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An Experimental Investigation of Overall Mass Transfer coefficient (KGa) of CO_2 absorption using Monoethanolamine (MEA) and Diethanolamine (DEA) in a Bubble Column Reactor (BCR)

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ABSTRACT

In this work, an absorption technology was used actually to investigate the mass transfer coefficient of carbon dioxide from a gaseous mixture (air, carbon dioxide) in blended solution Monoethanolamine (MEA) and Diethanolamine (DEA) in a bubble column reactor (BCR). The bubble column reactor(BCR) was made of Plexiglas with 1.5 m high and 0.1 m inside diameter. The overall mass transfer coefficient (K_{Ga}) was evaluated at different operating conditions, gas flow rate, air Flow rate, liquid flow rate. Where the gas flow rates were 10, 15, and 20 L /min, air flow rate 100,150 and 200 L/h, and liquid flow rate 5,10,15 L /min. This experiment by using a continuous process with helping the centrifugal pump. High-performance gas chromatographic (GC) was performed to evaluate CO_2 loading during absorption experiment . The experimental results have shown that the CO_2 loading in range of 0.581-1.367 (mol CO_2 /mole amine), and the maximum value of overall mass transfer coefficient (K_{Ga} was 0.04 S^{-1}).

1. Introduction

With regard to this century, elevation in the emissions regarding atmosphere's anthropogenic(CO_2) is considered to be challenging due to the fact that it is mainly contributing to the global warming. Fossil fueled plants are main emission's source, particularly plants using coal as main fuel. CO_2 is one of the gasses that are naturally-occurring, also it has main impact in reflection related to the solar radiation back to Earth, and that will keep the surface temperature of planet in suitable levels for the life. Furthermore, throughout the past tens of years, there has been an increase in the emissions related to other greenhouse gases (GHGs), in addition to CO_2, such as CH4, N2O, HFC, per fluorocarbons as well asSF6 [1], [2].Worldwide, CO_2 which is emitted from the power plants is considered to be about 40% of the overall emissions of CO_2 and within the ongoing businesses and industries, it is anticipated to be elevating to about 60% prior to the end of this century [3]. As CO_2 is released excessively via power plants, industries, in addition to other sources is of high importance in life cycle of earth and also to the global climate [1]. For the purpose of preventing excessive CO_2 release in atmosphere, carbon capture and storage (CSS) is of high importance in the industry of fossil fuel. Such approach includes CO_2 capturing, compress it to transport and after that store it permanently (in gas fields and depleted oil). The major application regarding CSS is in the industrial point sources as fossil-fuel power plants, production of fossil fuel, facilities for hydrogen production, industrial

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Nomenclature

K_{Ga}	overall mass transfer coefficient (S^{-1})
k_l	liquid side mass transfer coefficient (m/s)
k_g	gas film physical mass transfer coefficient (m/s)
Q_g	gas flow rate, ($\frac{L}{S}$)
F_1	molar flow rate of CO_2 at inlet, [$\frac{mol}{s}$]
$n_{co_2,abs}$	number of moles of CO_2 absorption [mol]

Greek symbols

δ	film thickness (m)
ρ_{Amine}	density of amine [Kg/m^3]
α	CO_2 loading [mol CO_2/mol amine]
ρ_{CO_2}	density of CO_2 [Kg/m^3]

Subscripts

BCR	bubble column reactor

plants (steel and iron blast furnaces, chemical processes, and cement kilns) [4].

Today, the absorption is the most important approach to remove CO_2 from the industrial waste gases as well as for synthesizing and for purification of natural gas. Such process pass flue gas via liquid which have the ability of absorbing CO_2 (in absorber vessel) and after that releasing CO_2 at increased temperatures in regenerator vessel (stripper**)** [5]–[7]**.** Aqueous alkanolamines are the major chemical solvent for capturing acid gaseous. Alkanolamines have been generally applied as absorbents for the capturing of CO_2, alkanolamine's structures involve primary, secondary, ternary amines including no less than single (OH) as well as amine group. With regard to the chemical solvents, primary amines like MEA, secondary amines DEA, Aminoethoxyethanol (DGA) as well as Diisopropanolamine (DPA), also tertiary amines like TEA and MDEA, as well as alternatives to amines like the hot potassium carbonate are utilized. Such alkanolamines were applied as chemical absorbents for removing acidic gases like (H_2S ,CO_2). A lot of the works on the chemical absorption with the tertiary alkanolamines like DEA, TEA, in addition to their associated apply of mixed amine absorbents, particularly blends the primary and tertiary amines (like TEA and MEA) or the secondary as well as tertiary amines (like TEA and DEA) has increased or them together [8]. The main benefits related to the technology of chemical absorption are as follows [9]:

1. Chemical absorption can be considered as major developed approach to capture CO_2, operating at normal pressure and temperature.
2. For tens of years it was commercialized, though not for the capture of CO_2 from power plants.
3. It can be used efficiently to dilute CO_2 system (general flue gas from power plants) .

Also, there are certain disadvantages related to this approach, as follows:

1. Amine oxidative degradation through SO_2, NO_2, and O_2 in flue gases that induce high absorbent makeup rate.
2. The energy consumption is high throughout high temperature absorbent regeneration.
3. The equipment corrosion rate is high.
4. The equipment size is large.

2. Theoretical background

As a result of the benefits and drawbacks of single amine solvents, blended amines became one of the attractive directions in the existing research area. Blended amines combine the benefits of the primary and the secondary amines, reacting fast with the CO_2.Through the combination of those advantages, and as a result, tailoring the solvent, it is possible achieving more sufficient absorption efficiency at low partial pressure, in addition to high kinetics of absorption for the reactions with the CO_2 [10]. The several reaction steps can be occurred through absorption process using aqueous blend of (MEA+DEA).The mechanism of the "zwitterions" which has been first presented in 1958 by Caplow and re-introduced in 1979 by Danckwerts, is, in general acknowledged as the mechanism of the reaction for the formation of the carbamate between CO_2 with primary amines and secondary amines. Based on Caplow, the bond of hydrogen is created between amine and molecules of water prior to any reactions with CO_2. At first, an unstable intermediate has been created as a result of bonding between the molecules of the carbon dioxide and the amine. Then, carbamate is created through the transfer of an amine proton. The base which is typically utilized is either an amine or a water molecule .Generally, the industrial amine sorbents' utilization was centered on the aqueous solutions of the primary amines as well as the secondary amines, reacting with CO_2 directly for forming ions of the carbamate $RNHCOO^-$. The chemical equations may be reduced to 2 significant steps, i.e., carbamate formation, bi-carbonate formation, and carbamate reversion. Eqution (2) illustrates the carbamate ion formation for the primary amine. A comparable reaction takes place for the secondary amines.

$$\mathbf{RNH_2 + CO_2 \rightarrow RNHCOO^- + RNH_3{}^+} \quad (1)$$

$$\mathbf{RNHCOO^- + CO_2 \rightarrow RNH_2 + HCO_3{}^-} \quad (2)$$

According to blended amines, in the combination of (primary and secondary amines) , the over-all reaction rate for the capture of $\mathbf{CO_2}$ can be reduced to [11]:

$$r_{overall} = k_{obs}(CO_2) \quad (3)$$

2.1. Mass Transfer for Gas Absorption

Mass transfer can be considered as one of the common phenomena which happen in simple, daily life in addition to the engineering process . In the case of absorption, the absorption of the gas in the liquid happens in the case of the transfer of the gaseous components from gas- to liquid-phase. In the process of the chemical absorption, the gaseous component is undergoes the absorption by liquid phase through combining the reaction and the diffusion mechanism. The processes of the chemical absorption are like systems that are aqueous amine-based, systems that are based on the ionic liquids, and ammonia manufacturing systems. As an explanation, the entire process rate can be viewed a layer of gas–liquid contact. The mass transfer must be enhanced with the increase of the turbulence in each of the liquid as well as the gas phases. The mass transfer happens through combining the diffusional and the mechanism of the chemical reaction in the boundary layer so the entire rate may be represented with each of the mass transfer and the chemical reaction. Numerous hypotheses may define the process of the gas absorption, like the penetration theory, film theory, boundary layer theory, and the surface renewal theory.

The film model which is simpler mathematically, compared to the models of penetration is usually utilized, based on the film theory, a stagnant film of thickness δ_L is supposed to be existing at gas and liquid interface as has been illustrated in **Fig. 1**. The mass transfer through the molecular penetration takes place via a thin liquid gas layer which is δ thick, and there isn't any concentration gradient in liquid bulk. In the theory of the film, the coefficient of the mass transfer k_L and kg are proportionate to the coefficient of the diffusion DCO2-amine and inversely proportionate to the thickness of the film. k_L stands for the mass transfer coefficient for the liquid side and is equal to:

$$\delta_L = \frac{DCO_2-amine}{k_L} \quad (4)$$

In a similar way, the equation below may be resulted for the coefficient of the mass transfer in gas phase:

$$\delta_G = \frac{DCO_2-amine}{kg} \quad (5)$$

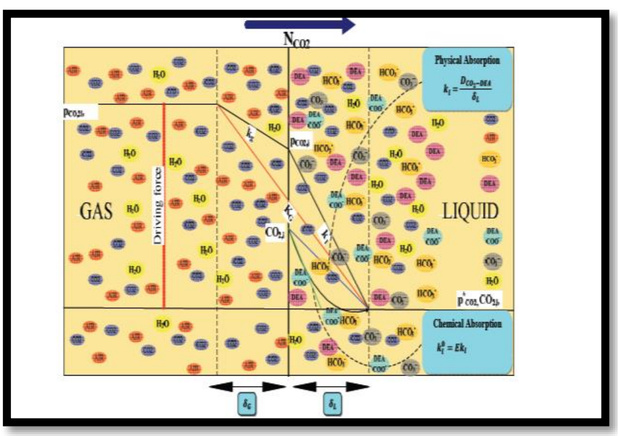

Figure 1. Carbon dioxide mass transfer into the liquid phase with chemical reaction based on the film theory

2.2. Determining the Overall Mass Transfer Coefficient (K_{Ga})

Mass transfer coefficient is an important part of this research. Mass transfer occurs when a component. In the scrubber, a simulated mix of gas which contains A (CO_2) and B (air) which flow to a bubble column from bottom continuously contacts with the solution of the amine which flows from the top in the column. The two streams contact with the column countercurrent in a simultaneous manner. In the present study, has been a reasonable theory. Taking under consideration the ideal gas law for inlet and outlet gases at a variety of temperature values, F_1/F_2 may be substituted by $(P_1/P_2)(T_2/T_1)(y_1/y_2)$. Which is why, the coefficients of the general volumetric mass transfer becomes [12]:

$$K_{Ga}\,(s^{-1}) = \frac{Q_g\,(\frac{L}{s})}{V_L\,(L)} \ln \frac{F_1(\frac{mol}{s})}{F_2(\frac{mol}{s})} \quad (6)$$

Where :

Q_g=Gas flow rate, $(\frac{L}{S})$

F_1=Molar flow rate of CO_2 at inlet, $[\frac{mol}{s}]$

F_2=Molar flow rate of CO_2 at outlet, $[\frac{mol}{s}]$

V_L=is the volume of liquid in the absorber.

3. Experimental Design

A continuous bubble column was used to study the capture. The concentration of blended amine was 10V/v% MEA+5 V/v% DEA. In order to reduce the large amount of experiments, the Taguchi method was used as the experimental design [13]. This study utilized three levels for the variables. When using the Taguchi method, a minimum number of experiments are required to be calculated, as based on the following equation:

$$N = 1 + \sum_{i=1}^{NV} (Li - 1) \quad (7)$$

Table 1 presents the combination of experiments in the orthogonal array for continuous process.

Table 1. Orthogonal arrays for experimental design for continuous process

Experiment No.	(gas flow) L/min	(air flow) L/h	(Liquid flow) L/min
1	10	100	5
2	10	150	5
3	10	200	5
4	15	100	10
5	15	150	10
6	15	200	10
7	20	100	15
8	20	150	15
9	20	200	15

4. Experimental Procedure

A continuous bubble-column scrubber is a powerful process in the removal of CO_2 as compared with other scrubbers since it has a simple construction, higher heat and mass transfer coefficients, higher removal efficiency, and effective control of the liquid residence time. So, a continuous bubble column reactor has become the absorber adopted by some researchers. The chemical solvent employed that used are shown in **Table 2.**

Table 2. Chemical materials(Amines) used in this work

Chemical Name	Abbrev	Chemical formula	Molecular weight [g/mol]	Density g/cm^3
Monoethanolamine	MEA	C_2H_7NO	61.084	1.0117
Diethanolamine	DEA	$C_4H_{11}NO_2$	105.137	1.097

Initially , flue gas was simulated by combining individual streams of CO_2 from gas cylinder and air from air compressor. Rotameters of the unit Liter per minute (Lmin−1) and (Lh-1) were installed for controlling the gas flow rates and air flow rate respectively . For CO_2 gas the range of (CO_2 flow rate) was 10-20 L min−1 and for air it was 100-200 L h-1. The experiment set up were carried out in a bubble column shown in **Fig. 2.** Aqueous solution of amines prepared (solvent) was pumped from the solution tank at a given flow rate range between (5-15)L/min to the top of the column , and a needle valve was installed on the top of the column to control the liquid flow rate so as to create counter current contact between gas and liquid.

After absorbing CO_2 and traveling through the column ,this operation was continued for at least 10 minutes to allow the system to reach steady state conditions , the CO_2-rich solution was then collected continuously in the liquid receiving tank. A drain valve was introduced at the bottom of the column for emptying the column after the process and collecting the sample liquid. At the same time, liquid samples were taken from the bottom of the column and analyzed for their concentrations and CO_2 loading.

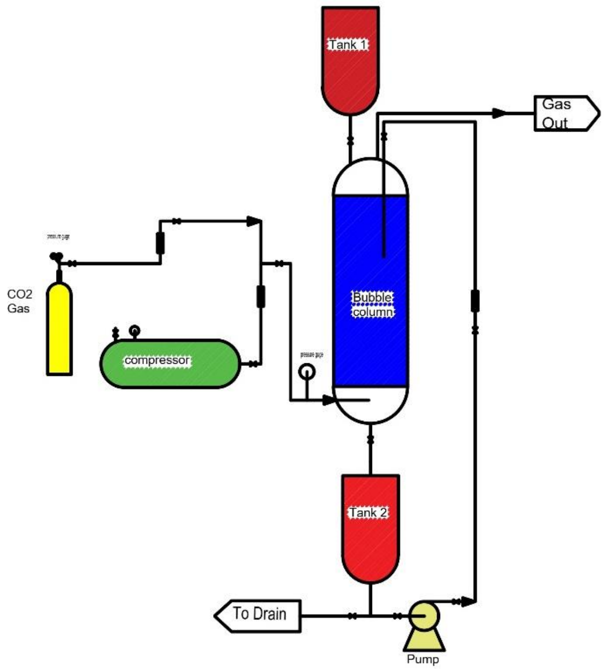

Figure 2. Schematic diagram of Bubble column reactor for absorp tion process

5. Results and Discussion

The experiments for mass transfer in a bubble column were studied based on CO_2 absorption into blended solution from MEA-DEA. Sample taken after absorption experiments were analyzed for CO_2 and amine content .In order to determine the CO_2 loading capacity in term of (moles of CO_2 per moles of amine).Gas chromatography (GC) was used to analyze the concentration of CO_2. In this work high performance a Shimadzu GC-8A Gas Chromatograph was used for analysis the samples that were obtained in experimental work in the laboratory of scientific studies and research in the region of Algiers - Al-Diwaniya (Iraq) .Block diagram of a typical gas chromatograph is shown in **Fig. 3**.

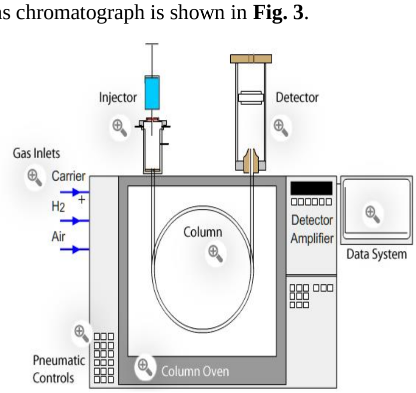

Figure 3. Block diagram of a typical gas chromatograph

The instrument is a gas chromatograph-mass spectrometer or GC-MS ,where a thermal conductivity detector TCD was used with 60 m /Amp detector current and temp.270°C ,it is measures changes in the exiting gas stream. A Porapak-Q column (2 x 2.5 m, the initial and final temp. of column was 120°C-240°C) . One of the gases called the carrier gas (here used helium gas, Helium (IG) with flow rate 20 milliliters/minute)flows into the injector, through the column and then into the detector. A sample is introduced into the injector usually with a syringe or an exterior sampling device. CO_2 loading was calculated by integrating differences between the concentrations of injected CO_2 and the concentrations of emitted CO_2.All the absorbents used in the experiments reached equilibrium at an appropriate time ,when completion of the reactions between CO_2 and the absorbents. The amount of the CO_2 before being injected into the reactor and the amount of the CO_2 emitted after reactions were calculated by applying the ideal gas equation. The absorption loading of CO_2 of (MEA +DEA) as shown in **Table 3.** which is in the range of(0.581–1.367) moles of CO_2 absorbed per mole of amine.The overall mole of CO_2 absorbed in the absorbent can be calculated by subtract mol of CO_2 inlet from out let and the CO_2 loading can be calculated through. CO_2 loading is defined as mole of CO_2 absorbed per mole of amine.

$$n_{co_2,abs} = n_{CO_2,IN} - n_{CO_2,out} \tag{8}$$

$$\boldsymbol{\alpha} = \frac{\textbf{mol of CO}_2}{\textbf{mol of amine}} \tag{9}$$

In **Fig. 4** we found that an increase in the CO_2 loading of an absorbent with increasing time and mean that the solubility of carbon dioxide is increased under various parameters condition.

It can be prediction that the CO_2loading capacity for aqueous blended amine solution increases, as the contact time (in the pilot unit) between the solutions and the CO_2, and the amount of absorbed CO_2 also increases .

Table 3. The results of CO_2 loading of the third set of experiments for *continuous process* by using (MEA=10% and DEA=5%) as blended solution

Group	Gas flow $Lmin^{-1}$	Air flow Lh^{-1}	Liquid flow $Lmin^{-1}$	Abso. time/min	CO_2 loading (mol CO_2/mol amine)	Absor. Capa.
A/10 min	10	100	5	10	0.581	0.128
B/10 min	10	100	5	10	0.742	0.164
C/10 min	10	100	5	10	0.863	0.191
D/10 min	15	150	10	10	0.836	0.185
E/10 min	15	150	10	10	0.884	0.197
F/10 min	15	150	10	10	1.225	0.305
G/10 min	20	200	15	10	0.997	0.233
H/10 min	20	200	15	10	1.180	0.254
I/10 min	20	200	15	10	1.367	0.329

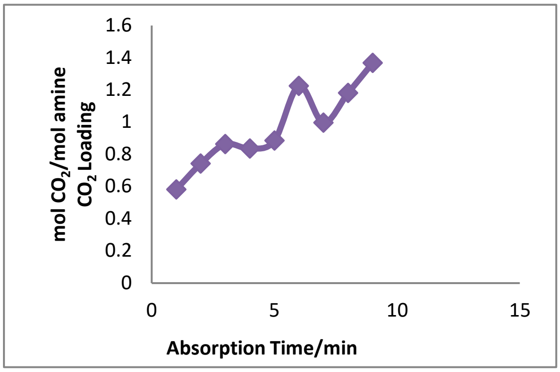

Figure 4. Comparison of the results obtained for CO_2 loading capacity Vs. reaction time for the tested aqueous amine solution

5.1. Effect of CO_2 Loading on Overall Mass Transfer Coefficient K_{Ga}:

Equation (6) show the calculation of K_{Ga} for continuous process ,the results of K_{Ga} for continuous process at 10% MEA+ 5%DEA, the overall mass transfer coefficient of the solutions was range between minimum and maximum value (0.01- 0.04) S^{-1}

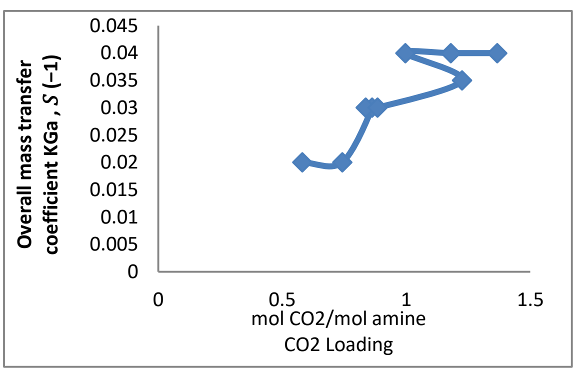

Figure 5- Comparison of the results obtained for CO_2 loading capacity Vs. reaction time for the tested aqueous amine solution (10%MEA+5%DEA)

The effect CO_2 loading on overall mass transfer coefficient of **Fig. 5** ,it is obvious that an increase of CO_2loading in amine solutions leads to adecrease in the existing active amine concentration, which consequently decreases the overall mass transfer coefficient .This effect is mainly attributed to the amount of CO_2loading in the amine solution is high. Where (MEA+DEA) blended amine solution was used , the mass transfer driving force from the gas phase to the liquid phase will decrease.

5.2 Effect of Liquid and Gas Flow Rates on Overall Mass Transfer Coefficient(K_{Ga})

5.1.1. For liquid flow rate :

The influence of liquid flow rate on the overall mass transfer coefficient has been studied for a blended amine solution (10%MEA+5%DEA) for continuous process.

The influence of the liquid flow rate on the overall mass transfer coefficient has been studied on the set 3 using blended amine solution (MEA+DEA) solution was of concentration by volume percent (v/v%) , 10%MEA ,5% DEA respectively . **Fig. 6** presents the evolution of K_{Ga} in function of the time for various liquid flow rates. The obtained mass transfer coefficient after 10 minutes of experiment was (0.04 S^{-1} at flow rate 20 L/min. The first observation is that increasing of the liquid flow rate, the overall mass transfer coefficient also increase with increasing time ,and that opposite with Circulation process.

5.1.2. For Gas flow rate :

One of the key parameters, which can affect the mass transfer performance, is the gas flow rate. Many researchers showed that when the gas flow rate increased, K_{Ga} increased as well.

The blended amine solution was in the form of volume percent concentration 10%,5% respectively. **Fig. 6** presents the evolution of the overall mass transfer coefficient in function of the time for various gas flow rates. The K_{Ga} was (0.04 S^{-1}) at gas flow 20 L/min ,and the air flow was 200 L/h which indicates that more CO_2,is absorbed at saturation step when more gas pass through the column.

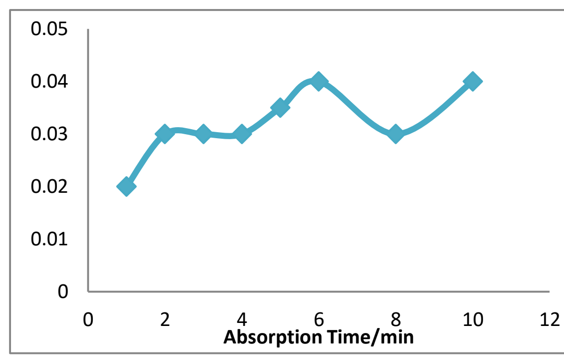

Figure 6- Overall mass transfer in function of time for continuous processes (10% MEA+ 5%DEA)

6. Conclusion

The main objective of this study is to investigate the carbon dioxide absorption in bubble column reactor at different blended amine solution

Monoethanolamine (MEA) and Diethanolamine (DEA) were used as solvent.To achieved this , it was necessary to calculation of the best overall mass transfer coefficient with the help of Taguchi method as an experimental design, in order to reduce the large amount of experiments. This purpose was made using Continuous process. The motivation of this thesis focuses on Study the effect of all parameters {CO_2 loading ,Liquid flow rate , gas flow rate , absorption time} on (k_{Ga}). This study showed that the increasing by the gas flow rate, the liquid flow rate, the k_{Ga} values increased. Also, Increasing the CO_2 loading of amines lead to a k_{Ga} decrease .

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