

# Performances of Automated Control System for Membrane Gas Absorption: Optimization Study

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**Abstract** – Membrane gas absorption (MGA) can overcome the major drawbacks of the processes that have been used commercially for the removal of CO<sub>2</sub>. Using produced thin film composite (TFC) membrane, performances of automated control system of MGA was optimized using central composite design (CCD) of Response Surface Methodology (RSM). ANOVA result showed that the temperature, concentration, velocity and flow rate of DEA played a significant role. The optimum DEA temperature was found at 50°C, DEA concentration at 2M, velocity at 3770m/s and 80 ml/min of DEA flow rate with 0.90 of desirability. **Copyright** © 2015 Penerbit Akademia Baru - All rights reserved.

**Keywords:** Membrane Gas Absorption; DEA; RSM

## 1.0 INTRODUCTION

Membrane gas absorption (MGA) is a hybrid of membrane and solvent separation that seeks to exploit the advantages of both processes [1,2]. MGA involves the transfer of CO<sub>2</sub> through a non-selective membrane before chemically absorption into a liquid absorbent. The polymeric membrane facilitates a controlled flow of gas into the solvent and provides high gas-liquid contact surface area. This physical separation of the liquid and gas flows eliminates foaming and channeling problems that can occur in classical solvent absorption processes.

In MGA, polymer membrane is should from hydrophobic materials. Hydrophobic materials have little or no tendency to adsorb water and water tends to “bead” on their surfaces (i.e discrete droplets). Hydrophobic materials possess low surface tension values and lack active groups in their surface chemistry for formation of “hydrogen- bonds” with water [3]. Table 1 shows the hydrophobic materials and its surface tension. Lower the surface tension shows higher the hydrophobic character of the materials.

Due to the enhanced greenhouse effect, MGA has been considered to be a promising alternative to conventional and potential large scale application technology for the recovery and removal of CO<sub>2</sub> [4]. The various factors such as porosity, membrane dimension, liquid

viscosity, chemical reaction on mass transfer in membrane [5-7] gave the impact for the MGA performance.

**Table 1:** Hydrophobic materials level [3]

Chemical Name	Surface Tension (dynes/cm)
Polytetrafluoroethylene (Teflon*)	18
Polyvinylidene fluoride (PVDF)	25
Polypropylene	29
Polyethylene	31
Polystyrene	33
Amylopectin	35
Polyepichlorohydrin	35
Amylose	37

To develop a MGA system, the focus is not only on liquid absorption type but improving the characteristic of membrane is also important. Table 2 is shown the MGA system performance with selected several of liquid absorbents.

**Table 2:** MGA system performance with selected chemical as liquid absorbents.

Type of polymer membrane	Module	Liquid Absorbent	Durability	Reference
PP <sup>1</sup>	Hollow Fiber	Aqueous NaOH and DEA solution	poor	[8]
PP <sup>1</sup>	Celgard X40-200 and X50-215, Hollow Fiber	Aqueous DEA solution	poor	[9]
PP <sup>1</sup>	Hollow Fiber	MEA	Wetting after some hours	[10]
PES <sup>2</sup> coated with PDMS <sup>3</sup>	Hollow Fiber	MEA	Wetting after 6 hours	[10]
PP <sup>1</sup> coated with PDMS <sup>3</sup>	Hollow Fiber	MEA	Wetting after 7 days	[10]
PTFE <sup>4</sup>	Hollow Fiber	5 M MEA	More than 6600 hours	[11]
PP <sup>1</sup>	Hollow Fiber	2M DEA	Over 3 months	[5]

PP<sup>1</sup>= Polypropylene, PES<sup>2</sup>= Polyether Sulfone, PDMS<sup>3</sup>= polydimethylsiloxane (silicon rubber), PTFE<sup>4</sup>= Polytetrafluoroethylene

Commercial MGA system are available on the market, however they tend to produce mass transfer coefficients that are significantly lower than those obtained in modules that are carefully built by hand [12]. The poor performance of commercial modules had been attributed to an uneven spacing of flat sheet membrane within the system, resulting in liquid channeling [13]. Furthermore, the experimental analysis of commercial modules is limited because they only have data sampling ports at the inlets and outlets. Hence, in this study, an automated control system of MGA was designed and fabricated in-house for the purpose to enhance the membrane performances. Performances of MGA were investigated based on selected operating parameters. A CCD and RSM were used to identify the significant operating parameters and developed a model to predict the response of the mass transfer rate of CO<sub>2</sub>.

## 2.0 METHODS/THEORY

### 2.1 Materials

Thin film composite (TFC) membranes were used. A 99% grade of diethanolamines (DEA) were purchased from Merck (M) Sdn. Bhd. and were mixed with deionized water, respectively to prepare aqueous liquid absorbents with desired concentrations (1M, 2M and 3M). The properties of TFC membranes are listed in Table 3.

**Table 3:** Properties of TFC membrane

Properties	
TFC membrane type	PDMS based 0.1 $\mu$ m PVDF membrane
Contact angle with water	130.2°
Contact angle with 1M of DEA	144.2°
Contact angle with 2M of DEA	138.1°
Contact angle with 3M of DEA	131.4°

### 2.2 Design of automated control system of MGA

In this study, an automated control system of MGA was designed and fabricated in-house. The schematic diagram for experimental setup is listed in Table 4 together part of shown in Figure 1.

The gas stream was passed through the upside of membrane cell and diffused through membrane pores into the liquid absorbent. Here, supply pressure regulator was ranged 0 to 5 bars applied. Gas flow meters with digital display were applied which ranged 0 to 400 ml/min. To detect CO<sub>2</sub> flow, CO<sub>2</sub> composition sensors was located before and after membrane cell for determine the composition of CO<sub>2</sub> which ranged 0- 20%. Two units of bourdon type pressure gauges were attached to detect the CO<sub>2</sub> and N<sub>2</sub> at inlet which ranged 0 to 5 bars. 10 liters hot water bath with centrifugal circulating pump and digital temperature controller (30-70°C) was used to heat up the liquid absorbent. Rotameter was used to feed

liquid absorbents. Three liters stainless steel tank was provided as feed tank with liquid feed pump. Electrical control consoled with indicator lamps, safety circuit and emergency cut out switch was allocated at control panel.

**Figure 1:** Schematic diagram for automated control system of MGA

**Table 4:** Part of list.

Part Number	Description
1	Frame
4	Stainless steel membrane cell
6	Hot water tank for temperature controller
8	Pump for hot water circulation
9	CO <sub>2</sub> gas sensor
11	Control panel
12	Gas tank to supply CO <sub>2</sub> and N <sub>2</sub>
15	Feed tank for supply liquid absorbent
18	Dosing pump as chemical resistant pump
23	Product tank

Before each run of an experiment, the system was cleaned for at least 10 min by deionized water to eliminate the influence of the former experiment. And all data were obtained at steady state, after at least 30 min of operating time. When CO<sub>2</sub>/N<sub>2</sub> mixture was used as the feed gas, Gas Chromatography (Perkin Elmer, TCD) was used to analyze the inlet and outlet gases concentrations. The CO<sub>2</sub> concentration of the outlet liquid was measured by a CO<sub>2</sub> electrode (Thermo Orion Model 95-02) to verify the mass balance via the gas analysis. The measurement range of the electrode was 4.4–440 ppm CO<sub>2</sub> with a reproducibility of  $\pm 2\%$ . All the data were collected after experiment had been operated for 10 min to ensure the system to reach the steady state. Steady state was indicated by a constant CO<sub>2</sub> concentration in the outlet gas stream. The results of each run were averaged from five times of sampling.

### 2.3 Calculation of experimental data

For chemical absorption, the overall mass transfer coefficient was experimentally calculated by following [14]:

$$K_i = \frac{V_g (C_{i,g,in} - C_{i,g,out})}{A_m (\Delta C_m)} \quad (1)$$

where  $V_g$  is the volumetric flow rate of gas phase,  $A_m$  is the area of the membrane and  $\Delta C_m$  is the logarithmic mean driving force based on gas phase concentration:

$$\Delta C_m = \frac{(C_{i,g,in} - C_{g,in}^*) - (C_{i,g,out} - C_{g,out}^*)}{\ln[(C_{i,g,in} - C_{g,in}^*) / (C_{i,g,out} - C_{g,out}^*)]} \quad (2)$$

where  $C_{g,out}^*$  and  $C_{g,in}^*$  in gas phase concentrations in equilibrium with corresponding liquid-phase CO<sub>2</sub> concentrations  $C_{i,L}$ . Due to liquid –phase CO<sub>2</sub> concentrations at inlet of the module equal to 0,  $C_{g,out}^*$  is 0.  $C_{g,in}^*$  is expressed by Henry's law as:  $C_{g,in}^* = C_{i,L} / m$ , the value of  $m$  is estimated by literature [15].

### 2.4 Experimental design

The CO<sub>2</sub> mass transfer optimization was studied with a standard Response Surface Methodology (RSM) using central composite design (CCD). CCD was used to examine the relationship between one or more response variables and set of quantitative experimental factors and finally necessary to find the factor settings that optimize the response. It was used to fit a quadratic surface as well. This method helps to optimize the individual and interaction effects of operating parameters of MGA system and its potential of CO<sub>2</sub> removal on DEA as liquid absorbent.

**Table 5:** Variables and levels for two-level fractional study of MGA system

Symbol	Variables	Range	
A	Liquid absorbent temperature	30	50
B	Liquid absorbent concentration	1	3
C	Liquid absorbents velocity	943	3770
D	Gas flow rate	50	120
E	Liquid absorbents flow rate	25	80

<b>F</b>	Volumetric concentration of CO <sub>2</sub> in inlet	10	100
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**Table 6:** Design layout and experimental variables for CCD

Run	Factor A	Factor B	Factor C	Factor D	Factor E	Factor F
1	40	2	2356.5	85	52.5	100
2	30	3	943.0	120	80.0	100
3	50	1	943.0	120	25.0	10
4	40	2	2356.5	85	52.5	55
5	40	2	2356.5	120	52.5	55
6	30	2	2356.5	85	52.5	55
7	30	1	3770.0	120	80.0	100
8	30	3	943.0	120	25.0	10
9	50	2	2356.5	85	52.5	55
10	50	3	943.0	120	80.0	10
11	30	1	943.0	120	80.0	10
12	30	1	943.0	50	80.0	100
13	40	1	2356.5	85	52.5	55
14	30	3	943.0	50	80.0	10
15	50	3	3770.0	50	25.0	100
16	30	1	3770.0	120	25.0	10
17	50	1	3770.0	120	25.0	100
18	50	3	3770.0	50	80.0	10
19	40	2	2356.5	85	52.5	55
20	30	1	943.0	50	25.0	10
21	40	2	2356.5	85	52.5	10
22	50	1	3770.0	120	80.0	10
23	30	3	3770.0	50	80.0	100
24	30	3	3770.0	120	25.0	100
25	50	3	943.0	50	25.0	10
26	50	1	943.0	50	25.0	100
27	50	3	943.0	50	80.0	100
28	50	3	3770.0	120	80.0	100
29	40	3	2356.5	85	52.5	55
30	30	1	3770.0	50	80.0	10
31	40	2	2356.5	85	80.0	55
32	50	3	943.0	120	25.0	100
33	50	1	3770.0	50	25.0	10
34	50	1	943.0	120	80.0	100
35	30	1	3770.0	50	25.0	100
36	40	2	2356.5	85	25.0	55
37	30	3	3770.0	50	25.0	10
38	40	2	943.0	85	52.5	55
39	40	2	2356.5	50	52.5	55
40	30	3	3770.0	120	80.0	10
41	50	1	943.0	50	80.0	10
42	30	3	943.0	50	25.0	100
43	40	2	3770.0	85	52.5	55
44	30	1	943.0	120	25.0	100
45	50	1	3770.0	50	80.0	100
46	50	3	3770.0	120	25.0	10

In this study, a half-fraction central composite face centered design with single replicate at each point was used to optimize the MGA system. Six variables were investigated in this

study, they are coded as; liquid absorbent temperature (30 to 50°C) (**A**), liquid absorbent concentration (1 to 3M) (**B**), liquid absorbents velocity (943 to 3770 cm/min) (**C**), gas flow rate (50 to 120 ml/min) (**D**), liquid absorbents flow rate (25 to 80 ml/min) (**E**), and volumetric concentration of CO<sub>2</sub> in inlet (10 to 100%) (**F**). Meanwhile, CO<sub>2</sub> mass transfer (mol/ (m<sup>2</sup> s)) (**Y**) was analyzed as response. The experimental conditions for each system studied as shown in Table 5.

The variables which are identified as important or significant are then investigated more thoroughly in subsequent experiment. The CCD consisting of 6 center points and 14 axial points that rendered a total of 46 run of experiment, which used to analyze the data acquired from the experimental design, as shown in Table 6. All experiments were done in a randomized order to minimize the effect of unexplainable variability in the observed responses due to irrelevant factor. Design expert software version 6.0.6 [16] was used to develop the mathematical model and evaluate the subsequent regression analyses, analyses of variance (ANOVA) and response surfaces. Based on the optimum operating parameters calculated by CCD, the optimum condition was repeated and validated.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Response Surface Analysis for DEA as liquid absorbent

Responses for each experimental run and predicted value are as shown in Table 7. The regression model equation generated for the CO<sub>2</sub> mass transfer by discarding the insignificant effects which was obtained after performing 46 experiments, are listed in Table 7. The mathematical models were also inspected for its validity by comparing the experimental data and the predicted data given by the models. The data can be observed also in Table 7. This data can be observed using visual inspection by plotting the experimental data versus the predicted data corresponding to the respective responses in the DOE software. The results demonstrated that there are tendencies in the linear regression fit, and the model explained the experimental range studied adequately.

The fitted regression equation showed good fit of the models and was successful in capturing the correlation between the variables. From all these validity tests, the model was found to be adequate for predicting the optimized CO<sub>2</sub> mass transfer for MGA system using DEA as liquid absorbent.

#### 3.2 ANOVA Analysis

Apart from that, significant effects of regression model generated for the CO<sub>2</sub> mass transfer were tabulated in Table 8. The significant effects included the DEA temperature (*A*), DEA concentration (*B*), DEA velocity (*C*), DEA flow rate (*E*), second-order effects of DEA concentration (*B*<sup>2</sup>), as well interaction effect of (*AB*), (*AC*), (*AE*), (*BC*), (*BE*) and (*CE*). The regression model equations were evaluated by F-test ANOVA which revealed that these regressions model equation are statistically significant at 95% confidence level. All these significant effects had the value of Prob > *F* less than 0.05. A quadratic empirical model for CO<sub>2</sub> mass transfer is as shown in Eqn. 3.

**Table 7:** Experimental and response results.

Standard order	CO <sub>2</sub> mass transfer (mol/(m <sup>2</sup> s))	
	Experimental values	Predicted values
1	0.00140	0.00158
2	0.00410	0.00416
3	0.00180	0.00278
4	0.00220	0.00309
5	0.00270	0.00241
6	0.00490	0.00325
7	0.00170	0.00167
8	0.00460	0.00428
9	0.00120	0.00132
10	0.00310	0.00303
11	0.00220	0.00230
12	0.00480	0.00503
13	0.00120	0.00086
14	0.00310	0.00357
15	0.00280	0.00304
16	0.00460	0.00422
17	0.00230	0.00241
18	0.00280	0.00325
19	0.00220	0.00167
20	0.00470	0.00428
21	0.00140	0.00158
22	0.00310	0.00416
23	0.00280	0.00278
24	0.00310	0.00309
25	0.00050	0.00086
26	0.00420	0.00357
27	0.00280	0.00304
28	0.00440	0.00422
29	0.00140	0.00132
30	0.00300	0.00303
31	0.00260	0.00230
32	0.00470	0.00503
33	0.00410	0.00585
34	0.00830	0.00668
35	0.00290	0.00199
36	0.00370	0.00383
37	0.00510	0.00588
38	0.00680	0.00666
39	0.00620	0.00627
40	0.00650	0.00627
41	0.00670	0.00626
42	0.00620	0.00628



43	0.00610	0.00627
44	0.00620	0.00627
45	0.00640	0.00627
46	0.00660	0.00627

**Table 8:** ANOVA and variance analysis for CO<sub>2</sub> mass transfer model.

Response	Sum of Squares (SS)	Mean Square (MS)	F- Value	Prob > F	Remark
Quadratic Model	1.44 x 10 <sup>4</sup>	1.31 x 10 <sup>5</sup>	28.62	< 0.0001	Significant
A	5.76 x 10 <sup>6</sup>	5.76 x 10 <sup>6</sup>	12.59	0.0012	Significant
B	2.86 x 10 <sup>5</sup>	2.86 x 10 <sup>5</sup>	62.53	< 0.0001	Significant
C	5.20 x 10 <sup>6</sup>	5.20 x 10 <sup>6</sup>	11.36	0.0019	Significant
E	2.65 x 10 <sup>9</sup>	2.65 x 10 <sup>9</sup>	5.78 x 10 <sup>3</sup>	0.0093	Significant
B <sup>2</sup>	9.98 x 10 <sup>5</sup>	9.98 x 10 <sup>5</sup>	218.03	< 0.0001	Significant
AB	1.13 x 10 <sup>8</sup>	1.13 x 10 <sup>8</sup>	0.025	0.0087	Significant
AC	1.51 x 10 <sup>7</sup>	1.51 x 10 <sup>7</sup>	0.33	0.0056	Significant
AE	2.81 x 10 <sup>7</sup>	2.81 x 10 <sup>7</sup>	0.61	0.0438	Significant
BC	1.25 x 10 <sup>7</sup>	1.25 x 10 <sup>7</sup>	0.27	0.0060	Significant
BE	5.00 x 10 <sup>7</sup>	5.00 x 10 <sup>7</sup>	1.09	0.0030	Significant
CE	3.64 x 10 <sup>5</sup>	3.64 x 10 <sup>5</sup>	7.96	0.0079	Significant
Lack of Fit	1.56 x 10 <sup>5</sup>	4.71 x 10 <sup>7</sup>	23.56	0.1620	Not Significant

Model of CO<sub>2</sub> mass transfer:

$$Y = 6.267\text{E-}003 + 4.118\text{E-}004 (A) + 9.176\text{E-}004 (B) + 3.912\text{E-}004 (C) + 8.824\text{E-}006 (E) - 3.355\text{E-}003 (B^2) + 1.875\text{E-}005 (AB) + 6.875\text{E-}005(AC) - 9.375\text{E-}005 (AE) - 6.250\text{E-}005 (BC) + 1.250\text{E-}004 (BE) + 3.375\text{E-}004 (CE) \quad (3)$$

**Table 9:** Summary of ANOVA and regression analysis for CO<sub>2</sub> mass transfer

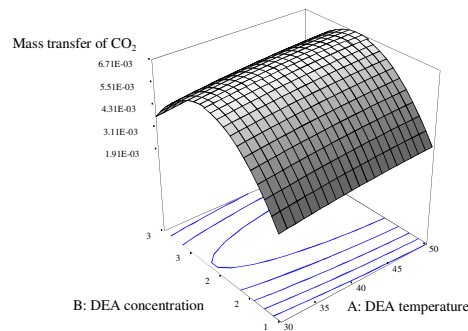
Model	Significant	Standard	R <sup>2</sup>	Adj-R <sup>2</sup>	Pred-R <sup>2</sup>	Adequate
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	Model Terms	Deviation	Precision			
Quadratic Model	A,B,C,E,B <sup>2</sup> , AB,AC, AE, BE, CE	6.767 x 10 <sup>-3</sup>	0.9025	0.8710	0.8277	16.846

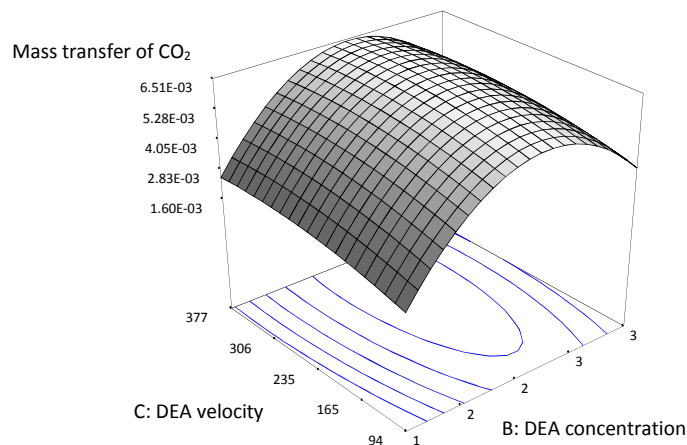
In this study, the regression model of CO<sub>2</sub> mass transfer (Equation 3) provided high values of  $R^2$  (0.9025), Adj- $R^2$  (0.8710) and Pred-  $R^2$  (0.8277) as shown by Table 9. The high determination coefficient of  $R^2$  indicated that the variability in the response could be explained by the mathematical model. For the model of equation, the predicted  $R^2$  is in reasonable agreement with the adjusted  $R^2$  because they are within 0.10 to each other.

### 3.3 Analysis of response surface

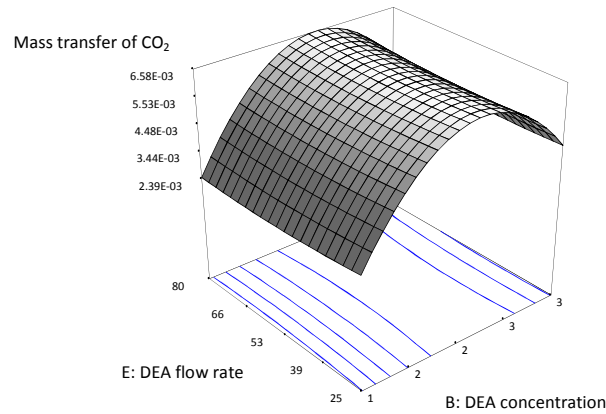
Impacts of DEA temperature, DEA concentration, DEA velocity and liquid absorbent flow rate were significant as indicated by response surface plot in Figure 2 to Figure 7. The maximum mass transfer of CO<sub>2</sub> was attained at intermediate DEA concentration (1M to 3M) in Figure 2, Figure 3 and Figure 4, respectively.



**Figure 2:** Response surface plotted on DEA concentration: DEA temperature.



**Figure 3:** Response surface plotted on DEA concentration: DEA velocity.

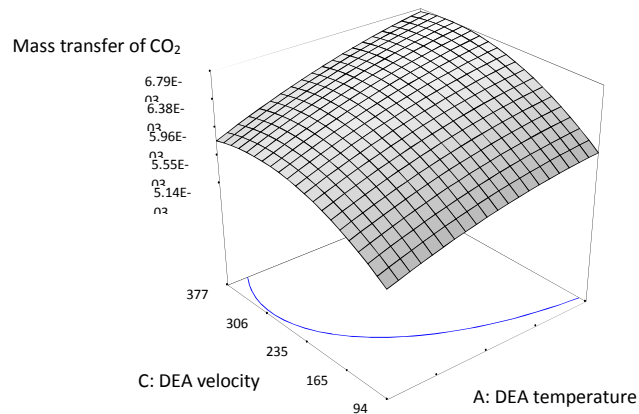


**Figure 4:** Response surface plotted on DEA concentration: DEA flow rate.

At DEA concentration of less than 2M, the effects of elongation contributed to greater mass transfer of  $\text{CO}_2$ , as shown in Figure 2. However, at DEA concentration more 2M, the elongation gave minor effect on the mass transfer of  $\text{CO}_2$  where an almost straight line was observed on the contour plot in Figure 2. This could be due to the DEA was consumed with continuous supplied of  $\text{CO}_2$ . However, increased in the DEA temperature resulting in drop in DEA concentration, which was lead to drop in  $\text{CO}_2$  mass. Hence, the MGA system still needed to be run under appropriate level of DEA concentration and DEA temperature; so that the  $\text{CO}_2$  mass transfer would be in good performance.

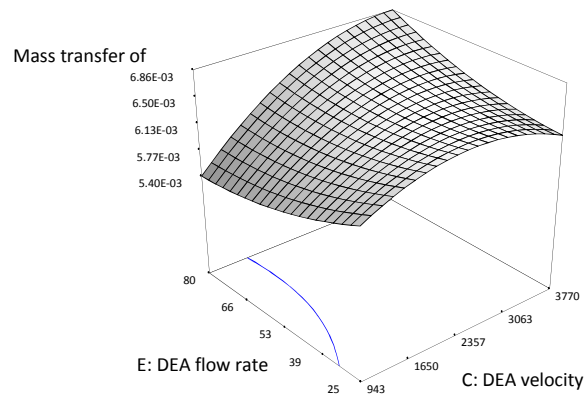
On the other hand, in Figure 3, higher mass transfer of  $\text{CO}_2$  was noted when the fast DEA velocity and intermediate of DEA concentration were introduced during the MGA system operated. In Figure 4, a similar trend was observed, where intermediate DEA concentration and the fast DEA flow rate were necessary for maximum mass transfer of  $\text{CO}_2$ .

Referring to the three- dimensional surface counter plots in Figure 5, mass transfer of  $\text{CO}_2$  was found lower when DEA run under low temperature and high elongation. The maximum of  $\text{CO}_2$  mass transfer was found at  $5.96 \times 10^{-3} \text{ mol/m}^2\text{s}$  when the DEA temperature was  $30^\circ\text{C}$  and 2357 m/s of DEA velocity.



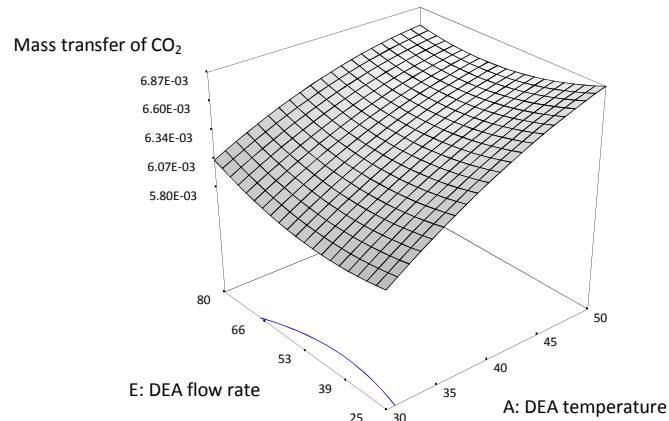
**Figure 5:** Response surface plotted on DEA velocity: DEA temperature.

Impacts of DEA flow rate, DEA velocity and DEA temperature were shown in Figure 6 and 7. At higher DEA flow rate, the MGA system still needed higher DEA velocity and DEA temperature, where long elongation as can be seen in Figure 6 and 7. Hence, at 80 ml/min of DEA flow rate and 943 m/s of DEA velocity,  $\text{CO}_2$  mass transfer was found at  $4.93 \times 10^{-3} \text{ mol/m}^2\text{s}$ . Meanwhile, at 80 ml/min of DEA flow rate and  $30^\circ\text{C}$  of DEA temperature,  $\text{CO}_2$  mass transfer was found at  $5.61 \times 10^{-3} \text{ mol/m}^2\text{s}$ . Thus, it can be concluded that  $\text{CO}_2$  mass



transfer depends appropriate value of DEA temperature, velocity and flow rate.

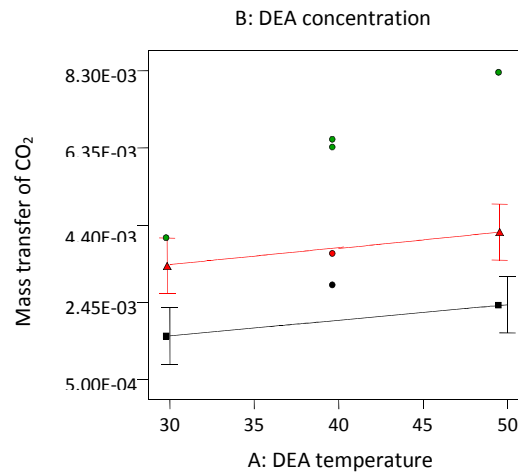
**Figure 6:** Response surface plotted on DEA flow rate: DEA velocity.



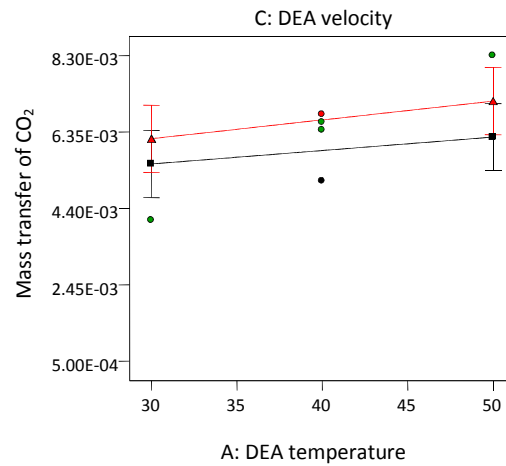
**Figure 7:** Response surface plotted on DEA flow rate: DEA temperature.

### 3.4 Verification and statistical models and diagnostic statistic

RSM has the advantages of observing the interaction effects among independent parameters. Fig. 8-13 show the binary interactions between DEA concentration and DEA temperature (Fig. 8); DEA temperature and DEA velocity (Fig. 9); DEA temperature and DEA flow rate (Fig. 10); DEA flow rate and DEA velocity (Fig. 11); DEA concentration and DEA velocity (Fig. 12) and DEA concentration and DEA flow rate (Fig. 13), respectively.

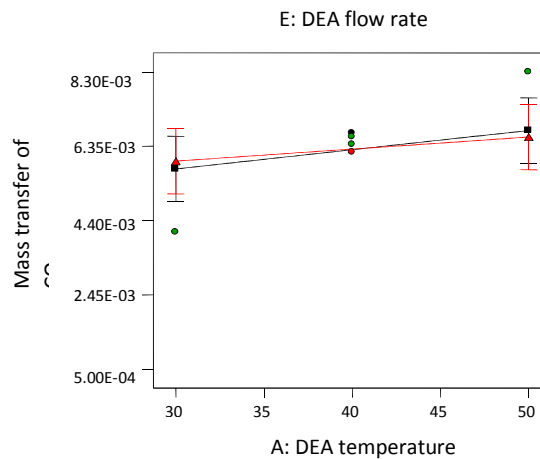


**Figure 8:** Interaction via DEA temperature: DEA concentration (▲ for 1M, ■ for 3M and ● is design point)

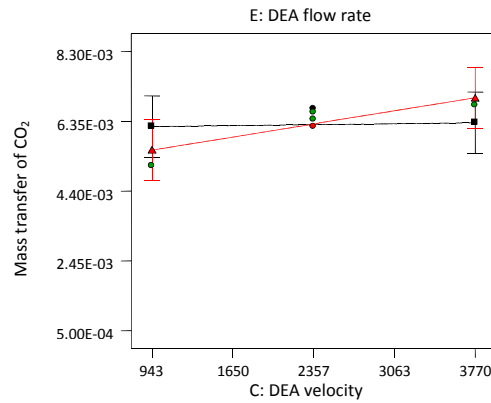


**Figure 9:** Interaction via DEA temperature: DEA velocity (▲ for 3770 m/s, ■ for 943 m/s and ● is design point)

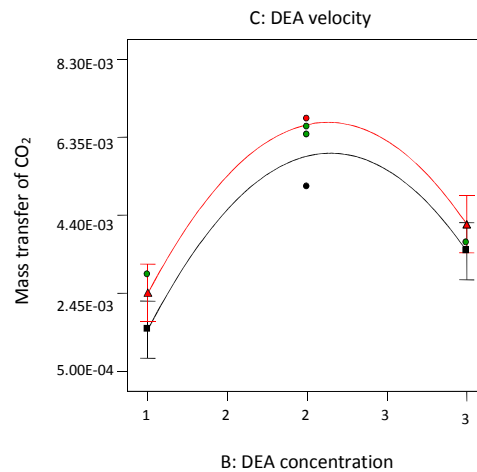
As can be seen in Fig. 8 to Fig. 11, the parallel curvatures implied that there was a weak interaction between variables. However, the non-parallel curvatures of Fig. 12 and Fig. 13 indicated that there was relatively strong interaction between variables. In this case, DEA concentration (B), DEA velocity (C) and DEA flow rate (E). As the result of this strong interaction, BC and BE appeared as significant terms in Eqn. 3. According the model, the maximum operating condition of MGA system was predicted around the region of middle of the variables.



**Figure 10:** Interaction via DEA temperature: DEA flow rate (▲ for 80 ml/min, ■ for 25 ml/min and ● is design point)

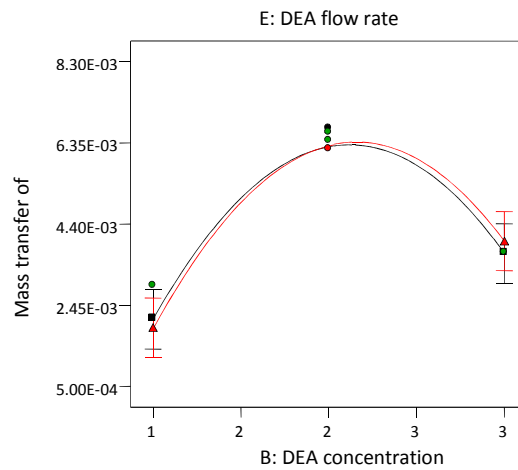


**Figure 11:** Interaction via DEA velocity: DEA flow rate ( $\blacktriangle$  for 80 ml/min,  $\blacksquare$  for 25 ml/min and  $\bullet$  is design point)

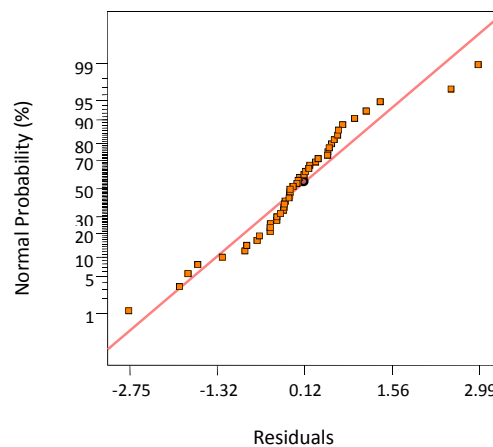


**Figure 12:** Interaction via DEA concentration: DEA flow rate ( $\blacktriangle$  for 3770 m/s,  $\blacksquare$  for 943 m/s and  $\bullet$  is design point)

Diagnostic plots in Figure 14 and Figure 15 were used to determine the residual analysis of response surface design, ensuring that the statistical assumptions fit to analysis data. Figure 14 shows the normal probability of the residuals, to verify whether the standard deviations between actual and predicted response values do follow the normal distribution [17]. The general impression from the figure explained that underlying errors were distributed normally as the residuals fall near to a straight line and thus there was no severe indication of non-normality of the experimental results.

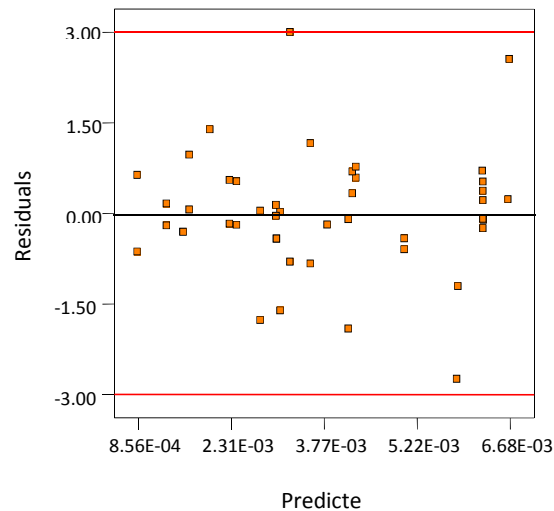


**Figure 13:** Interaction via DEA concentration: DEA flow rate ( $\blacktriangle$  for 80 ml/min,  $\blacksquare$  for 25 ml/min and  $\bullet$  is design point)



**Figure 14:** Normal probability plot of residual for mass transfer of  $\text{CO}_2$

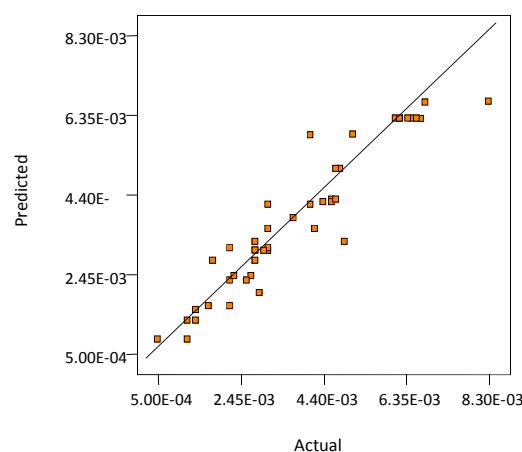




**Figure 15:** Plot of residual versus predicted response.

The plots of residuals versus predicted response was presented in Fig. 15. All points of experimental runs were scattered randomly within constant range of residuals across the graph i.e. within the horizontal lines at point  $\pm 3.0$ . This implied that the proposed models were adequate and the assumption of constant variance was confirmed.

Reliability and adequacy of empirical models (Eqn. 3) were confirmed when the actual values obtained from experimental studies were well-matched to the estimated values from regression model (Fig. 16). Points above the diagonal line were those over-estimates and vice versa. Fig. 16 generally indicated that all experiment design points were distributed along the diagonal line.



**Figure 16:** Predicted versus actual value plot for mass transfer of  $\text{CO}_2$

Responses from experimental results shown in Figure 16 were well-fitted in acceptable variance range compared to predicted values from the respective empirical model. This

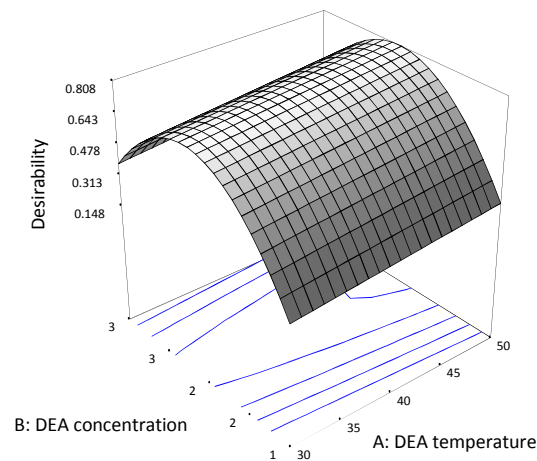
indicated that discrepancy occurred due to uncontrollable experimental error could be neglected. Thus, regression model obtained from CCD could be further use a predictor for the optimization of CO<sub>2</sub> mass transfer using MGA system.

### 3.5 Optimization analysis

In this section, the ultimate goal was to get CO<sub>2</sub> mass transfer with moderate DEA concentration and DEA temperature while maintaining others operating conditions. Figure 17, the surface response plot clearly shows that the desirable DEA tends to shift to lower concentration and moderate temperature, around 50°C.

From Table 10, it can be seen that the most desirable operating conditions were set at DEA temperature of 50°C, DEA concentration of 2M, DEA velocity of 3770 m/s and DEA flow rate of 80 ml/min, respectively. Meanwhile, for operating condition has no effect to the response; gas flow rate and CO<sub>2</sub> inlet concentration were set at 101 ml/min and 33 %v, respectively.

To validate the optimal point generated by CCD, an experimental run was conducted at operating conditions were set as the most desirable operating conditions as shown in Table 10. In the Table 11, the experimental value ( $7.97 \times 10^{-3}$  mol/m<sup>2</sup>s) was found to be in good agreement with the values predicted by CCD ( $7.47 \times 10^{-3}$  mol/m<sup>2</sup>s). Error estimations between predicted and actual values fell within 5%. This indicates that the process optimization in CCD is good and reliable to achieve high CO<sub>2</sub> mass transfer when the MGA system is operated using the suggested optimal operating conditions.



**Figure 17:** Response surface plot of desirability

**Table 10:** Numerical optimization for central composite design

Operating conditions	1	2	3	4	5
DEA temperature (°C)	50	50	49	48	48
DEA concentration (M)	2	2	2	2	2
DEA velocity (cm/min)	3770	3770	3763	3763	3763
Gas flow rate (ml/min)*	101	110	72	70	103
DEA flow rate (ml/min)	80	80	79	79	78
CO <sub>2</sub> inlet concentration (%v)*	33	71	15	62	94
Predicted Responses					
Mass transfer of CO <sub>2</sub> (mol/(m <sup>2</sup> s))	7.47x10 <sup>-3</sup>	7.47x10 <sup>-3</sup>	7.46x10 <sup>-3</sup>	7.45x10 <sup>-3</sup>	7.45x10 <sup>-3</sup>
Desirability (D <sub>f</sub> )	0.90 (Selected)	0.90	0.89	0.89	0.88

\*Has no effect on optimization results.

**Table 11:** Confirmation between optimized mass transfers of CO<sub>2</sub> calculated from mathematical design and experimental study

Factor A: DEA temp. (°C)	Factor B: DEA con. (M)	Factor C: DEA velocity (cm/min)	Factor D: Gas flow rate (ml/min)*	Factor E: DEA flow rate (ml/min)	Factor F: CO <sub>2</sub> inlet con. (%v)*	Response: Mass Transfer of CO <sub>2</sub> (mol/(m <sup>2</sup> s))
Predicted values from central composite design:						
50	2	3370	101	80	33	7.47x10 <sup>-3</sup>
Actual value from confirmation study:						
50	2	3370	101	80	33	7.97x10 <sup>-3</sup>
Standard deviation (%):						0.04

## 4.0 CONCLUSIONS

ANOVA result showed that the temperature, concentration, velocity and flow rate of DEA played a significant role. The optimum DEA temperature was found at 50°C, DEA concentration at 2M, velocity at 3770m/s and 80 ml/min of DEA flow rate with 0.90 of desirability. In the study, the optimum response predicted via CCD was  $7.47 \times 10^{-3}$  mol/m<sup>2</sup>s shown good agreement with the actual experiment value  $7.97 \times 10^{-3}$  mol/m<sup>2</sup>s with the deviation within 5% between actual and predicted data.

## REFERENCES

- [1] Y. Zhang, R. Wang, Novel method for incorporating hydrophobic silica nanoparticles on polyetherimide hollow fiber membranes for CO<sub>2</sub> absorption in a gas-liquid membrane contactor, *Journal of Membrane Science* 452 (2014) 379-389.
- [2] S. Wongchitphimon, R.Wang, R. Jiratananon, Surface modification of polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) hollow fiber membrane for membrane gas absorption, *Journal of Membrane Science* 381 (2011) 183-191.
- [3] R. Wang, Polymeric Membrane preparation and surface modification for water treatment, the 7<sup>th</sup> International Pre Conference Workshop on Membrane Science & Technology, Kuala Lumpur, (2009).
- [4] J.L. Li, B. H. Chen, Review of CO<sub>2</sub> absorption using chemical solvents in hollow fiber membrane contactors, *Separation and Purification Technology* 41(2005) 109–122.
- [5] N A.L. Ahmad, A.R. Sunarti, K.T. Lee, W.J.N. Fernando, CO<sub>2</sub> removal using membrane gas absorption, *International Journal of Greenhouse Gas Control* 4 (2010) 495-498.
- [6] A. Mansourizadeh, Z. Aslmahdavi, A.F. Ismail, T. Matsuura, Blend polyvinylidene fluoride/surface modifying macromolecule hollow fiber membrane contactors for CO<sub>2</sub> absorption, *International Journal of Greenhouse Gas Control* 26 (2014) 83-92.
- [7] Gh. Bakeri, A.F. Ismail, M. Rahimnejad, T. Matsuura, Porous polyethersulfone hollow fiber membrane in gas-liquid contacting processes. *Chemical Engineering Research and Design* 92 (2014) 1381-1390.
- [8] H.A. Rangwala, Absorption of Carbon Dioxide into aqueous solutions using hollow fiber membrane contactors, *Journal of Membrane Science* 112 (1996) 229-240.
- [9] R. Wang, D.F. Li, C. Zhou, M. Liu, D.T. Liang, Impact of DEA solutions with and without CO<sub>2</sub> loading on porous polypropylene membranes intended for use as contactors, *Journal of Membrane Science* 229 (2004) 147–157.
- [10] F.O. Pedersen, H. Dannstrom, Separation of carbon dioxide from offshore gas turbine exhaust, *Energy Conversion Management* 38 (1997) 81-86.
- [11] N. Nishikawa, M. Ishibashi, H. Ohta, N. Akutsu, H. Matsumoto, T. Kamata, H. Kitamura, CO<sub>2</sub> removal by hollow-fiber gas-liquid contactor, *Energy Conversion Management* 36 (1995) 415–418.

- [12] S.R. Wickramasinghe, M.J. Semmens, E.L. Cussler, Hollow fiber modules made with hollow fiber fabric, *Journal of Membrane Science* 84 (1993) 1–14.
- [13] K.L. Wang, E.L. Cussler, Baffled membrane modules made with hollow fiber fabric, *Journal of Membrane Science* 85 (1993) 265–278.
- [14] J.G. Lu, Y.F. Zheng, M.D. Cheng, Wetting mechanism in mass transfer process of hydrophobic membrane gas absorption, *Journal of Membrane Science* 308 (2008) 180–190.
- [15] R.J. Little, G.F. Versteeg, W.P.M. van Swaaij, Kinetics of CO<sub>2</sub> with primary and secondary amines in aqueous solutions I. Zwitterion deprotonation kinetics for DEA and DIPA in aqueous blends of alkanolamines, *Chemical Engineering Science* 47 (1992) 2027-2035.
- [16] D.C. Montgomery, *Design and Analysis of Experiments*. John Wiley & Sons, New York (2005).
- [17] K.M. Lee, D.F. Gillmore, Formulation and process modeling of biopolymer (polyhydroxyalkanoates: PHAs) production from industrial wastes by novel crossed experimental design, *Process Biochemistry* 40 (2005) 229-246.