

Separation of CO₂ from Flue Gas via Absorption of Alcohol Amines

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Abstract The separation of CO₂ from flue gas by alcohol amine method was investigated in this paper. We conducted the absorption and desorption experiments using different alcohol amines: monoethanolamine (MEA), diethanolamine (DEA), methyl diethanolamine (MDEA), triethanolamine (TEA), piperazine (PZ), and their binary mixtures. Relevant absorption rate and desorption rate of CO₂ were obtained and reported. Aspen Plus was applied to simulate the process of recovering CO₂ from flue gas via absorption of PZ-MEA solution. The influences of the lean liquid CO₂ load, lean liquid temperature and desorber pressure on the reboiler duty were investigated, and the optimal operating parameters were obtained on the basis of the minimum reboiler duty.

Keywords Absorption, Desorption, CO₂, Flue Gas, Alcohol Amines

1. Introduction

The emission of greenhouse gases brings about the increasing severe greenhouse effect. The global average temperature has increased by 0.3 to 0.7 °C in the past century, and it may increase by about 3 °C at the end of 21st century without effective actions to control the greenhouse effect.^{1,2} Among all of the greenhouse emissions, CO₂ is the main component with a proportion more than 60 %, and the major source of the CO₂ in the atmosphere is the flue gas released from the combustion of fossil fuel.^{3,4} Consequently, capture of CO₂ from flue gas could effectively mitigate the greenhouse effect, and make economic sense as well.⁵

One of the most suitable and mature methods for capture of CO₂ from flue gas is the absorption using alcohol

amines.⁶⁻¹⁰ The most widely used amine is monoethanolamine (MEA), which is successfully applied in industry.¹¹⁻¹³ However, the limitation of MEA is high energy consumption in desorption process, which is reported as 4.2 to 5.2 kJ/(kgCO₂).^{14,15} Consequently, we investigated the separation of CO₂ from the flue gas using different alcohol amines in this paper.

2. Experimental Section

1. Materials and apparatus

The absorbents used in this work are MEA, diethanol amine (DEA), methyl diethanol amine (MDEA) and piperazine (PZ), which are supplied by Sinopharm Chemical Reagent Co., Ltd. The composition of the flue gas is CO₂: 15 mol% and N₂: 85 mol%. Figure 1 and 2 show the apparatus of the absorption and desorption experiments.

2. Experimental procedure

An appropriate amount of absorbent solution was first added into the reaction flask. The magnetic stirrer was turned on and the temperature was set to the experimental value. Then the flue gas was introduced into the flask with a constant flow rate of 4 ml/s. The gas flows of the two soap film flow meters were recorded with time. While the difference between the two meters was less than 5 ml/min, the absorption experiment was considered finished. Then the desorption experiment was conducted at atmospheric pressure. After the flow of the desorption gas, measured by the soap film meter, was less than 10 ml/min, the desorption process was considered as completed.

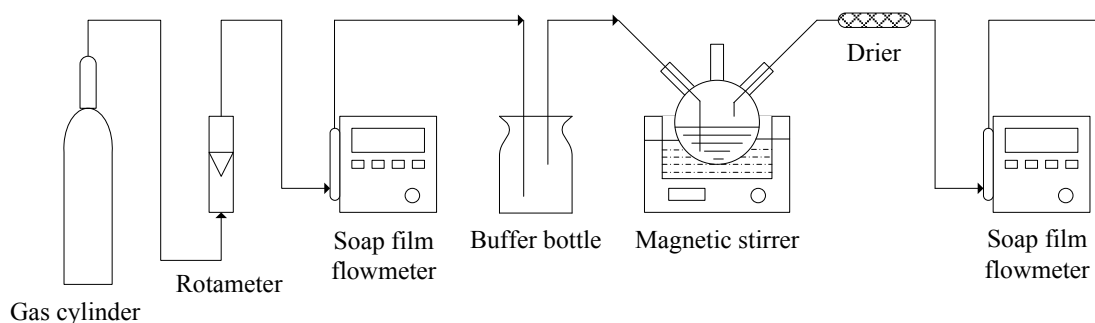


Figure 1. Schematic diagram of the apparatus for the absorption of CO₂ from flues gas using hydramines.

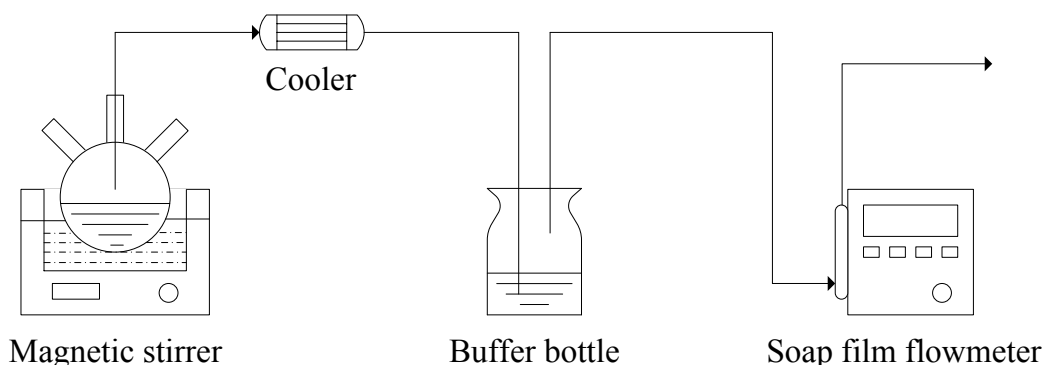


Figure 2. Schematic diagram of the apparatus for the desorption of CO₂ from flues gas using hydramines.

3. Calculation

The absorption rate (R_a) is defined as the number of moles of CO₂ absorbed in the solution per second.¹⁶ It could be calculated by the following equation.

$$n = \frac{p(V_1 - V_2)}{RT} \quad (1)$$

$$R_a = \frac{n}{60} \quad (2)$$

where n is the number of moles of the absorbed CO₂ in amine solution. V_1 and V_2 are the gas flows per minute measured by the soap film flowmeters, respectively. p , T are the given pressure and temperature of the soap film flowmeter. R is the gas constant with a value of 8.3145 J/(mol·K). The desorption rate (R_d) is defined as the number of moles of CO₂ desorbed from the absorption liquid per second.¹⁷ It is obtained using the same calculation method.

4. Simulation Using Aspen Plus

1. Materials

The equilibrium stage model was used in the simulation. The compositions of flue gas are CO₂: 9 mol%, N₂: 88 mol% and O₂: 3 mol%, and the flow rate is 54000 Nm³/h, which is given by Tarim Oilfield Petrochemical Company. The absorbent is PZ-MEA mixed solution with a total mass

concentration of 30 wt%. The molar ratio of PZ and MEA in the absorption solution is 1:1. ELECNRTL equation is chosen as the property method for CO₂-PZ-MEA-H₂O system.

2. Calculation

The recovery of CO₂ (R) is calculated using the following equation:

$$R = \frac{F_r}{F_f} \quad (3)$$

where F_r and F_f are CO₂ molar flow in the gas product of the desorber and feed gas, respectively.

CO₂ load is defined as the number of moles of CO₂ absorbed by 1 mole alcohol amine.¹⁸ There are rich liquid CO₂ load and lean liquid CO₂ load in the simulation. Rich liquid, i.e., high CO₂ content liquid, is the liquid out from the bottom of absorber. Lean liquid is the liquid entering into the absorber to absorb CO₂ from flue gas. The absorbent is PZ-MEA binary solution. One PZ molecule has two amidogens, and one MEA molecule has one amidogen. Consequently, one mole PZ could absorb two moles of CO₂ in theory, and one mole MEA in the same way. CO₂ load (L_{CO_2}) is calculated as follows:

$$L_{CO_2} = \frac{F_{CO_2}}{2F_{PZ} + F_{MEA}} \quad (4)$$

where F_{CO_2} , F_{PZ} and F_{MEA} are the molar flows of CO₂,

PZ and MEA in the liquid, respectively.

5. Results and Discussion

1. Absorption by single alcohol amine

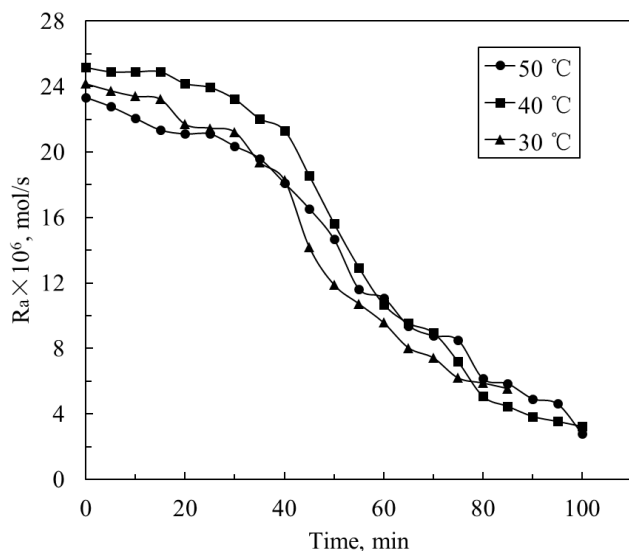


Figure 3. The absorption rate of flue gas in 0.5 mol/L MEA solution at different temperatures.

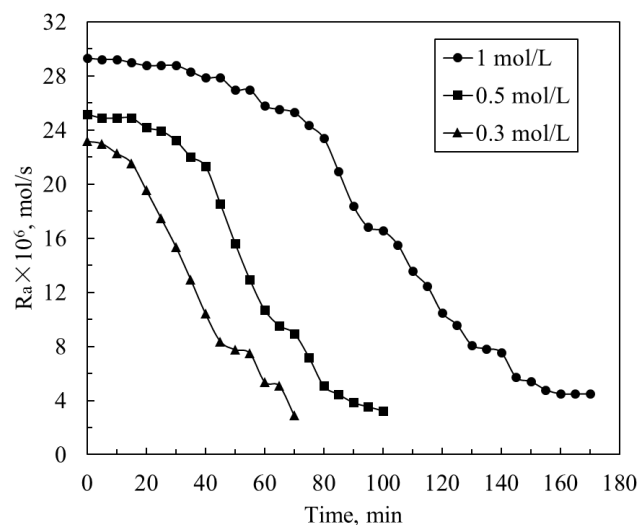


Figure 4. The absorption rate of flue gas in MEA solutions with different concentrations at 40 °C.

First, we measured the absorption rates of flue gas in 0.5 mol/L MEA solutions at 30 °C, 40 °C and 50 °C, respectively. As shown in Figure 3, the absorption rate at 40 °C is the highest. The absorption rate increases with the temperature. However, higher temperature will inhibit the absorption as the reaction between MEA and CO₂ is exothermic. Consequently, we chose 40 °C as the optimal reaction temperature in this work. Figure 4 shows the absorption rates of flue gas in different MEA solutions at 40 °C. We can find that the absorption rate increases with the MEA concentration. However, higher concentration of amine brings about higher cost and faster erosion of equipment.

Consequently, the concentration of amine with more than 1 mol/L was not investigated in this work. Then, we measured the absorption rates of flue gas using various absorbents with the same concentration of 1 mol/L at 40 °C. Figures 5 and 6 show R_a and R_d of flue gas using different single amines, respectively.

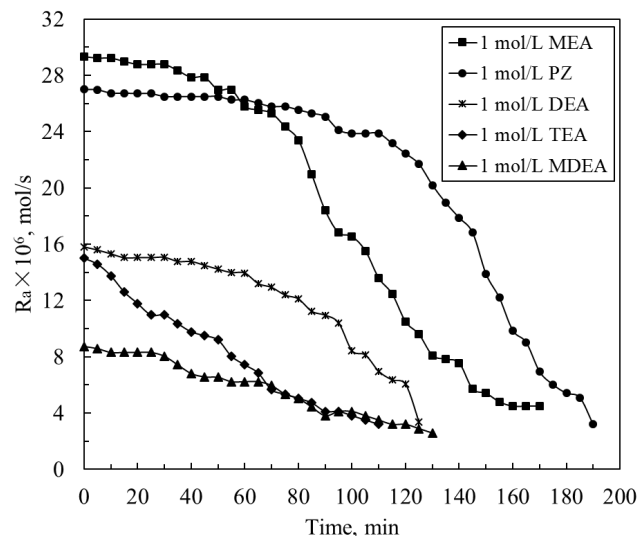


Figure 5. The absorption rate of flue gas at 40 °C.

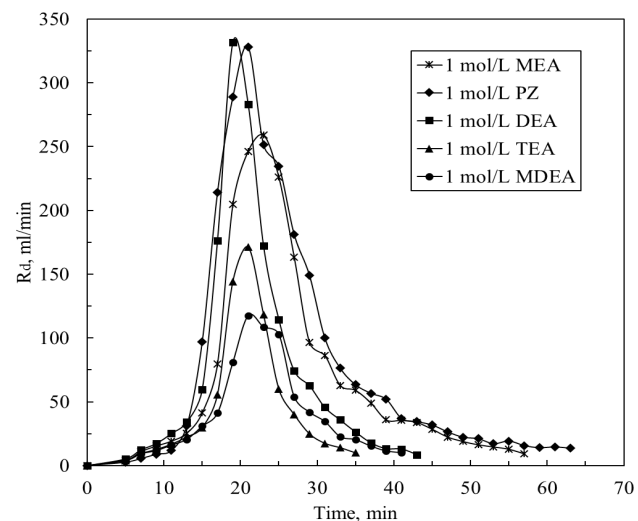


Figure 6. The desorption rate of CO₂.

We can find that PZ and MEA have much higher adsorption rate of CO₂ than the other three amines. The initial adsorption rate of MEA is slightly higher than that of PZ, but the situation reverses after 60 min. It shows that the overall absorption effect of PZ is the best among the five amines. The adsorption rate of TEA and MDEA are the slowest, because they are tertiary amines and they have different reaction mechanism from the other three amines.¹⁹ Due to the absence of hydrogen atoms around the nitrogen atom, TEA and MDEA can not form NCOO⁻ with CO₂. The reaction between tertiary amines and CO₂ could be expressed using equation (3).²⁰ It indicates that tertiary amines only behaves as the catalyst of CO₂ hydrolysis. Consequently, the

reaction rate is much slower than that between primary amine, secondary amine and CO₂ at the same conditions.²¹

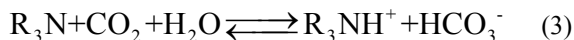


Figure 6 shows that the maximum R_d appears at about 22 minutes after the desorption reaction starts. The desorption time of TEA/CO₂ and MDEA/CO₂ are relatively short, i.e., the desorption of TEA/CO₂ and MDEA/CO₂ are relatively easy.

2. Absorption Using Mixed Alcohol amines

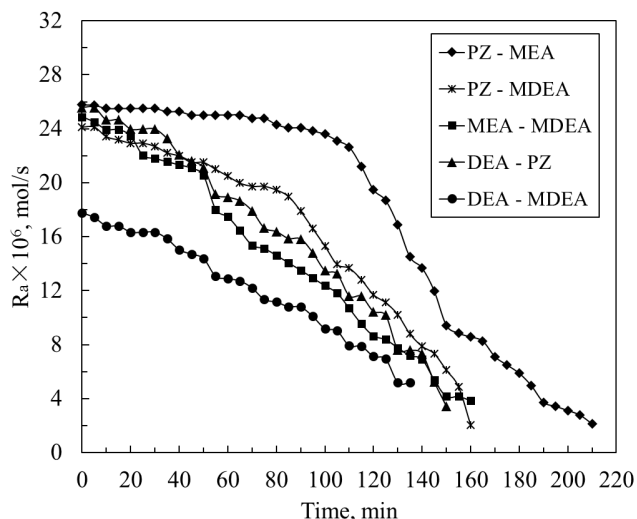


Figure 7. The absorption rate of flue gas of binary mixed alcohol amines at 40 °C.

Different amines have different absorbing quality. In order to develop more effective absorbent, we investigated the absorption of flue gas using various binary amines: MEA-MDEA, DEA-MDEA, PZ-MDEA, PZ-MEA and PZ-DEA. The total mole concentration of the two amines are

1 mol/L. Based on the experiments in this work, we found that the binary amines with equal concentration, i.e., 0.5 mol/L-0.5 mol/L, has the best performance in consideration of both absorption and desorption processes. Figures 7 and 8 show the adsorption rate and desorption rate of mixed amines. Table 1 presents the desorption temperature of mixed amines.

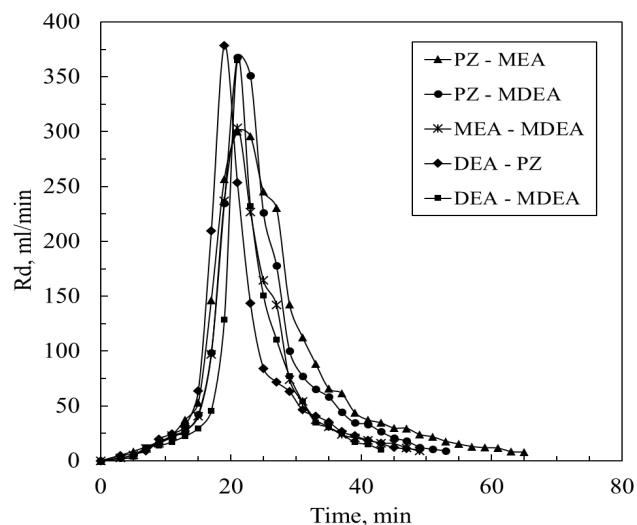


Figure 8. The desorption rate of CO₂ of mixed alcohol amines.

Table 1. The desorption temperature of mixed amines

Amines	Temperature of desorption, °C	Azeotropic temperature, °C
0.5mol/L MEA-0.5mol/LMDEA	42	100
0.5mol/L DEA-0.5mol/LMDEA	46	102
0.5mol/L PZ-0.5mol/L MDEA	45	101
0.5mol/L PZ-0.5mol/L MEA	43	100
0.5mol/L PZ-0.5mol/L DEA	45	101

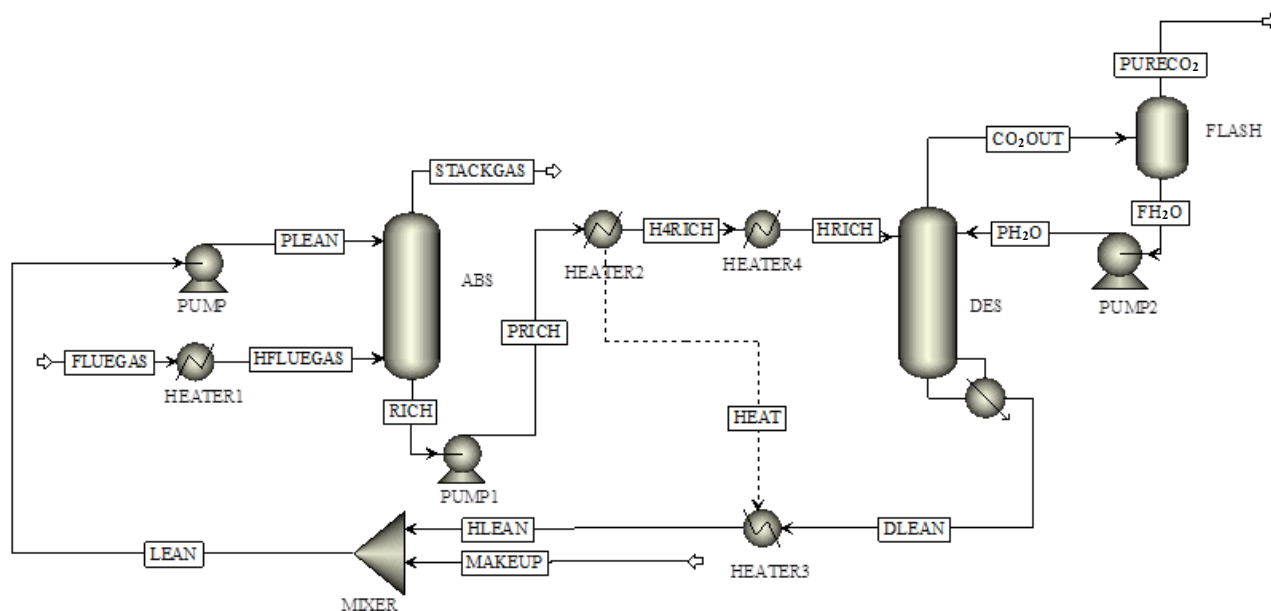


Figure 9. Flow diagram of simulation of CO₂ absorption from flue gas using Aspen Plus.

It shows that PZ-MEA has the largest absorption capacity, and it has the lowest azeotropic temperature as well, resulting in low energy consumption in CO₂ desorption process. It also indicates that there is interaction between different alcohol amines because the absorption rate of mixed alcohol amines is not a simple adding of two single amines. PZ-MEA has the best performance in both CO₂ absorption and desorption processes in this work.

3. Simulation of Aspen Plus

The flow diagram of simulation is shown in Figure 9. The concentration of CO₂ in the product is defined as 98 mol%, and the recovery of CO₂ is 85 %. The influences of lean liquid CO₂ load, lean liquid temperature, and the desorber pressure on the reboiler duty are investigated and shown in Figure 10 to 12. The optimal operating parameters based on the minimum reboiler duty are presented in Table 2.

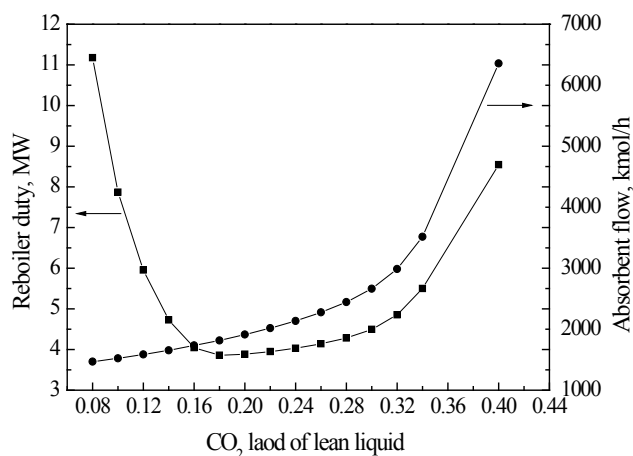


Figure 10. Influence of lean liquid CO₂ load on absorbent flow and reboiler duty.

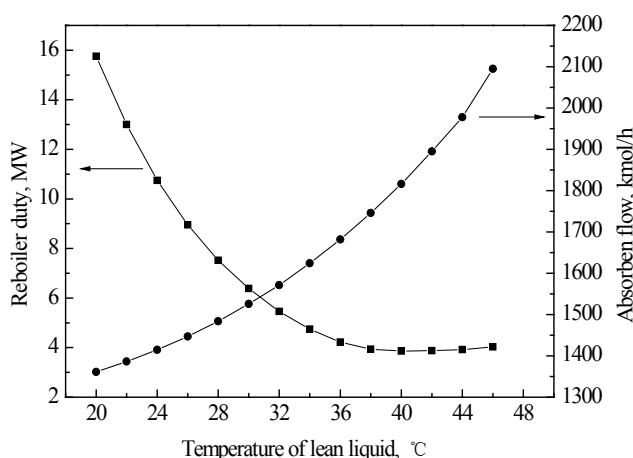


Figure 11. Influence of lean liquid temperature on absorbent flow and reboiler duty.

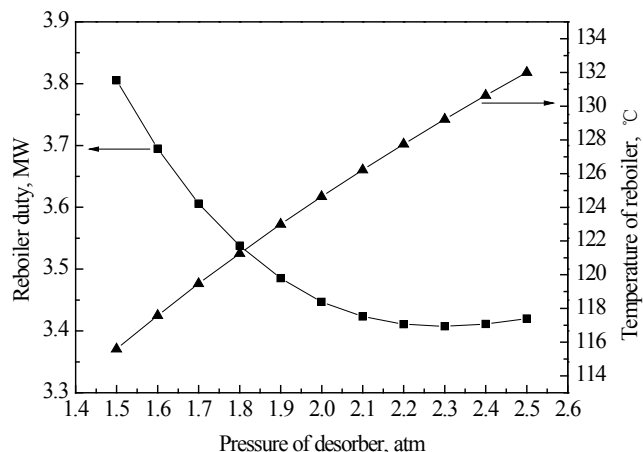


Figure 12. Influence of desorber pressure on reboiler temperature and duty.

Table 2. The optimal operating parameters of simulation based on the minimum reboiler duty

Parameters	Values
Flue gas flow, m ³ /h	54000
Absorbent flow, kmol/h	1815.42
PZ concentration in absorbent, wt%	17.5
MEA concentration in absorbent, wt%	12.5
CO ₂ load of lean liquid	0.18
Absorbent temperature, °C	40
Temperature of stream HRICH, °C	100
Absorber stages	10
Desorber stages	12
Desorber pressure, atm	2
Reboiler temperature, °C	124.64
Reboiler duty, MW	3.45
Temperature of flash tank, °C	17
PZ concentration in the gas out of absorber, ppm	14
MEA concentration in the gas out of absorber, ppm	16
CO ₂ recovery, %	85
CO ₂ concentration in product, mol%	98.04

Table 2 shows that at the optimum operating condition, the duty of reboiler is 3.45 MW, accounting for about 45 % of the energy consumption of the whole system, i.e., the highest energy consumption part of the CO₂ recovery.

6. Conclusions

In this paper, we systematically studied the separation of CO₂ from flue gas using different alcohol amines. The absorption and desorption rates of CO₂ were obtained and reported. The results demonstrate that PZ - MEA binary mixed amines have the best performance in all of the amines studied in this work in consideration of both absorption and desorption effects. Aspen Plus was also applied to simulate the process of recovering CO₂ from flue gas. We investigated the influences of lean liquid CO₂ load, lean liquid temperature and desorber pressure on reboiler duty, and optimized the operating parameters on the basis of the minimum reboiler duty.

Acknowledgements

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