4th Post Combustion Capture Conference (PCCC4)

Modelling CO_2 capture with AMP in NMP system

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Keywords: precipitating systems; modelling; sterically hindered amine; organic solvents; biphasic

1. Introduction

Novel solutions with sterically hindered amine, 2-amino-2-methyl-1-propanol (AMP), in organic solvents N-methyl pyrrolidinone (NMP) and triethylene glycol dimethyl ether (TEGDME) have been of interest in post combustion CO_2 capture [1,2]. Usage of organic solvents, NMP and TEGDME, facilitates formation of AMP carbamate which is of lower stability when compared to the bicarbonate formed in the aqueous solutions. This makes it possible to regenerate the amine at lower temperatures (70-90˚C), which in turn makes it possible to regenerate using low grade heat in the plant. Furthermore, the AMP carbamate precipitates in the organic solvents mentioned. By separating the precipitate from the organic solvent before regeneration, only the CO_2 rich stream with the precipitate needs to be heated. Such a separation could make the process further economical. Additionally, the carbamate formed is very reactive and could open new paths for the utilization of CO_2 captured.

2. Model development

An equilibrium model was developed for the AMP in NMP system as per the following reaction mechanism:

$$CO_2(sol) + RNH_2(sol) \leftrightarrow RNH_2^+COO^-(sol)$$
$$RNH_2^+COO^-(sol) + RNH_2(sol) \leftrightarrow RNH_3^+(sol) + RNHCOO^-(sol)$$
$$RNH_3^+(sol) + RNHCOO^-(sol) \leftrightarrow RNH_3^+RNHCOO^-(s)$$

ENRTL-RK method was used in Aspen Plus with unsymmetrical reference state which requires H_2O in the system. On the contrary, the system being modelled does not contain any water; this discrepancy is handled by correcting the dielectric constant in the model and having negligible concentrations of water in the streams. Properties of $RNH_3^+(sol)$ and $RNHCOO^-(sol)$ were found in literature [3] and properties of $RNH_2^+COO^-(sol)$ and $RNH_3^+RNHCOO^-(s)$ were approximated to that of H^+PZCOO^- (zwitterion formed with piperazine) and KCl respectively [4]. The zwitterion being an active center is found in very low concentrations and errors in the properties of the zwitterion would not influence the results significantly. Approximating the solid properties with KCl however, is a current limitation of the model.

The molecular weights, charge, ion types and zwitter type were declared as required. The dielectric constant for AMP is available in Aspen database [5] for the entire temperature range while that of NMP is available for 25˚C [6] and it is assumed to be constant with temperature. The NRTL parameters of CO_2 in NMP and AMP are assumed to be the same as that of CO_2 in H_2O available in the Aspen databases [7]. The NRTL parameters for AMP in NMP are also approximated to be same as that of AMP in H_2O [3]. The electrolyte pair parameters are assumed as per [4]. The parameters for PZH^+ (protonated piperazine) and $PZCOO^-$ (piperazine carbamate ion) in H_2O (from [4]) have been used for $RNH_3^+(sol)$ and $RNHCOO^-(sol)$ in H_2O and NMP. The Henry's constant with temperature was derived for CO_2 in NMP solvent. The same was assumed for CO_2 in AMP.

The flowsheet shown in Fig. 1, was modelled for CO_2 capture using AMP in NMP system, to evaluate the equilibrium performance of the system. The exhaust gases from an industry (GI-NA) were sent into an absorber (NMP-ABS) where a lean organic stream (LI-NA) absorbed CO_2 and the rich outlet liquid stream (LO-NA) was sent to a crystalliser (NMP-CRYS) through a heat exchanger (HX). The outlet of the crystalliser in the present case does not have any solid concentration owing to the solid property approximations. Therefore, a separator was not installed after the crystalliser. The outlet of the crystalliser was pumped to a regeneration column (NMP-REG) using a liquid pump (SLPUMP). The outlet of the regeneration column was pumped back to the absorption column via a MIXER where make-up streams are introduced, followed by a heat exchanger HX2. The PURGE stream was introduced to take care of any accumulating impurities in the system. Mole balances on NMP (NCAL), AMP (ACAL) and H_2O (HCAL) in the system were established to calculate the required make-up flows.

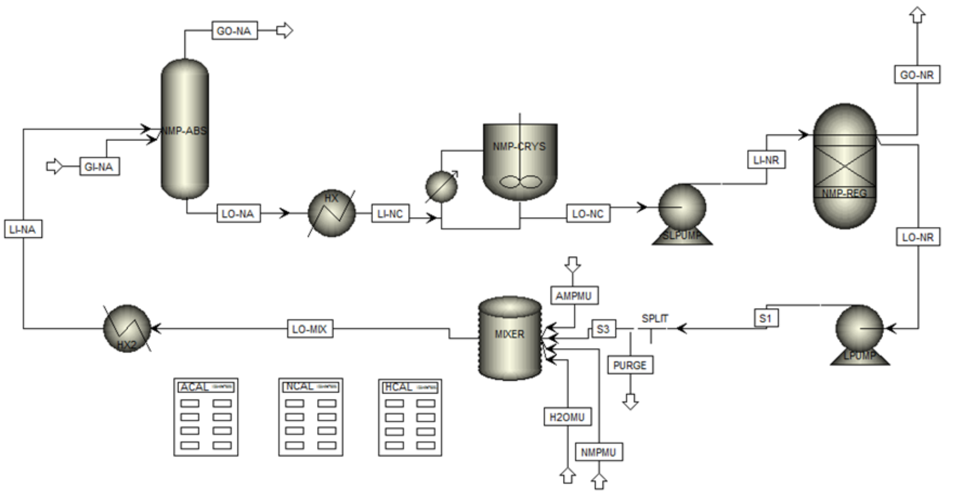

Fig. 1 The flowsheet used for modelling the AMP in NMP system

3. Results

Preliminary results from the model show that capture of CO_2 is better with higher concentrations of AMP as compared to lower concentrations of AMP, which is in agreement with previous experimental results. Further, the capture of CO_2 is better at lower temperatures as compared to higher temperatures, which is expected and also in agreement with experimental results. There was no solid observed in the model as opposed to experiments, as a result of the erroneous solid properties. The regeneration unit was separately modelled to check the effects of separating solvent from the CO_2 rich stream, and it was found that separation would favour regeneration as well, i.e., more CO_2 is regenerated from a single pass if solvent is separated before regeneration when compared to regeneration of the entire stream. Comparison with experimental data shows that the model currently over-predicts the energy requirement for regeneration of the amine. The results obtained from the model can therefore be considered as a conservative estimate, but show a significant reduction of the energy requirement for regeneration of the amine as compared to aqueous solutions of MEA (monoethanolamine).

The properties of the crystals, especially Gibbs energy and heat of formation of the solids will be determined and incorporated into the model. The model will be further validated using experimental results obtained from continuous operation.

References

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