

Optimization of MDEA-PZ Ratio and Concentration for CO₂ Removal in Semi-Lean Membrane Contactor Process

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Abstract. Membrane contactor has garnered interest in the recent decade due to its advantages. This study looks at optimisation of the amine concentration, comprising of methyldiethanolamine (MDEA) with piperazine (PZ) in membrane contactor to remove CO₂ from 25mol% down to 6.5mol%. 37 experiments were carried out and the results were analysed through response surface analysis. Model is found to be significant with R² of 0.9854. Based on contour plot produced, there exists a trade-off between amine concentration and viscosity that greatly impacts the performance. For better overall evaluation, the amine regeneration side is considered by running process simulation through gPROMS to obtain data on expected hydrocarbon co-absorption and amine regeneration energy required. The optimum amine is found to be at 45wt% concentration and MDEA-to-PZ ratio of 0.047 where the process would meet outlet spec whilst minimising amine regeneration duty and the amine rich loading.

1 Introduction

Membrane contactor integrates membrane separation with conventional phase contacting operation, like extraction of absorption, with the intent to fully exploit the benefits of both technologies [1]. This technology offers higher packing density, eliminates foaming, provides independent control of gas and liquid flow, modular and linear scale-up, gives easier prediction of performance and not sensitive to motion [2, 3, 4].

Selecting an effective absorbent is one of the key parameters to optimize the CO₂ capture in the membrane absorption process [5]. About 90% of the acid gas treating processes in operation use alkanolamines solvents due to their versatility and ability to remove acid gases to ppm levels [6]. In this study, blended solutions of methyldiethanolamine (MDEA) with piperazine (PZ) are used due to its higher CO₂ capacity, low vapor pressure, thermal stability and less significant corrosive nature [5, 7].

MDEA is a tertiary amine and has a low reaction rate to CO₂. The CO₂ reaction only takes place after the CO₂ dissolves in the water to form a bicarbonate ion. Acid-base reaction then occurs between the bicarbonate with the amine to yield the overall CO₂ reaction [8, 9]. PZ is a cyclic amine used as a promoter to enhance absorption rate of aqueous MDEA [10]. Aqueous solution of Piperazine-activated MDEA was disclosed and introduced to market by many leading companies such as BASF, Dow Chemical Company, UOP LLC, Huntsman Corporation and Shell [8].

The absorbent concentration has tremendous impact on specific rate of absorption of CO₂ [10]. Increasing the PZ concentration with MDEA/ PZ blend has a significant effect on CO₂ absorption [11]. However, there is a restriction of using higher mass proportion of PZ since both viscosity and crystallization affinity of PZ hampers its usability mostly at higher concentration [10]. This is more crucial for a membrane contactor where the mass transfer resistance in the liquid phase represents 69–93% of the total mass transfer resistance [12]. Hence, there is trade-off between increasing the absorbent concentration and minimizing the liquid mass transfer resistance. Previous studies show that increasing amine concentration will lead to higher CO₂ absorbing capacity [5], however solvent viscosity would also increase which will hinder mass transfer in membrane contactor system [13].

Work on optimizing solvent concentration and ratio for membrane contactor application for CO₂ removal is scarcely found in literature. Saidi (5) is among the few that carried out sensitivity analysis on various amine concentration in membrane contactor and found that increasing the PZ concentration to more than 5 wt% has no significant effect on the CO₂ absorption flux. His conclusion however focused on improving the performance through increasing liquid temperature, solvent concentration, fiber numbers and the liquid flow rate [5]. Chan et al. [12] alternatively pointed out that most published works of membrane contactor used excessive amine flow in order to achieve better performance, but this leads to high liquid-to-gas ratio (L/G) which results in high energy requirement for pumping and regeneration process

The objective of this paper is to determine the optimized solvent concentration and MDEA-to-PZ ratio for removal of CO₂ from 25 mol% to 6.5 mol%. The liquid flowrate in these experiments is limited in order to achieve low L/G ratio of 0.6 – 1.0 liter of liquid per mol CO₂ absorbed. The outcome of this study is to illustrate the trade-off between increasing amine concentration and reducing liquid side mass transfer resistance in membrane contactor process in order to improve CO₂ absorption performance. The significance of this work is to achieve optimum solvent condition for both CO₂ removal and solvent regeneration process.

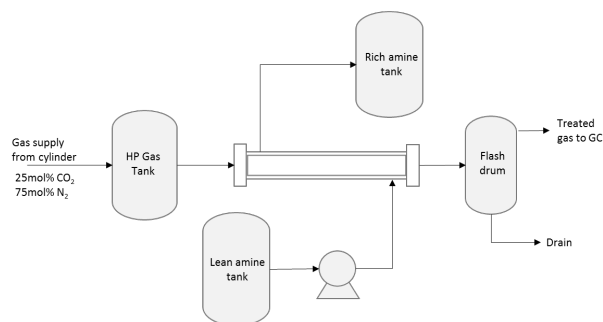


Fig. 1. Membrane contactor lab test rig setup

2 Methodology

2.1 Materials

Methyldiethanolamine (MDEA) and piperazine (PZ) were purchased from Sigma Aldrich. Different mixtures of MDEA, PZ and distilled water were prepared according to experimental design with range as shown in Table 2

The membrane module used is of 2-metre long and consist of polytetrafluoroethylene (PTFE) hollow fibre membranes. The module was prepared and supplied by Dalian Institute of Chemical and Physics (DICP). The details of the membrane module used for the experiments are as follows:

Table 1. Membrane module details and specification

Membrane material	PTFE
Membrane outer Diameter (mm)	1.11
Membrane inner Diameter (mm)	0.41
Membrane thickness (mm)	0.35
Membrane porosity (%)	0.42
Max pore size (µm)	0.67
Liquid entry pressure using amine (bar)	2.37
Membrane module length (m)	2
No. of fibers in module	120
Module packing density	47%
Specific membrane area (m ² /m ³)	1700

2.2 CO₂ Removal Experiment

Membrane contactor lab test rig setup as shown in Figure 1 was used for CO₂ removal experiments. Testing was conducted at various amine concentration and MDEA to PZ ratio such as shown in Table 2. The experiments were carried out using inlet gas of 25mol% CO₂ (balance N₂) with targeted CO₂ outlet of 6.5mol%. All experiments were carried out at high pressure of 53 barg and amine inlet temperature of 40°C. Gas is flowed on the lumen side, with liquid MDEA-PZ solution on the shell side at constant flow rate of 10 kg/hr (i.e. liquid velocity of 0.01 m/s), counter-currently. This configuration is similar to work reported by Kang et al. [14]. All experiments were run at least for an hour or until process is stable before results were recorded.

Table 2. Range of parameters varied in experiment

Gas flowrate (kg/hr)	1.20 – 2.70
MDEA (wt%)	28 – 45
PZ (wt%)	0 – 7
Total amine concentration (wt%)	32 – 45
MDEA to PZ ratio	0 – 0.18
Semi lean amine loading (mol/mol)	0.20 – 0.28

2.3 Amine analysis for concentration and CO₂ loading

Amine analysis to measure for its concentration was carried out through titration against 0.5N hydrochloric acid (Reference method DOW43000020). The volume of acid used is then entered into formula below to calculate for wt% of amine.

$$\left(\frac{V \times N \times 9.102}{W_1} \right) = \text{wt \% amine} \quad (1)$$

Where:

- N = normality of HCl, up to 0.0001N;
- V = mL of HCl used to titrate sample, up to 0.05 mL;
- 9.102= amine factor;
- W₁ = weight of sample, up to 0.0001g

To measure the CO₂ loading in the amine, the sample is added with 100mL methanol and then titrated against 0.5N potassium hydroxide (KOH) (Reference method DOW43000055). The volume of KOH used is recorded and the amount of CO₂ in the amine sample is calculated through formula below. Lean solution is used as basis of comparison.

$$\left(\frac{V_1}{W_1} - \frac{V_2}{W_2} \right) \times N \times 4.4 = \% \text{ CO}_2 \text{ in amine} \quad (2)$$

Where:

- V₁= mL of KOH to titrate sample, up to 0.05 mL;
- V₂= mL of KOH to titrate fresh solution, up to 0.05 mL;
- W₁= g of sample titrated, up to 0.0001g;
- W₂= g of lean solution titrated, up to 0.0001g;
- N= normality of KOH, up to 0.0001N.

2.4 Data analysis and process simulation

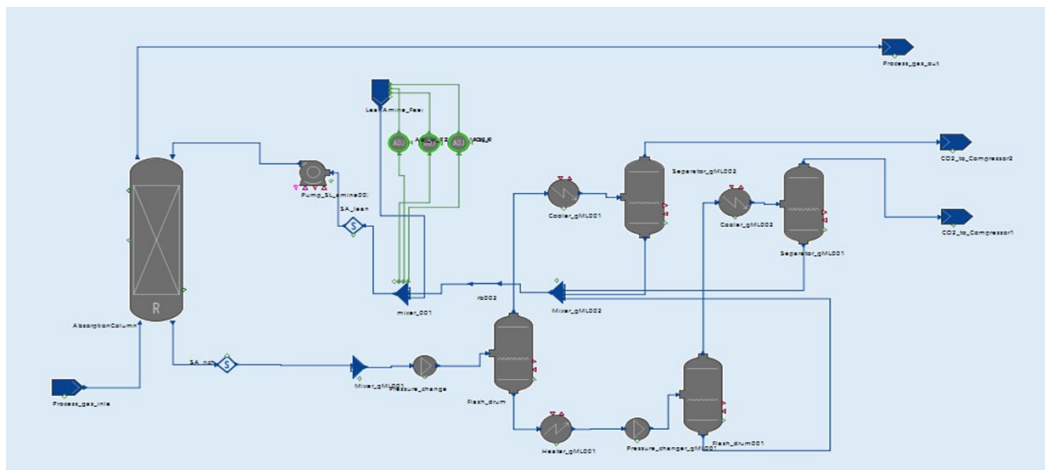


Fig. 2. Process simulation flowsheeting using gPROMS

Results from the experiments were analysed as response surface using DesignExpert software (Version 10). Model produced is evaluated and used to predict the best amine condition for the process.

Additionally, since the experiments are limited to just the absorption side, data on the amine regeneration section is obtained through process simulation using gPROMS ProcessBuilder 1.2 software. Simulation is done to evaluate on hydrocarbon loss through co-absorption and heating duty required for various concentration of amine used; The flowsheeting for process simulation is as shown in Figure 2.

For semi-lean CO₂-removal process, high pressure and low pressure flash vessels are for amine regeneration, as shown in Figure 2. Feed gas flowrate of 900 mmsfd is used, with feed composition consisting of 25mol% CO₂. Heater temperature is set constant at 90°C and amine flowrate at 2900 kg/s. The flowrate chosen are based on similar L/G ratio as lab experiments. Amine concentration as well as MDEA to PZ ratio were varied, similar to lab experiments; and the resulted hydrocarbon loss and heating duty required were recorded and used to evaluate optimized amine.

3 Result and Discussion

3.1 Response surface analysis

Total of 37 experiments were carried out and response surface analysis was carried out. The resulted ANOVA response surface model is as presented in Table 3. Confidence level chosen in this analysis is 95%, therefore parameters with p-value of less than 0.05 is consider significant. All parameter interactions and squares are considered significant with 95% confidence level, which shows that there are strong relations between the target CO₂ outlet performance with

operating parameters and their interactions. The model has a regression, R² of 0.9854. The model is deemed adequate to navigate the design space.

Table 3. Result of ANOVA response surface model; where A is gas flowrate, B is amine loading, C is amine concentration, D refers to MDEA to PZ ratio, and E is the liquid flowrate

Source	Sum of Squares	df	Mean Square	F Value	p-value (Prob>F)
Model	97.09	16	6.07	79.12	< 0.0001
A	23.93	1	23.93	312.00	< 0.0001
B	2.71	1	2.71	35.34	< 0.0001
C	1.48	1	1.48	19.27	0.0003
D	1.16	1	1.16	15.13	0.0009
E	0.078	1	0.078	1.02	0.3251
AB	1.28	1	1.28	16.70	0.0006
AC	2.17	1	2.17	28.33	< 0.0001
AE	0.56	1	0.56	7.35	0.0134
BC	4.14	1	4.14	53.95	< 0.0001
BD	8.68	1	8.68	113.15	< 0.0001
BE	10.96	1	10.96	142.95	< 0.0001
CD	7.34	1	7.34	95.72	< 0.0001
CE	10.22	1	10.22	133.27	< 0.0001
A ²	0.45	1	0.45	5.85	0.0253
B ²	3.22	1	3.22	41.95	< 0.0001
D ²	6.22	1	6.22	81.15	< 0.0001
Residual	1.53	20	0.077		
Cor Total	98.62	36			

3.2 Effect of PZ concentration

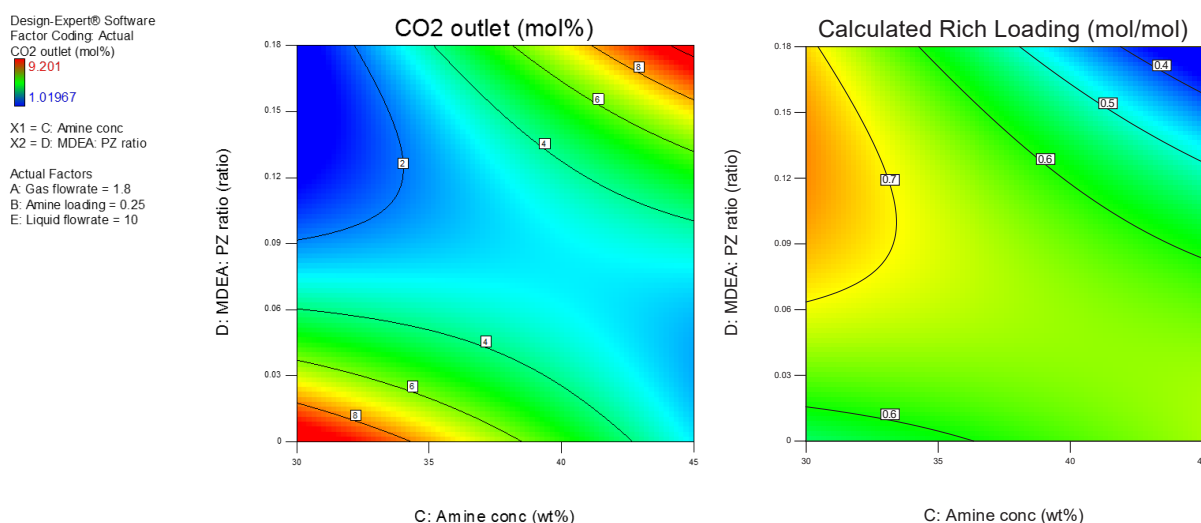


Fig. 3. Contour plot of CO₂ outlet (mol%) (left) and rich amine loading (mol/mol) (right) based on gas flowrate 1.8kg/hr and amine loading 0.25 mol/mol

Figure 3 shows the optimum amine conditions in order to meet the CO₂ outlet specification of 6.5mol% using membrane contactor process. Based on contour plot on CO₂ outlet, for lower amine concentration of between 30 – 35 wt%, the rate of absorption efficiency dramatically increases with increase of PZ concentration, similar to findings by Ibrahim et al. [8] and Khan et al. [10]. In contrast, using less PZ at this amine concentration would lead to insufficient CO₂ removal, resulting the outlet to be off-spec. This is because of MDEA low reaction rate to CO₂ and when lacking of activator PZ, it is unable to remove CO₂ effectively.

At higher concentration of between 40 – 45wt%, the contour plot shows an obvious change of behaviour where the membrane contactor process now prefers lower PZ for better performance. Using more PZ in the solution would resulted in a more viscous solution and this will increase the liquid mass transfer resistance.

Hence, the CO₂ outlet contour plot above clearly shows how membrane contactor is sensitive to changes that affects absorbent viscosity. The optimised absorbent conditions for CO₂ removal are those that are in blue and green plot. The accompanying contour plot on Calculated Rich Loading (mol/mol) shows plot for rich amine loading based on the same operating range. The rich amine loading when using less concentrated amine (30 – 35wt%) has reached to more than 0.7 mol CO₂/mol amine. This is because at low amine concentration, the absorbent has limited absorption capacity and it is proven from these experiments that the rich loading has already reached the rich loading amine limit.

The two plots however only convey the optimisation in terms of CO₂ removal at the absorption. The last section of this paper will look at the amine regeneration side

(through process simulation) to account for hydrocarbon carry-over and regeneration energy required for the different amine conditions.

3.3 Effect of increasing gas flowrate

The capacity limit of the membrane module is stretched further by increasing gas flowrate. As shown in Figure 4 shows the contour plot of membrane contactor performance for when gas flowrate is increased to 2.5 kg/hr, instead of 1.8kg/hr previously

Based on Figure 4 on CO₂ outlet plot, the operating range is much smaller and the only suitable amine concentration is between 40 – 45wt% and MDEA-to-PZ ratio of between 0 to 0.12 in order to meet the CO₂ outlet specification of 6.5mol%. This is because with increasing gas flowrate, more amine is required for the absorption process to occur, thus, higher amine concentration if more favourable. Additionally, the use of PZ in the absorbent is also limited to less than 5wt% to ensure that the liquid does not get too viscous and limits mass transfer. The 5wt% limit of PZ seems consistent as the finding reported by Saidi [5].

The advantage of increasing membrane module capacity (through increasing gas flowrate) is that it reduces the number of modules required for processing and this shall reduce the overall capital expenditure (CAPEX). However, looking at rich amine contour plot in Figure 4 (with similar operating range), the rich amine will be very rich and above 0.8 mol CO₂/mol amine. The risk of very rich amine is the potential for sudden flashing inside pipeline which could lead to severe vibration.

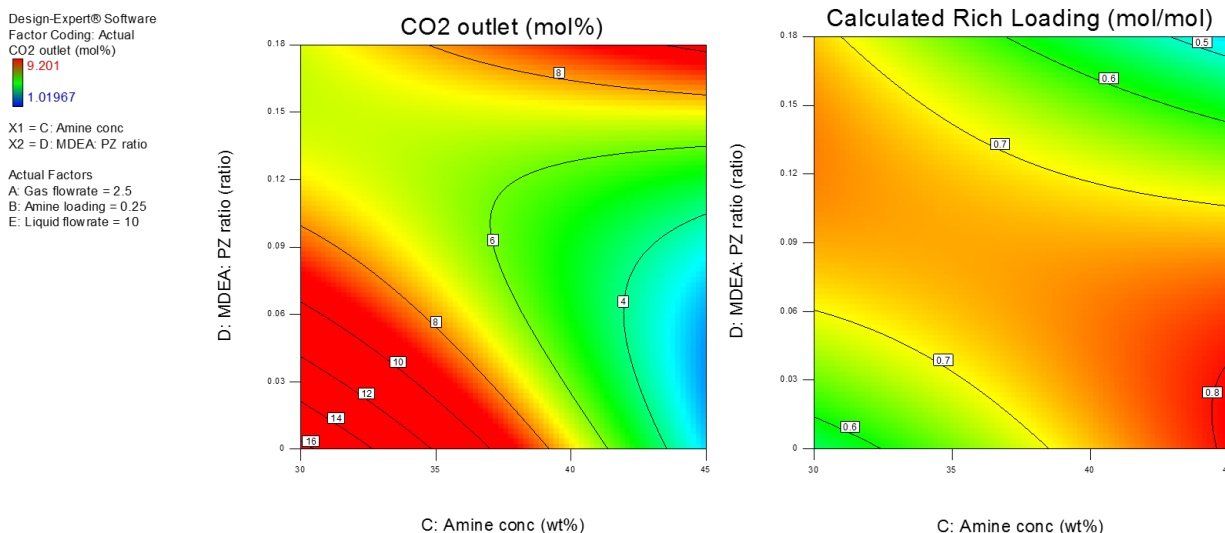


Fig. 4. Contour plot CO₂ outlet (mol%) (left) and rich amine loading (mol/mol) (right) based on gas flowrate 2.5kg/hr at amine loading 0.25 mol/mol

3.4 Effect of amine concentration on heating duty and hydrocarbon loss

Based on contour plot obtained in Figure 3, 12 simulation cases were run using gPROMS varying the amine total concentration at 30, 35, 40 and 45wt%, and MDEA to PZ ratio at 0.047, 0.098 and 0.184. The process flowsheet is as shown previously in Figure 2.

Figure 5 charted the resulted hydrocarbon loss (in %) against the amine concentration used. This is based on the flash gas stream at the outlet of low pressure flash vessel. It shows that using a higher concentration of amine, co-absorption of hydrocarbon is more likely to occur.

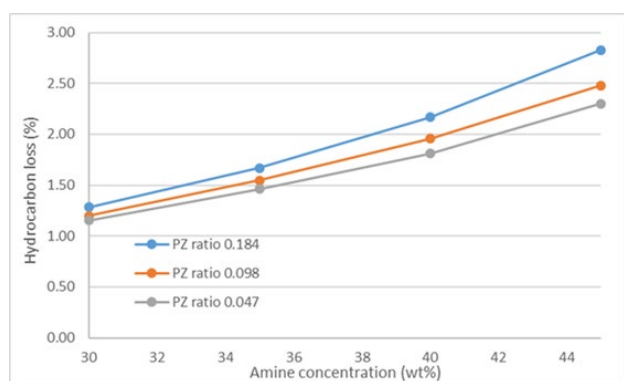


Fig. 5. Hydrocarbon loss (%) based on process simulation with feed gas 25mol% CO₂ at varied amine concentration and ratio

The co-absorption can be reduced by using lower amine concentration. However, similar to as reported by Kang et al. [14], since this hydrocarbon loss is based on flash gas stream, it could be rerouted back as fuel gas. Hence, no significant loss or economic implication.

Figure 6 below shows the required heating energy for amine regeneration is higher for lower concentration amine. This is because MDEA at lower concentration of 30-35wt% has higher water content, thus its heat capacity (J/g.K) is much higher [15] and more amount of heat need to be supplied to produce a unit change in its temperature in order to regenerate the amine.

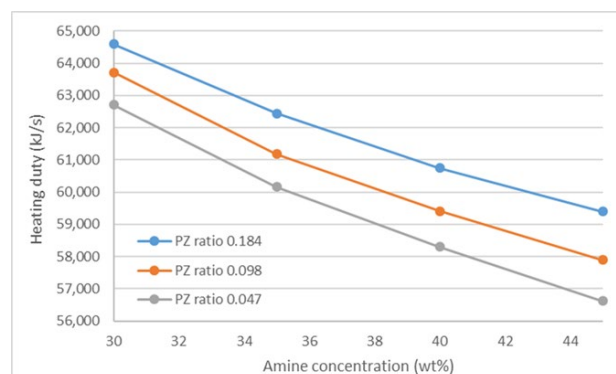


Fig. 6. Heating duty (kJ/s) based on process simulation with gas flowrate 900 mmscf and feed gas 25mol% CO₂ at varied amine concentration and ratio

The result from Figure 6 is translated into operating cost as shown in Table 5. Only the numbers for cases that would meet CO₂ specification outlet of 6.5mol% are considered.

Table 5. Heating duty (RM mil/year)

MDEA:PZ ratio	Amine concentration (wt%)			
	30	35	40	45
0.184	0.89	0.86		
0.098	0.87	0.84	0.81	
0.047			0.80	0.78

Evaluating the table above, together with result in contour plot in Figure 3 and 4, it seems that it is most advantageous to use MDEA-PZ at 45wt% and MDEA-to-PZ ratio of 0.047. At this concentration and amine ratio, it would meet the desired CO₂ spec whilst minimising amine regeneration duty and the amine rich loading.

4 Conclusion

Membrane contactor offers several advantages against conventional technology but the process need to be economic and efficient by keeping the L/G ratio low and minimising the liquid mass transfer resistance. Optimising the MDEA-PZ concentration for CO₂ removal from 25mol% down to 6.5mol% demonstrates that there is a trade-off between amine concentration and viscosity. The optimum amine for the said case is found to be at 45wt% concentration and MDEA-to-PZ ratio of 0.047 where the process would meet outlet spec whilst minimising amine regeneration duty and the amine rich loading. Increasing the gas flowrate could lead to less number of membrane module required for the separation process, however more attention need to be put on the risk of too high rich amine loading at the outlet of the process as very rich amine could lead to risk of severe vibration in pipeline.

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