

## Effect of Operating Conditions on CO<sub>2</sub> Absorption into Aqueous Alkanol amine Solutions in Packed Column

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### Abstract

This paper highlights the importance of operating parameters to mass-transfer in CO<sub>2</sub> absorption in columns with different packings. The study compares the performance of two packings, Gempak 4A and Raschig ring. Mass-transfer efficiency of these packings was determined by carrying out absorption experiments in a pilot-scale absorption unit with aqueous solutions of monoethanolamine (MEA), Diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA) as test solvent.

The overall mass-transfer coefficient ( $K_{Gav}$ ) can be considered to be indicative of the CO<sub>2</sub> removal efficiency of the system and can be calculated from experimentally gas-phase CO<sub>2</sub> concentration profiles within the test columns. The results of this study indicate that mass-transfer coefficient of these packings tested varies significantly not only with operating parameters such as liquid load, liquid CO<sub>2</sub> loading, solvent concentration, solvent type and feed CO<sub>2</sub> concentration but also with packing arrangement.

In absorption experiments the results show the typical behavior of liquid controlling system. Gas flow rate has no influence on overall mass transfer coefficient ( $K_{Gav}$ ), and an increase in liquid flow rate yields a greater ( $K_{Gav}$ ). CO<sub>2</sub> loading lowers the ( $K_{Gav}$ ) and an increase in amine concentration induces a higher ( $K_{Gav}$ ). Increasing the CO<sub>2</sub> concentration within the feed gas was found to reduce the value of ( $K_{Gav}$ ) within the system.

Structured packing offers superior performance to random packings, structured packing provides almost twice greater ( $K_{Gav}$ ) than random packings.

**Keywords: operating conditions; carbon dioxide; Amine solution, packed column.**

## تأثير الظروف التشغيلية على عملية امتصاص غاز ثاني أكسيد الكربون باستخدام المحاليل الأمينية خلال الأبراج المحشوة

### المستخلص

يسلط هذا البحث الضوء على الاحداثيات المهمة في عمليات انتقال المادة عن طريق امتصاص غاز ثاني اوكسيد الكربون في الابراج المحشوة كما يهدف البحث الى المقارنة بين الحشوات المنتظمة والحشوات العشوائية للأبراج. تم بحث كفاءة انتقال المادة بأجراء تجارب عملية في وحدة امتصاص ريادية باستعمال محاليل أمينية مختلفة ولكلا النوعين من الحشوات.

أن معامل انتقال المادة الاجمالي يمكن ان يعد دليل على كفاءة ازالة غاز ثاني اوكسيد الكربون الذي يحسب من خلال التجارب العملية باتباع تدرج التركيز لغاز ثاني اوكسيد الكربون في جزء البرج المعد لذلك. دلت النتائج على ان معامل انتقال المادة يتغير ليس فقط مع احداثيات التشغيل ( تركيز المذيب ونوعه، تركيز غاز ثاني اوكسيد الكربون في السائل والغاز الداخل ومعدل جريان السائل) ولكن أيضاً مع ترتيب الحشوات. تبين أن طور السائل هو المسيطر على عملية الامتصاص وأن معدل جريان الغاز ليس له تأثير على معامل انتقال المادة الاجمالي بينما ينتج زيادة معدل جريتان السائل وتركيزه زيادة في معامل انتقال المادة الاجمالي وان زيادة تركيز غاز ثاني اوكسيد الكربون في الغاز الداخل يؤدي الى تقليل معامل انتقال المادة الاجمالي. أن الحشوات المرتبة بانتظام تعطي اداء افضل بالمقارنة مع الحشوات العشوائية حيث وجد ان هذا الترتيب للحشوات يعطي تقريبا " ضعف قيمة معامل انتقال المادة الاجمالي بالمقارنة مع الحشوات العشوائية.

### 1. Introduction

The removal of carbon dioxide from gas streams, commonly referred to as acid gas treating, is necessary in many industrial processes. In natural gas processing, CO<sub>2</sub> is removed to reduce the costs compression and transportation. In ammonia manufacture, CO<sub>2</sub> needs to be removed from the hydrogen streams, since it poisons the catalyst for the reaction between hydrogen and nitrogen. Power plant flue gases are a new application of CO<sub>2</sub> removal processes, compared to the first two. In this case, CO<sub>2</sub> is removed only to reduce greenhouse emissions. This issue is of increasing interest, because global warming is an important environmental and political issue. With the Kyoto protocol of 1997 forty-one industrialized countries agreed to cut the carbon dioxide emissions to approximately 5% less than the emissions in 1990, in a five year period going from 2008 to 2012[1]. To achieve the agreement target, separation of CO<sub>2</sub> from industrial waste gases, which would otherwise be vented to atmosphere, becomes essential. A wide range of technologies currently exist for separation and capture CO<sub>2</sub> from gas streams. There are a number of methods available for effectively

capturing CO<sub>2</sub> and depending on the nature of the problem one process will be favored over another. Some of the more common separation methods includes absorption, low temperature distillation, adsorption, and membrane[2]. The most common method used to remove carbon dioxide is absorption into a liquid solvent, particularly aqueous alkanolamine solutions. The alkanolamine treating process was first introduced in 1930 when R. R. Bottoms patented the process[3]. Since that time, the process has remained virtually unchanged. The objective of this study is to obtain the mass transfer performance of the CO<sub>2</sub> absorption process using different packing type and different aqueous alkanolamine solutions as the column internal and absorption solvent, respectively. The performance of the process is presented in terms of the volumetric overall mass transfer coefficient. The effect of various operating parameters, such as the liquid flow rate, gas flow rate, CO<sub>2</sub> feed percent, and liquid CO<sub>2</sub> loading were also evaluated.

## 2. Theory

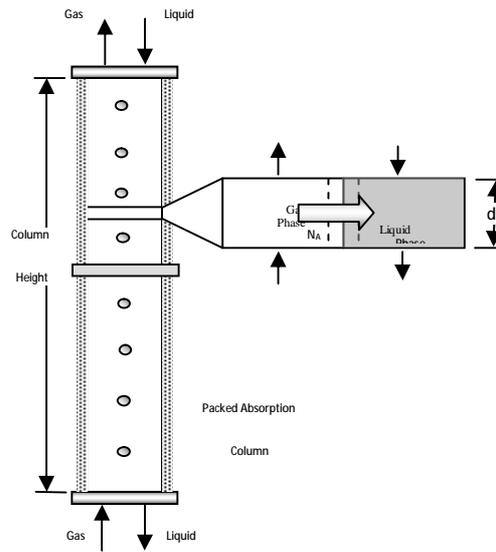
The height of the absorption column required to reduced the concentration of a particular component in the gas stream to a certain level can be calculated by combining the degree of mass transfer and the differential material balance. Considering a segment of the column with height  $dZ$  as shown in Figure (1), the material balance of the transferred component A can be written as:

$$N_A A_e = G_i A_c dY_{A,G} \quad (1)$$

$$N_A A_e = G_i \frac{V_c}{dZ} d \left[ \frac{y_{A,G}}{1 - y_{A,G}} \right] \quad (2)$$

Generally, the gas - liquid interfacial area for mass transfer is presented in terms of the area per unit volume of the absorption column. Therefore, Equation (2) can be expressed by:

$$N_A a_v dZ = G_i d \left[ \frac{y_{A,G}}{1 - y_{A,G}} \right] \quad (3)$$



**Figure (1) Schematic diagram of a packed column.**

According to the aforementioned mass flux equation, the material balance equation can be further arranged as:

$$K_G (Py_{A,G} - HC_{A,L}) a_V dZ = G_i d \left[ \frac{y_{A,G}}{1 - y_{A,G}} \right] \quad (4)$$

Based on equation (4), the required height (Z) can be integrating over the column:

$$Z = G_i \int_{Bottom}^{Top} \frac{1}{K_G a_V (1 - y_{A,G})^2 (Py_{A,G} - HC_{A,L})} dy_{A,G} \quad (5)$$

In many cases it is assumed that the mass transfer coefficient is independent of the concentration of the absorbed component in the system[4], in other words the volumetric  $K_G a_V$  coefficient is constant over the height of the column. Thus this term can be removed from the integral and equation (5) may be simplified as:

$$Z = \left( \frac{G_i}{K_G a_V P} \right) \int_{Bottom}^{Top} \frac{dy_{A,G}}{(1 - y_{A,G})^2 (y_{A,G} - HC_{A,L} / P)} \quad (6)$$

The term  $(G_i / K_G a_V P)$  has the dimension of length and is designated the height of packing required for transfer unit, commonly known as the height of a transfer unit (HTU).

The integral on the right hand side of equation (6) is dimensionless and represents the total number of these transfer units required to make up the whole column. Consequently, it is called the number of transfer units (*NTU*). Equation (6) may therefore be written as:

$$Z = (HTU) (NTU) \quad (7)$$

Where

$$HTU = \left( \frac{G_i}{K_G a_V P} \right) \quad (8)$$

and

$$NTU = \int_{Bottom}^{Top} \frac{dy_{A,G}}{(1 - y_{A,G})^2 (y_{A,G} - HC_{A,L} / P)} \quad (9)$$

By differentiating Equation (6) we get:

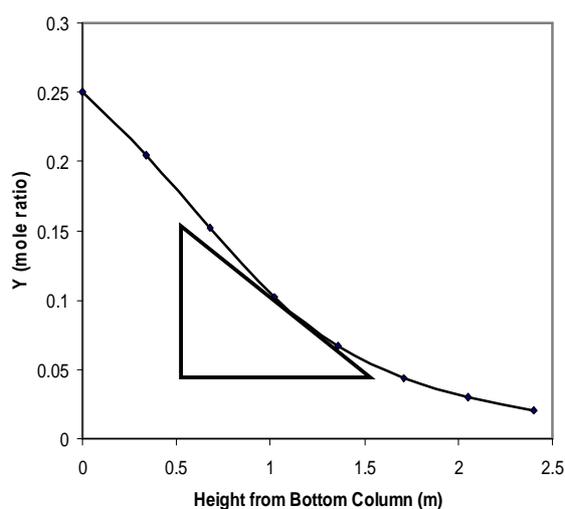
$$dZ = \left( \frac{G_i}{K_G a_V P} \right) \left( \frac{dy_{A,G}}{(1 - y_{A,G})^2 (y_{A,G} - HC_{A,L} / P)} \right) \quad (10)$$

Rearranging and simplifying, the final expression for  $K_G a_V$  can be given as:

$$K_G a_V = \left( \frac{G_i}{P y_{A,G} - HC_{A,L}} \right) \left( \frac{dY_{A,G}}{dZ} \right) \quad (11)$$

The first term on the right-hand side of equation (11) was determined from the values of the operating conditions of the absorption experiment. The second term of the equation (concentration gradient ( $dY_{A,G}/dZ$ )) was obtained from slope of the measured  $CO_2$  concentration profile, which was converted to a plot of the mole ratio  $Y_{A,G}$ . Figure (2) aid in illustrating the mechanics of the problem. It should be noted that this slope was not the global measure of entire profile but the local value, determined at a specific point of interest to give the  $K_G a_V$  value at that particular condition. Finally, the relationship between mole fraction and mole ratio is defined:

$$y_{A,G} = \frac{Y_{A,G}}{1 + Y_{A,G}} \quad (12)$$



**Figure (2) .Determining  $dY_A/dZ$  from the  $\text{CO}_2$  mole ratio concentration profile.**

### 3. Absorption System

The absorption columns are made out of acrylic plastic and have a height of 2.4 m and diameter of 0.2 m. Sampling points for the gas composition are located at regular intervals along the sides of each column. Column A has ten sampling points, while column B has eight gas sampling points. This is because of the types of packing used in the columns. The absorption process is carried out in a counter-current mode of operation. The feed gas composed of  $\text{CO}_2$  and air enters at the bottom of the column and flows upwards. The prepared alkanolamine solution is pumped to the top of the column and flows downwards by gravity. The absorption  $\text{CO}_2$  into alkanolamine solution occurs as the counter-current gas and liquid phases contact one another inside the absorption column. The packing promotes mixing and provides a surface area for contact between the two phases. Treated gas leaves at the top of the absorption column and the rich solution leaves at the bottom. Column A is randomly packed with 19 mm Raschig rings. Column B is packed with Gempak 4A and rotated  $90^\circ$  with respect to each other in succession[5], and the data for the packing types used in this study are provided in Table (1). This is standard arrangements for structured packing in order to achieve optimum performance, as recommended by the manufactures.

**Table (1). Packing data [6].**

Packing Type	Surface area ( $\text{m}^2/\text{m}^3$ )	% Voids
19 mm Raschig	245	80
Gempak 4A	446	92

#### 4. Experimental Procedures

In the present work, CO<sub>2</sub> absorption experiments were carried out to generate mass transfer efficiency data of different solvents over ranges of operating and design parameters. The experiments were carried out in the Engineering Process Laboratory, School of Chemical Engineering and Analytical Science, The University of Manchester as shown in Figure (3). Prior to a specific experimental run of the pilot plant, the variables for considerations had to be determined. Such variables consisted of the Amine solution concentration, the solution CO<sub>2</sub> loading, the percent of CO<sub>2</sub> in the feed gas, the liquid flow rate, the inert gas flow rate and the column packing type.

An aqueous solution of MEA, DEA, AMP, or MDEA was prepared in the feed tank, at a given concentration. The absorption experiment began by introducing a gas mixture of compressed air from air from a central supply and CO<sub>2</sub> from a cylinder to the bottom of an absorption column at a desired flow rate. The prepared aqueous solution was simultaneously pumped to the top of the column to create counter current contact between gas and liquid. The operation was continued for at least 30 minutes to allow the system to reach the steady state. At this point, the CO<sub>2</sub> concentrations in the gas phase at different positions along the column were measured through a series of a sampling points by switching the sampling point from one port to another using the IR analyzer. Finally, a liquid sample was taken from the bottom of the column and analyzed for its composition. The system operating conditions used in the present work are summarized in Table (2).

**Table (2). List of operating conditions.**

Conditions	Range
Liquid Flow Rate (m <sup>3</sup> /m <sup>2</sup> .hr)	7.69-19.22
Gas Flow Rate (mol/m <sup>2</sup> .s)	9-17
CO <sub>2</sub> Feed %	5-20
Amine Concentration (kmol/m <sup>3</sup> )	1-3
Inlet CO <sub>2</sub> loading (mol CO <sub>2</sub> /mol MEA)	0-0.2
Inlet Gas Temperature (°C)	23-27
Inlet Liquid Temperature (°C)	23-26

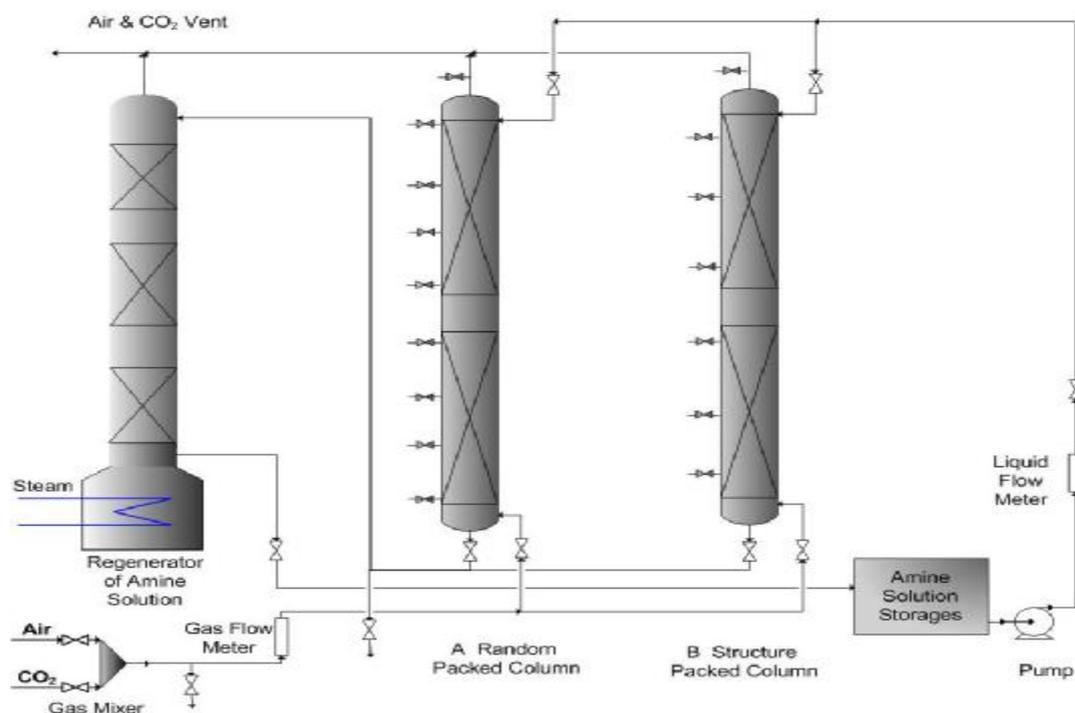


Figure (3). Experimental apparatus for CO<sub>2</sub> absorption.

## 5. Results and Discussion

### 5.1. Effect of Liquid Flow Rate

Figure (4) shows that the liquid load or flow rate has an influence on the value of  $K_{GA_v}$ ; i.e., an increase in liquid load generally yields a greater  $K_{GA_v}$  value. The possible reason for this behavior is that a higher liquid load leads to a greater liquid side mass-transfer coefficient, which is directly proportional to the overall  $K_{GA_v}$  in the case of liquid-phase controlled mass transfer, and a greater effective area, which is caused by more liquid spreading on the packing surface.

### 5.2. Effect of Gas Flow Rate

According to Figure (5), the  $K_{GA_v}$  value unaffected by the gas flow rate through the absorber over a range of 9-17 mol/m<sup>2</sup>s. Logically, an increase in the gas load allows more CO<sub>2</sub> molecules to travel from gas bulk to the gas liquid interface, which would result in higher

mass transfer performance. However, the rate of gas absorption is not exclusively dependent upon the mass-transfer phenomenon in the gas phase. The mass-transfer behavior in the liquid phase also plays an important role. In the case when the  $K_{Ga_v}$  value is unaffected by an increasing gas load, the liquid-phase mass transfer is considered to be the major factor controlling the absorption process.

### 5.3. Effect of Solvent Concentration

According to Figure (6), an increase in the solvent concentration induces a higher  $K_{Ga_v}$ . This effect is simply due to an increase in the enhancement factor, which is functionally related to the absorbent concentration. The possible explanation for this behavior is that increasing the solvent concentration reflects higher amounts of solvent molecules per unit volume available for absorbing more CO<sub>2</sub> at the gas-liquid interface.  $K_{Ga_v}$  values rise to a maximum and then fall as solution concentration increase beyond 3 kmol/m<sup>3</sup>. The reduction in  $K_{Ga_v}$  values is blamed on an increase in solution viscosity as concentration rise, thus hindering molecular diffusion.

### 5.4. Effect of Feed CO<sub>2</sub> Loading

The effect of feed CO<sub>2</sub> loading on overall mass transfer coefficient  $K_{Ga_v}$  of absorption column is shown in Figure (7). As feed CO<sub>2</sub> loading increases the concentration of free amine decrease, which leads to lower absorbent concentration. The enhancement factor is expected to reduce and the  $K_{Ga_v}$  decreases.

### 5.5. Effect of Feed CO<sub>2</sub> Concentration

From Figure (8),  $K_{Ga_v}$  is reduced by 72% when the feed CO<sub>2</sub> concentration is raised from 5% to 20%. However, the opposing effects of the reducing  $K_{Ga_v}$  and the increasing inlet CO<sub>2</sub> partial pressure caused the actual mass flux of CO<sub>2</sub> absorbed in the system to remain relatively constant. The restricted diffusion of solvent molecules in the liquid phase is speculated to be the cause of this behavior. As mentioned previously, the restricted diffusion in the liquid phase basically results in a constant amount of CO<sub>2</sub> absorbed. Therefore, higher CO<sub>2</sub> concentrations lead to a reduction in the  $K_{Ga_v}$  value.

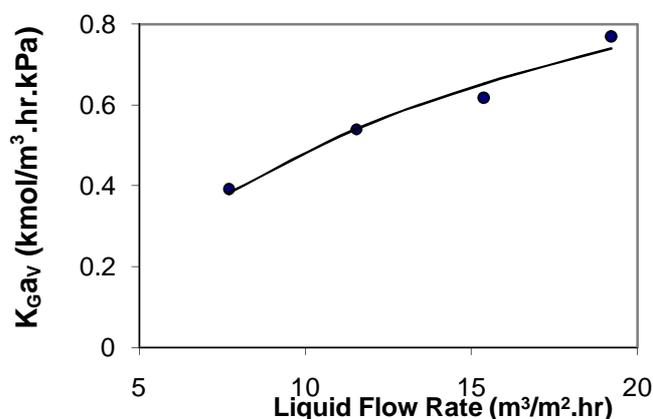
### 5.6. Effect of Solvent Type

The  $K_{Ga_v}$  comparison between the all systems at a specific operating condition is also illustrated in Figure (9), the CO<sub>2</sub>-MEA system provides approximately 3 times higher  $K_{Ga_v}$  than the CO<sub>2</sub>-AMP system does. The difference between the  $K_{Ga_v}$  values of the absorption systems is primarily influenced by the rate constant ( $k_2$ ). The greater the rate constant, the higher the  $K_{Ga_v}$  value would be expected.

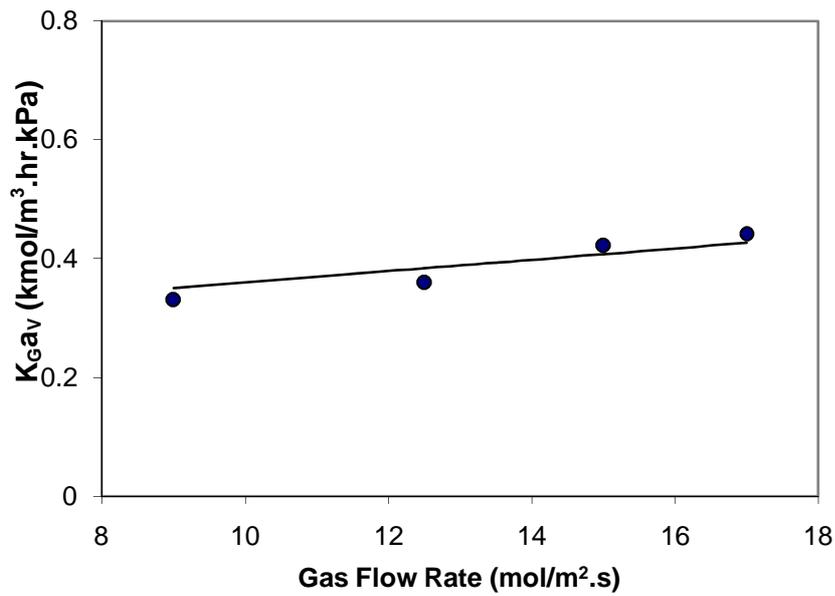
The  $k_{2,MEA-CO_2} > k_{2,DEA-CO_2} > k_{2,AMP-CO_2} > k_{2,MDEA-CO_2}$  thus leading to higher  $K_{Ga_v}$ . Besides the influence of  $k_2$ , the surface tension of the liquid solvents also plays an important role on  $K_{Ga_v}$ . In general, a lower surface tension would allow a greater effective mass transfer area, resulting in a greater  $K_{Ga_v}$ .

### 5.7. Effect of Packing Type

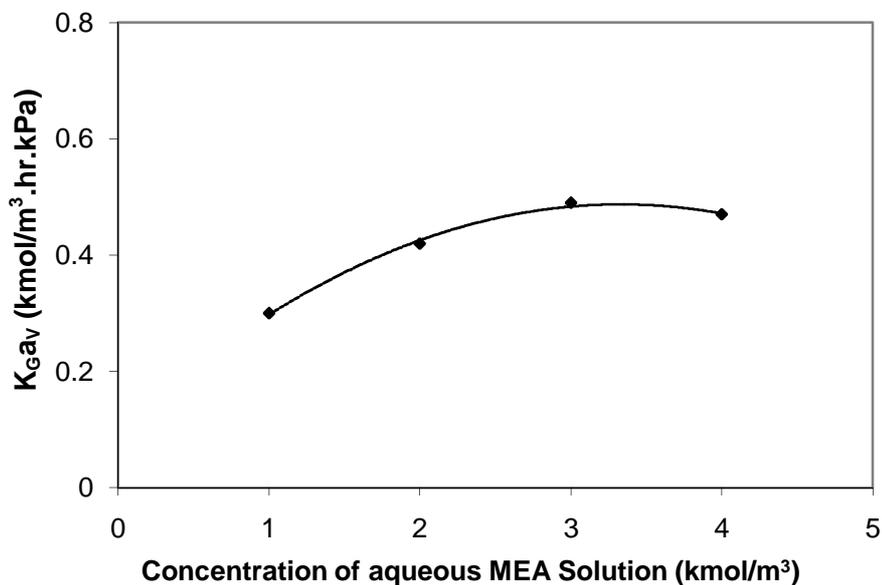
The column packing plays a very important role in the absorption process as it provides a surface area for the gas and liquid phases to contact upon. Furthermore, it also promotes mixing of the two phases. Figure (10) shows the  $K_{Ga_v}$  values obtained for the two types of packings used in this study. These experimental runs are conducted under identical conditions. With only difference being the packing itself. The Gempak 4A packing produces  $K_{Ga_v}$  values are well over twice as large as those obtained in a randomly packing of Rasching ring. This due to the significantly larger contacting surface area and improved flow distribution for the contacting phases.



**Figure (4). Effect of liquid flow rate on overall mass transfer coefficient for CO<sub>2</sub>-MEA system (gas flow rate 9 mol/m<sup>2</sup>.s, solution concentration 3 kmol/m<sup>3</sup>, CO<sub>2</sub> feed 20% , CO<sub>2</sub> loading of lean solution 0.18 mol/mol).**



**Figure (5).** Effect of gas flow rate on overall mass transfer coefficient for CO<sub>2</sub>-MEA system (liquid flow rate 7.69 m<sup>3</sup>/m<sup>2</sup>.hr, solution concentration 3 kmol/m<sup>3</sup>, CO<sub>2</sub> feed 20% , CO<sub>2</sub> loading of lean solution 0.2 mol/mol).



**Figure (6).** Effect of solution concentration on overall mass transfer coefficient for CO<sub>2</sub>-MEA system (gas flow rate 9 mol/m<sup>2</sup>.s, liquid flow rate 7.69 m<sup>3</sup>/m<sup>2</sup>.hr, CO<sub>2</sub> feed 10% , CO<sub>2</sub> loading of lean solution 0.18 mol/mol).

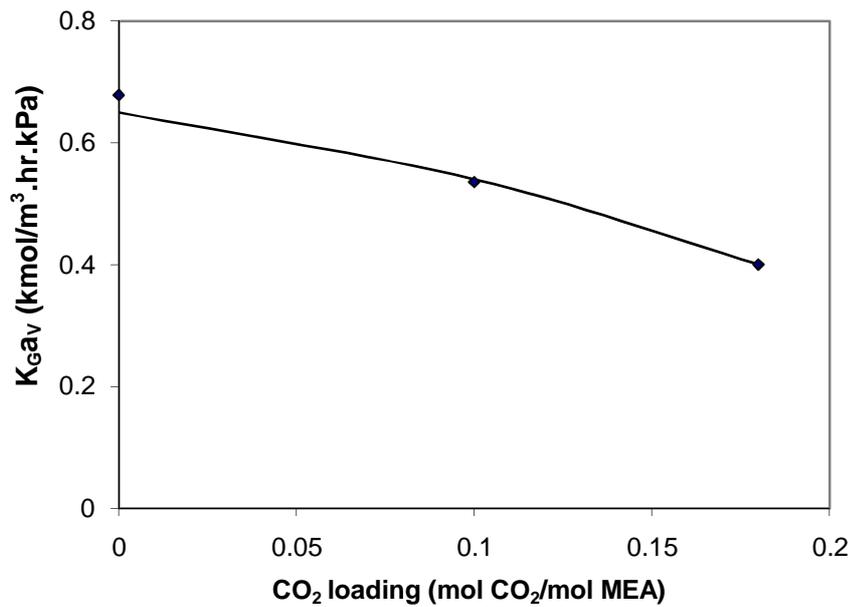


Figure (7). Effect of CO<sub>2</sub> loading of lean solution on overall mass transfer coefficient for CO<sub>2</sub>-MEA system (gas flow rate 9 mol/m<sup>2</sup>.s, liquid flow rate 7.69 m<sup>3</sup>/m<sup>2</sup>.hr, solution concentration 3 kmol/m<sup>3</sup>, CO<sub>2</sub> feed 15%).

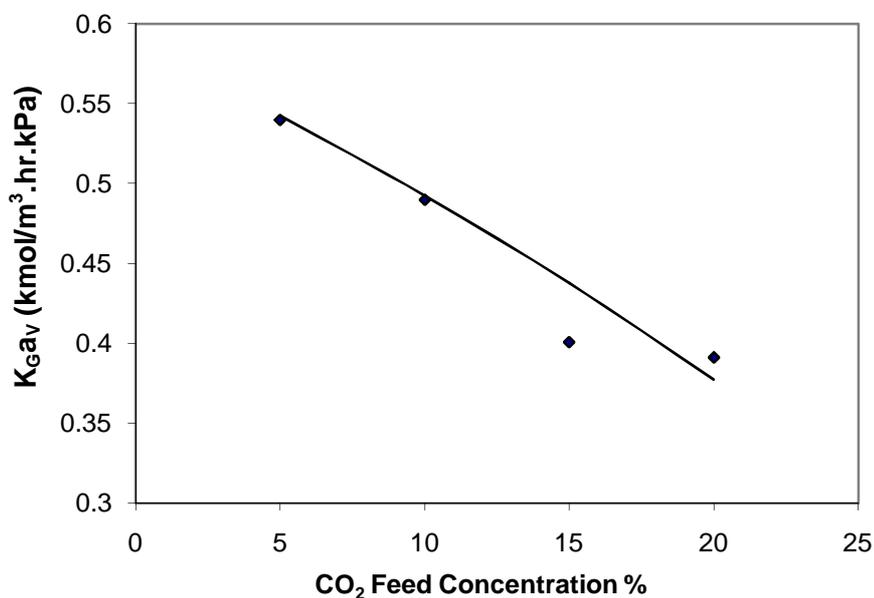
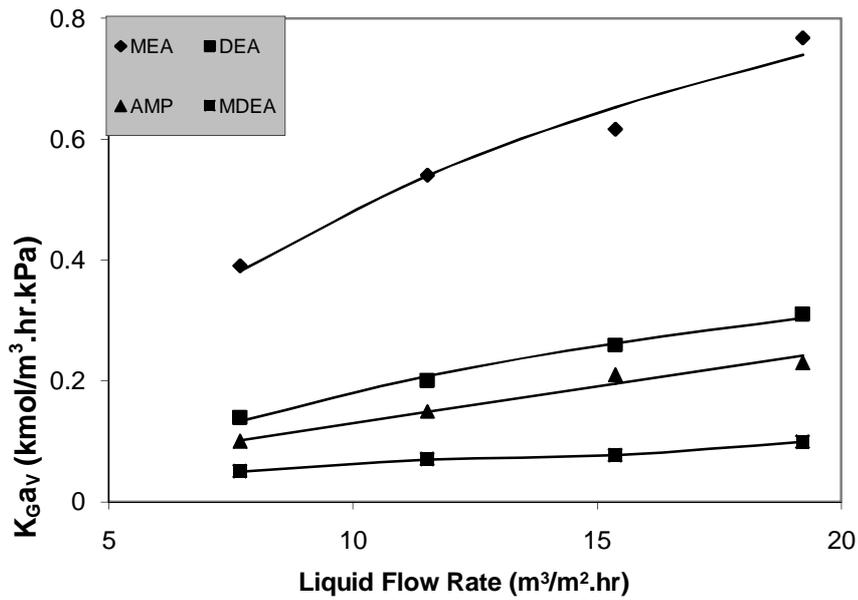
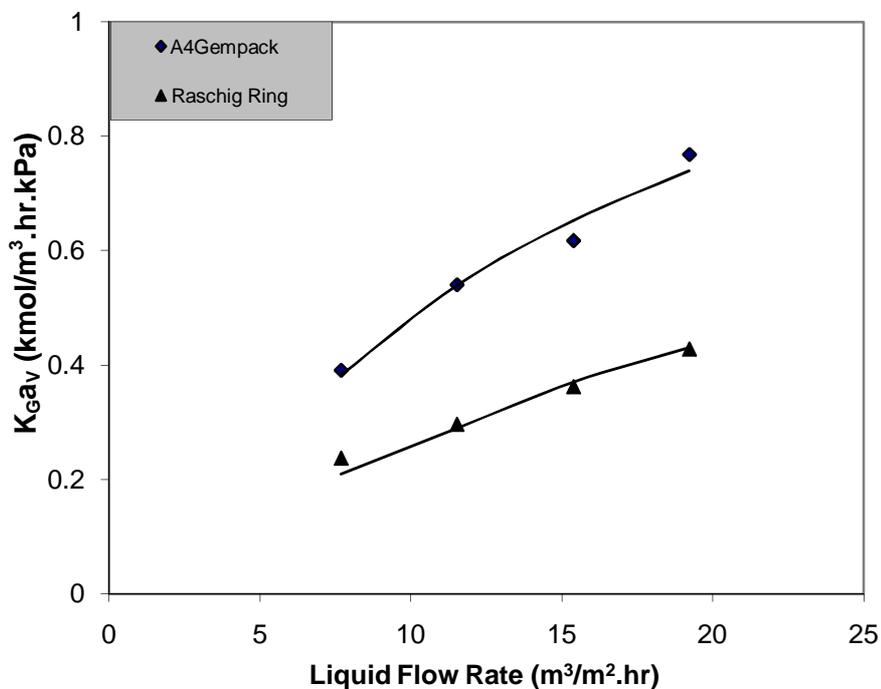


Figure (8). Effect of feed CO<sub>2</sub> concentration on overall mass transfer coefficient for CO<sub>2</sub>-MEA system (gas flow rate 9 mol/m<sup>2</sup>.s, solution concentration 3 kmol/m<sup>3</sup>, liquid flow rate 7.69 m<sup>3</sup>/m<sup>2</sup>.hr, CO<sub>2</sub> loading of lean solution 0.18 mol/mol).



**Figure (9).** Effect of liquid flow rate on overall mass transfer coefficient for CO<sub>2</sub>-MEA system (gas flow rate 9 mol/m<sup>2</sup>.s, solution concentration 3 kmol/m<sup>3</sup>, CO<sub>2</sub> feed 20%, CO<sub>2</sub> loading of lean solution 0.18 mol/mol ).



**Figure (10).** Effect of packing type on overall mass transfer coefficient (gas flow rate 9 mol/m<sup>2</sup>.s, solution concentration 3 kmol/m<sup>3</sup>, CO<sub>2</sub> feed 20% , CO<sub>2</sub> loading of lean solution 0.18 mol/mol).

## 6. Conclusions

The following conclusions may be drawn:

- (1) An increase in liquid load generally yields a greater  $K_{GaV}$ .
- (2) Gas load has no influence on  $K_{GaV}$ .
- (3) Increasing the reagent concentration therefore increases the value of  $K_{GaV}$  and improves the CO<sub>2</sub> removal performance of the system.
- (4) Solvent type also has an effect on  $K_{GaV}$ . In summary the  $K_{GaV}$  of the systems investigated can be expressed in the order CO<sub>2</sub>-MEA > CO<sub>2</sub>-DEA > CO<sub>2</sub>-AMP > CO<sub>2</sub>-MDEA.
- (5) Structured packing offers superior performance to random packings. Structured packing (Gempak4A) provides almost twice greater  $K_{GaV}$  than random packings (Raschig rings).
- (6) Increasing the CO<sub>2</sub> concentration within the gas stream to values of up to 20% was found to reduce the value of  $K_{GaV}$  within the system.
- (7) As the CO<sub>2</sub> loading increases the concentration of active reagent molecules in the liquid is reduced and hence the  $K_{GaV}$  value decreases.

## 7. References

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## 8. Nomenclature

symbol	Description	Unit
$A_C$	cross-section area of column	$m^2$
$A_e$	gas-liquid interfacial area	$m^2$
$a_v$	effective interfacial area per unit volume of packing	$m^2/m^3$
$C_A$	concentration of component A	$kmol/m^3$
$C_{A,i}$	concentration of component A at gas-liquid interface	$kmol/m^3$
$C_{A,L}$	concentration of component A in the liquid bulk	$kmol/m^3$
$G_i$	inert molar gas load	$kmol/m^2.s$
$H$	Henry's law constant	$m^3.kPa/ kmol$
$K_G$	overall gas mass-transfer coefficient	$kmol/m^2.s.kPa$
$N_A$	mass transfer flux of component A	$kmol/m^2.s$
$P$	total pressure	kPa
$Y_A$	mole ratio of component A in gas bulk	mol/mol
$y_{A,G}$	mole fraction of component A in gas bulk	mol/mol
$y_{A,i}$	mole fraction of component A at gas-liquid interface	mol/mol
$Z$	packing height	m