GHGT-11

Rate-Based Modeling of CO_2 Absorption in Aqueous NH_3 in a Packed Column

Guojie Qi[1], Shujuan Wang[1], Hai Yu[2]*, Paul Feron[2], Changhe Chen[1]

[1]*Department of Thermal Engineering, Tsinghua University, Beijing, 100084, P.R. China*
[2]*CSIRO Energy Centre, 10 Murray Dwyer Circuit, Mayfield West, NSW 2304, Australia*

Abstract

A rigorous rate-based model for the aqueous ammonia (NH_3) based CO_2 absorption in a packed column has been used to simulate the recently available results from pilot plant trialing of aqueous NH_3 based post combustion process (PCC) at the Munmorah power station, New South Wales, Australia. The model is based on RateSep module, a rate-based absorption & stripping unit operation model in Aspen Plus®, and uses an improved thermodynamic model for NH_3-CO_2-H_2O system to predict the performance of CO_2 capture. The evaluation of the thermodynamic model via validation of vapor liquid equilibrium and heat of absorption of the NH_3-CO_2-H_2O system shows that the model can satisfactorily predict experimental results from the published literatures. The predicted results from the rate-based model also agree reasonably well with pilot plant results including CO_2 absorption rate and NH_3 loss rate. The rate-based model is then utilized for the extended study of the effect of operation pressure, aqueous NH_3 concentration and liquid inlet temperature on the CO_2 absorption and NH_3 loss. Two different absorber configurations split flow and inter-cooling have been investigated as possible options for control of the NH_3 loss.

Keywords: Aqueous ammonia, post combustion capture, PCC, pilot plant, Aspen Plus, rate-based

1. Introduction

Aqueous NH_3 is one of the promising solvents for CO_2 capture and has recently received extensive attention all over the world. Compared to traditional amines, aqueous NH_3 is a low cost solvent, has less corrosion and degradation issues, can achieve a high CO_2 removal capacity and capture multiple components, such as NO_x, SO_2 and CO_2[1-3]. However, NH_3 loss is a challenge for the application of the aqueous NH_3 based CO_2 absorption process[4].

*Corresponding authors. Tel: +86-10-62788668; Fax: +86-10-62770209. E-mail: wangshuj@tsinghua.edu.cn;
Tel: +61-(02)4960 6201; Fax: +61-(02)4960 6021; E-mail: Hai.Yu@csiro.au

A number of pilot plants have been constructed and operated in the last few years to test the technical and economic feasibility of aqueous NH_3 based post combustion capture processes[5-7]. However, the results from these trials are not available in public domain, which prevents the development and validation of a reliable model. Recently we have reported the results from pilot plant trials of aqueous NH_3 based post combustion capture process under real flue gas conditions in a pilot plant at Munmorah power station[8-9]. The availability of pilot plant results makes it possible to validate the rigorous model for the aqueous NH_3 based post combustion capture process.

In this paper, a rigorous rate-based model for CO_2 absorption is developed using an improved thermodynamic model for NH_3-CO_2-H_2O system and RateSep Module in ASPEN Plus® V7.3. The thermodynamic model is validated with experimental data from published literatures including vapor liquid equilibrium and heat of absorption of the NH_3-CO_2-H_2O system. The results of pilot plant trials are used to compare the predicted CO_2 absorption and NH_3 loss rates. The validated model is used to investigate the effect of operation pressure, NH_3 concentration and solvent inlet temperature on the CO_2 absorption and NH_3 loss rates and to gain an understanding of the characteristics of the absorption process. What is more, the split flow and inter-cooling configurations in the absorber are analyzed as the potential methods for the NH_3 loss control.

2. Model development

The thermodynamic model for CO_2-NH_3-H_2O used in this paper has been described in detail elsewhere[10]. The electrolyte NRTL model is used to calculate activity coefficients, enthalpies, Gibbs energies for the non-ideal CO_2 loaded NH_3 liquid phase thermodynamic behavior[11]. The PC-SAFT equation of state is applied to the calculation of fugacity coefficients for the vapor phase[10]. The thermodynamic model can describe accurately the vapor liquid equilibrium and heat of absorption of the NH_3-CO_2-H_2O system and many other chemical physical properties.

The rate-based model embedded in the Aspen plus® RadFrac distillation model (RateSep Module) is used to model the CO_2 absorption process using aqueous NH_3. The rate-based model adopts the two film theory and discretizes the film to several segment on each stage, and completely characterize the material and energy balance, chemical kinetics, mass and heat transfer, hydrodynamics and column properties of the whole absorption system[12-14].
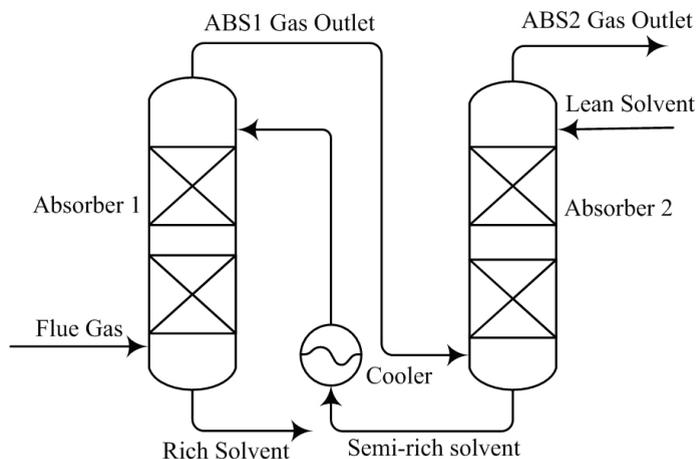

Figure 1. Schematic flow_sheet of the CO_2 absorbers in series

The model flow-sheet and stream specifications are based on the pilot plant trials at the Munmorah power station. The flow-sheet for the rate-based absorber model is shown in Figure 1. Two absorbers are operated in series. The flue gas containing CO_2 is introduced into the bottom of absorber 1 and the lean solvent to the top of the absorber 2. Since in the pre-treatment column aqueous NH_3 is used to remove SO_2, the flue gas at the inlet of the absorber contains a certain amount of NH_3. One cooler is used between the two absorbers in order to reduce the temperature of the semi-rich solvent which leaves absorber 2.The absorber and inlet streams specifications in the rate-based model are the same as those used in the pilot plant trials in campaigns 3, tests 30-39 (16 tests in total) and given in the Table 1.

Table 1. Rate-based absorber model input specifications

Parameter	Value	Parameter	Value
Packing type	25mm Pall ring	CO_2 concentration in the flue gas, vol.%	7.5-12
Absorber inner diameter, m	0.6	NH_3 concentration in the flue gas, vol.%	0.028-0.5
Total packing height, m	5.8-7.8 (two absorbers in total)	H_2O concentration in the flue gas, vol.%	1.2-2.5
NH_3 concentration, wt%	1.9-5.8	Gas temperature, °C	12-30
lean solvent CO_2 loading, mole CO_2/mole NH_3	0.21-0.41	Gas flow rate, kg/hr	632-916
Liquid temperature, °C	14-33	Gas pressure, kPa	101-105
Liquid flow rate, L/min	67-134	Cooler temperature, °C	13-31

3. Model validation

3.1. Thermodynamic model validation

Figure 2 shows comparison between the predicted CO_2 and NH_3 partial pressures and the measured results as a function of NH_3 and CO_2 molalities at the temperature of 20 °C [15], which are close to the trials conditions used in the pilot plant. In general there is a good agreement between the model prediction and the experimental results.
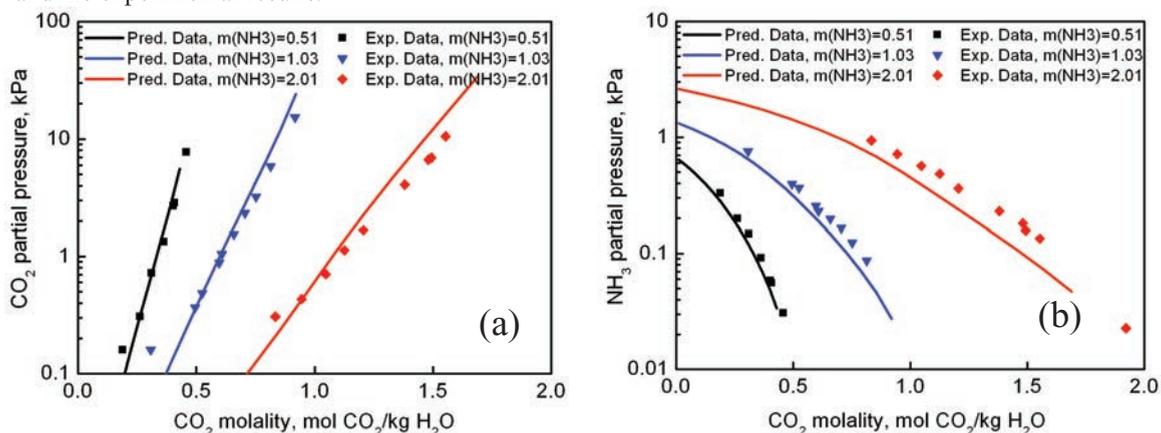

Figure 2. Comparison of predicted and experimental (a) CO_2 and (b) NH_3 partial pressure for the NH_3-CO_2-H_2O system, 20 °C.

The heat of CO_2 absorption results are compared with the experimental calorimetric data measured using a reaction calorimeter by Qin et al[16]. The experimental data are differential in temperature and

semi-differential in loading. Figure 3 shows that the predicted heat of CO_2 absorption are in a good agreement with the experimental data at 40 °C and 2.5 wt.% and 5 wt.% NH_3, respectively.
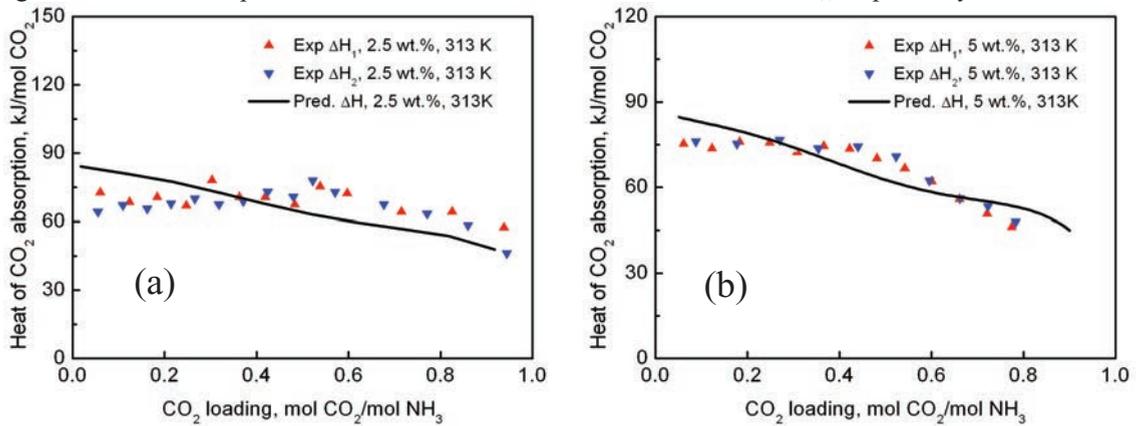

Figure 3. Comparison of predicted and experimental heat of CO_2 absorption at (a) 40 °C, 2.5 wt% NH_3 and (b) 40 °C, 5 wt% NH_3

3.2. Rate based model validation

Figure 4 shows the parity plot of (a) CO_2 absorption rate in both absorbers 1 and 2 and (b) NH_3 concentration on the gas outlet of absorber 1 obtained experimentally and from the rate-based and equilibrium model in Aspen Plus. The rate-based model can give a satisfactory CO_2 absorption rate prediction for most of tests in the pilot plant, and the maximum relative deviation between the predicted and experimental results is 15 %. The equilibrium based model (switch the RadFrac model approach option from rate-based to equilibrium model) significantly over predicts the CO_2 absorption rates. The NH_3 concentrations on the gas outlet of absorber 1 agree well with the experimental results and the maximum relative deviation between the predicted and experimental results is about 10%.

In summary, the rate-based model can predict the absorber performance reasonably. The aqueous NH_3 based absorber can achieve high CO_2 absorption but the NH_3 loss is significant at the absorber gas outlet. Therefore, the typical operation parameters and the absorption configurations are analyzed aimed to further understand and improve the absorber performance.
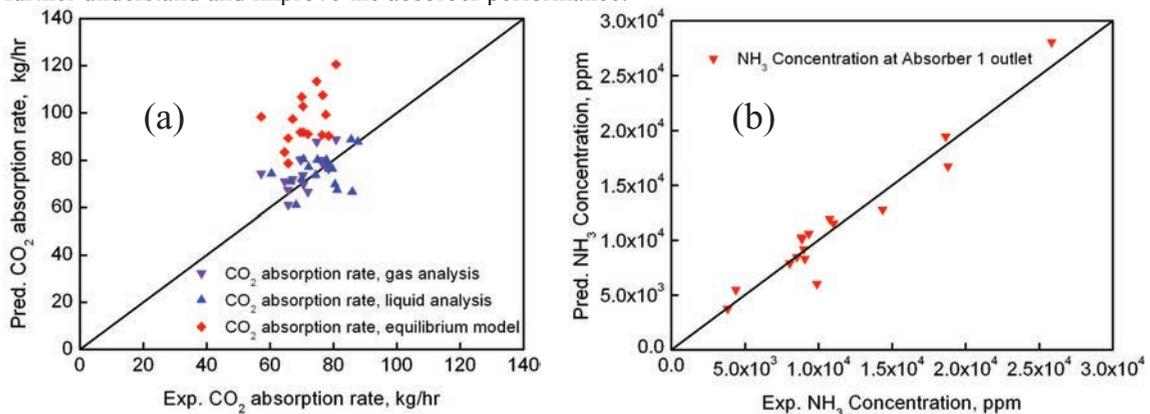

Figure 4. Parity plot of (a) CO_2 absorption rate in both absorbers 1and 2 and (b) NH_3 concentration after absorber 1.

4. Absorber performance

4.1. The effect of operation pressure

Figure 5 shows the effect of absorber operation pressure on (a) the CO_2 removal and NH_3 loss rate, (b) CO_2 removal efficiency and rich CO_2 loading. With an increase in absorber pressure, the CO_2 removal rate increases and since the CO_2 mass flow rate is fixed at the inlet, the CO_2 removal efficiency and the CO_2 loading in rich solvent increase accordingly. The CO_2 removal efficiency is close to 100% at pressure above 3 bar. The NH_3 loss rate decreases dramatically with an increase in operation pressure. It is clear that the higher absorber pressure is very beneficial to enhance CO_2 absorption and to an even larger extent reduce the NH_3 loss. However, pressurisation of the flue gas requires a significant amount of energy. Therefore, it is important to investigate the CO_2 absorption and NH_3 recovery in the follow up work and assess if the high pressure operation can make the capture process economically more feasible.
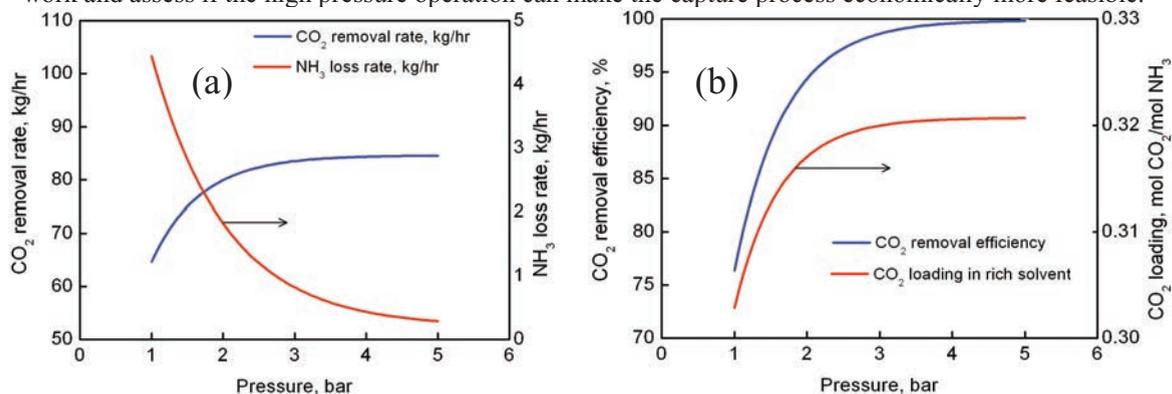

Figure 5. Effect of operation pressure on (a) CO_2 removal and NH_3 loss rate and (b) CO_2 removal efficiency and rich loading. Packing height = 7.8 m; liquid and gas temperature = 15 °C ; solvent flow rate = 134 L/min; gas flow rate = 700 kg/h; CO_2 concentration of the flue gas = 8 vol.%; CO_2 loading = 0.23 mol CO_2/mol NH_3; NH_3 concentration = 4.5 wt%.

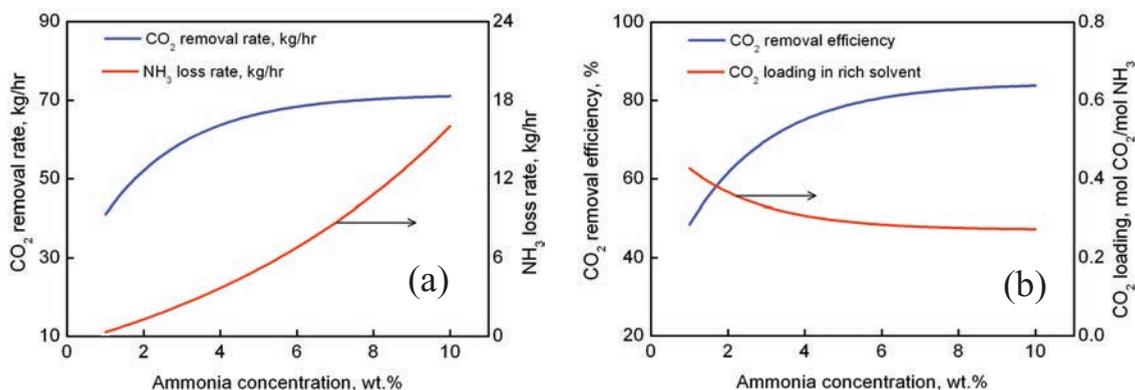### 4.2. The effect of aqueous NH_3 concentration

Figure 6. Effect of aqueous NH_3 concentration on (a) CO_2 removal and NH_3 loss rate and (b) CO_2 removal efficiency and rich loading. Packing height = 7.8 m; liquid and gas temperature = 15 °C ; solvent flow rate = 134 L/min; operation pressure = 1 bar; gas flow rate = 700 kg/h; gas CO_2 concentration of the flue gas = 8 vol.%; CO_2 loading = 0.23 mol CO_2/mol NH_3.

Figure 6 shows the effect of aqueous NH_3 concentration on (a) CO_2 removal and NH_3 loss rate and (b) CO_2 removal efficiency and rich loading. As expected, the CO_2 removal efficiency increases and rich CO_2 loading decreases with an increase in NH_3 concentration. However, the effect of NH_3 concentration on CO_2 removal rate is limited and further increase in NH_3 concentration at NH_3 concentration above 6% leads to a marginal increase in CO_2 removal rate while NH_3 loss tends to increase to a greater extent. So the NH_3 concentration needs to be optimised to achieve high CO_2 removal rate and to limit NH_3 loss to an acceptable level.

4.3. The effect of liquid inlet temperature

Figure 7 shows the effect of liquid inlet temperature on (a) CO_2 removal and NH_3 loss rate and (b) CO_2 removal efficiency and rich loading. Both the CO_2 removal and NH_3 loss rates increase with an increase in liquid inlet temperature, but to a much different extent. An increase in liquid inlet temperature leads to a slight increase in CO_2 removal rate but a much larger increase in NH_3 loss. Under conditioned studied, the absorber can achieve approximately 80% CO_2 removal efficiency at the temperature of 20 °C vs 83% at 40 °C, while NH_3 loss at 20 °C is reduced to one third of the value at 40 °C. It is evident that the CO_2 capture by aqueous NH_3 should be operated at low temperature in order to reduce NH_3 loss.
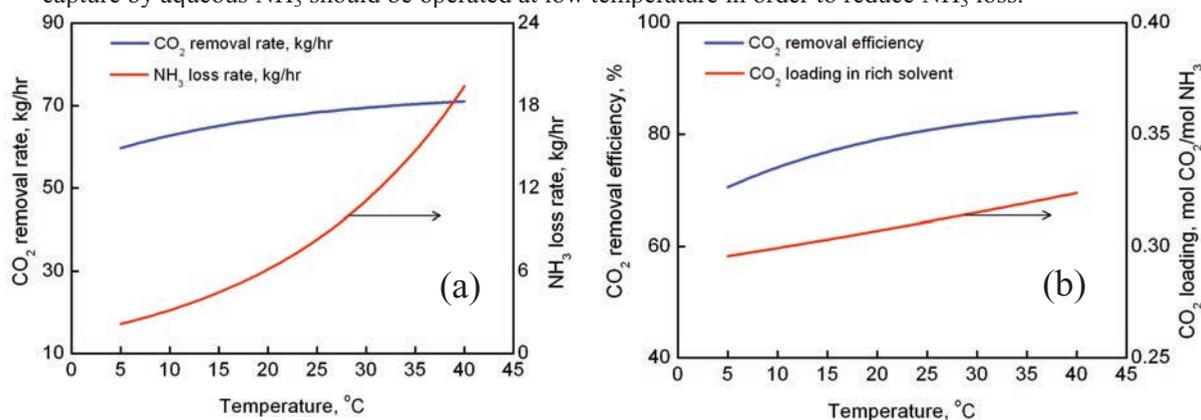

Figure 7. Effect of liquid inlet temperature on (a) CO_2 removal and NH_3 loss rate and (b) CO_2 removal efficiency and rich loading. Packing height = 7.8 m; solvent flow rate = 134 L/min; operation pressure = 1 bar; gas flow rate = 700 kg/h; gas CO_2 concentration of the flue gas = 8 vol.%; CO_2 loading = 0.23 mol CO_2/mol NH_3; NH_3 concentration = 4.5 wt%.

5. Case study

5.1. Inter-cooling

As discussed above, low liquid temperature can limit the NH_3 loss. Therefore, a study is carried out to determine the possibility of the inter-cooling process in the absorber as one of effective approaches for the NH_3 loss control. Figure 8 (a) shows an inter-cooling process used to control the absorber temperature distribution and promote the CO_2 absorption thermodynamically. The downward solvent flow in the absorber is drawn off and cooled down by an external cooler, and then sent back to the same level of the absorber.

Figure 8 (b) shows the effect of intercooler position on the NH_3 gas concentration profiles along the packing height. The NH_3 gas outlet concentrations maintain similar at the top of the absorber, despite the fact that the inter-cooling process can reduce the solvent temperature and NH_3 gas concentration below

the intercooler. This is because the NH_3 loss is a fast process and the NH_3 concentration in the gas phase is mainly determined by its equilibrium concentration. Since the inlet liquid conditions are fixed, different liquid temperature profiles as shown in Figure 8 (c) in the column has little effect on the NH_3 concentration at the outlet. So the inter-cooling process can not achieve the suppression of the NH_3 loss. However, it indicates that optimizing the solvent inlet conditions is the main way to limit the NH_3 loss.
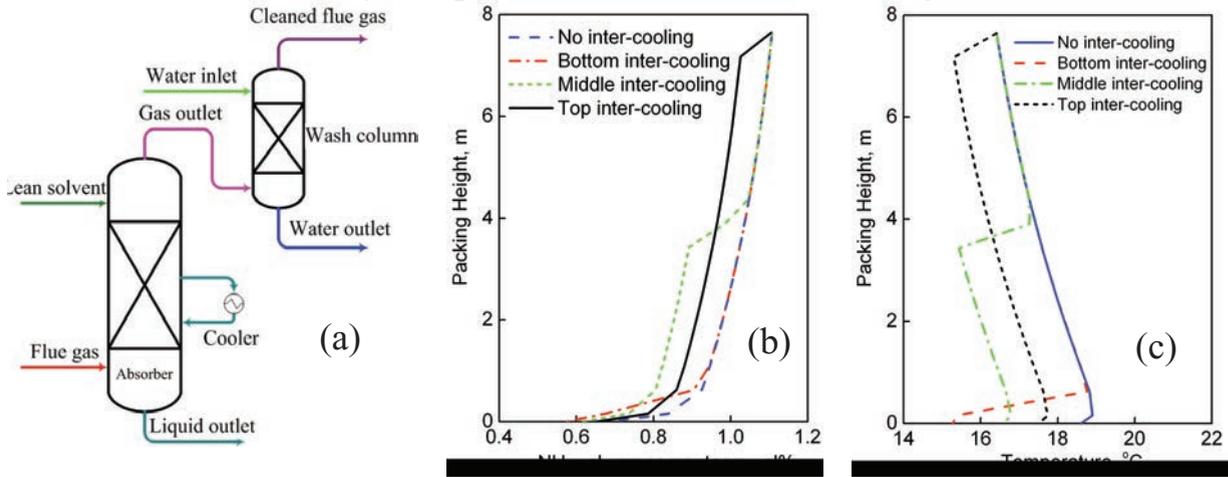

Figure 8. (a) Flow sheet, (b) NH_3 percentage and (c) temperature profiles along the packing height for operation of an aqueous NH_3 based absorber with an inter-cooling section. Base case condition: packing height = 7.8 m (divided to 50 stages); liquid and gas temperature = 15 °C ; solvent flow rate = 134 L/min; operation pressure = 1 bar; gas flow rate = 700 kg/h; gas CO_2 concentration of the flue gas = 8 vol.%; CO_2 loading = 0.23 mol CO_2/mol NH_3; NH_3 concentration = 4.5 wt%, intercooler temperature = 15.3 °C .
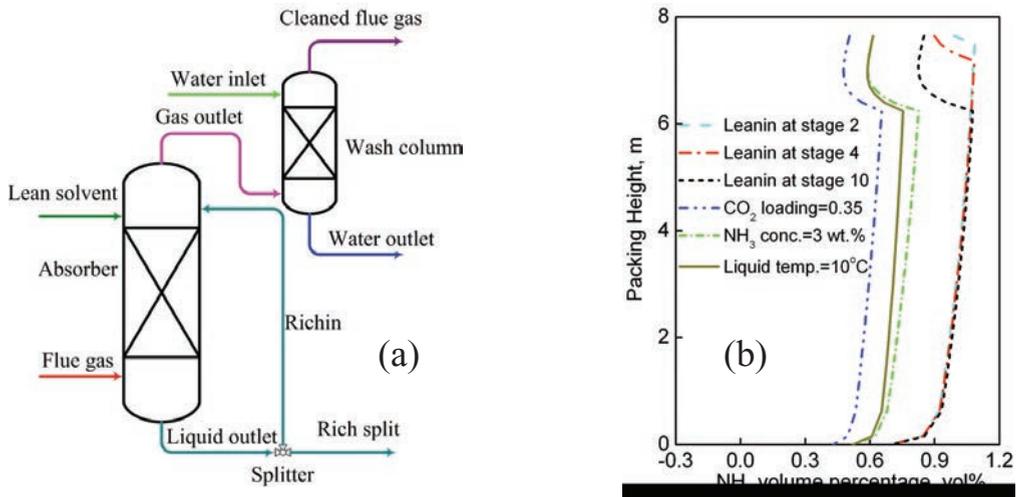
5.2. Split flow

Figure 9. (a) Flow sheet and (b) NH_3 percentage along the packing height for operation of an aqueous NH_3 based absorber with a split section of the rich solvent. Base case condition: packing height = 7.8 m (divided to 50 stages); liquid and gas temperature = 15 °C ; lean solvent flow rate = 134 L/min; split fraction = 0.1; operation pressure = 1 bar; gas flow rate = 700 kg/h; gas CO_2 concentration of the flue gas = 8 vol.%; CO_2 loading = 0.23 mol CO_2/mol NH_3; NH_3 concentration = 4.5 wt%.

Figure 9 (a) shows a split flow process used to reduce NH_3 loss. The rich solvent at the bottom of the absorber is divided into two streams. One stream recycles back to the top of the absorber. The other feeds into the stripper for the regeneration. A preliminary study is carried out with a split flow injecting to the top of the absorber (stage 1) and the lean solvent inlet is varied along the absorber height.

Figure 9 (b) shows the effect of split flow on the NH_3 concentration in the gas phase along the packing height. The gas outlet NH_3 concentration decreases as the lean solvent inlet location drops from the second to the tenth stage, while the NH_3 concentrations below the lean solvent inlet are close to each other along the packing height. In addition, the lean solvent inlet conditions can also affect the NH_3 loss process. As shown in Figure 9 (b), the NH_3 loss decreases with the increasing of inlet lean CO_2 loading and decreasing of the inlet solvent temperature and aqueous NH_3 concentration.

6. Conclusions

This paper describes a rigorous rate-based model for CO_2 absorption in aqueous NH_3 in a packed column and validates it with results from a pilot plant. The availability of the model allows detailed analysis of the capture process and can guide process improvement.

Parametric analysis of CO_2 absorption using the validated model reveals that the operation parameters can be optimized taking into account the CO_2 absorption and NH_3 loss. The high absorber pressure is very beneficial to enhance CO_2 absorption and to an even larger extent reduce the NH_3 loss. The higher NH_3 concentration above 6% leads to a marginal increase in CO_2 removal rate while NH_3 loss tends to increase to a greater extent. An increase in absorber liquid inlet temperature from 20 to 40 ^{o}C leads to a small increase in CO_2 removal efficiency but a significant increase in ammonia loss.

The inter-cooling and split flow configurations are investigated as two options for the NH_3 loss control. The inter-cooling configuration can not achieve the suppression of the NH_3 loss while the split flow configuration has the potential to achieve reduction of the gas outlet NH_3 concentrations. The lean solvent inlet conditions have been found to play a major role on the NH_3 loss process.

Acknowledgements

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