Carbon Dioxide Capturing via a Randomly Packed Bed Scrubber Using Primary and Poly Amine Absorbents

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ABSTRACT

Greenhouse gases (GHGs) cause global warming and climate change, making their emission and synthesis a global issue. Employing a pilot-scale scrubber packed with a Rashing ring randomly, where experimentally examined the absorption performance of carbon dioxide capturing by using an aqueous solvent of primary and poly alkanol amines; the investigations on carbon dioxide capturing were carried out at atmospheric pressure (1 atm), using simulated feed gas of carbon dioxide balanced with nitrogen. Monoethanolamine, Triethylenetetramine, and Diethylenetriamine are the primary and poly alkanol amine absorbents examined for this work. The impact of operating conditions, including amine inlet concentrations, liquid flow rates, gas flow rate, lean amine loading, inlet carbon dioxide concentration, absorbent temperature, and alkanol amine type, were examined according to the two-film concept. Regarding the removal of carbon dioxide efficiency and volumetric mass transfer coefficient based on the gas side, the absorption performance was presented. A lab-scale investigation revealed that employing DETA absorbent possesses higher carbon dioxide removal efficiency of up to 28.9% and a higher coefficient of mass transfer of up to 165.7% in comparison to conventional MEA absorbent while employing TETA absorbent possesses higher carbon dioxide removal efficiency of up to 18.86% and higher coefficient of mass transfer of up to 69.64% in comparison to the conventional MEA absorbent. Based on these findings, it is reasonable to assume that DETA would serve as an efficient chemical absorbent for the removal of carbon dioxide.

Keywords: carbon dioxide capture; overall mass transfer coefficients; packed bed scrubber; diethylenetriamine; triethylenetetramine; monoethanolamine, two-film concept; chemical absorption.

INTRODUCTION

Due to the adverse ecological impacts of greenhouse gases (GHG), such as global warming and climate change; thus, the emission and synthesis of GHGs have become a severe problem worldwide [1, 2, 3]. One of the most significant gases among GHGs is carbon dioxide [4]; the conventional carbon dioxide concentration in the stream of flue gases from different sources is listed in Table 1; carbon dioxide accounts for 76% of all GHGs globally [5]. The greenhouse gases absorb infrared light, which traps heat and causes the Earth's surface to warm; the term "greenhouse effect" refers to this phenomenon [6]; above this, in sour-gas production, the primary corrosion-causing species is carbon dioxide since the corrosion rate dramatically increases with the existence of carbon dioxide gas [7, 8, 9]. In order to control the environmental effects of greenhouse gas emissions and overcome the corrosion problems in downstream gas processing, it requires advancing effective technologies for carbon dioxide capturing produced by large stationary sources. Emissions of carbon dioxide can be reduced through the use of post-combustion, oxy-fuel, and pre-combustion, combustion technologies [10]; Synthesis gas, a reformed fossil fuel gas stream that primarily contains carbon dioxide and hydrogen, is retained during pre-combustion operations [11]. Post-combustion involves separating carbon dioxide from a stream of nitrogen-rich exhaust gases in order to remove carbon dioxide from already-existing flue gas [12]. Oxy-fuel combustion involves burning fuels in the recycled exhaust gas and oxygen, resulting

Table 1. Typical concentration of carbon dioxide exhausted from a different source

Industry	The concentration of carbon dioxide exhausted (v/v %)	Ref
Power generation	13–15	[21]
Natural gas processing	0–70	[22]
Iron, steel	20–30	[23]
Glass	35–45	[24]
Refineries	10–15	[25]
Cement	20–30	[23]
Quicklime	20–28	[24]
Hydrogen production	20–25	[22]
Oil-fired boilers	11–13	[26]
Pulp and paper	~13	[22]
petrochemical	5–10	[23]
Natural gas-fired boilers	7–10	[26]
Aluminum production	1–2	[26]
Gas turbine	3–4	[26]

in a significant carbon dioxide concentration in the exit stream [13]. Although oxy-fuel combustion technology is still being developed, the pre- and post-combustion are well-established technologies used in many commercial facilities [14]. Accordingly, new methods and materials for capturing and storing carbon dioxide have received significant attention during the last decade, such as membrane separation, adsorption, cryogenics, and chemical and physical absorption, which have been suggested to capture carbon dioxide [15]. The best post-combustion capture technique that can be used to capture carbon dioxide in fossil fuel power plants is chemical absorption [16], amine-based chemical absorption has been identified as a potential mitigation alternative for reducing emissions of carbon dioxide in other energy-intensive sectors, like the production of cement, oil refineries, and steel and iron industry [17], due to their commercial maturity, chemical absorption utilizing amine solutions is commonly regarded as a useful technique for industrial-scale development [18]; absorption scrubbers, commonly packed bed structures, contact gas mixtures with amine solution counter currently to selectively removal of carbon dioxide, these separation techniques can remove carbon dioxide because of its high reaction rate with carbon dioxide [1]. However, low carbon dioxide capturing capability, equipment corrosion, high volatility, and environmental issues were only a few of the downsides of first-generation solvents like monoethanolamine [19]; to overcome these problems,

New solvents are being sought after by researchers to use instead of conventional ones. Poly alkanol amines are a type of amine absorbent with promising properties in terms of thermodynamic capabilities as well as kinetics as carbon dioxide absorbents because of their distinctive structure consisting of two or more groups of amine within a single molecule like DETA and TETA [20]. To our knowledge, a few studies have looked at the impact of poly alkanol amines and operating factors on carbon dioxide capturing in a packed bed absorption scrubber. In the present study, a lab-scale packed bed scrubber was used to assess the removal of carbon dioxide efficiency and volumetric mass transfer coefficient based on the gas side; the absorption performance was presented of three different types of alkanol amine solvent, based on the two-film concept, the effects of the operating variables, absorbent flow rate, absorbent concentration, gas flow rate, lean amine temperature, inlet carbon dioxide concentration, absorbent type, and solvent flow rate, have been investigated. Experimental findings showed that poly alkanol amine solution had the best performance of mass transfer; these findings show that poly amine absorbent would be an effective carbon dioxide chemical absorbent in a packed scrubber.

Reaction mechanism

Many researchers provided extensive information on the carbon dioxide and alkanol amines

reaction kinetics; Saha et al. and Vaidya & Kenig Provided a useful description of the specifics of the reactions mentioned [27, 28]. The reaction between a variety of secondary and primary alkanol amines with carbon dioxide can be described by the zwitterion mechanism. Initially, Caplow [29] proposed the zwitterion mechanism by Danckwerts, who then reintroduced it; this mechanism can be simplified using either secondary or primary alkanol amines (mentioned as R_1R_2NH) in a two-step reaction with carbon dioxide, which reacts reversibly with secondary or primary amine and a zwitterion intermediate ($R_1R_2NH^+COO^-$) where formed in the first step, carbamate ($R_1R_2NCOO^-$) is formed in the second step, through the deprotonation of the intermediate zwitterion through the base (identified by B) according to the Eqs. 1 and 2 [30].

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2NH^+COO^- \qquad (1)$$

where: R_1 – alkyl, $R_2 - H$ for primary amine, and alkyl is for secondary amine.

$$R_1R_2NH^+COO^- + B \leftrightarrow BH^+ + R_1R_2NCOO^- \quad (2)$$
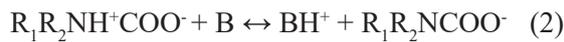
Equation 2, B refers to the base and may involve R_1R_2NH, H_2O, or OH^- [27]. If R_1R_2NH is the most significant contribution in Eq. (3), as proposed by Saha et al. [27], so the following equation will describe the complete reaction of carbon dioxide with amine:

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \quad (3)$$

According to Eq. 3, The maximum amount of carbon dioxide that can be loaded into equilibrium with primary or secondary amine is 0.5 (CO_2 mol/amine mol). However, only relatively stable carbamate species (like DEA and MEA) qualify for this statement [29].

Determination of carbon dioxide removal efficiency

The carbon dioxide removal efficiency (η), one of the most critical responses in this study, is defined as the quantity of carbon dioxide captured by an alkanol amine absorbent under standard conditions of use. The equation for this is as follows. It is derived by estimating the change in carbon dioxide content between the feed and the treated gas [31]:

$$\eta = \left(1 - \frac{y_{CO2,out}}{1-y_{CO2,out}} * \frac{1-y_{CO2,in}}{y_{CO2,in}}\right) * 100 \% \quad (4)$$

where: $y_{CO2,in}$ and $y_{CO2,out}$ – denote mole fractions of carbon dioxide gas phase feeding and releasing the packed scrubber.

Determination of the overall coefficient of mass transfer based on the gas side per unit volume (K_{G*av})

The classic two-film concept

The two-film concept states that there is a very thin film of gaseous and liquid on both sides of the interface, with the diffusion of molecules through each of the two films acting as the controlling factor; the total mass transfer coefficient (K_G) for chemical absorption according to the distinct gas (k_g) and liquid-phase (k_l) mass transfer coefficients, as well as the factors of enhancement (β) [30].

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{H}{\beta * k_l} \qquad (5)$$

The effective liquid-gas interfacial area (a_v), in addition to the coefficients of mass transfer, is regarded as an essential variable in the process of mass transfer in a gas-absorption device like a packed scrubber; designing absorption scrubbers has traditionally depended on the transfer unit principle, and it is within this notion that the K_{G*av} arises in the process of engineering design. Therefore, calculating the K_{G*av} is more practical:

$$\frac{1}{K_{G*a_v}} = \frac{1}{k_{g*a_v}} + \frac{H}{\beta * k_{l*a_v}} \qquad (6)$$

Obviously, Eq. 6 can be used to directly calculate the overall coefficient; however, due to the complicated methodologies required for experimental determination of the individual coefficients of mass transfer; thus, this methodology is not commonly used. The mass transfer coefficient K_{G*av} can be determined by the measured carbon dioxide concentrations in experiments at the sour and sweet pipelines.

Determination of K_{G*av} from experimental carbon dioxide concentrations at the sour and sweet pipelines

Three primary factors influence the mass transfer coefficient: the wetting area between gases and liquids, liquid phase resistance, and gas phase resistance [32]. Equation 7 is used to compute the K_{G*av} kmol/m³·h·kPa, an equation comparable to Eq. 7 has been described in preceding investigations [33–37]:

$$K_{G*a_v} = \frac{G}{P*Z} * \left[\frac{\ln \left(\frac{y_{CO2,in} * (1 - y_{CO2,out})}{y_{CO2,out} * (1 - y_{CO2,in})} \right) +}{\left(\frac{y_{CO2,in}}{(1 - y_{CO2,in})} - \frac{y_{CO2,out}}{(1 - y_{CO2,out})} \right)} \right] \quad (7)$$

where: $y_{CO2,in}$, $y_{CO2,out}$ – represent the feed and treated gas stream molar carbon dioxide concentration through the packed tower, Z – the packed height of the scrubber, G – represents the total inert gas molar flow, P – the operational pressure.

MATERIALS AND METHODS

Distilled water; Monoethanolamine (MEA, Thomas Baker, >98%); Diethylenetriamine (DETA, Fluka, >97%); Triethylenetetramine (TETA, Fluka, >60%), Four amines are used to make this product: two cyclical, one with branching, and one linear, Only 60% of the total is represented by the linear form; CO_2 gas cylinder (>99.6 vol.% (and N_2 gas cylinder) >99.8 vol.% (were purchased from Albilal Gas Company located in Baghdad; the supplies material were utilized in the same condition as when they were first received, all amine solutions were prepared using distilled water and volumetric glassware.

METHODOLOGY AND EXPERIMENTAL SETUP

In this study, a lab-scale carbon dioxide capture unit was used to evaluate the mass transfer performance of the carbon dioxide capture system for a simulated exhaust gas of a comparable cement factory with a comparable composition and alkanol amine solution as absorbent. The experimental setup's schematic diagram of the absorption lab unit is shown in Figure 1. The packed scrubber was made of acrylic with a 2 m total height and 40 mm inner diameter, the packing scrubber height was 1.8 m, and the packed material was a glass Rashing ring with a size of 6 mm diameter, and with 0.8 mm of a wall thickness which is dumped to the scrubbed randomly, the percentage of free space in the packing section is 62%, and the contact surface area is about 794 m²/m³. To control the lean alkanol amine solution temperature, it stores in a 1000 ml glass flask; the 1000 ml glass flask was kept at a constant temperature set by an electric heater with a stirrer and temperature controller (Dragon Lab, MS-H-Pro, China). The simulated exhaust gas is

provided using a two-gas flow meter that mixes the desired concentration of carbon dioxide balanced with nitrogen; the feed pressure of gases pipeline is set to 1.2 atm, which is controlled via pressure regulator valves which then flow controlled with a flow meter; after that, fed two streams to a gas mixing T shape connection to mix both gases before feeding them to the packed scrubber. The simulated gas passed through the scrubber from its base to the top. The lean amine absorbent is provided into the scrubber at the top of the scrubber; it is pumped to the column top at a specific flow rate via a diaphragm pump (Diaphragm pump, TYP-2500NH, China); the rotameter and bypass valve are installed on the lean amine pipeline to control the liquid flow rate and the head of the pump. Thus, the simulated gas and alkanol amine solvent were in a counter-current flow pattern; it is beneficial to make simulated gas and aqueous alkanol amine solution contact and react effectively. When the scrubber top outlet concentration of carbon dioxide is constant (0.1 vol.%), a steady state is reached, which was approximately reached after 10 minutes of operation, IR gas analyzer (Geotechnical Instruments, BIOGAS 5000, United Kingdom) by dual wavelength infrared sensor with reference channel 0–100% vol, with an accuracy ±0.5% vol for the range 0–60%, and 60–100% is 1.5%, response time for measuring carbon dioxide gas ≤10 seconds, pump with a flow of 550 ml/min [38], gas analyzer typically was used during the tests to purge samples and measure the carbon dioxide concentrations. All tests were performed at the ambient pressure (1 atm). Table 2 provides further information on the operational conditions.

RESULTS AND DISCUSSION

Effect of liquid flow rate

As indicated in Figure 2 and Figure 3 with all types of alkanol amine absorbent, the values of both carbon dioxide removal efficiency (η) and the overall volumetric mass transfer coefficients based on the gas phase ($K_G a_v$) follow a rising trend with increasing the alkanol amine flow rate. An increase in alkanol amine flow rate from 0.9549 m³/m²·h to 1.9099 m³/m²·h yielded the following: in the case of DETA, the η increased from 72.65% to 99.59%, in case of TETA, η increased from 58.49% to 96.37% and, in case of MEA, η increased from 42.33% to 93.90%. In term of $K_G a_v$
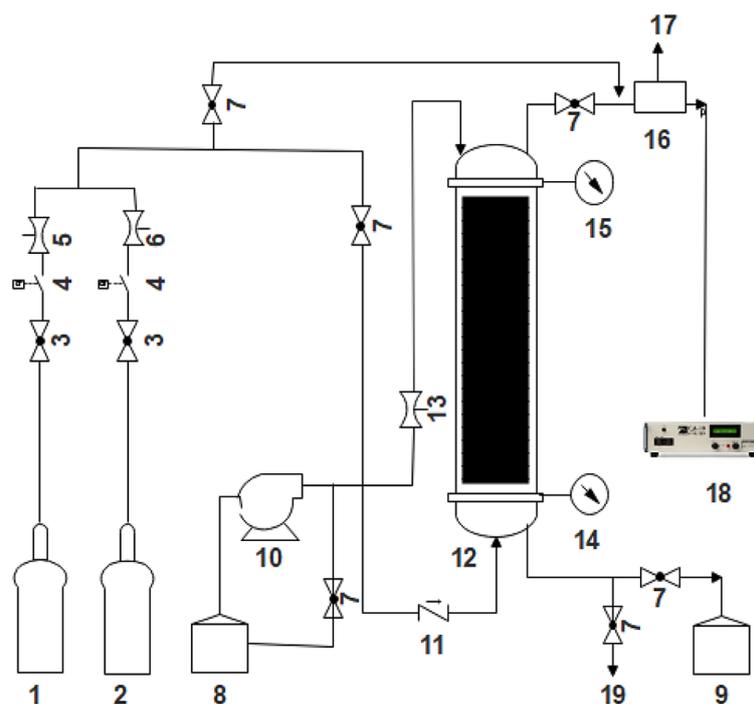
Figure 1. Experimental schematic for carbon dioxide capture in a packed bed absorber

Table 2. Range of experimental operating conditions

Parameters	Range
Gas flow rate	3.8408, 7.6817, 11.5225 (kmol/m²·h)
Lean amine flow rate	0.9549, 1.4324, 1.9099 (m³/m²·h)
Lean amine loading	0, 0.15, 0.30 (mol CO_2/molamine)
Inlet lean amine temperature	298.15–323.15 K
Average inlet simulated gas temperature	298.15 K
Total amine concentrations	10, 20, 30 wt.%
Carbon dioxide inlet concentration	20, 30, 40 v/v.%
Amine type	MEA, DETA, TETA
Operating pressure	101.325 kPa
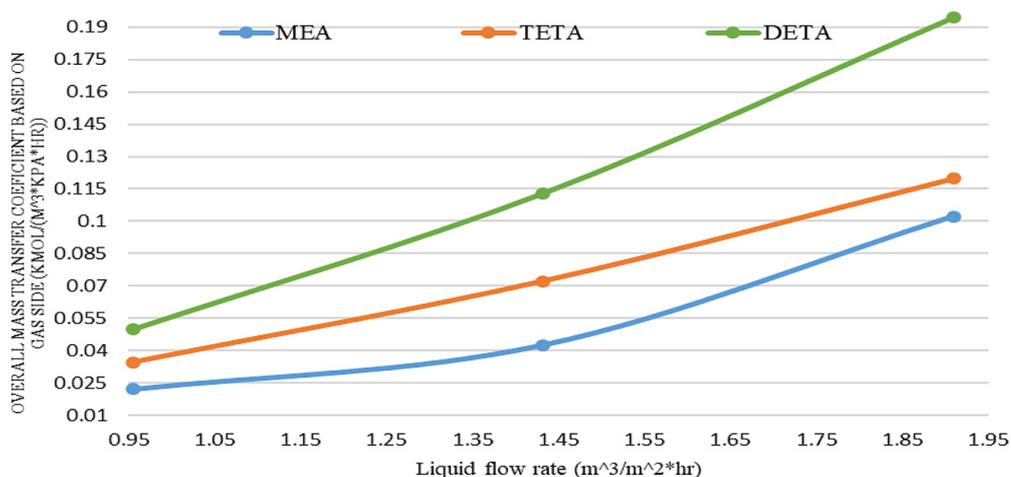
Figure 2. Liquid flow rate's impact on $K_G a_v$ at T = 298.15 K, P_{opp} = 101.325 kPa, unloaded. Lean amine, CO_2 inlet = 20% v/v, G = 7.6817 kmol/m²·h, wt. = 30%
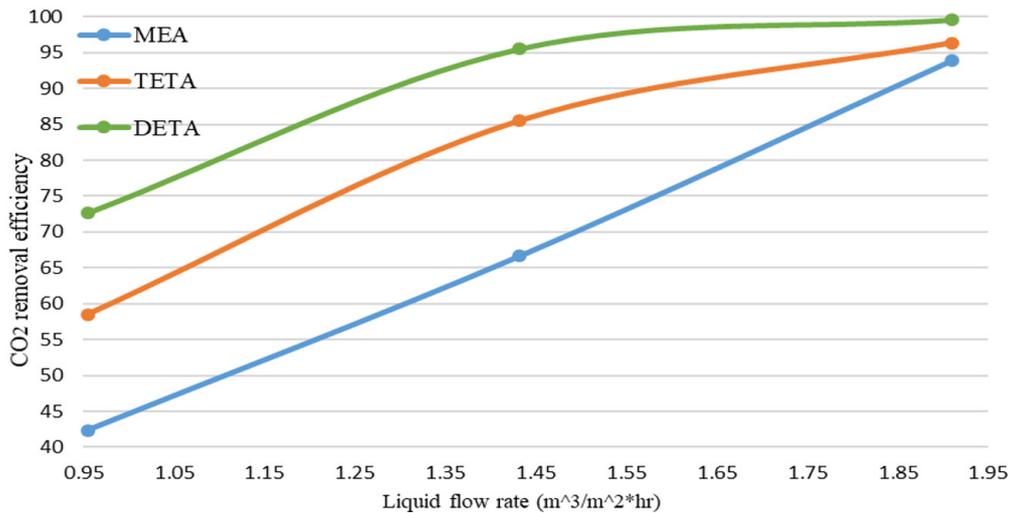
Figure 3. Liquid flow rate's impact on carbon dioxide removal efficiency at $T = 298.15$ K, $P_{opp} = 101.325$ kPa, unloaded. Lean amine, CO_2 inlet = 20% v/v, wt. = 30%, $G = 7.6817$ kmol/m²·h

and with the increasing of alkanol amine flow rate from 0.9549 m³/m²·h to 1.9099 m³/m²·h yielded the following; in the case of DETA, the K_Ga_v increased from 0.0498 to 0.194 kmol/m³·h·kPa, in case of TETA, K_Ga_v risen from 0.0346 to 0.1198 kmol/m³·h·kPa and, in case of MEA, K_Ga_v increased from 0.0221 to 0.102 kmol/m³·h·kPa. The enhancement of both K_Ga_v and η, which may result from a rise in the liquid flow rate, could lead to an increase in the alkanol amine flow that covers the packing elements' outer surface; this is based on our observations. According to Vaewhongs et al. (2020), a packed column with a higher liquid flow rate could additionally encounter turbulent mixing of the liquid inside that case, a reduction in the liquid film thickness [36]; another possible explanation is that the chemical enhancement in the absorbent, which is related to K_Ga_v values, increased as a result of the greater number of chemical molecules accessible to react with carbon dioxide during absorption processes [39]. These findings were in line with research on carbon dioxide absorption via alkanol amine [36, 39, 40]. However, a rise in the liquid flow rate has a negative impact on the system's energy and costs [42]. In conclusion, the mass transfer performance of carbon dioxide capturing via alkanol amine is significantly influenced by the liquid flow rate.

Effect of gas flow rate

As shown in Figure 4 and Figure 5, both Carbon dioxide removal efficiency (η) and the overall volumetric mass transfer coefficients based on the gas phase (K_Ga_v) were strongly affected by changes in gas flow rate. The obtained experimental results show an increase in the total gas flow rate which was led to a slight increase in K_Ga_v value with DETA absorbent for the gas flow rate increased from 3.8408 kmol/m²·h to 7.6817 kmol/m²·h then decreased as gas flow rate exceed 7.6817 kmol/m²·h, this slight increase can be due to many reasons one of them is that DETA is categorized as a Polyamines, a class of potential amine absorbent; due to their unique structure of two or more amino groups inside one molecule, they have been shown to have a high kinetics and, absorption capacity making them promising absorbents for carbon dioxide capturing [42]; However, turbulent column conditions are induced by a higher gas flow rate which is more favorable to mass transfer; although to the fact that gas's detention time in the solution decreased as the gas flow rate increased; thus, the K_Ga_v increases as the driving force between carbon dioxide and the amine is increased, where as there are more molecules of carbon dioxide available to move from the gas bulk side to the gas-liquid boundary layer [43]. The sharp decrease in K_Ga_v value over the progression of the study with DETA absorbent when the gas flow rate exceeded 7.6817 kmol/m²·hr and both MEA and TETA take the same trend over the range of gas flow rate used in the test; this is because using a higher gas flow rate resulted in a lesser contact time between the gas and liquid [44]. In general, there are more carbon dioxide molecules available for absorption when the gas flow rate is increased while there is
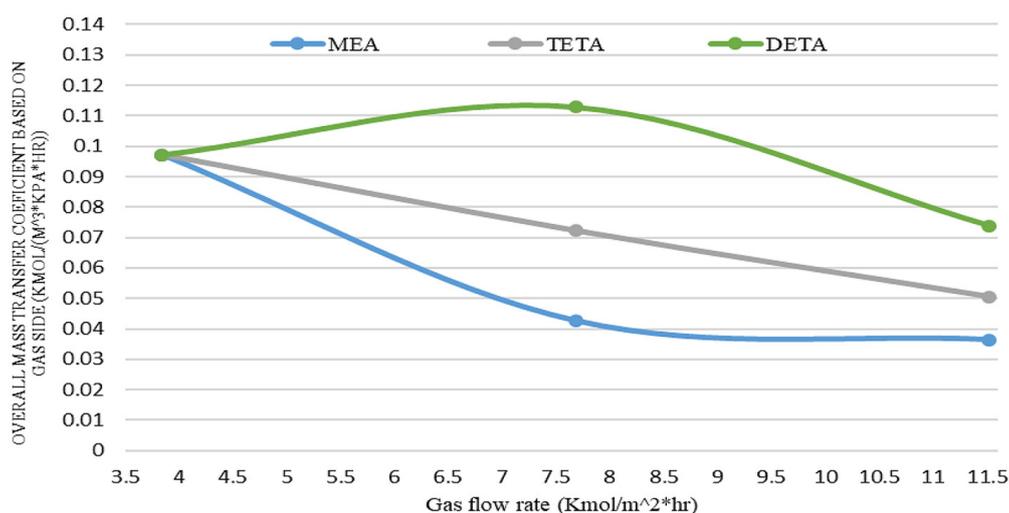
Figure 4. Gas flow rate's impact on K_Ga_v at $T = 298.15$ K, $P_{opp} = 101.325$ kPa, unloaded. Lean amine, CO_2 inlet = 20% v/v, L = 1.4324 m³/m²·h, wt. = 30%
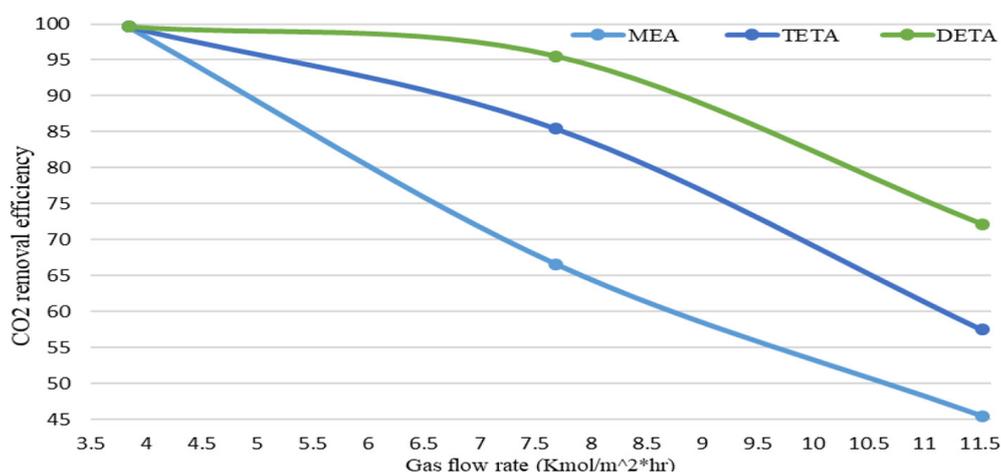

Figure 5. Gas flow rate's impact on carbon dioxide removal efficiency at $T = 298.15$ K, $P_{opp} = 101.325$ kPa, unloaded. Lean amine, CO_2 inlet = 20% v/v, $L = 1.4324$ m³/m²·h, wt. = 30%

a fixed amount of free active amine; the performance of mass transfer is controlled by the liquid flow rate and the reactive amine availability in the liquid phase when the gas flow rate exceeds 7.6817 kmol/m²·h with DETA absorbent and with using MEA and TETA over the range of gas load used in test; thus, the overall gas coefficient is not just dependent on the gas flow rate [45]. On the other hand, in terms of carbon dioxide removal efficiency (η), it followed a reduction trend for all types of amine: in the case of DETA, the η decreased from 99.59% to 72.19%, in the case of TETA, η decreased from 99.59% to 57.52%, and in the case of MEA, η decreased from 99.59% to 45.45%; this is due to a higher gas flow rates resulted in more molecules of carbon dioxide fed to the column, while constant amine molecules

in the liquid; furthermore, the increased gas flow rate further reduces the gas's residence time in the absorption scrubber and lessens the possibility of the carbon dioxide and amine molecules reacting [46]. These findings were in line with research on carbon dioxide absorption via alkanol amine [39, 40]. In conclusion, the carbon dioxide removal efficiency and K_Ga_v in carbon dioxide and alkanol amine absorption systems are significantly influenced by the gas flow rate.

Effect of total absorbent concentration

As indicated in Figures 6 and 7 with all types of alkanol amine absorbent, the values of both carbon dioxide removal efficiency (η) and the overall volumetric mass transfer coefficients based on
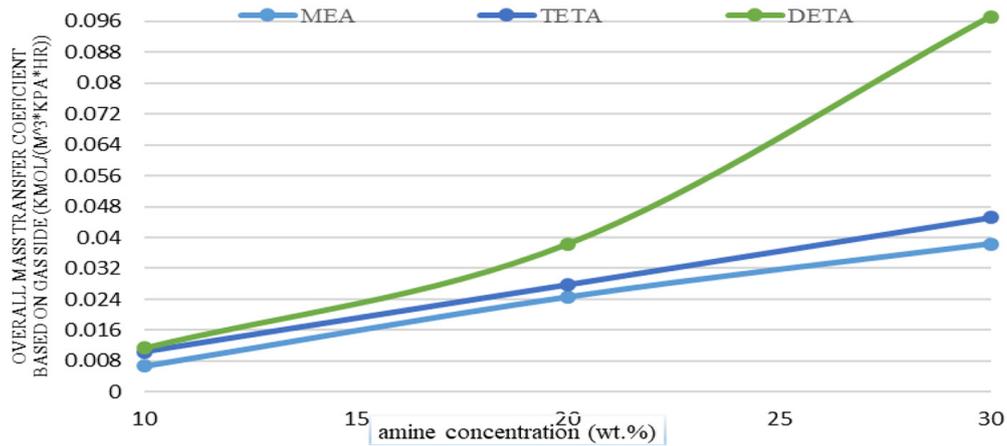
Figure 6. Total absorbent concentration's impact on K_Ga_v at $T = 298.15$ K, $P_{opp} = 101.325$ kPa, unloaded. Lean amine, CO_2 inlet =20% v/v, $G = 3.8410$ kmol/m²·hr), L= 0.9549 m³/m²·h
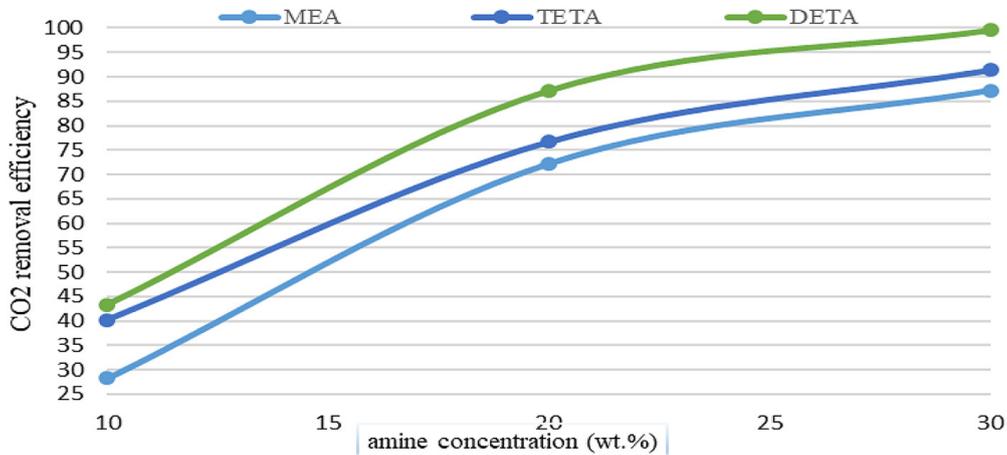

Figure 7. Total absorbent concentration's impact on **carbon dioxide removal efficiency** at $T = 298.15$ K, $P_{opp} = 101.325$ kPa, unloaded lean amine, CO_2 inlet = 20% v/v, $G = 3.8410$ kmol/m²·h, $L = 0.9549$ m³/m²·h

the gas phase (K_Ga_v) follow a rising trend with increasing the total absorbent concentration. An increase in the total absorbent concentration from 10% wt. to 30% wt. yielded the following: in the case of DETA, the η increased from 43.38% to 99.60%, in the case of TETA, η rose from 40.23% to 91.42%, and in case of MEA, η increased from 28.3% to 87.2%; In term of K_Ga_v and with an increase in the total absorbent concentration from 10% wt. to 30% wt. yielded the following; in the case of DETA, the K_Ga_v increased from 0.0114 to 0.0972 kmol/m³·h·kPa, in case of TETA, K_Ga_v risen from 0.0104 to 0.0452 kmol/m³·h·kPa and, in case of MEA, K_Ga_v increased from 0.0068 to 0.0383 kmol/m³·h·kPa. The fundamental reason for this is that higher solution concentrations would result in more free active molecules of alkanol amine per unit volume, which could raise the enhancement factor and allow for faster

carbon dioxide absorption into alkanol amine solvent [47], from a chemical dynamics perspective, increasing the concentration of the absorbent is analogous to raising the concentration of the reactant, this leads to a positive shift in the response, thereby enhancing the reaction rate [48]. However, the solution's viscosity would rise as the solution concentration increased. However, it is difficult for carbon dioxide to diffuse from the gas/liquid boundary to the bulk liquid phase due to the high viscosity [47].

Effect of inlet absorbent temperature

As indicated in Figures 8 and 9 with all types of alkanol amine absorbent, the values of both Carbon dioxide removal efficiency (η) and the overall volumetric mass transfer coefficients based on the gas phase (K_Ga_v) follow a slight
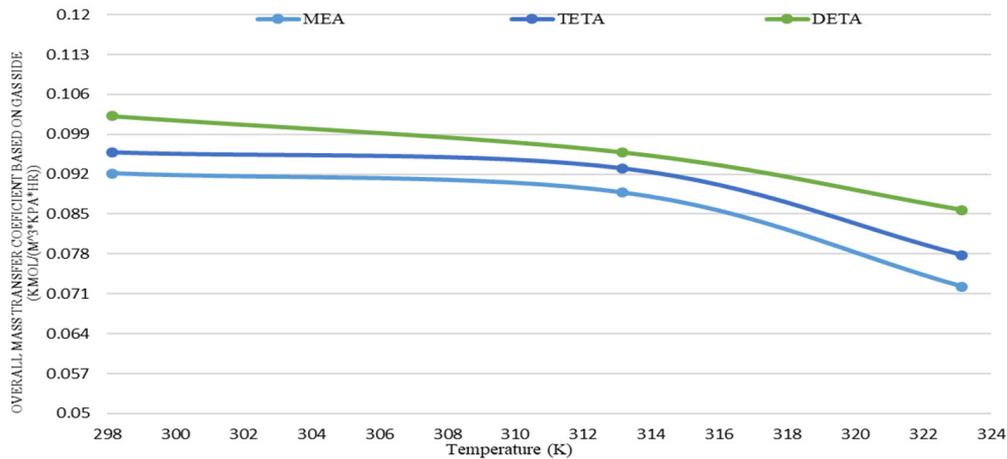
Figure 8. Effect of inlet absorbent temperature on $K_G a_v$ at wt. = 20% G = 7.6817 kmol/m³·h, L = 1.9099 m³/m²·h, P_{opp} = 101.325 kPa, unloaded. Lean amine, CO_2 inlet = 20% v/v
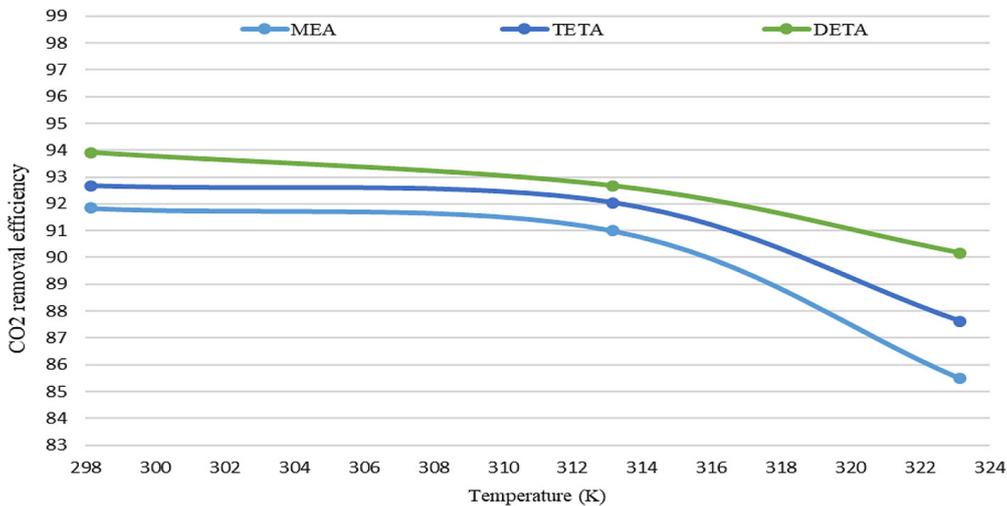

Figure 9. Effect of inlet absorbent temperature on carbon dioxide removal efficiency at G = 7.6817 kmol/m³·h, L = 1.9099 m³/m²·h, P_{opp} = 101.325 kPa, unloaded. Lean amine, CO_2 inlet = 20% v/v, wt. = 20%

reduction trend with increasing the inlet absorbent temperature. An increase in inlet absorbent temperature from 298.15 K to 323.15 K yielded the following: in the case of DETA, the η reduced from 93.90% to 90.16%; in the case of TETA, η reduced from 92.67% to 87.63% and, in case of MEA, η reduced from 91.84% to 85.49%; In term of $K_G a_v$ with an increase in inlet absorbent temperature from 298.15 K to 323.15 K yielded the following; in the case of DETA, the $K_G a_v$ decreased from 0.1022 to 0.0857 kmol/m³·h·kPa, in case of TETA, $K_G a_v$ decreased from 0.0959 to 0.0778 kmol/m³·h·kPa and, in case of MEA, $K_G a_v$ decreased from 0.0922 to 0.0723 kmol/m³·h·kPa. This was because, at high enough temperatures, reverse reactions may occur in the exothermic reaction of absorption of carbon dioxide

mechanism; also, carbon dioxide's physical solubility in the absorbent decreases as the temperature rises because of an increase in the carbon dioxide vapor pressure above the solution [49]. Above that, due to the fact that alkanol amine absorption capacity is temperature dependent, the effect of temperature on absorption capacity plays an important role; it drops when the temperature rises [43].

Effect of lean amine loading

The lean amine loading is a parameter in an absorption process that is an interesting dynamic variable since their values change with the packed scrubber height; while the absorbent concentration and liquid flow rate are static factors,

the carbon dioxide loading rises as the liquid descends from the top of the scrubber, the carbon dioxide molecules transferred from the gas phase into the liquid phase is what caused this [50]. As indicated in Figures 10 and 11 with all types of alkanol amine absorbent, the values of both carbon dioxide removal efficiency (η) and the overall volumetric mass transfer coefficients based on the gas phase ($K_G a_v$) follow a reduction trend with increasing the lean amine loading. In terms of carbon dioxide removal efficiency, an increase in the lean amine loading from 0 to 0.3 (CO_2 moles/ moles amine) yielded the following: in the case of DETA, the η reduced from 95.55% to 65.22%, in the case of TETA, η reduced from 85.49% to 56.05% and in case of MEA, η reduced from

66.6% to 37.04%; In term of $K_G a_v$ with an increase in the lean amine loading from 0 to 0.3 (CO_2 moles/ moles amine); yielded the following; in the case of DETA, the $K_G a_v$ decreased from 0.1129 to 0.0411 kmol/m³·h·kPa, in case of TETA, $K_G a_v$ decreased from 0.0723 to 0.0324 kmol/m³·h·kPa and, in case of MEA, $K_G a_v$ decreased from 0.0426 to 0.0187 kmol/m³·h·kPa. Reasons for this when the solution is fully loaded or at its maximum capacity, which occurs, for example, in MEA solution when the carbon dioxide loading reaches a maximum of about 0.50 CO_2 moles /moles amine, absorption stop to occur; also, the mass transfer driving force of steadily decreases as liquid loading grows throughout the column's length. Less free alkanol amine molecules are accessible to interact with
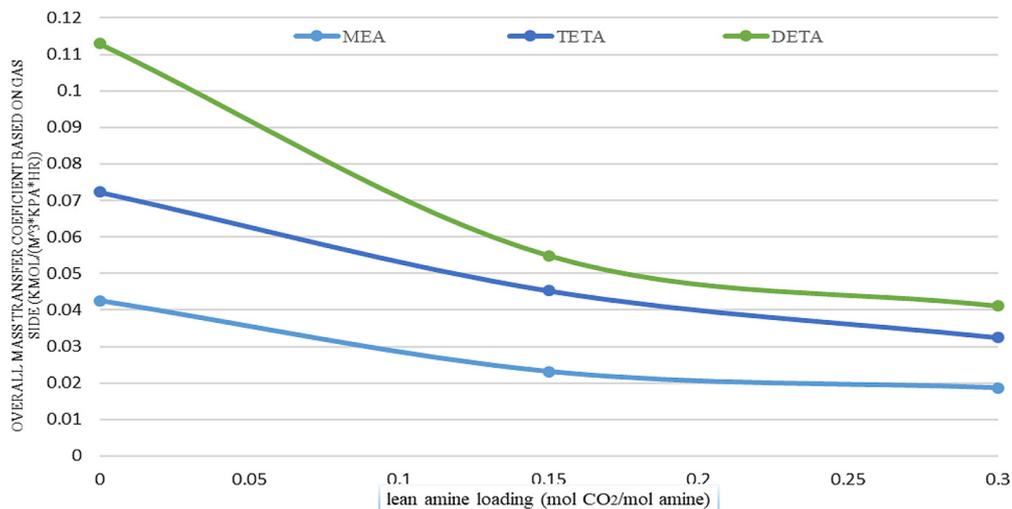

Figure 10. Effect of lean amine loading on $K_G a_v$ at T = 298.15 K, P_{opp} = 101.325 kPa, CO_2 inlet = 20% v/v, wt. = 30%, G = 7.6817 kmol/m³·h, L = 1.9099 m³/m²·h
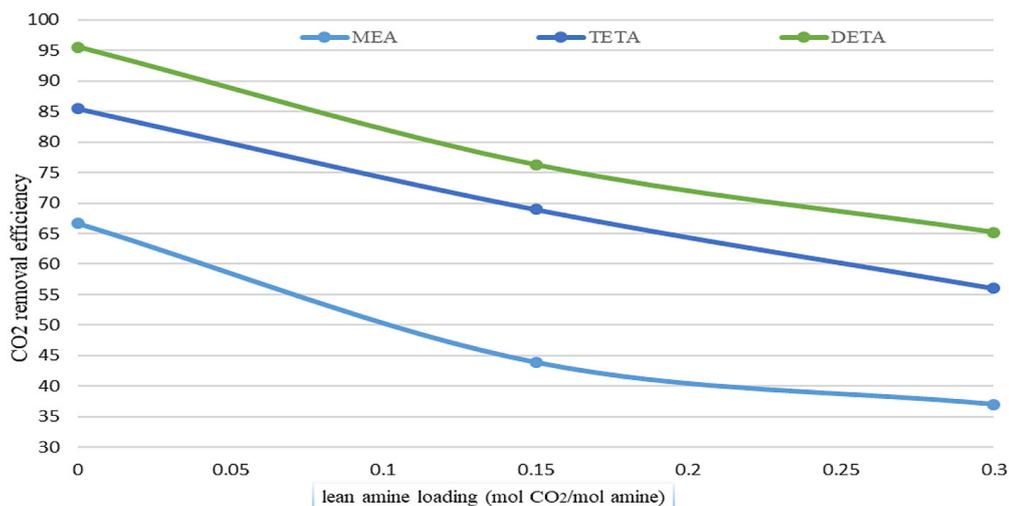

Figure 11. Effect of lean amine loading on carbon dioxide removal efficiency at T = 298.15 K, P_{opp} = 101.325 kPa, CO_2 inlet = 20% v/v, G = 7.6817 kmol/m³·h, L = 1.9099 m³/m²·h, wt. = 30%

carbon dioxide molecules, which has this effect as a result of the mass transfer being less efficient due to the increased carbon dioxide lean amine loading, as well as the K_Ga_v value being decreased [50], to achieve lower lean amine loadings in the absorption process, significant energy is required to be used throughout the desorption process in order to release carbon dioxide; Consequently, it is not recommended to pursue low carbon dioxide loadings [47].

Effect of inlet concentration of carbon dioxide

Investigations were also conducted on the impact of inlet concentration of carbon dioxide on K_Ga_v and η. As indicated in Figures 12 and 13

with all types of alkanol amine absorbent, the values of both carbon dioxide removal efficiency (η) and the overall volumetric mass transfer coefficients based on the gas phase (K_Ga_v) follow a slight reduction trend with increasing the inlet concentration of carbon dioxide. In terms of carbon dioxide removal efficiency, an increase in the inlet concentration of carbon dioxide from 20% to 40% (v/v) yielded the following: in the case of DETA, the η reduced from 76.72% to 65.73%, in the case of TETA, η reduced from 50.56% to 47.02% and in case of MEA, η reduced from 41.28% to 28.76%; In term of K_Ga_v with an increase in the inlet concentration of carbon dioxide from 20% to 40% (v/v); yielded the following; in the case of DETA, the K_Ga_v decreased
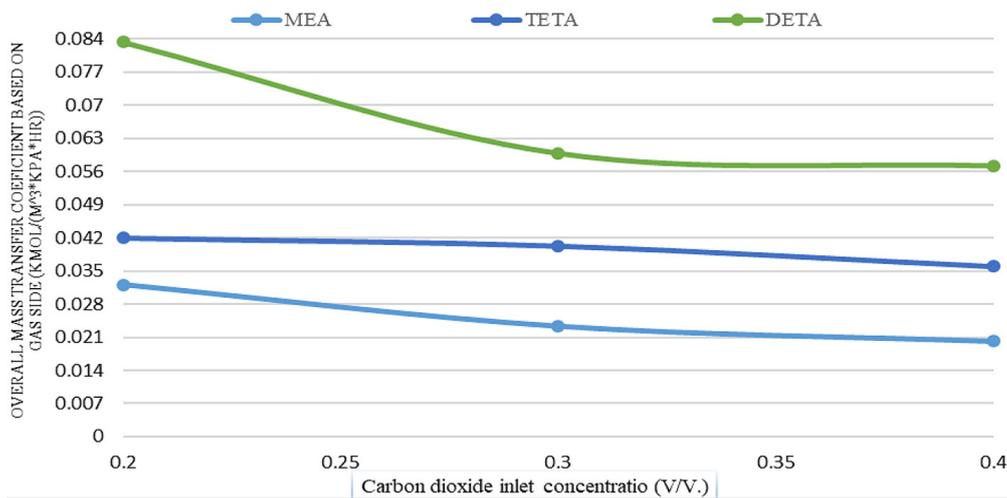

Figure 12. Inlet Carbon dioxide concentration effect on K_Ga_v at $T = 298.15$ K, $P_{opp} = 101.325$ kPa, unloaded. Lean amine, wt. = 20%, $G = 11.5225$ kmol/m²·h, $L = 1.4324$ m³/m²·h
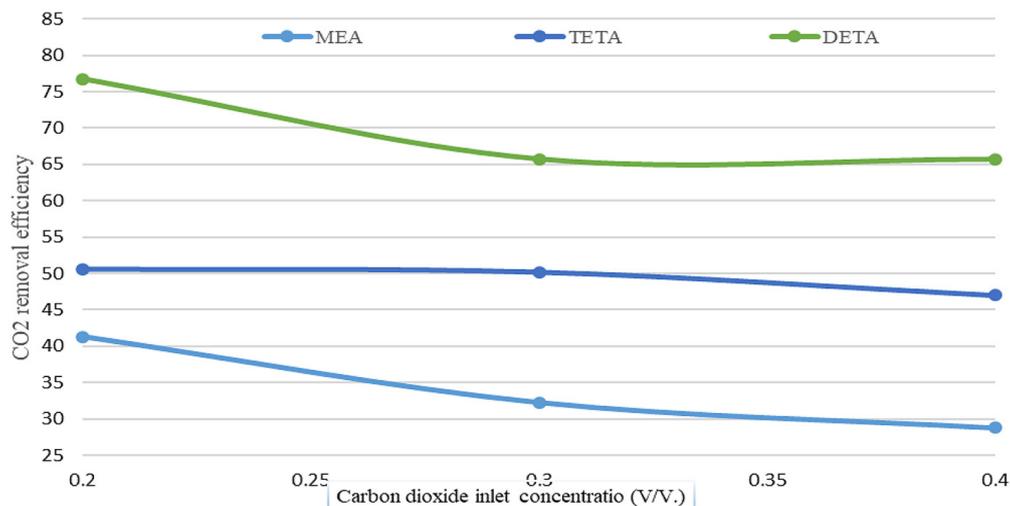

Figure 13. Effect of inlet carbon dioxide concentration on carbon dioxide removal efficiency at $T = 298.15$ K, $P_{opp} = 101.325$ kPa, unloaded. Lean amine, wt. = 20%, $G = 11.5225$ kmol/m²·h, $L = 1.4324$ m³/m²·h

from 0.0834 to 0.0572 kmol/m³·h·kPa, in case of TETA, K_Ga_v decreased from 0.0419 to 0.0359 kmol/m³·h·kPa and, in case of MEA, K_Ga_v decreased from 0.0321 to 0.0201 kmol/m³·h·kPa. This phenomenon is caused by the restricted diffusion of absorbent molecules in the liquid phase, in which a consistent amount of carbon dioxide is absorbed as a result of the restricted diffusion in the liquid side [51, 52].

Effect of alkanol amine type

As indicated in Figures 14 and 15, both carbon dioxide removal efficiency (η) and the overall volumetric mass transfer coefficients based on the gas phase (K_Ga_v) are strongly affected by the types of alkanol amine absorbent. The better order ranked in terms of carbon dioxide removal

efficiency is DETA>TETA> MEA under similar operating conditions. It was observed, that the carbon dioxide removal efficiency was 95.55% for DETA, 85.49% for TETA, and 66.63% for MEA under the same operating condition to ensure the objectivity of the comparison. It was also observed under the same condition that the overall mass transfer coefficient takes the same bitterness rank in which K_Ga_v was 0.1129 kmol/m³·h·kPa for DETA, which is higher than the TETA, and MEA, by 56.3%, 165.7% respectively. These results suggest that the carbon dioxide removal efficiency and gas side mass transfer coefficient within DETA was the highest compared to other alkanol amines TETA and MEA. These consistent results would be attributed to the difference in the absorption capacity, which is limiting the absorption rate of carbon dioxide; a
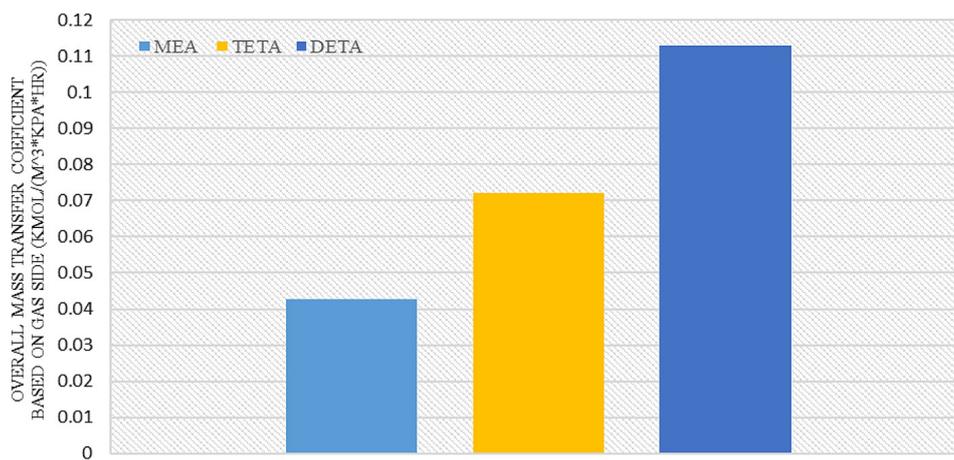

Figure 14. Effect of alkanol amine type on K_Ga_v at T = 298.15 K, P_{opp} = 101.325 kPa, unloaded. Lean amine, CO_2 inlet =20% v/v, wt. = 30%, G = 7.6817 kmol/m²·h, L = 1.4324 m³/m²·h

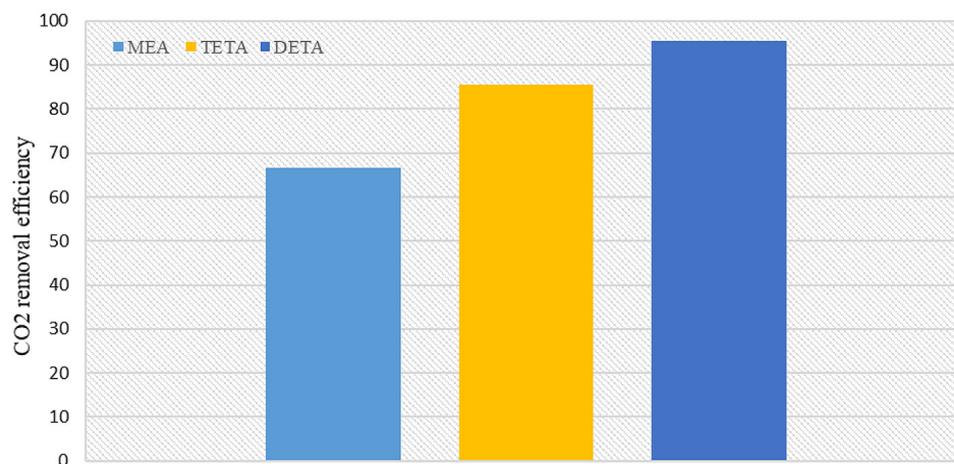**Figure 15.** Effect of alkanol amine type on carbon dioxide removal efficiency at T = 298.15 K, P_{opp} = 101.325 kPa, unloaded. Lean amine, CO_2 inlet = 20% v/v, wt. = 30%, G = 7.6817 kmol/m²·h, L = 1.4324 m³/m²·h

comparison of DETA with other types of alkanol amine proved that the capacity of absorption in a unit of (g carbon dioxide/kg solution amine) was in the order of DETA (156.89 g CO_2/kg solution) > TETA (130.51 g CO_2/kg solution) > MEA (125.4 g CO_2/kg solution) [53, 54], thus higher absorption capacity resulting in the enhancement of carbon dioxide mass transfer rate, However, in addition to the absorption capacity, performance of mass transfer is also an essential criteria for evaluating a new solvent due to its significant impact on packing height and operating conditions, as well as direct effects on investment and operating costs [42]. In addition, a simulation of an actual carbon dioxide capture process can be obtained through research on mass transfer performance in a packed scrubber.

CONCLUSION

Three different absorbent solutions were used in this study; DETA, TETA, and MEA as a solvent for carbon dioxide absorption in a randomly packed bed scrubber with Rashing rings packing. The impact of operating conditions, including amine inlet concentrations, liquid flow rates, gas flow rate, lean amine loading, inlet carbon dioxide concentration, absorbent temperature, and alkanol amine type, were examined based on the two-film concept regarding the volumetric overall mass transfer coefficient based on the gas side (K_Ga_v), and carbon dioxide removal efficiency (η); where the absorption performance was presented. The investigated outcomes demonstrate that DETA and TETA could enhance carbon dioxide capturing performance, the more impressive enhancing effects from the DETA absorbent than conventional MEA absorbent. In line with the order of the absorption capacity and reaction rate constant, the carbon dioxide capturing performance is ranked as follows: DETA > TETA > MEA. The other operational parameters significantly influence carbon dioxide absorption performance regardless of the type of absorbent, which demonstrated that the performance of absorption could be enhanced by increasing liquid flow rate and total amine concentration while decreasing with increasing gas flow rate, lean amine loading, inlet carbon dioxide concentration, and absorbent temperature. Additionally, K_Ga_v first increased and then declined with a rise in gas flow rate using the DETA solution. These

investigations show that a DETA solution could be an effective carbon dioxide absorbent.

REFERENCE

1. Cao, Y., Seyed Alizadeh, S.M., Fouladvand, M.T., Khan, A., Taghvaie Nakhjiri, A., Heidari, Z., Pelalak, R., Kurniawan, T.A., Albadarin, A.B. 2021. Mathematical modeling and numerical simulation of CO_2 capture using MDEA-based nanofluids in nanostructure membranes. Process Safety and Environmental Protection, 148, 1377–1385. https://doi.org/10.1016/j.psep.2021.03.007

2. Al-Obaidi, D.A., Al-Mudhafar, W.J., Al-Jawad, M.S. (2022). Experimental evaluation of Carbon Dioxide-Assisted Gravity Drainage process (CO2-AGD) to improve oil recovery in reservoirs with strong water drive. Fuel, 324, 124409. https://doi.org/10.1016/j.fuel.2022.124409.

3. Cheage Chamgoué, A., Kombou, C.L., Tchouate Ngankap, M., Metsebo, J., Armstrong Akoteh, A. (2023). Improving the Recovery of Hydrocarbons in a Well in the Gullfaks Field by Injecting Sequestrated CO_2. Iraqi Journal of Chemical and Petroleum Engineering, 24(1), 1–4. https://doi.org/10.31699/ijcpe.2023.1.1

4. Hason, M.M., Al-Sulttani, A.O., Abbood, I.S., Hanoon, A.N. 2020. Emissions Investigating of Carbon Dioxide Generated by the Iraqi Cement Industry. IOP Conference Series: Materials Science and Engineering, 928(2), 022041. https://doi.org/10.1088/1757-899x/928/2/022041

5. Orozco-Agamez, J., Tirado, D., Umana, L., Alviz-Meza, A., Garcia, S., Pena-Ballesteros, D. 2022. Effects of Composition, Structure of Amine, Pressure and Temperature on CO_2 Capture Efficiency and Corrosion of Carbon Steels Using Amine-based Solvents: a Review. Chemical Engineering Transactions, 96, 505–510.

6. Majeed, N.S., Majeed, J.T. 2017. Study the Performance of Nanozeolite NaA on CO2 Gas Uptake. Iraqi Journal of Chemical and Petroleum Engineering, 18(2), 57–67. https://doi.org/10.31699/IJCPE.2017.2.5.

7. Yaro, A.S., Rashid, K.H. 2016. Modelling and

Optimization of Carbon Steel Corrosion in CO_2 Containing Oilfield Produced Water in Presence of HAc. Iraqi Journal of Chemical and Petroleum Engineering, 16(2), 1–8. https://ijcpe.uobaghdad.edu.iq/index.php/ijcpe/article/view/249

8. AL-Sammarraie, A.M. 2020. Role of Carbon Dioxide on the Corrosion of Carbon Steel Reinforcing Bar in Simulating Concrete Electrolyte. Baghdad Science Journal, 17(1), 0093. https://doi.org/10.21123/bsj.2020.17.1.0093

9. Hadi Jasim, H. 2019. Evaluation the Effect of Velocity and Temperature on the Corrosion Rate of Crude Oil Pipeline in the Presence of CO_2/H2S Dissolved Gases. Iraqi Journal of Chemical and Petroleum Engineering, 20(2), 41–50. https://doi.org/10.31699/ijcpe.2019.2.6

10. Sang Sefidi, V., Luis, P. 2019. Advanced Amino Acid-Based Technologies for CO_2 Capture: A Review. Industrial & Engineering Chemistry Research, 58(44), 20181–20194. https://doi.org/10.1021/acs.iecr.9b01793

11. Scholes, C.A., Smith, K.H., Kentish, S.E., Stevens, G.W. 2010. CO_2 capture from pre-combustion processes—Strategies for membrane gas separation. International Journal of Greenhouse Gas Control, 4(5), 739–755. https://doi.org/10.1016/j.ijggc.2010.04.001

12. Helei, L., Tantikhajorngosol, P., Chan, C., Tontiwachwuthikul, P. 2021. Technology development and applications of artificial intelligence for post-combustion carbon dioxide capture: Critical literature review and perspectives. International Journal of Greenhouse Gas Control, 108, 103307. https://doi.org/10.1016/j.ijggc.2021.103307

13. Yin, C., Yan, J. 2016. Oxy-fuel combustion of pulverized fuels: Combustion fundamentals and modeling. Applied Energy, 162, 742–762. https://doi.org/10.1016/j.apenergy.2015.10.149

14. Theo, W.L., Lim, J.S., Hashim, H., Mustaffa, A.A., Ho, W.S. 2016. Review of pre-combustion capture and ionic liquid in carbon capture and storage. Applied Energy, 183, 1633–1663. https://doi.org/10.1016/j.apenergy.2016.09.103

15. Waisi, B.I., Majeed, J.T., Majeed, N.S. 2021. Carbon dioxide capture using nonwoven activated carbon nanofiber. IOP Conference Series: Earth and Environmental Science, 779(1), 012056. https://doi.org/10.1088/1755-1315/779/1/012056

16. Vega, F., Cano, M., Gallego, L.M., Camino, S., Camino, J.A., Navarrete, B. 2017. Evaluation of MEA 5 M performance at different CO_2 concentrations of flue gas tested at a CO_2 capture lab-scale plant. Energy Procedia, 114, 6222–6228. https://doi.org/10.1016/j.egypro.2017.03.1760

17. Rubin, E.S., Mantripragada, H., Marks, A., Versteeg, P., Kitchin, J. 2012. The outlook for improved carbon capture technology. Progress in Energy and Combustion Science, 38(5), 630–671. https://doi.org/10.1016/j.pecs.2012.03.003

18. Chu, F., Yang, L., Du, X., Yang, Y. 2016. CO_2 capture using MEA (monoethanolamine) aqueous solution in coal-fired power plants: Modeling and optimization of the absorbing columns. Energy, 109, 495–505. https://doi.org/10.1016/j.energy.2016.04.123

19. Dash, S.K., Parikh, R., Kaul, D. 2022. Development of efficient absorbent for CO_2 capture process based on (AMP + 1MPZ). Materials Today: Proceedings, 62, 7072–7076. https://doi.org/10.1016/j.matpr.2022.01.148

20. Luo, X., Fu, K., Yang, Z., Gao, H., Rongwong, W., Liang, Z., Tontiwachwuthikul, P. 2015. Experimental Studies of Reboiler Heat Duty for CO_2 Desorption from Triethylenetetramine (TETA) and Triethylenetetramine (TETA) + N-Methyldiethanolamine (MDEA). Industrial & Engineering Chemistry Research, 54(34), 8554–8560. https://doi.org/10.1021/acs.iecr.5b00158

21. Husebye, J., Brunsvold, A.L., Roussanaly, S., Zhang, X. 2012. Techno Economic Evaluation of Amine based CO_2 Capture: Impact of CO_2 Concentration and Steam Supply. Energy Procedia, 23, 381–390. https://doi.org/10.1016/j.egypro.2012.06.053

22. Roussanaly, S., Berghout, N., Fout, T., Garcia, M., Gardarsdottir, S., Nazir, S.M., Ramirez, A., Rubin, E.S. 2021. Towards improved cost evaluation of Carbon Capture and Storage from industry. International Journal of Greenhouse Gas Control, 106, 103263. https://doi.org/10.1016/j.ijggc.2021.103263

23. Baker, R.W., Freeman, B., Kniep, J., Huang, Y.I., Merkel, T.C. 2018. CO_2 Capture from Cement Plants and Steel Mills Using Membranes. Industrial & Engineering Chemistry Research, 57(47), 15963–15970. https://doi.org/10.1021/acs.iecr.8b02574

24. Wilk, A., Więcław-Solny, L., Tatarczuk, A., Krótki, A., Spietz, T., Chwoła, T. 2017. Solvent selection for CO_2 capture from gases with high carbon dioxide concentration. Korean Journal of Chemical Engineering, 34(8), 2275–2283. https://doi.org/10.1007/s11814-017-0118-x

25. Madugula, A.C.S., Sachde, D., Hovorka, S.D., Meckel, T.A., Benson, T.J. 2021. Estimation of CO_2 emissions from petroleum refineries based on the total operable capacity for carbon capture applications. Chemical Engineering Journal Advances, 8, 100162. https://doi.org/10.1016/j.ceja.2021.100162

26. Wang, X., Song, C. 2020. Carbon Capture From Flue Gas and the Atmosphere: A Perspective. Frontiers in Energy Research, 8. https://doi.org/10.3389/fenrg.2020.560849

27. Saha, A.K., Bandyopadhyay, S.S., Biswas, A.K. 1995. Kinetics of absorption of CO_2 into aqueous solutions of 2-amino-2-methyl-1-propanol. Chemical

Engineering Science, 50(22), 3587–3598. https://doi.org/10.1016/0009-2509(95)00187-a

28. Vaidya, P.D., Kenig, E.Y. 2007. CO_2-Alkanolamine Reaction Kinetics: A Review of Recent Studies. Chemical Engineering & Technology, 30(11), 1467–1474. https://doi.org/10.1002/ceat.200700268

29. Caplow, M. 1968. Kinetics of carbamate formation and breakdown. Journal of the American Chemical Society, 90(24), 6795–6803. https://doi.org/10.1021/ja01026a041

30. Sema, T., Naami, A., Liang, Z., Shi, H., Rayer, A.V., Sumon, K.Z., Wattanaphan, P., Henni, A., Idem, R., Saiwan, C., Tontiwachwuthikul, P. 2012. Part 5b: Solvent chemistry: reaction kinetics of CO_2 absorption into reactive amine solutions. Carbon Management, 3(2), 201–220. https://doi.org/10.4155/cmt.12.13

31. Aroonwilas, A., Veawab, A. 2004. Characterization and Comparison of the CO_2 Absorption Performance into Single and Blended Alkanolamines in a Packed Column. Industrial & Engineering Chemistry Research, 43(9), 2228–2237. https://doi.org/10.1021/ie0306067

32. Nair, P.S., Selvi, P.P. 2014. Absorption of carbon dioxide in packed column. International journal of scientific and research publication, 4(4), 1–11.

33. Aroonwilas, A., Tontiwachwuthikul, P. 1998. Mass Transfer Coefficients and Correlation for CO_2 Absorption into 2-Amino-2-methyl-1-propanol (AMP) Using Structured Packing. Industrial & Engineering Chemistry Research, 37(2), 569–575. https://doi.org/10.1021/ie970482w

34. Gao, H., Xu, B., Han, L., Luo, X., Liang, Z. 2017. Mass transfer performance and correlations for CO_2 absorption into aqueous blended of DEEA/MEA in a random packed column. AIChE Journal, 63(7), 3048–3057. https://doi.org/10.1002/aic.15673

35. Naami, A., Edali, M., Sema, T., Idem, R., Tontiwachwuthikul, P. 2012. Mass Transfer Performance of CO_2 Absorption into Aqueous Solutions of 4-Diethylamino-2-butanol, Monoethanolamine, and N-Methyldiethanolamine. Industrial & Engineering Chemistry Research, 51(18), 6470–6479. https://doi.org/10.1021/ie2008357

36. Vaewhongs, P., Photein, K., Nimcharoen, R., Limlertchareonwanit, T., Minakanishtha, K., Maneeintr, K., Charinpanitkul, T. 2020. Gas-phase mass transfer coefficient of CO_2 in different alkanolamine solutions within packed-bed absorption column. The second materials research society of thailand international conference. https://doi.org/10.1063/5.0023685

37. Sheng, M., Liu, C., Ge, C., Arowo, M., Xiang, Y., Sun, B., Chu, G., Zou, H. 2016. Mass-Transfer Performance of CO_2 Absorption with Aqueous Diethylenetriamine-Based Solutions in a Packed Column with Dixon Rings. Industrial & Engineering Chemistry Research, 55(40), 10788–10793. https://doi.org/10.1021/acs.iecr.6b02280

38. Qedenv environmental systems ltd. (n.d.). geotechuk. Retrieved June 2, 2023, from https://www.qedenv.com/search/?q=biogas5000

39. Mustafa, N.F.A., Mohd Shariff, A., Tay, W.H., Abdul Halim, H.N., Mhd Yusof, S.M. 2020. Mass Transfer Performance Study for CO_2 Absorption into Non-Precipitated Potassium Carbonate Promoted with Glycine Using Packed Absorption Column. Sustainability, 12(9), 3873. https://doi.org/10.3390/su12093873

40. Abdul Halim, H.N.M., Shariff, A., Tan, L.S., Bustam, M.A. 2015. Mass Transfer Performance of CO_2 Absorption from Natural Gas using Monoethanolamine (MEA) in High Pressure Operations. Industrial & Engineering Chemistry Research, 54(5), 1675–1680. https://doi.org/10.1021/ie504024m

41. Limlertchareonwanit, T., Maneeintr, K., Charinpanitkul, T. 2020. Measurement of Mass Transfer Coefficient of CO_2–Amine System from Absorption Process. IOP Conference Series: Materials Science and Engineering, 859(1), 012011. https://doi.org/10.1088/1757-899x/859/1/012011

42. Wen, L., Liu, H., Rongwong, W., Liang, Z., Fu, K., Idem, R., Tontiwachwuthikul, P. 2015. Comparison of Overall Gas-Phase Mass Transfer Coefficient for CO_2 Absorption between Tertiary Amines in a Randomly Packed Column. Chemical Engineering & Technology, 38(8), 1435–1443. https://doi.org/10.1002/ceat.201400606

43. Gul, A., Tezcan Un, U. 2022. Effect of Temperature and Gas Flow Rate on CO_2 Capture. European Journal of Sustainable Development Research, 6(2), em0181. https://doi.org/10.21601/ejosdr/11727

44. Al-Sudani, F. 2020. Absorption of Carbon Dioxide into Aqueous Ammonia Solution using Blended Promoters (MEA, MEA+PZ, PZ+ArgK, MEA+ArgK). Engineering and Technology Journal, 38(9), 1359–1372. https://doi.org/10.30684/etj.v38i9a.876

45. Kuntz, J., Aroonwilas, A. 2009, February. Mass-transfer efficiency of a spray column for CO_2 capture by MEA. Energy Procedia, 1(1), 205–209. https://doi.org/10.1016/j.egypro.2009.01.029

46. Rajiman, V., Halim, H.N.A., Shariff, A.M., Ali, U.F.M., Dzahir, M.I.H.M. 2021. Potential of 2-Amino-2-Methyl-1-Propanol Solution as Absorbent for CO_2 Absorption from Biogas. IOP Conference Series: Earth and Environmental Science, 765(1), 012054. https://doi.org/10.1088/1755-1315/765/1/012054

47. Fu, K., Sema, T., Liang, Z., Liu, H., Na, Y., Shi, H., Idem, R., Tontiwachwuthikul, P. 2012. Investigation of Mass-Transfer Performance for CO_2 Absorption into Diethylenetriamine (DETA) in a Randomly Packed Column. Industrial & Engineering

Chemistry Research, 51(37), 12058–12064. https://doi.org/10.1021/ie300830h

48. Peng, Y., Zhao, B., Li, L. 2012. Advance in Post-Combustion CO_2 Capture with Alkaline Solution: A Brief Review. Energy Procedia, 14, 1515–1522. https://doi.org/10.1016/j.egypro.2011.12.1126

49. Tan, L., Shariff, A., Lau, K., Bustam, M. 2012. Factors affecting CO_2 absorption efficiency in packed column: A review. Journal of Industrial and Engineering Chemistry, 18(6), 1874–1883. https://doi.org/10.1016/j.jiec.2012.05.013

50. Demontigny, D., Tontiwachwuthikul, P., Chakma, A. 2001. Parametric studies of carbon dioxide absorption into highly concentrated monoethanolamine solutions. The Canadian Journal of Chemical Engineering, 79(1), 137–142. https://doi.org/10.1002/cjce.5450790121

51. Aroonwilas, A., Veawab, A., Tontiwachwuthikul, P. 1999. Behavior of the Mass-Transfer Coefficient of Structured Packings in CO_2 Absorbers with Chemical Reactions. Industrial & Engineering Chemistry Research, 38(5), 2044–2050. https://doi.org/10.1021/ie980728c

52. Najim, S.E., Ateik, A.A., Haweel, C.K. 2011. Effect of Operating Conditions on CO_2 Absorption into Aqueous Alkanol amine Solutions in Packed Column. University of Thi-Qar Journal for Engineering Sciences, 2(1), 103–117.

53. Kim, Y.E., Moon, S.J., Yoon, Y.I., Jeong, S.K., Park, K.T., Bae, S.T., Nam, S.C. 2014. Heat of absorption and absorption capacity of CO_2 in aqueous solutions of amine containing multiple amino groups. Separation and Purification Technology, 122, 112–118. https://doi.org/10.1016/j.seppur.2013.10.030

54. Bernhardsen, I.M., Knuutila, H.K. 2017. A review of potential amine solvents for CO_2 absorption process: Absorption capacity, cyclic capacity and pKa. International Journal of Greenhouse Gas Control, 61, 27–48. https://doi.org/10.1016/j.ijggc.2017.03.021