot d_v^2 \cdot \rho / \sigma)^{0.375} \quad (14)$$

$$d_v = 26 (D_{CO_2}^2 \cdot g \cdot \rho / \sigma)^{-0.5} (g \cdot D_C^3 / \eta^2)^{-0.21} (u_g / (g \cdot D_C)^{0.5})^{-0.2} \quad (15)$$

## 4. Reaction Kinetic Type and Regime

### I. Reaction Kinetic Type

Carbone dioxide undergoes a second-order reaction with hydroxyl ions, OH<sup>-</sup>, and the absorption of carbon dioxide in to K<sub>2</sub>CO<sub>3</sub> and MEA solution conforms to the model just described ; in this case so,, the absorption rate is given by Eq.(16)[29]:

$$N = C_{CO_2}^* a \sqrt{D_{AB} k_2 C_{B_0} + k_L^0} \quad (16)$$

$k_2 = k_{OH}$  rate constant for K<sub>2</sub>CO<sub>3</sub> - CO<sub>2</sub> system and  $k_2 = k_{MEA}$  rate constathe nt for MEA - CO<sub>2</sub> system.

If the carbon dioxide absorption into a thin film is occurring according to a pseudo-first-order regime in which the concentration of K<sub>2</sub>CO<sub>3</sub> and MEA is not depleted across the film, so that the absorption rate can be described as follows [29]:

$$N = C_{CO_2}^* a \sqrt{D_{AB} k_2 C_{B_0}} \quad (17)$$

Where:-

C<sub>B0</sub> = Concentration of liquid reactant (B) in the bulk (K<sub>2</sub>CO<sub>3</sub>, MEM)

D<sub>AB</sub> = Diffusion coefficient of CO<sub>2</sub> in K<sub>2</sub>CO<sub>3</sub> solution or Diffusion coefficient of CO<sub>2</sub> in MEA solution

The certain conditions of the reaction kinetic type must satisfy the following condition [29]: -

$$(D_{CO_2} C_{O_2} K)^{0.5} < \frac{1}{2} k_L^0 (1 + (C_{O_2} / Z \cdot C^*)) \quad (18)$$

### II. Reaction Regime

Hatta number (Ha) can be calculated as following [29]:

$$\text{Hatta number} = (k_2 \cdot D_{CO_2} \cdot C_{K_2CO_3}^0)^{0.5} / k_L^0 \quad (19)$$

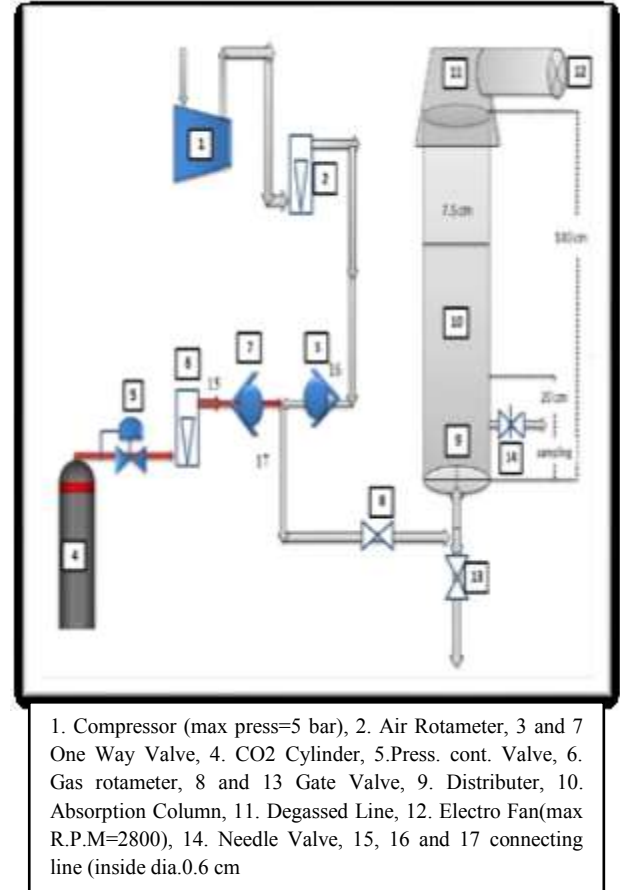


Figure 1: Schematic diagram of the experimental apparatus

Table 1: Variables used in the experiment

| Type of Absorbent                                                          | Superficial Gas Velocity and Gas Flow Rate |                                   |                       |
|----------------------------------------------------------------------------|--------------------------------------------|-----------------------------------|-----------------------|
|                                                                            | Gas velocity (m/s)                         | Flow rate CO <sub>2</sub> (L/min) | Flow rate air (L/min) |
| 30% K <sub>2</sub> CO <sub>3</sub> (promoted and un-promoted)              | 0.014                                      | 0.36                              | 3.6                   |
| 30% MEA (un-promoted)                                                      | 0.019                                      | 0.5                               | 5                     |
| <b>Promoter</b>                                                            | 0.025                                      | 0.65                              | 6.5                   |
| Amino acid                                                                 | 0.03                                       | 0.79                              | 7.9                   |
| (Alanine, Arginine, Glycine, Taurine, Lysine, Proline, Serine) +Piperazine | 0.035                                      | 0.92                              | 9.2                   |

Table 2a: The reaction kinetic regime between 30%un-promoted K<sub>2</sub>CO<sub>3</sub> - CO<sub>2</sub>

| $U_g$<br>(m/sec) | $V_g$<br>(m <sup>3</sup> /sec) | $K_{OH}$<br>(m <sup>3</sup> /kmole.sec) | $k_L^o$<br>(m/sec) | $(D_{CO_2} \cdot C_{O(K_2CO_3)} \cdot K_{OH})^{0.5}$<br>(m/sec) | $\frac{1}{2} k_L^o (1 + (C_{O(K_2CO_3)}/Z \cdot C_{O_2}^*))$<br>(m/sec) |
|------------------|--------------------------------|-----------------------------------------|--------------------|-----------------------------------------------------------------|-------------------------------------------------------------------------|
| <b>0.014</b>     | $6.0 \times 10^{-5}$           | 8322.14                                 | 1.042              | $7.1 \times 10^{-3}$                                            | 7.81                                                                    |
| <b>0.019</b>     | $8.3 \times 10^{-5}$           | 8322.14                                 | 1.004              | $7.1 \times 10^{-3}$                                            | 7.53                                                                    |
| <b>0.025</b>     | $1.1 \times 10^{-4}$           | 8322.14                                 | 0.983              | $7.1 \times 10^{-3}$                                            | 7.37                                                                    |
| <b>0.03</b>      | $1.3 \times 10^{-4}$           | 8322.14                                 | 0.961              | $7.1 \times 10^{-3}$                                            | 7.20                                                                    |
| <b>0.035</b>     | $1.5 \times 10^{-4}$           | 8322.14                                 | 0.947              | $7.1 \times 10^{-3}$                                            | 7.10                                                                    |

Table 2b: The reaction kinetic regime between 30%MEA and CO<sub>2</sub>

| $U_g$<br>(m/sec) | $V_g$<br>(m <sup>3</sup> /sec) | $K_{DEA}$<br>(m <sup>3</sup> /kmole.sec) | $k_L^o$<br>(m/sec) | $(D_{CO_2} \cdot C_{O(DEA)} \cdot K_{DEA})^{0.5}$<br>(m/sec) | $\frac{1}{2} k_L^o (1 + (C_{O(DEA)}/Z \cdot C_{O_2}^*))$<br>(m/sec) |
|------------------|--------------------------------|------------------------------------------|--------------------|--------------------------------------------------------------|---------------------------------------------------------------------|
| 0.014            | $6.0 \times 10^{-5}$           | 576.10                                   | 1.042              | $1.6 \times 10^{-3}$                                         | 4.86                                                                |
| 0.019            | $8.3 \times 10^{-5}$           | 576.10                                   | 1.004              | $1.6 \times 10^{-3}$                                         | 4.68                                                                |
| 0.025            | $1.1 \times 10^{-4}$           | 576.10                                   | 0.983              | $1.6 \times 10^{-3}$                                         | 4.60                                                                |
| 0.03             | $1.3 \times 10^{-4}$           | 576.10                                   | 0.961              | $1.6 \times 10^{-3}$                                         | 4.48                                                                |
| 0.035            | $1.5 \times 10^{-4}$           | 576.10                                   | 0.947              | $1.6 \times 10^{-3}$                                         | 4.40                                                                |

## 5. Results and Discussion

### I. Reaction Kinetic Type

From Table 2, it can be noticed the results of Equation (18), which indicates that the reaction kinetics of carbon dioxide with 30% promoted and un-promoted potassium carbonate and 30% MEA solutions undergoes a pseudo-first-order reaction (i.e. where the concentration of the reactant in the neighborhood of the surface is very little different from that in the bulk of the liquid, and the dissolved gas undergoes as a pseudo-first-order reaction) [29]. It is worth noting that, in general, if the reaction between dissolved carbon dioxide and a reagent in solution is irreversible, then no matter what type of kinetics the reaction follows, the limiting rate of absorption when the reaction is intrinsically fast enough, or  $k_L^o$  is small enough. This is because, in the limit, the reaction can only proceed as fast as the reactants can diffuse to the reaction zone and the nature of the reaction proceeding there is then irrelevant, providing it destroys carbon dioxide and the reactant “instantaneously” and irreversibly. This would occur, for instance, if a sufficiently powerful catalyst and promoter were added in sufficient concentration to alkali carbonate solution [29]. The finding of Barifcani et al. [22] confirm our results.

### II. Reaction Regime

Figure 2 shows the results of Hatta number of CO<sub>2</sub> absorption into un-promoted and promoted K<sub>2</sub>CO<sub>3</sub>, from Hatta number, can compare the reaction rate in a liquid film to the diffusion rate of gas. It is noteworthy the reaction undergoes a pseudo-first order, so from this condition, Enhancement factor(E)  $\approx$  Hatta number (Ha)

[33]. From Figure 2 clarifies that all the results for Hatta number <0.02, this case indicates that the reactions occur only in the main body of liquid. Therefore, it was noted that after the addition of piperazine to the solution of (30% K<sub>2</sub>CO<sub>3</sub>), Ha increased, because piperazine accelerated the arrival of CO<sub>2</sub> to the main body of the solution, which enhanced the reaction between gas and solution.

### III. Effect of Operating Variables

#### a. Influence of superficial gas velocity

Figures 3 and 4 give the indication of superficial gas velocity on the absorption of carbon dioxide in un-promoted 30%(K<sub>2</sub>CO<sub>3</sub>, MEA) solution. It can be noticed that the high carbonate and MEA conversion were obtained at ( $U_g = 0.025$  m/s,  $V_g = 1.1 \times 10^{-4}$  m<sup>3</sup>/s), The superficial gas velocity cover approximately homogeneous to transition flow regime in present work the behavior of velocity, high absorption rate was obtained up to  $U_g = 0.025$  m/s (homogeneous flow regime). This is attributed to the fact that in the homogeneous flow regime give the smaller bubbles with lower rising velocity lead to form large residence time and consequently higher gas holdup and mass transfer. This increase in the gas holdup and mass transfer have been found to be proportional in lower superficial gas velocity up to a point then it will become less pronounced in higher superficial gas velocity (transition regime). This is attributed to the formation of large bubble which led to lower gas holdup. The present trends are in accordance with the findings of [33]. Furthermore, monoethanolamine gave % conversion in the absorption of carbon dioxide higher than of potassium carbonate solution. As

the absorption rate of  $\text{CO}_2$  in monoethanolamine solution reached  $R_A = 7.92 \times 10^{-3}$  ( $\text{kmol/m}^3 \cdot \text{s}$ ), which was greater than potassium carbonate by 1.9 times. This is attributed to the zwitterion mechanism was found that the reaction of  $\text{CO}_2$  into MEA involves the formation of zwitterion complex ( $\text{R}_2\text{NH}_2\text{COO}$ ) and subsequent deprotonation of zwitterions to produce carbamate ( $\text{R}_2\text{NHCOO}$ ), followed carbamate reversion by hydrolysis reaction. These results are in agreement with the previous findings of [34-35].

#### *b. Effect of absorbent type ( $\text{K}_2\text{CO}_3$ , MEA) on $\text{CO}_2$ absorption*

Figures 5 and 6 show the effect of absorbent type ( $\text{K}_2\text{CO}_3$ , MEA) on  $\text{CO}_2$  conversion at superficial gas velocity  $U_g = 0.025$  m/s and gas flow rate  $V_g = 1.1 \times 10^{-4}$   $\text{m}^3/\text{s}$ . As can be seen in these figures, the highest % conversion was obtained from absorption with 30%MEA and reached (94.1%) through (5400 s) because of formation zwitterion and subsequent deprotonation of zwitterions to produce carbamate and followed by carbamate reversion to bicarbonate by hydrolysis reaction. For un-promoted 30% $\text{K}_2\text{CO}_3$  were (29.3%) conversion reached through (5400 s) which the lower % conversion about (64.8%) than MEA absorbent. This result agrees with [36-38]. In the reaction regime, the reactions occur only in the main body of liquid (Eqs. (1)–(5)) for  $\text{CO}_2$  absorption into  $\text{K}_2\text{CO}_3$  solutions, Eq. (2) is fast but not fast enough to be treated as instantaneous. The pH of the absorbent is greater than 9, Eq.(4) is negligible in comparison with Eq.(2), hence the rate-limiting step of the absorption process is Eq. (2). Since Eq. (2) is not quite fast, the absorption kinetics is slow. The present trends are in accordance with the findings of [12, 14, 16 and 21-24].

#### *c. Promoter effect on the absorption rate of carbon dioxide*

Figures 7 to 11 illustrate 30%  $\text{K}_2\text{CO}_3$  conversion for  $\text{CO}_2$  absorption promoted with different types and concentration of amino acid salts and piperazine. Figures 7 to 9 illustrate that the piperazine continued to increase the % conversion of potassium carbonate by increasing the concentration and reached to ( $\%^{4.5}$ ) at 0.5  $\text{kmol/m}^3$  piperazine concentration, unlike of amino acid salts promoters which gave constant effectiveness by increasing the concentration of amino acid from 0.05 to 0.5  $\text{kmol/m}^3$ . As an increase in the concentration of promoter above the critical concentration up to 0.25  $\text{kmol/m}^3$  for Glycine, Taurine, Lysine, and 0.5  $\text{kmol/m}^3$  for

Proline, Serine, it could precipitate during  $\text{CO}_2$  absorption. The precipitate could cause a pore blocking of distributor and that leads to a decrease in the solubility of  $\text{CO}_2$ , this result agrees with finding [24-25, 41]. Figure 10 and Table 3 show the carbonate conversion in prompted and un-promoted 30%  $\text{K}_2\text{CO}_3$  with piperazine (promoter), and the results compared with the monoethanolamine conversion. The results indicated that the monoethanolamine conversion reached during 5400 sec (94.1%) which is higher than the un-promoted carbonate conversion (29.3%). In addition, the results exhibited that the conversion increased with increasing the concentration of piperazine added to potassium carbonate.

From Table 3, it can be noticed that (64.8%) increase in conversion when used MEA absorbent as compared with the un-promoted  $\text{K}_2\text{CO}_3$ . While after the addition of piperazine promoter from (0.05 to 1  $\text{kmol/m}^3$ ) the rate increased of conversion from 20.7 to 52.8%. Figure 11, shows the absorption rate of  $\text{CO}_2$  when adding (0.05 to 1  $\text{kmol/m}^3$ ) of piperazine to  $\text{K}_2\text{CO}_3$  which increased up to ( $7.67 \times 10^{-3}$ )  $\text{kmol/m}^3 \cdot \text{s}$  at 1  $\text{kmol/m}^3$  piperazine. This increase in absorption rate of gas is obtained after adding piperazine to  $\text{K}_2\text{CO}_3$  because piperazine increased the mass transfer of gas by rapidly absorbing  $\text{CO}_2$  near the gas-liquid interface, where the  $\text{CO}_2$  concentration is high and then penetrates into the solution. This result agrees with the work of [39].

Among the amino acid salts examined, Alanine, Arginine showed the fastest promoting effect in the carbonate conversion up to 0.25  $\text{kmol/m}^3$  concentration where carbonate conversion reached 62.5% and 60.7% respectively while piperazine up to 1  $\text{kmol/m}^3$  concentration where carbonate conversion reached 82.1%. This could be attributed to the reaction order between  $\text{CO}_2$  and the amino acids. The reaction order between Alanine, Arginine and carbon dioxide is between 1.22 and 2, but for the reaction between piperazine and  $\text{CO}_2$ , the reaction order has been reported to be second-order. This means that as the concentration of amino acids increases, the reaction rate between Alanine, Arginine, piperazine and  $\text{CO}_2$  increases with concentration to the power of 1.22–2. The present trends are in accordance with the findings of [40-42].

**Table 3: Comparison between reaction (MEA,**

| <b>K<sub>2</sub>CO<sub>3</sub>) with CO<sub>2</sub> during 5400 s.</b> |                                          |               |                          |
|------------------------------------------------------------------------|------------------------------------------|---------------|--------------------------|
| Con. of piperazine added (kmol/m <sup>3</sup> )                        | %React of K <sub>2</sub> CO <sub>3</sub> | %React of MEA | % increase in conversion |
| <b>0</b>                                                               | 29.3%                                    | 94.1%         | -                        |
| <b>0.05</b>                                                            | 50%                                      | -             | 20.7%                    |
| <b>0.25</b>                                                            | 64.3%                                    | -             | 35%                      |
| <b>0.5</b>                                                             | 74.3%                                    | -             | 45%                      |
| <b>1.0</b>                                                             | 82.1%                                    | -             | 52.8%                    |

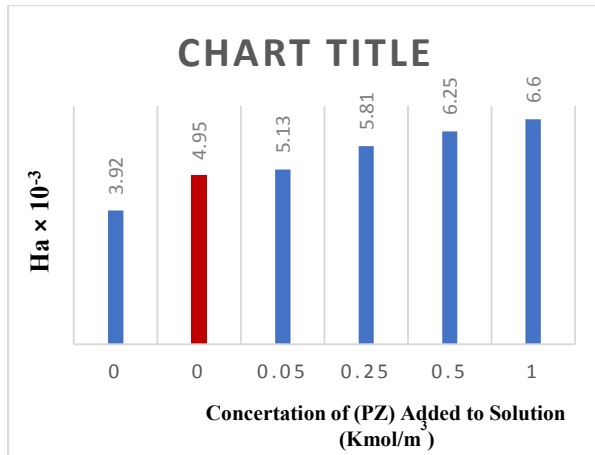


Figure 2: Hatta number of reaction between CO<sub>2</sub> with 30% (K<sub>2</sub>CO<sub>3</sub>, MEA) before and after adding Piperazine

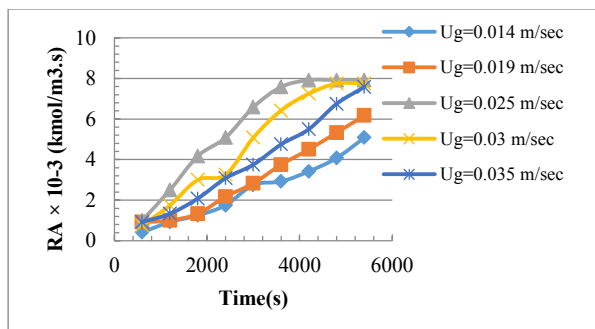


Figure 3: Absorption rate of CO<sub>2</sub> in monoethanolamine solution.

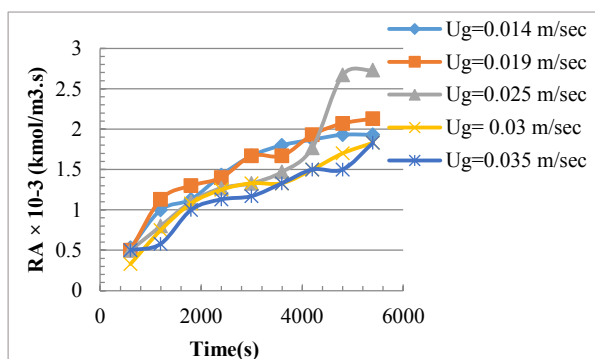
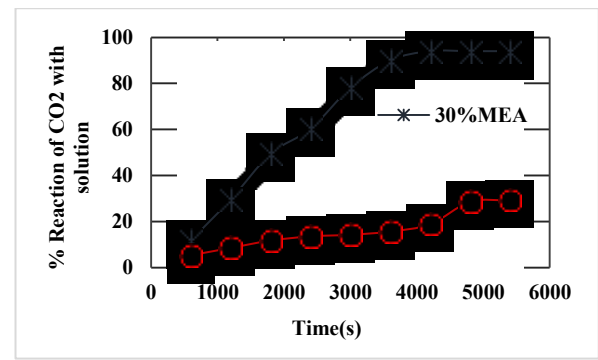


Figure 4: Absorption rate of CO<sub>2</sub> in potassium carbonate solution.



30% K<sub>2</sub>CO<sub>3</sub>, 30% MEA, (Promoted 30% K<sub>2</sub>CO<sub>3</sub>)

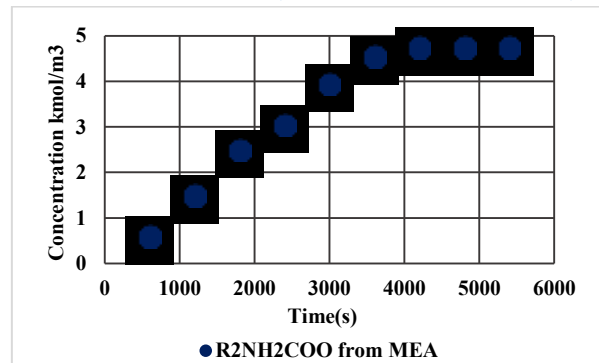


Figure 6: Concentration of Zwitterion (R<sub>2</sub>NH<sub>2</sub>COO) Kmol/m<sup>3</sup>

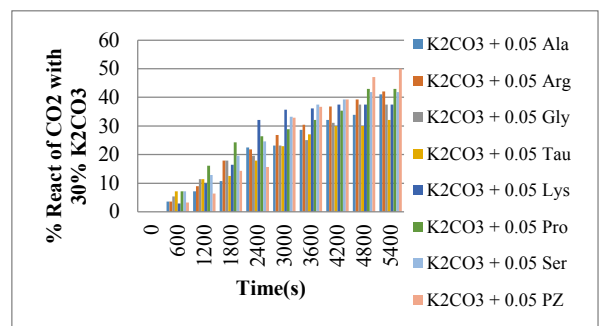


Figure 7: Rate of reaction between K<sub>2</sub>CO<sub>3</sub> and CO<sub>2</sub> after adding 0.05 kmol/m<sup>3</sup> of different type of promoters

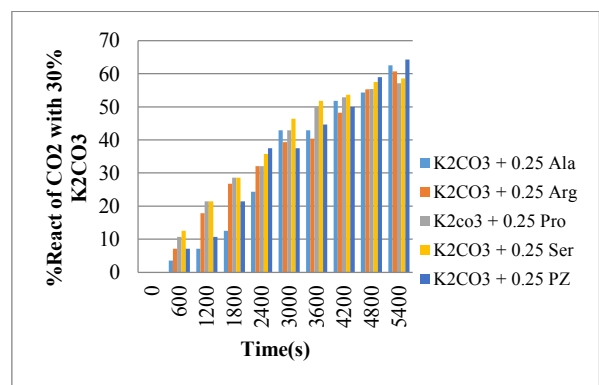


Figure 8: Rate of reaction between K<sub>2</sub>CO<sub>3</sub> and CO<sub>2</sub> after adding 0.25 kmol/m<sup>3</sup> of different type of promoters

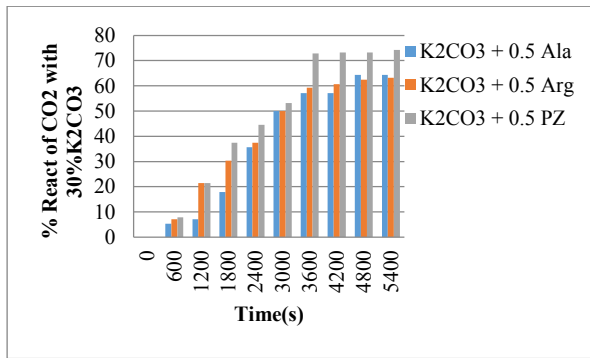


Figure 9: Rate of reaction between  $K_2CO_3$  and  $CO_2$  after adding 0.5 kmol/m<sup>3</sup> of different type of promoters

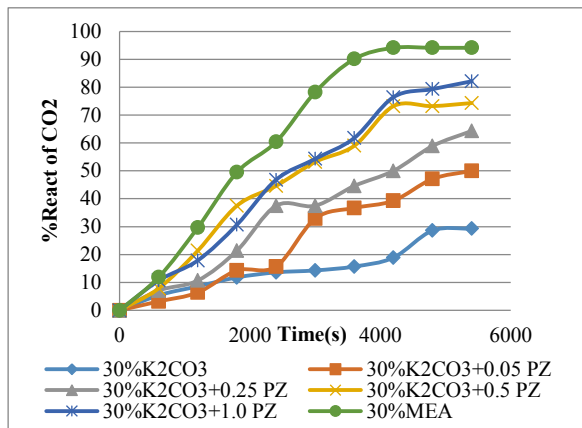


Figure 10: Rate of reaction between  $K_2CO_3$  and  $CO_2$  after adding different concentrations of Piperazine (PZ) and compared with MEA

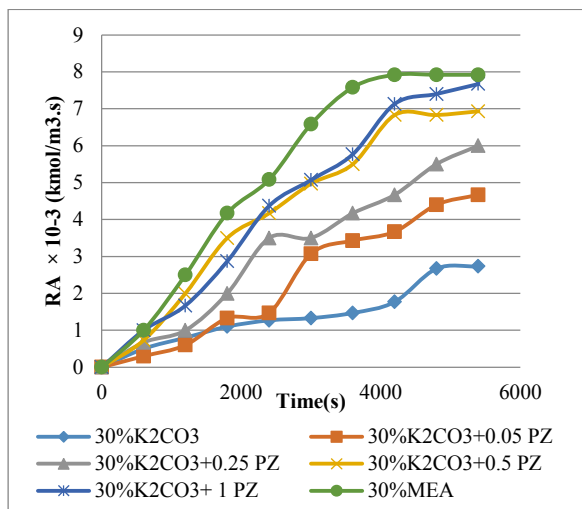


Figure 11: Absorption rate of  $CO_2$  in  $K_2CO_3$  before and after adding Piperazine (PZ) and compared with MEA

## 6. Conclusions

The main points concluded from the current study are:

1. The absorbent type has affected the carbon dioxide absorption because each absorbent has a different mechanism of reaction with gas from the other. The results showed that monoethanolamine

gave a higher reaction and MEA conversion from  $K_2CO_3$  absorbents.

2. Gas velocity has an effect on the absorption of carbon dioxide in a bubble column reactor when the velocity of the gas increased, the absorption rate of gas increased up to  $U_g = 0.025$  m/s which gives a higher conversion,

3. The promoters are added to the carbonate absorbent, which enhanced the absorption of  $CO_2$  by using potassium carbonate, and increased the reaction rate when increasing the concentration of promoters to the critical concentration.

4. Piperazine gave a high reaction rate of carbon dioxide with a solution and carbonate conversion as compared with amino acids salts.

5. The dissolved gas of carbon dioxide undergoes a pseudo-first order reaction, from this  $E \approx Ha$ , all the results showed that  $Ha < 0.02$ , indicating that the reactions occur only in the main body of liquid.

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## Abbreviations

|     |            |
|-----|------------|
| Ala | Alanine    |
| Arg | Arginine   |
| Gly | Glycine    |
| Lys | Lysine     |
| Pro | , Proline  |
| PZ  | Piperazine |
| Tau | Taurine    |
| Ser | Serine     |

## Nomenclature

|                    |                                                                       |
|--------------------|-----------------------------------------------------------------------|
| $A$                | : Interfacial area (m <sup>2</sup> /m <sup>3</sup> )                  |
| $C_{O(DEA)}$       | : Initial concentration of Diethanolamine(kmol/m <sup>3</sup> )       |
| $C_O$              | : Initial concentration of potassium carbonate(kmol/m <sup>3</sup> )  |
| $C_{(K_2CO_3)}^*$  | : Concentration at interface(kmole/m <sup>3</sup> )                   |
| $C_{O_2}^*$        | : Concentration of carbon dioxide at interface(kmole/m <sup>3</sup> ) |
| $D_C$              | : Diameter of column(m)                                               |
| $D_{CO_2}$         | : Diffusion coefficient of $CO_2$ in solution(m <sup>2</sup> /s)      |
| $D_{CO_2}^{water}$ | : Diffusion coefficient of $CO_2$ in pure water(m <sup>2</sup> /s)    |
| $D_{N_2O}^{water}$ | : Diffusion coefficient of $N_2O$ in pure water(m <sup>2</sup> /s)    |
| $D_{N_2O}$         | : Diffusion coefficient of $N_2O$ in solution(m <sup>2</sup> /s)      |
| $d_v$              | : Mean bubble diameter (m)                                            |
| $E$                | : Enhancement factor(-)                                               |

|               |                                                                                                            |
|---------------|------------------------------------------------------------------------------------------------------------|
| G             | :Acceleration due to gravity ( $\text{m/s}^2$ )                                                            |
| Ha            | :Hatta number(-)                                                                                           |
| H             | :Henry's constant ( $\text{atm.m}^3/\text{kmol}$ )                                                         |
| $H^0$         | :Henry's constant in pure water( $\text{atm.m}^3/\text{kmol}$ )                                            |
| $K_{AM}$      | :Reaction rate constant between $\text{CO}_2$ and $\text{NH}_3$ ( $\text{m}^3/\text{kmole.s}$ )            |
| $k_L^0$       | :Liquid side mass transfer coefficient (m/s)                                                               |
| $K_{MEA}$     | : Reaction rate constant between $\text{CO}_2$ and MEA( $\text{m}^3/\text{kmole.s}$ )                      |
| $K_{OH}$      | : Reaction rate constant between $\text{CO}_2$ and $\text{K}_2\text{CO}_3$ ( $\text{m}^3/\text{kmole.s}$ ) |
| N             | Absorption rate of $\text{CO}_2$ ( $\text{kmol/m}^3.\text{h}$ )                                            |
| M             | :Molarity of solution( $\text{kmol/m}^3$ )                                                                 |
| $P_{Ai}$      | : Partial pressure of the gas at the bulk(atm)                                                             |
| $R_A$         | Absorption rate of $\text{CO}_2$ ( $\text{kmol/m}^3.\text{h}$ )                                            |
| %             | :% React of $\text{K}_2\text{CO}_3$ with $\text{CO}_2$ (-)                                                 |
| $R_{K_2CO_3}$ | %                                                                                                          |
| %             | :% React of MEA with $\text{CO}_2$ (-)                                                                     |
| $R_{MEA}$     |                                                                                                            |
| T             | :Temperature(k)                                                                                            |
| $U_g$         | :Velocity of gas(m/s)                                                                                      |
| $V_g$         | :Volumetric gas flow rate( $\text{m}^3/\text{s}$ )                                                         |
| Z             | : Number of moles reactant with each mole of gas(-)                                                        |

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