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Modeling Energy Performance of Aqueous Methyldiethanolamine/Piperazine for CO_2 Capture

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Process modeling and experimental data have demonstrated that a blended amine solvent containing piperazine (PZ) and methyldiethanolamine (MDEA) exhibits favorable energy performance characteristics. By combining the high capacity of MDEA with the fast CO_2 absorption rate of PZ, MDEA/PZ blends are an attractive option for removing CO_2 from the flue gas of coal-fired power plants.

The solubility of CO_2 in 7m MDEA/2m PZ and 5m MDEA/5m PZ was measured over operationally significant loading ranges from 40 ^oC—160 ^oC using wetted wall column and total pressure apparatus. Applying the Gibbs-Helmholtz equation to the solubility curves, the heats of absorption for both 7m MDEA/2m PZ and 5m MDEA/5m PZ were estimated to be 68 kJ/mol CO_2, which is greater than the heat of absorption of 8m PZ (63 kJ/mol CO_2) but less than that of 7m MEA (84 kJ/mol CO_2). Assuming 90% removal from a flue gas containing 12 mol% CO_2, the capacities of 7m MDEA/2m PZ and 5m MDEA/5m PZ were estimated to be 0.83 and 0.94 mol CO_2/kg water + amine, respectively, both of which are greater than the capacities of 8m PZ (0.76 mol CO_2/kg water + amine) and 7m MEA (0.60 mol CO_2/kg water + amine).

The wetted wall column apparatus was also used to measure a liquid side mass transfer coefficient expressed in units of partial pressure (kmol/m^2-kPa-s), which will from this point on be referred to as kg'. At 40 ^oC and a CO_2 partial pressure of 1.5 kPa, kg' values for both 7m MDEA/2m PZ (9.0 x 10^{-7} kmol/m^2-kPa-s) and 5m MDEA/5m PZ (1.2 x 10^{-6} kmol/m^2-kPa-s) are comparable to kg' for 8m PZ (1.0 x 10^{-6} kmol/m^2-kPa-s) and better than that of 7m MEA (5.0 x 10^{-7} kmol/m^2-kPa-s).

A hot gas FTIR apparatus was used to measure loaded and unloaded amine volatility for 7m MDEA/2m PZ from 40 ^oC—70 ^oC. At 40 ^oC and lean loading conditions the equilibrium vapor contained 7 ppm MDEA and 6 ppm PZ, compared to 12.6 ppm for 8m PZ and 30 ppm for MEA under similar conditions. Though solvent losses due to amine volatility will be relatively low for MDEA/PZ blends, they do pose a potential environmental threat. Therefore, an amine water wash system is modeled as part of the absorber when optimizing the process.

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An Aspen Plus® model has been developed that predicts the aforementioned thermodynamic and kinetic rate data for 7m MDEA/2m PZ and 5m MDEA/5m PZ, as well as hydraulic parameters such as viscosity, density, and component diffusivity. Thermodynamic data was fit via a sequential regression in which separate MDEA and PZ models were first developed independently, allowing data for the blend to be regressed using only cross parameters. Hydraulic data was directly incorporated into Aspen Plus® using FORTRAN subroutines that calculate viscosity, density, and component diffusivity as a function of process parameters such as temperature, amine concentration, and CO_2 loading. Kinetic rate data was incorporated by adjusting rate constants in an Aspen Plus® wetted wall column simulation to fit CO_2 absorption rate data at various temperatures and loadings. Using thermodynamically consistent methodology, the Aspen Plus® model is able to predict CO_2 solubility, heat capacity, CO_2 activity coefficient, amine volatility, viscosity, density, diffusivity, and CO_2 absorption rate over operationally significant temperature, amine concentration, and loading ranges for MDEA, PZ, and MDEA/PZ systems.

A major advantage of MDEA/PZ blends is that they do not exhibit the insolubility issues associated with concentrated PZ. Running the absorber at lower temperatures will increase the rich loading, thus increasing the CO_2 pressure at the top of the stripper. If it is assumed that compression in the absorption/stripping process is more efficient than mechanical compression, lower absorber temperatures have the potential to increase overall process efficiency. An 8m solution of PZ will begin to precipitate at a loading of 0.42 mol CO_2/mol alkalinity, necessitating that the absorber be operated at temperatures at or above 40 ^oC. Preliminary modeling results suggest that the equivalent work of an absorption/stripping/compression process using 7m MDEA/2m PZ could be reduced by more than 20% (from 37.4 kJ/mol CO_2 to 28.8 kJ/mol CO_2) when the absorber temperature is decreased from 40 ^oC to 20 ^oC. Along with absorber intercooling, water wash configurations, and complex stripper configurations, absorber temperature is being used to optimize process performance for an absorption/stripping/compression process that utilizes MDEA/PZ to capture CO_2 from the flue gas of coal fired power plants.