

# Rate-Based Modelling and Simulation of Large-Scale CO<sub>2</sub> Capture Using a Piperazine-Promoted Aqueous Ammonia Solution

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Due to the fast reaction rate of piperazine (PZ) with CO<sub>2</sub>, it has the potential to act as a promoter in aqueous ammonia (NH<sub>3</sub>)-based CO<sub>2</sub> capture processes. A rigorous, rate-based model for the NH<sub>3</sub>-PZ-CO<sub>2</sub>-H<sub>2</sub>O system was developed using Aspen Plus<sup>®</sup>, and validated against experimental results. Absorption and desorption processes were simulated under real flue gas conditions to gain a practical understanding of the behaviour and characteristics of interactions between PZ-promoted NH<sub>3</sub> solution and CO<sub>2</sub>. Adding PZ significantly increased the CO<sub>2</sub> absorption rate in the NH<sub>3</sub>-based CO<sub>2</sub> capture process via a fast reaction between PZ carbamate and CO<sub>2</sub>. The temperature along the column was higher than in the absence of PZ, and additional NH<sub>3</sub> was released into the solution, which led to higher NH<sub>3</sub> loss. Adding PZ also reduced the stripping heat, resulting in a smaller energy requirement for solvent regeneration.

## 1. Introduction

Aqueous ammonia (NH<sub>3</sub>) has gained significant attention as a potential alternative to traditional amine solvents in post-combustion CO<sub>2</sub> capture process, due to its low cost, low regeneration energy, high CO<sub>2</sub> absorption capacity, and resistance to degradation (Mumford et al., 2015). Its commercial application for CO<sub>2</sub> capture is restricted by the low absorption rate of CO<sub>2</sub>, and the high volatility of NH<sub>3</sub> (Molina et al., 2015). Piperazine (PZ) is widely recognized as an effective rate promoter in amine solutions and the NH<sub>3</sub>-based PCC process. Fang et al. (2014) showed that the addition of PZ significantly increased the mass transfer coefficient of CO<sub>2</sub> into aqueous NH<sub>3</sub> by three to fourfold. Previous bench-scale research using wetted-wall columns has confirmed that the addition of small amounts of PZ to both unloaded and CO<sub>2</sub> pre-loaded aqueous NH<sub>3</sub> solutions can significantly increase the CO<sub>2</sub> absorption rate (Li et al., 2013).

To understand the overall performance of blended NH<sub>3</sub>/PZ solvent for CO<sub>2</sub> capture, a rigorous model is needed to accurately predict its thermodynamic properties, including vapour-liquid equilibrium, chemical reaction equilibrium, and kinetic performance such as mass and heat transfer, materials and energy balance, and chemical kinetics. Yu et al. (2016) investigated CO<sub>2</sub> absorption by NH<sub>3</sub>/PZ in a laboratory-scale packed column, and used the results to develop and validate a rate-based model. In this paper, a rigorous, rate-based model was developed using Aspen Plus<sup>®</sup> for CO<sub>2</sub> absorption and desorption using PZ-promoted aqueous NH<sub>3</sub>, and validated against experimental results. Process simulations under large-scale conditions provided us with insight into the thermodynamic properties and kinetic behaviour of the capture process. Our rate-based model and improved understanding of PZ-promoted, aqueous NH<sub>3</sub>-based CO<sub>2</sub> capture will guide further improvement, scale-up and techno-economic assessment of this process.

## 2. Model description and validation

### 2.1 Model description

The embedded models for the  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$  and  $\text{PZ-CO}_2\text{-H}_2\text{O}$  systems provided by Aspen Plus v8.4 were combined to develop a thermodynamic model for the  $\text{NH}_3\text{-PZ-CO}_2\text{-H}_2\text{O}$  system (Aspen Technology, 2010). The electrolyte non-random two-liquid (NRTL) model was chosen to calculate activity coefficients, enthalpies and Gibbs energies for non-ideal,  $\text{CO}_2$ -loaded  $\text{NH}_3$  solution. The Redlich-Kwong equation of state was applied to calculate fugacity coefficients for the vapour phase. Henry's law was applied to  $\text{CO}_2$ ,  $\text{NH}_3$ , and  $\text{N}_2$ . The chemical equilibrium constants were calculated using the following equation:

$$\ln K_{\text{eq},j} = a + \frac{b}{T} + c \ln(T) + dT \quad (1)$$

where  $K_{\text{eq},j}$  is the equilibrium constant of reaction  $j$ ;  $T$  is the temperature in Kelvin; and the constants  $a$ ,  $b$ ,  $c$  and  $d$  are retrieved from Aspen Plus databanks (Aspen Technology, 2010). The differential heat of absorption was calculated from the vapour-liquid equilibrium data obtained from the Flash module calculations. The commonly used equation derived from the Gibbs-Helmholtz equation was applied:

$$\Delta H_{\text{abs}} \approx R \left[ \frac{\partial \ln \hat{f}_{\text{CO}_2}}{\partial (1/T)} \right]_{P,x} \quad (2)$$

where  $\Delta H_{\text{abs}}$  is the differential heat of absorption;  $\hat{f}_{\text{CO}_2}$  is the fugacity of  $\text{CO}_2$ ; and  $R$  is the gas constant.

Transport properties are required when describing mass and heat transfer in a rate-based model. Various transport property models and corrections embedded in Aspen Plus were chosen to calculate the density, viscosity, thermal conductivity, diffusion coefficient and surface tension for the  $\text{NH}_3\text{-PZ-CO}_2\text{-H}_2\text{O}$  system. The detailed setting of transport properties models can be found in our previous work (Yu et al., 2016).

The rate-based model using the Aspen Plus RadFrac distillation module was employed to simulate  $\text{CO}_2$  absorption by PZ-promoted aqueous  $\text{NH}_3$ . The chemical reaction model was consistent with the electrolyte NRTL model. The reactions of the formation of bicarbonate and carbamate were considered to be kinetically controlled. Reduced power law expressions were used for the kinetically controlled reactions:

$$r_j = k_j T^n \exp\left(-\frac{E_j}{RT}\right) \prod_{i=1}^N (C_i)^{\partial_i} \quad (3)$$

where  $r_j$  is the rate of reaction;  $k_j$  is the pre-exponential factor;  $n$  is the temperature exponent;  $E_j$  is the activation energy;  $C_i$  is the concentration of component  $i$ ; and  $\partial_i$  is the stoichiometric coefficient of component  $i$ . In this study, the concentration basis was molarity, the factor  $n$  was set to zero, and  $k_j$  and  $E_j$  were derived from the work of Pinsent et al. (1956) and more recently Bishnoi and Rochelle (2002).

### 2.2 Model validation

The model was verified against experimental data in a relatively large temperature and  $\text{CO}_2$  loading range. VLE data and differential heat of absorption data were used to validate the model for subsystems, including  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$  system,  $\text{PZ-CO}_2\text{-H}_2\text{O}$  system and  $\text{NH}_3\text{-PZ-H}_2\text{O}$  system. For  $\text{NH}_3\text{-PZ-CO}_2\text{-H}_2\text{O}$  system, differential heat of absorption data and data from  $\text{CO}_2$  absorption process were used. In general, the proposed model can satisfactorily predict thermodynamic properties of the  $\text{NH}_3\text{-PZ-CO}_2\text{-H}_2\text{O}$  system.

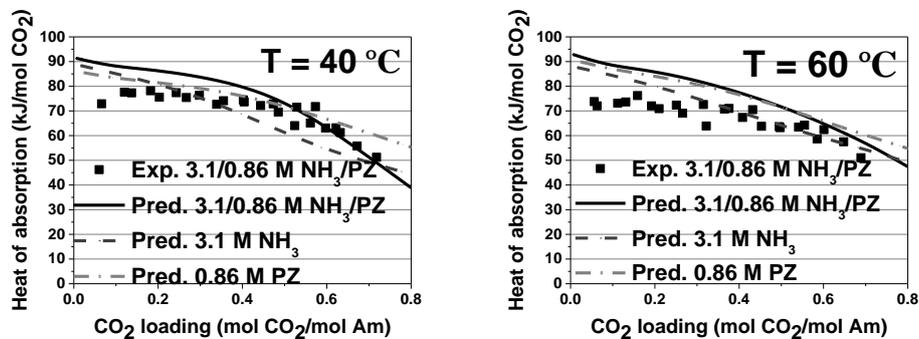


Figure 1: Calculated differential heat of absorption for 3.1/0.86 M  $\text{NH}_3\text{/PZ}$  system compared with experimental data at 40 °C and 60 °C from Liu et al. (2012), "Exp" means experimental data, "Pred" means model prediction.

Figure 1 shows that the model generally overestimates the heat of absorption at low loadings for the NH<sub>3</sub>-PZ-CO<sub>2</sub>-H<sub>2</sub>O system. Comparison of the heat of CO<sub>2</sub> absorption in aqueous NH<sub>3</sub> and aqueous PZ suggests that both the predicted and experimental heat of CO<sub>2</sub> absorption are higher in PZ than in NH<sub>3</sub> within the studied loading and temperature range. The heat of CO<sub>2</sub> absorption in NH<sub>3</sub>/PZ mixtures should be higher than in NH<sub>3</sub> alone, which is consistent with the model's prediction.

The rate-based model was validated using the experimental data of the CO<sub>2</sub> absorption process under various conditions at different NH<sub>3</sub> and PZ concentrations, temperatures and lean solution flow rates. To make a reliable comparison, the simulation conditions were consistent with the experimental conditions; detailed information of each case can be found elsewhere (Yu et al., 2016).

### 3. Process simulation

Using the developed model, the effect of PZ on the performance of both absorption and desorption in a large-scale, aqueous NH<sub>3</sub>-based CO<sub>2</sub> capture process was investigated. The simplified configuration used in this study is consisted of an absorber, a stripper and a heat exchanger. The concentrations of CO<sub>2</sub> and NH<sub>3</sub> in the flue gas were 11.60 % and 1.09 % and the temperature was 44.2 °C. The NH<sub>3</sub> present in the flue gas was recovered from the cooling water in the pre-treatment column.

As reported by Zhang et al. (2013), using aqueous NH<sub>3</sub> to absorb CO<sub>2</sub> in one absorber under typical 500 MW coal-fired power plant conditions will result in a large absorber (diameter = 40 m, packed height = 72 m) to achieve a high CO<sub>2</sub> removal efficiency, which is not practical. As discussed in our previous publications, it is more practical to use three identical trains of CO<sub>2</sub> capture in parallel. Each process train has a 12 m diameter absorber and deals with one-third of the total flue gas, which is approximately 1 Mt CO<sub>2</sub> per year (Li et al., 2015). The mass flow rate of flue gas for each process train was 794.6 t/h.

*Table 1: Summary of CO<sub>2</sub> capture system operating conditions and simulation results*

Case no.		1	2	3	4	5
	NH <sub>3</sub> conc. (mol/kg H <sub>2</sub> O)	4	4	4	4	3.2
Lean solvent	PZ conc. (mol/kg H <sub>2</sub> O)	0	0.4	0.2	0	0.4
conditions	CO <sub>2</sub> loading (mol CO <sub>2</sub> /mol alk)	0.25	0.25	0.25	0.25	0.25
	Temp of Leanin (°C)	35	35	35	35	35
Absorber	Packing height (m)	55	20	20	20	23
conditions	CO <sub>2</sub> removal efficiency (%)	82.4	82.7	75.6	68.5	82.5
and results	NH <sub>3</sub> conc. in outlet gas (%)	5.3	9.9	7.0	5.3	7.0
Stripper	Stripper/reboiler temp (°C)	139.4	139.9	140.8	139.4	142.3
conditions	CO <sub>2</sub> desorption rate (kg/h)	114,917	115,288	105,453	95,539	114,987
and results	Heat duty (MJ/kg CO <sub>2</sub> )	4.09	3.97	4.41	4.82	3.75

Five cases using different NH<sub>3</sub> and PZ concentrations were investigated. Packing heights were varied with the purpose of achieving an 80 % CO<sub>2</sub> capture efficiency. Detailed conditions are shown in Table 1. A low NH<sub>3</sub> concentration of 4 mol/kg H<sub>2</sub>O was chosen to reduce energy penalty from NH<sub>3</sub> slip, as optimised in our previous work (Li et al., 2015). PZ was introduced into the NH<sub>3</sub> solution in cases 2, 3 and 5 under a relatively low ratio to avoid precipitation and reduce degradation. To determine the effect of the total concentration of amino group, the concentrations of NH<sub>3</sub> and PZ in case 5 were set to 3.2 and 0.4 mol/kg H<sub>2</sub>O, to ensure that the total concentration of amino group in blended PZ/NH<sub>3</sub> solvent was equal to that of NH<sub>3</sub> alone.

### 4. Results and discussion

As shown in Table 1, comparing the packing height of the absorber in case 1 and case 2 indicates that PZ as a promoter increases absorption rate. The required packing height for achieving an 80 % CO<sub>2</sub> removal efficiency was reduced from 55 to 20 m. Comparing case 1 and case 5 also shows that PZ accelerates absorption, indicating the fast absorption is not solely due to the increase in the concentration of amino group. Introducing PZ also causes greater NH<sub>3</sub> loss. NH<sub>3</sub> concentration in the vent gas was almost doubled by introducing PZ at a mole ratio of 10:1 (NH<sub>3</sub> to PZ) in case 2. The trade-off between the reduction in capital costs and the increase in energy requirement for the NH<sub>3</sub> abatement process needs to be considered when determining the optimal amount of PZ introducing into the system. The regeneration energy requirement is decreased by introducing PZ, despite the larger heat of absorption of the PZ solution.

#### 4.1 Absorber performance

The rate-based model allows for a detailed analysis of absorber and stripper performance, improving our understanding of how PZ performs in the system. The temperature profiles, speciation profiles and reaction rates along the column in case 2 and case 4 were examined. The operating conditions for these two cases were the same, except for case 2, in which 0.4 M PZ was introduced into the solution. As shown by Figure 2, the reactions for PZ-related species primarily occurred near the top of the column, because of their relatively high concentrations and fast reaction rates with CO<sub>2</sub>. Figure 2(a) shows that PZ(COO<sup>-</sup>)<sub>2</sub> increased while PZ and PZH<sup>+</sup> decreased rapidly at the top of the column. As lean solvent entered the top of the column, the main reactants were PZCOO<sup>-</sup> and HPZCOO, and the main product was PZ(COO<sup>-</sup>)<sub>2</sub>. This indicates that the dominant reactions for PZ-related species were as follows:



As the concentration of PZ carbamate decreased, PZ became the main reactant for PZ-related species. In Figure 2(b), PZ and PZH<sup>+</sup> became reactants near the top of the column, which is consistent with the speciation profile.

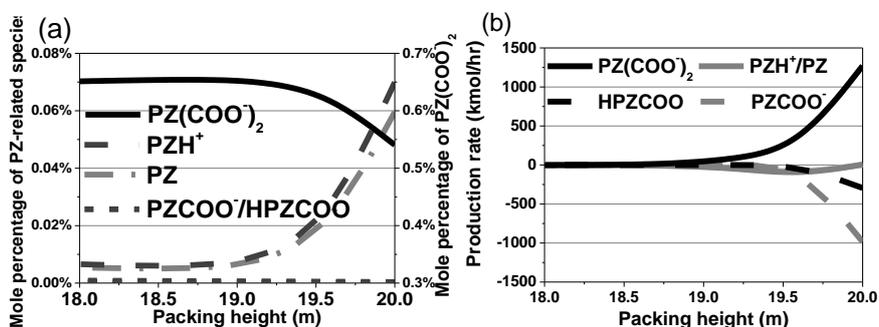


Figure 2: Predicted profiles along the packing height in case 2: (a) PZ-related speciation in the liquid phase at the upper stages of the column; (b) production rates of PZ-related species at the upper stages of the column. Positive production rate value means net production in the liquid phase

As shown in Figure 3(a), NH<sub>3</sub> concentration generally decreased from top to bottom in both cases, as expected, while it increased slightly near the top of the column in case 2. Figure 3(b) shows that the reaction rates of NH<sub>3</sub>-related species were almost the same in both cases, except for the reactions occurred near the top of the column. Instead of being a reactant, NH<sub>3</sub> became a product, while NH<sub>2</sub>COO<sup>-</sup> became a reactant in case 2. This indicates that the reactions occurring for NH<sub>3</sub>-related species near the top of the column were as follows:



Combined with the reactions for PZ-related species, the total reactions occurring near the top of the column were:



As indicated in Eq(4) – (9), no apparent HCO<sub>3</sub><sup>-</sup> is involved, which is consistent with the speciation prediction in Figure 3(a). The rate of consumption of NH<sub>2</sub>COO<sup>-</sup> in Figure 3(b) and the rate of formation of PZ(COO<sup>-</sup>)<sub>2</sub> in Figure 2(b) were almost the same at the top of the column, which again confirms the reaction between NH<sub>3</sub> carbamate and PZ carbamate. In general, PZ accelerates CO<sub>2</sub> absorption by reacting with CO<sub>2</sub> directly in the form of PZ carbamate, which releases additional NH<sub>3</sub> into the solution through Eq(6).

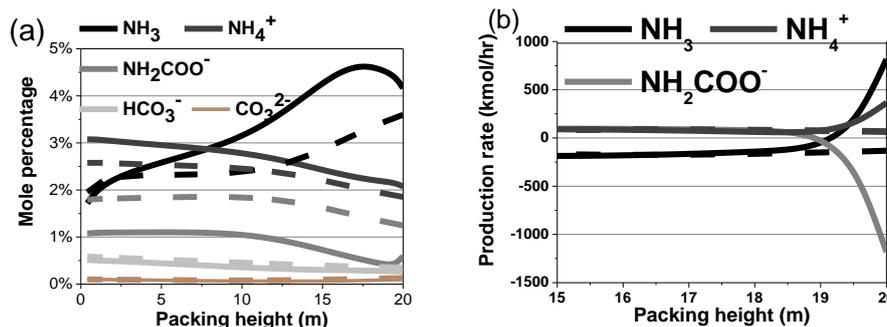


Figure 3: Predicted profiles along the packing height in case 2 (solid line) and case 4 (dash line): (a) HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and NH<sub>3</sub> related species profiles in the liquid phase; (b) production rates of NH<sub>3</sub>-related species.

Figure 4 shows the liquid and vapour temperatures along the column. The addition of PZ increased the temperature, because of the larger heat of absorption of PZ and greater amount of CO<sub>2</sub> absorbed. The increase of temperature can both accelerate the reaction and increase NH<sub>3</sub> loss.

In summary, introducing PZ into the NH<sub>3</sub> solution in the absorption process has two effects. One is that additional NH<sub>3</sub> is released via the reaction between PZCOO<sup>-</sup> and NH<sub>2</sub>COO<sup>-</sup> in the solution. The other is that more heat of reaction is released, which increases the temperature along column. Both effects contribute to a faster reaction rate between NH<sub>3</sub> and CO<sub>2</sub>, and greater NH<sub>3</sub> loss in the absorber.

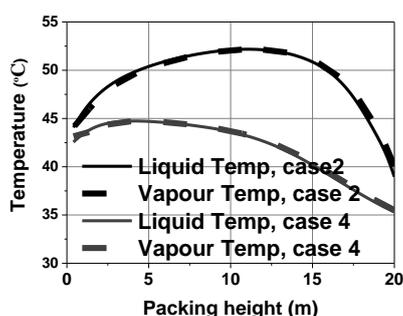


Figure 4: Predicted temperature profile along the packing height in case 2 and case 4.

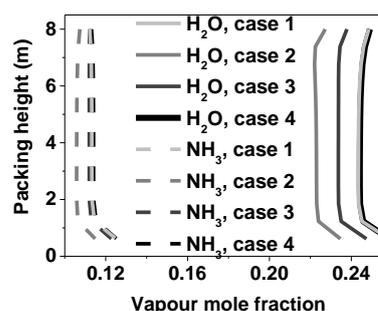


Figure 5: Vapour fraction of H<sub>2</sub>O and NH<sub>3</sub> along the column in cases 1 – 4.

#### 4.2 Stripper performance

Assuming that no heat loss occurred in the CO<sub>2</sub> stripping process, the energy requirement for CO<sub>2</sub> regeneration can be calculated using the following equation:

$$Q_R = H_S + H_D + Q_C \quad (10)$$

where the sensible heat,  $H_S$ , is the energy required to heat the solvent from inlet temperature to outlet temperature; desorption heat,  $H_D$ , is the energy required for CO<sub>2</sub> desorption reactions; and stripping heat,  $Q_C$ , is the energy required for H<sub>2</sub>O and NH<sub>3</sub> vaporisation.

Table 2 shows the distribution of the regeneration energy consumption calculated by Eq(11) in cases 1 – 4. In cases 2 – 4, regeneration energy decreased when PZ concentration was increased under the same operating conditions. The desorption heat remained almost the same because of similar CO<sub>2</sub> loadings. Due to the similar composition of solvents in all cases, sensible heat is mainly determined by the amount of CO<sub>2</sub> desorbed by the stripper, which is determined by the amount of CO<sub>2</sub> absorbed in the absorption process. This indicates that increasing CO<sub>2</sub> capacity of the solvent is the key to reducing sensible heat. CO<sub>2</sub> capacity is increased by adding PZ, which is in favour of reducing the sensible heat.

Figure 5 shows that H<sub>2</sub>O and NH<sub>3</sub> concentration decreased when PZ concentration increased in cases 2 – 4. Since temperature and total vapour flow rates were similar among these cases, adding PZ decreased the stripping heat, as shown in Table 2. Comparing case 1 and 2 considers the situation when the desorbed CO<sub>2</sub> flow rate is fixed. The regeneration energy of case 2 was slightly lower than that of case 1. The sensible heat and desorption heat of both cases were similar, due to the similar compositions of rich solvents. The lower

regeneration duty in case 2 is attributed to the smaller stripping heat, which is due to the lower  $\text{NH}_3$  and water concentrations in the vapour phase as shown in Figure 5.

*Table 2: Distribution of the regeneration energy consumption*

Case no.	$\text{NH}_3/\text{PZ}$ molality	$H_s$ (MJ/kg $\text{CO}_2$ )	$H_D$ (MJ/kg $\text{CO}_2$ )	$-Q_c$ (MJ/kg $\text{CO}_2$ )	Regeneration energy (MJ/kg $\text{CO}_2$ )
1	4/0	1.89	1.59	0.61	4.09
2	4/0.4	1.84	1.61	0.52	3.97
3	4/0.2	2.04	1.61	0.76	4.41
4	4/0	2.27	1.60	0.95	4.82

## 5. Conclusions

Detailed analysis of the simulation results reveals that PZ addition can effectively accelerate the absorption rate in the  $\text{NH}_3$ -based  $\text{CO}_2$  capture process, and reduce the height of absorber required to achieve a high  $\text{CO}_2$  removal efficiency. The temperature along the column was higher in the presence of PZ due to its larger heat of absorption. Reactions happened along the packing of the absorber were studied. Additional  $\text{NH}_3$  was released into the solution via the reaction between PZ carbamate and  $\text{NH}_3$  carbamate at the upper stages of the absorber. However,  $\text{NH}_3$  loss also increased due to higher temperature and higher free  $\text{NH}_3$  concentration. With PZ as a promoter in the system, the capital costs of the absorption process can be largely reduced and the energy requirement for solvent regeneration is decreased by reducing stripping heat for the conditions evaluated.

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