

## Evaluation of Stripper Performance for Carbon Dioxide Removal in an Ammonia Plant

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### Abstract

*Ammonia plant provides some key roles in the fertilizer industry. This plant converts natural gas, steam, and air as raw materials into ammonia and carbon dioxide (CO<sub>2</sub>) as the products. Both ammonia and CO<sub>2</sub> products will become the feeds for urea plant. One of the units in the ammonia plant is CO<sub>2</sub> removal unit. It functions to separate CO<sub>2</sub> gas from syngas prior to final conversion into urea in the urea plant. One of the equipment that supports the CO<sub>2</sub> removal unit is a stripper. This study aims to evaluate the performance of the stripper by arranging a mathematical model and solves it for steady-state operating condition. The mass transfer, chemical, and phase equilibrium are employed in the development of the mathematical model. One of the stripping performance parameters is CO<sub>2</sub> lean loading. The mathematical equations were solved with the assistance of MATLAB software and resulted in the profiles of the mole flow rate and temperature along the bed packing stripper. Variables that affect stripper performance include temperature and pH. The simulation shows satisfactorily results compared with the operational plant data as indicated by a total error of less than 5%. The optimum operating conditions for the stripping process that allow minimum CO<sub>2</sub> lean loading at bottom stripper are temperature of 120°C – 123°C and inlet stripper pH between 7.9-8.1.*

**Keywords:** Chemical equilibrium; lean loading; mass transfer; modeling; phase equilibrium

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### INTRODUCTION

The need for urea fertilizer in Indonesia is relatively increasing every year. Association of Indonesian Fertilizer Producers (APPI) data shows that from 2014-2019 there was an average increase in consumption of urea fertilizer by 3.69% per year, both in the domestic and export markets. The need for urea fertilizer is met by several fertilizer industries spread across parts of Indonesia. The existence of several national fertilizer industries and coupled with the global fertilizer industry, has led to competition at the

inter-company level. Indicators of competitiveness at this level can be measured by the ability to generate profits, market share productivity, and cost of production (HPP). The most dominant component of the HPP is the cost of raw materials, which accounts for 50%-70% of the total HPP of urea fertilizer. (PIM, 2021).

The main raw material used for the production of urea fertilizer is natural gas. First, natural gas is processed into ammonia and carbon dioxide (CO<sub>2</sub>), then processed into urea fertilizer.

Apart from natural gas, an ammonia plant also requires other raw materials, are steam, and air. The process in ammonia plants can be divided into several units, are the front-end (Gas Treating, Reforming), middle-end (Shift Converter, CO<sub>2</sub> Removal, Methanator), and back-end (Ammonia Converter, Refrigerant System). The CO<sub>2</sub> removal unit functions are separate CO<sub>2</sub> gas from syngas to be sent to urea plant, so the performance of the CO<sub>2</sub> removal unit is very crucial for the plant. One of the pieces of equipment that supports the performance of the CO<sub>2</sub> removal unit is a stripper. This study analyzes in more detail the performance of the stripper and studies the effect of the performance of the stripper on the lean solvent.

This study applies the principles of mass and heat transfer, phase equilibrium, and chemical equilibrium in the evaluation of the packing column stripper system. With this principle, mathematical modeling has been developed as an explanation of the phenomena that occur in the CO<sub>2</sub> stripping process. The mathematical modeling that has been made is completed using the Matlab simulator. Based on previous literature reviews conducted by Oyenekan (2007), Arhanu and Eldi (2015), and Ariani *et al.* (2021), this study offers several differences from other model development approaches such:

1. The modeling assumptions used in this study are non-isothermal systems. In addition, there is also a change in pressure throughout the bed packing system.
2. The solvent used in this study was aMDEA (activated methyl diethanolamine) with activators piperazine, while in previous studies it was MEA (monoethanolamine) and KHCO<sub>3</sub> (potassium bicarbonate).
3. This study uses real industrial data, whereas previous research partially used experimental data in the process or its validation.

This research has focused on developing mathematical models and solutions that can be used to predict CO<sub>2</sub> values in lean solutions (CO<sub>2</sub> lean loading) and obtain the optimum process conditions for minimum CO<sub>2</sub> lean loading where this parameter is one of the test parameters for stripping performance contained in the CO<sub>2</sub> removal unit. (Anugrah *et al.*, 2023)

## RESEARCH METHOD

The research was carried out theoretically by developing a mathematical model of the system studied. Mathematical equations were then solved using Matlab software. The system reviewed in this study is depicted in Figure 1.

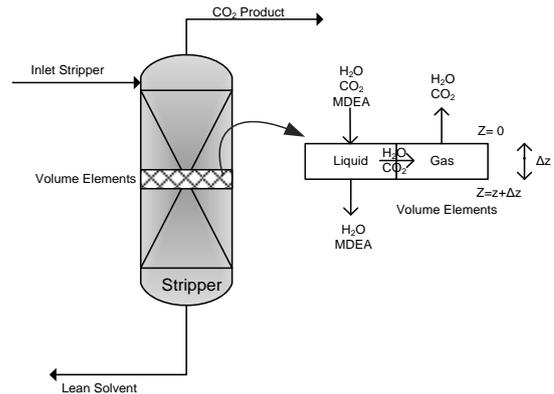


Figure 1. Overview of the stripping system volume elements.

Based on the theoretical and operational considerations, the following assumptions were taken into account:

- Steady state operating condition (accumulation = 0).
- The system is ideal.
- The chemical reaction is very fast (mass transfer as rate controlling) due to the use of piperazine as an activator.
- The reaction occurs in the liquid film, so the resistance is in the gas phase ( $k_G=K_G$ ). (Levenspiel, 1999)

Employing the principles of mass balance and heat balance, the following derivative equations are obtained.

Carbon dioxide mass balance in liquid phase/gas phase in volume elements:

$$\frac{dF_{CO_2}}{dz} = -K_{G_{CO_2}} \cdot a \cdot (P^*_{CO_2} - P_{CO_2}) \cdot S \quad (1)$$

Water mass balance in liquid phase/gas phase in volume elements:

$$\frac{dF_{H_2O}}{dz} = -K_{G_{H_2O}} \cdot a \cdot (P^*_{H_2O} - P_{H_2O}) \cdot S \quad (2)$$

Liquid phase heat balance in volume elements:

$$\frac{dT_L}{dz} = (-h \cdot a \cdot S \cdot (T_L - T_G) + \frac{Q_{reb}}{z} - N_{H_2O} \cdot \Delta H_{v_{H_2O}} - N_{CO_2} \cdot \Delta H_{v_{CO_2}} - N_{CO_2} \cdot \Delta H_R) / (\Sigma F_i \cdot C_{p_i}) \quad (3)$$

Gas phase heat balance in volume elements:

$$\frac{dT_G}{dz} = (h \cdot a \cdot S \cdot (T_L - T_G)) / (\Sigma G_i \cdot C_{p_i}) \quad (4)$$

To calculate the values of the equation above, the concept of phase equilibrium (Green and Perry, 2008) and chemical equilibrium (Nisa *et al.*, 2019; Guštin and Marinšek-Logar, 2011) is required with the scheme in Figure 2.

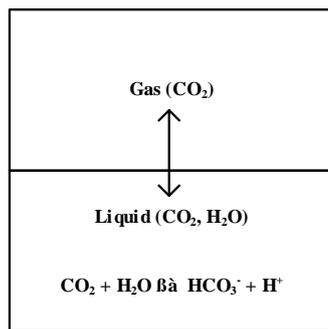


Figure 2. Schematic of the phase equilibrium and chemical equilibrium of the stripping process

Phase equilibrium:

$$P_{\text{CO}_2} = H_{\text{CO}_2} \cdot x_{\text{CO}_2} \quad (5)$$

$$P_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}^\circ \cdot x_{\text{H}_2\text{O}} \quad (6)$$

Chemical equilibrium in the liquid phase:

$$[CO_{2\text{total}}] = [CO_2] \cdot \left[ 1 + \frac{K_A}{K_W} \cdot 10^{-pOH} \right] \quad (7)$$

The equation used to calculate the overall mass transfer coefficient in the gas phase ( $K_{GA}$ ) is the Onda method (Onda *et al.*, 1968). This is based on the type and size of packing applied to the stripper column. Meanwhile, to calculate the convection heat transfer coefficient ( $h$ ) apply the Chilton & Colburn method equation. After the coefficients are obtained, the derivative equations that have been compiled are solved using the ode45 solver in the Matlab software. Solving the simultaneous order differential equations obtained profiles of the total mole flow rate, component mole flow rate, and temperature along the bed packing stripper.

## RESULT AND DISCUSSION

### Simulation validation results on plant design.

Model validation is done by comparing the data obtained from the simulation results with the plant design data. The available plant design data is the result of the design (specification) without being equipped with a calculation process. The results of modeling validation are presented in table 1.

Based on table 1 the percent error for the parameters of the mole flow rate of  $H_2O$ , the mole fraction of MDEA and the temperature at the bottom of the stripper is below one percent. For the  $CO_2$  mole flow rate parameter on the bottom stripper there is a relatively high percent error. This is because, by design, the amount of  $CO_2$  that is at the bottom of the stripper is 0 kmole/hr. This value is the theoretical ideal value, while the chance of achieving this value is very small. In the book *Amine Treating and Sour Water Stripping* (Sheilan *et al.*, 2008), the rules of thumb/recommended lean solution loadings are explained based on the type of amine used in the system. For the amine type MDEA, the recommended lean loading is 0.002 – 0.005 mole/mole. If calculated, a maximum  $CO_2$  mole flow rate of  $\pm 13$  kmole/hr is obtained.

### Profile of the Total Mole Flow Rate of Liquid Phase and Gas Phase

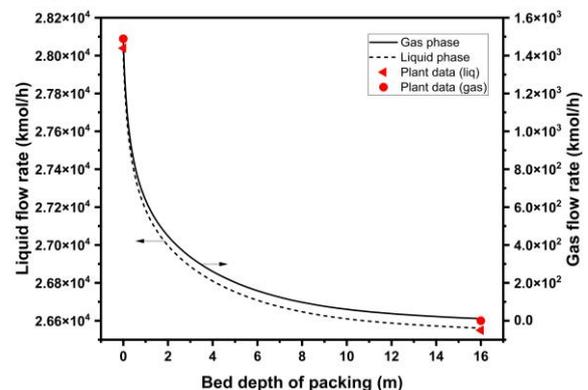


Figure 3. Profile of the total mole flow rate of the liquid phase and gas phase

Table 1. The results of the simulation validation of the plant design on the stripping system

No	Parameter	Unit	Simulation	Error
<b>Top Bed (Feed/Product condition) = initial condition</b>				
1.	$CO_2$ mole rate (l)	kmole/hr	1,411.12	-
2.	$H_2O$ mole rate (l)	kmole/hr	24,075.96	-
3.	$CO_2$ mole rate (g)	kmole/hr	1,411.12	-
4.	$H_2O$ mole rate (g)	kmole/hr	64	-
5.	MDEA mole frac	-	0,090	-
6.	Temperature	$^\circ C$	80.8	-
<b>Bottom Bed</b>				
1.	$CO_2$ mole rate	kmole/hr	10.88	-
2.	$H_2O$ mole rate	kmole/hr	24,012.4	0.002%
3.	MDEA mole frac	-	0.0955	0.00%
4.	Temperature	$^\circ C$	123.86	0.048%

Figure 3 shows the mole flow rate of the liquid phase at a depth of packing  $z = 0$  m, which is 28,024.85 kmole/hr to a depth of packing of 16 m, is 26,561.08 kmole/hr. In the liquid phase, there was a reduction in the mole flow rate along the packing bed by 1,463.76 kmole/hr, meaning that 1,463.76 kmole/hr changed the phase to gas. In the gas phase, there was an increase in the mole flow rate from the bottom stripper position ( $z = 16$  m) 11.35 kmole/hr to 1,475.12 kmole/hr on the top stripper.

**The Component Mole Flow Rate Profiles**

The dominant mass flux transfer of  $CO_2$  occurs at positions zero to five meters from the top bed packing, with the percent of moles transferred in that position reaching 91% of the total moles transferred overall. The amount of  $CO_2$  at 10 m to 16 m positions is relatively constant (average 20 kmole/hr), but the  $CO_2$  level at that position has decreased from 2.5% to zero percent. This explains that the bottom of the stripper tower (10-16 m depth) continues to function (although the  $CO_2$  levels are relatively constant) to reduce  $CO_2$  levels towards the target function of zero percent. The  $CO_2$  mole rate profile along the stripper column has a suitable slope with similar research that has been conducted by previous researchers such as the results research by (Park, 2014).

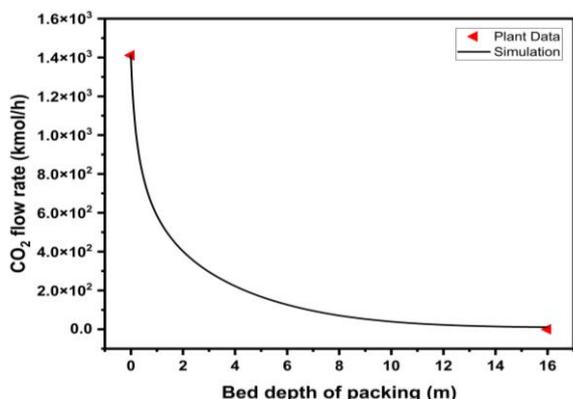


Figure 4. Carbon dioxide mole flow rate profile

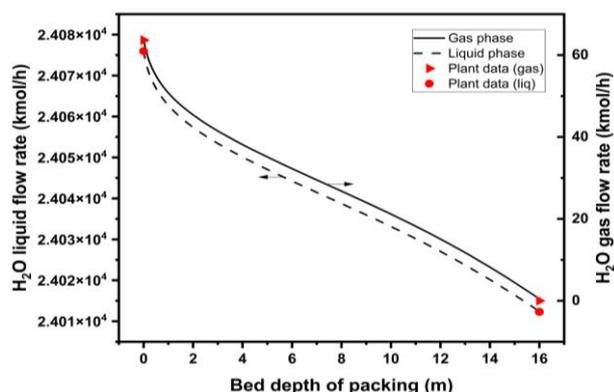


Figure 5. Water mole flow rate profile

Figure 5 displays the mole flow rate profiles of the liquid and gas phases of  $H_2O$ . The amount of

$H_2O$  in the liquid phase on the top bed packing (inlet stripper) was 24,075.96 kmole/hr. Along the stripper column, there is a mass transfer of  $H_2O$  from the liquid phase to the gas phase of 63.7 kmol/hr so that at the bottom stripper ( $z = 16$  m), the amount of  $H_2O$  in the liquid phase is 24,012.30 kmole/hr. For the gas phase, the amount of  $H_2O$  at the bottom stripper ( $z = 16$  m) is zero and increases along the stripper column to 63.7 kmole/hr at the top stripper. A total of 63.7 kmole/hr of  $H_2O$  in the gas phase needs to be separated from  $CO_2$  and inert gas, if  $CO_2$  gas this product will be compressed to the urea reactor. The results of the  $H_2O$  profile simulation show that they are in appropriate with plant data.

The  $H_2O$  mole flow rate profile has a different trend from the  $CO_2$  mole flow rate profile, where the mass transfer of  $H_2O$  from the liquid phase to the gas phase occurs evenly along the column, forming a nearly linear profile.

**Liquid Phase Temperature Profile**

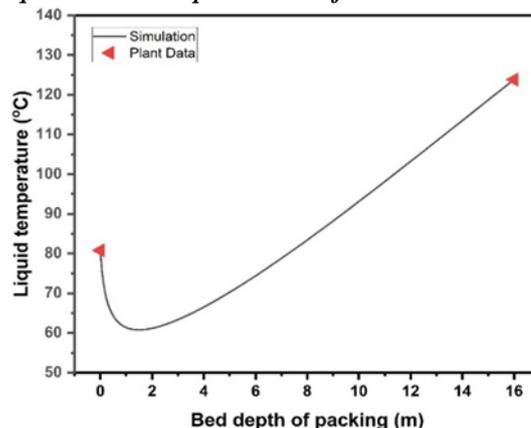


Figure 6. Liquid phase temperature profile

Figure 6 shows the trend of liquid temperature along the bed packing stripper. The stripper inlet temperature ( $z = 0$  m) is 80.8°C. Along the column, the temperature increases due to the heat supply from the reboiler, so that at the bottom stripper ( $z = 16$  m) the temperature reaches 123.8°C. The simulation results show the same value as the plant data.

At the top of the stripper (0-2 m), there is a decrease in temperature from 80.8°C to 60°C because the available heat is used for the  $CO_2$  stripping reaction from the MDEA solvent (endothermic reaction). In addition, the energy from the reboiler is also used as the latent heat of  $CO_2$  vaporization. At 2 m-16 m bed depth, the temperature increases as it approaches the reboiler direction indicating energy consumption for the sensible heat of the solvent solution. In addition, reboiler heat is also used as convection heat and  $H_2O$  vaporization, but it is relatively small. As for research which displays the stripper temperature profile along the column has been carried out by (Krótki *et al.*, 2020) and (Bui *et al.*, 2014). The comparison results show suitability or the similarity of the slope of the

simulated temperature profile with the resulting temperature profile experimental studies that have been carried out in these two studies.

**Effect of Operating Conditions on CO<sub>2</sub> Lean Loading Bottom Stripper Temperature**

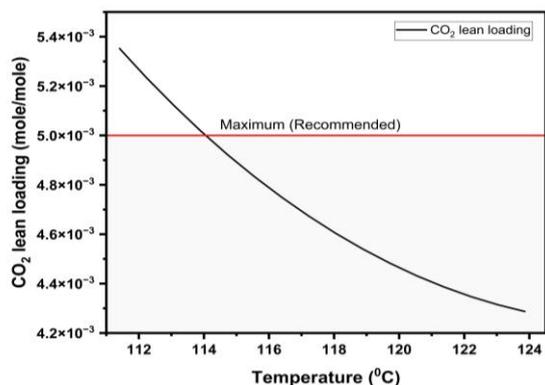


Figure 7. Effect of bottom stripper temperature on CO<sub>2</sub> lean loading

Based on figure 7, the higher the bottom stripper temperature, the lower the CO<sub>2</sub> lean loading value. This proves that the stripping performance will be better at relatively high temperatures. At a temperature of 123.8°C, CO<sub>2</sub> lean loading is 4.28 x 10<sup>-3</sup> mol/mol, this value is still below the recommended maximum CO<sub>2</sub> lean loading. The maximum value of CO<sub>2</sub> lean loading is 5 x 10<sup>-3</sup> mol/mol. This value is

obtained when the bottom stripper temperature is lowered to 114.8°C. That is, it is recommended to maintain a minimum temperature of 115°C so that the lean loading CO<sub>2</sub> value does not exceed its maximum limit.

**The pH of the Inlet Stripper**

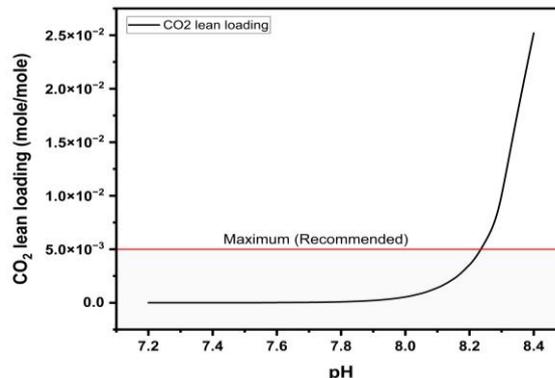


Figure 8. Effect of inlet stripper pH on CO<sub>2</sub> lean loading

Based on Figure 8, the lower pH will result in a lower total CO<sub>2</sub> in the liquid because the CO<sub>2</sub> balance shifts to the gas phase (as shown in Figure 2). The optimum pH of the stripping process is between 7.9-8.1. Based on this value, the ideal solvent concentration for the absorption and stripping process can be determined later.

Table 2. Simulation results of actual operating conditions

No	Parameter	Bottom bed			
		Rate 80%	Rate 85%	Rate 88%	Rate 95%
1	CO <sub>2</sub> lean loading, mol/mol	0.0056	0.0052	0.0045	0.0041
2	Temperature, °C	109.68	109.75	114.05	121.31
3	% Error of temperature	-7.05	-7.63	-4.95	1.01

**Simulation Results of Actual Operating Conditions**

Simulations at various operating rate conditions show results that are relatively close to the actual operating data at the plant. At the plant operating rate of 80% and 85%, the simulated CO<sub>2</sub> lean loading is still above the maximum recommended value (0.005 mole/mole). This can be caused by the actual bottom stripper temperature which is still relatively low. The cause of the low actual temperature is the low operating rate, so the amount of gas (hot syngas) that becomes the heating medium in the reboiler becomes less. Meanwhile, at operating rates of 88% and 95%, the CO<sub>2</sub> loading value is relatively good, because the bottom stripper temperature reaches 120°C. Because the average error is still below five percent, this simulation can be used to design or evaluate stripper and lean solvent conditions.

**CONCLUSION**

From the results obtained in this study, it can be concluded as follows.

1. The simulation that has been prepared can be used for designing or evaluating stripper operating conditions with a percent error below five percent.
2. The optimum operating conditions for the stripping process to obtain a minimum CO<sub>2</sub> lean loading are:
  - a. Bottom stripper temperature = 120°C-123°C.
  - b. pH = 7.9-8.1.

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**LIST OF NOMENCLATURES**

$a$	: Mass transfer area per bed volume, $m^2/m^3$
$F_i$	: Mole flow rate component $i$ (liquid), kmole/hr
$G_i$	: Mole flow rate component $i$ (gas), kmole/hr
$H$	: Henry constant, atm
$h$	: Convection heat transfer coefficient, $kJ/(m^2.hr.K)$
$K_G$	: Overall mass transfer coefficient in gas phase, $kmole/(m^2.hr.atm)$
$K_A$	: The equilibrium constant for the hydrolysis reaction $CO_2$ in water
$K_w$	: The equilibrium constant for the ionization reaction of water
$k_G$	: mass transfer coefficient in gas phase, $kmole/(m^2.hr.atm)$
$N_i$	: The flux rate of transfer of component $i$ to the gas from the solvent per unit area $kmole/(m^2.jam)$
$P_i$	: The partial pressure of component $i$ in the gas phase, atm
$P_i^o$	: pure vapor pressure of component $I$ , atm
$P_i^*$	: The partial pressure of component $i$ in interface, atm
$Q_{reb}$	: Heat of reboiler, $kJ/hr$
$S$	: Column cross-sectional area, $m^2$
$T_L$	: Liquid temperature, $^oC$
$T_G$	: Gas temperature, $^oC$
$x_i$	: Mole frac component $I$ in liquid phase
$z$	: Bed depth, $m$
$\Delta H_R$	: Heat of reaction, $kJ/kmole$
$\Delta H_v$	: Heat latent of vaporazion, $kJ/kmole$

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