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Reaction sensitivity analysis of regeneration process of CO_2 capture using aqueous ammonia

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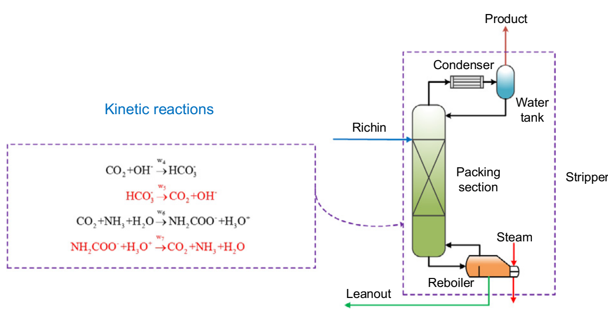
HIGHLIGHTS

- Reaction sensitivity analysis of CO_2 regeneration process was performed.
- Reaction sensitivities were obtained at different operating conditions.
- The formation and decomposition of HCO_3^- significantly affect CO_2 output.
- The formation and decomposition of NH_2COO^- significantly affect NH_3 slip.
- A novel concept for reducing regeneration energy was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to improve the regeneration efficiency of CO_2 capture using aqueous ammonia, it is important to recognize the characteristics of the kinetic reactions in the regeneration process. At first, the reaction sensitivity analysis method was determined to identify which kinetic reactions playing important roles in the regeneration process. Then, the reaction sensitivity analysis of this process was performed at different operating conditions of the rich solvent flowing into the stripper. The formation and decomposition reactions of bicarbonate both play important roles on the CO_2 output, and the sensitivity of the CO_2 output to the decomposition reaction of bicarbonate is mostly a bit larger than that to the formation reaction of bicarbonate. Based on the results of the reaction sensitivity analysis, a novel concept that is changing the reaction rates of the kinetic reactions that play important roles in the CO_2 capture process was proposed for reducing the regeneration energy. For the tested process, this novel concept can reduce the regeneration energy by 30.31%.

1. Introduction

With the advantages of high CO_2 absorption capacity and no degradation, CO_2 capture using aqueous ammonia is a promising technical route for reducing the CO_2 emissions from power plants [1,2]. For NH_3-based CO_2 capture, the regeneration process as shown in Fig. 1 is an important segment since its energy performance is a key consideration in actual applications [3]. In the regeneration process, almost pure CO_2 is produced in the stripper by heating the rich solvent (Richin) and the lean solvent (Leanout) flowing out of the stripper is recycled [4,5]. Therefore, a comprehensive understanding of the regeneration process is quite necessary.

Currently, many efforts have been devoted to studying the regeneration process of CO_2 capture using aqueous ammonia. Ma et al. [6] investigated the effects of water bath temperature, ammonium bicarbonate concentration, CO_2 loading, and solution pH on the solvent regeneration capacity with a thermostatic water bath apparatus. Ma et al. [7] also used this water bath apparatus for

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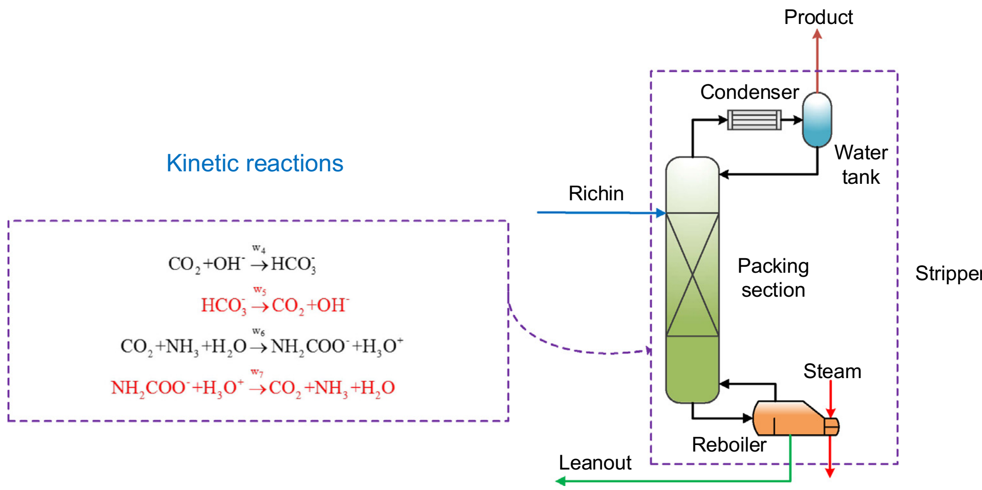

Fig. 1. Simplified diagram of the regeneration process of CO_2 capture using aqueous ammonia.

kinetic studies on regeneration reactions. Chen et al. [8] carried out kinetic studies on the regeneration reaction of heating the ammonium bicarbonate using thermogravimetry analysis method. Yu et al. [9,10] reported the regeneration performances of the Munmorah pilot plant, such as the CO_2 output, reboiler heat duty, regeneration energy, gas purity, and solid precipitation. Qin et al. [11] studied the regeneration energy by analyzing the heat of absorption. Jiang et al. [12] considered the simultaneous removal of CO_2 and SO_2 and carried out studies on the solvent regeneration process by heating the rich solution, where the ammonium bicarbonate and ammonium sulfate both exist. Experimental results showed that the ammonium sulfate in the rich solvent has a restrained effect on the solvent regeneration. In addition to the experimental studies, simulation studies have also been performed. Henrik et al. [13] evaluated the heat requirement for solvent regeneration based on equilibrium-based simulations of the overall CO_2 capture process at different NH_3 concentrations and CO_2 loadings of the lean solvent. Duan et al. [14] simulated the regeneration process with the equilibrium-based model and optimized its process operating parameters, such as the temperature of the rich solvent flowing into the stripper and the stripper pressure. But, the equilibrium-based model overestimates the heat/-mass transfer rates significantly and is usually inadequate for describing the reactive separation process [15]. Although the Murphree efficiency can be introduced to improve the prediction of heat/mass transfer rates by the equilibrium-based model [16], it is difficult to give the appropriate Murphree efficiencies at the different stages [17]. The rate-based model can overcome the limitations of the equilibrium-based model by considering the actual heat/mass transfer rates. Yu et al. [18] performed the rate-based modeling of the regeneration process and analyzed the Munmorah pilot plant results. In our previous work [19], a comprehensive model was built for the CO_2 regeneration process based on simultaneous considerations of the hydrodynamics in the packed tower, non-ideal thermodynamic behaviors of the vapor and liquid phases, rate-based heat/mass transfer, and finite reaction rates. Predicted target parameters of the regeneration process agree well with the experimental results.

Although many studies on the regeneration process of NH_3-based CO_2 capture have been carried out, there is no report studying which chemical reactions play important roles in the regeneration process as far as we know. The chemical reactions taking place in the regeneration process are usually described by the kinetic reaction model, as shown in Table 1 [20]. The reactions of CO_2 with NH_3 and the reactions of CO_2 with OH^- are kinetically controlled,

Table 1
Kinetic reaction model for the NH_3–CO_2–H_2O system.

Reaction ID	Reaction type	Chemical equation
1	Equilibrium	$NH_3+H_2O \leftrightarrow NH_4^++OH^-$
2	Equilibrium	$2H_2O \leftrightarrow H_3O^+ + OH^-$
3	Equilibrium	$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$
4	Kinetic	$CO_2 + OH^- \rightarrow HCO_3^-$
5	Kinetic	$HCO_3^- \rightarrow CO_2 + OH^-$
6	Kinetic	$NH_3 + CO_2 + H_2O \rightarrow NH_2COO^- + H_3O^+$
7	Kinetic	$NH_2COO^- + H_3O^+ \rightarrow NH_3 + CO_2 + H_2O$
8	Salt	$NH_4HCO_3(S) \leftrightarrow NH_4^+ + HCO_3^-$

while the other reactions are chemical equilibrium reactions. The solvent regeneration is mainly controlled by the kinetic reactions. For the important kinetic reactions in the regeneration process, increasing the reaction rates of the kinetic reactions beneficial to the solvent regeneration or decreasing the reaction rates of the kinetic reactions not beneficial to the solvent regeneration would help to increase the CO_2 output when the reboiler heat duty keeps constant. Compared with only optimizing the operating parameters of the regeneration process, changing the properties of kinetic reactions that play important roles in this process for increasing the CO_2 output when the reboiler heat duty keeps constant is a more fundamental solution for improving the energy performance of this process.

In this paper, we mainly focused on investigating which kinetic reactions play important roles in the regeneration process of CO_2 capture using aqueous ammonia. The reaction sensitivity analysis method, which is based on the method for reducing the combustion reaction mechanism [21], is established for this study. Details of this method will be presented in Section 2. To get information of which kinetic reactions play important roles in different regeneration processes, different operating conditions such as temperature, NH_3 concentration, and CO_2 loading of rich solvent flowing into the stripper, and different stripper pressures were all considered when performing reaction sensitivity analysis. Here, it should be pointed out that considering the components in the solution are H_2O, CO_2, NH_3, N_2, NH_2COO^-, HCO_3^-, CO_3^{2-}, NH_4^+, H_3O^+, OH^-, and NH_4HCO_3, the CO_2 loading used in this paper is the molar ratio of CO_2 to NH_3 in the solvent and defined in Eq. (1), where [] is the concentration of components, mol/L. The distributions of the main components in the vapor and liquid phases were obtained for further understanding the reaction sensitivity analysis results. Finally, based on these results, a novel concept that is changing the