Abstract

Concentrated aqueous piperazine has been proposed as a possible evolutionary step from monoethanolamine (MEA) as a solvent for post-combustion capture. High concentration piperazine (>5 m) has volatility similar to MEA but provides CO₂ absorption rate and capacity that is almost double that of 7 m MEA. It is also more resistant to oxidative and thermal degradation and can be used up to 150°C. In order to demonstrate these benefits a one month pilot plant campaign was conducted in November 2008 at The University of Texas at Austin with 5 m, 8 m and 9 m PZ. An absorber model for concentrated PZ was developed in Aspen Plus® RateSep™. The model was validated with the pilot plant results and served to assess the quality of the pilot plant data using the reconciliation tool in Aspen Plus®. The model simulates the temperature profile of the absorber. Loadings are matched within 0.03 and the deviation of the removal fraction is no more than 0.03. The absorber model was used to study intercooling and determine optimum conditions for its implementation. Based on pilot plant data and model results, 90% CO₂ removal can be achieved with 8 m piperazine, 9 meters of packing, and intercooling with a loading shift from 0.32 (lean) to 0.39 (rich) mol CO₂/mol alkalinity and steam heat rate in the stripper of 148 kJ/mol CO₂ and an equivalent work of 33.6 kJ/mol CO₂.

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1. Introduction

Concentrated Piperazine (PZ) has been suggested as a possible improvement to the industry standard monoethanolamine (MEA) for CO₂ capture from flue gas. Freeman et al.[1] showed that 8 m PZ has a volatility similar to MEA but the advantage of faster kinetics (more than twice) and higher capacity (double) than MEA. It is also more resistant to oxidative and thermal degradation (degrades at temperatures higher than 150°C). PZ has previously been used as a promoter to increase absorption rates and capacity in solvents. It has been blended with K₂CO₃ [2-4] and with MDEA for natural gas sweetening [5, 6]. Freeman et al. [1] showed that 8 m PZ can be used without solids precipitation at the optimum loading range of 0.3 to 0.4 mol CO₂/mol alkalinity. This greater PZ concentration requires the implementation of a new model. Frailie et al.[7] describe the development of the thermodynamic framework for concentrated PZ. This framework was used to implement a kinetic representation for concentrated PZ based on work by Dugas[8] and Cullinan[2]. Once the kinetic framework was established, an absorber model was built for a PZ pilot plant campaign at The University of Texas at Austin. The model uses a FORTRAN subroutine to implement the Tsai
interfacial area correlation and a viscosity correlation used to fit the data by Freeman et al. [1]. The absorber model was used to reconcile pilot plant data, validate the model, and analyze the performance of the solvent.

2. Initial pilot plant data evaluation

A simple evaluation of the absorber data was performed to estimate the overall gas-side mass transfer coefficient (K_G) at isothermal conditions with a log mean driving force by the equation:

\[ K_G = \frac{N_{CO_2}}{a_{eff} \sqrt{V_e} \text{LMPD}} \]  \hfill (1)

The effective packing area, a_{eff} was calculated by the Tsai et al.[9] correlation. The total CO_2 flux, N_{CO_2}, was estimated from the reported gas CO_2 inlet and outlet. V_e is the packing volume. LMPD is the log mean of the inlet and outlet CO_2 partial pressure driving force. Figure 1 shows the resulting K_G as a function of the arithmetic average between inlet and outlet CO_2 equilibrium pressures. K_g data from the pilot plant campaign were consistent with the values of k_g obtained by Dugas[8] in the wetted wall column. The K_G with the PZ solvents is 4 to 5 times greater than results with 7 m MEA and 5 m K+/2.5 m PZ.

![Figure 1. Comparison between K_G and kg’ data for concentrated PZ. Lines are kg’ data by Freeman et al.[1] Circles are data from other campaigns and solvents. [4, 8, 10, 11]](image)

3. Kinetic model development

A wetted wall column (WWC) model was developed in Aspen Plus® RateSep™. It uses the thermodynamic framework by Fraile et al.[7] and FORTRAN subroutines for liquid and gas mass transfer coefficients, and interfacial area implemented by Dugas [8]. These subroutines include correlations found in Cullinane [2]. For the gas film transfer coefficient (k_g):

\[ k_g = \frac{1.075}{RT} D_{CO_2}^{0.15} d^{0.7} \left( \frac{V}{R} \right)^{0.05} \]  \hfill (1)

where:  
R is the gas constant  
D_{CO_2} is the diffusion coefficient of CO_2  
d is the hydraulic diameter of the WWC  
v is the linear velocity of the gas  
h is the height of the contact cylinder in the WWC

The liquid film transfer coefficient is defined taking into account that the WWC experiments are conducted at conditions for which the dimensionless penetration distance (\eta) is less than 0.01. The penetration distance is defined as:

\[ \eta = D_{CO_2} h \left( \frac{2}{3} \right)^{4/3} \left( \frac{W}{Q} \right)^{4/3} \left( \frac{\rho g}{\mu} \right)^{1/3} \]  \hfill (2)

where:  
W is the circumference of the contact cylinder  
Q is the volumetric flow rate of the liquid
ρ is the liquid density

\( g \) is the gravity constant

\( \mu \) is the liquid viscosity

For these conditions the liquid mass transfer coefficient \( (k_L^0) \) follows equation 3. Here \( A \) is the gas-liquid contact area.

\[
k_L^0 = \frac{Q_s}{A} \left( \frac{1}{\pi} \right)
\]

(3)

Gas and liquid specifications were taken from WWC experimental data in Dugas [8]. Reported flux data was used to obtain the kinetic constants \( (k_n) \) in the activity \( (a) \) based reactions in the WWC (Table 1). The reverse rates are calculated from the equilibrium constant \( (K_{eq}) \) for each reaction as:

\[
k_{n-r} = \frac{k_{n-f}}{K_{eq}}
\]

(4)

Kinetic constants in Aspen Plus® RateSep™ are represented by the power law equation. The experimental data were used to generate the pre-exponential factor \( (k_0) \) and energy of activation \( (E_a) \) in the power law:

\[
k_n = k_0 \left( \frac{T}{298.15} \right)^n \exp \left( -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right)
\]

(5)

Figure 2 shows the flux fit between reported data by Dugas [8] and the WWC model with the calculated kinetic constant values. Results match reported flux data within 20% for 40, 60, and 80 °C as seen in Figure 1. However, deviation increases for 100 °C. This might be related to other phenomena taking a larger role in the absorption/desorption process such as the diffusion of reactants and products.

Table 1 Kinetic expressions used in the PZ model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2PZ + CO_2 \rightarrow PZH^+ + PZCOO^- ) (6)</td>
<td>( r = k_{n-f} a_{PZ} a_{CO_2} a_{PZCOO^-} ) (6a) ( r = k_{1-r} \frac{a_{PZH^+} a_{PZCOO^-}^2}{a_{PZ}} ) (6b)</td>
</tr>
<tr>
<td>( 2PZCOO^- + CO_2 \rightarrow PZ(COO^-)_2 + H^+PZCOO^- ) (7)</td>
<td>( r = k_{2-f} a_{PZCOO^-}^2 a_{CO_2} ) (7a) ( r = k_{2-r} a_{H^+PZCOO^-} a_{PZ(COO^-)_2} ) (7b)</td>
</tr>
<tr>
<td>( PZCOO^- + CO_2 + H_2O \rightarrow HCO_3^- + H^+PZCOO^- ) (8)</td>
<td>( r = k_{3-f} a_{PZCOO^-} a_{CO_2} ) (8a) ( r = k_{3-r} \frac{a_{H^+PZCOO^-} a_{HCO_3^-}}{a_{H_2O}} ) (8b)</td>
</tr>
</tbody>
</table>

*Reaction 7 is included as an equilibrium reaction.

*Subscripts \( f \) and \( r \) refer to the direction of the reaction (forward and reverse respectively)

4. Pilot plant absorber modeling

The resulting kinetic values and the developed thermodynamic framework[7] were used to implement an absorber model in Aspen Plus® RateSep™ for the pilot plant at The University of Texas at Austin. The absorber at the pilot plant has a diameter of 0.427 m and was packed with 6.10 m of Mellapak 2X divided into two equal beds. It was fed at the bottom with a blend of air and recycled CO₂ from the stripper. The lean solvent was introduced at the top of the column. Total packing was represented in the model using 30 segments with counter current flow. The liquid mass transfer film was divided into 20 segments optimized to adequately capture the absorption enhancement effect of the amine. Heat loss was neglected.

The analyzed pilot plant campaign data consisted of 12 runs with constant volumetric gas flow (= 0.165 actual m³/s) and a CO₂ content around 12%. Amine concentration varied from 5 m to 9 m with most data around 8 m. Lean loading, and solvent flow rate were also varied. Table 2 summarizes the conditions of the analyzed pilot plant runs.
Table 2. Pilot plant conditions for the concentrated PZ campaign at The University of Texas at Austin. Absorber packing height = 6.1 m Mellapak 2X. Diameter = 0.427 m. Gas flow rate ≈0.165 actual m³/s.

<table>
<thead>
<tr>
<th>PZ concentration (m)</th>
<th>L/G (mol L/mol G)</th>
<th>Loading (mol CO₂/mol alkalinity)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.46</td>
<td>5.5</td>
<td>0.285</td>
<td>0.340</td>
</tr>
<tr>
<td>7.88</td>
<td>5.5</td>
<td>0.308</td>
<td>0.370</td>
</tr>
<tr>
<td>9.18</td>
<td>4.9</td>
<td>0.254</td>
<td>0.330</td>
</tr>
<tr>
<td>7.82</td>
<td>4.3</td>
<td>0.284</td>
<td>0.360</td>
</tr>
<tr>
<td>8.22</td>
<td>6.0</td>
<td>0.302</td>
<td>0.360</td>
</tr>
<tr>
<td>8.06</td>
<td>5.6</td>
<td>0.305</td>
<td>0.360</td>
</tr>
<tr>
<td>7.85</td>
<td>6.7</td>
<td>0.267</td>
<td>0.340</td>
</tr>
<tr>
<td>7.67</td>
<td>5.7</td>
<td>0.331</td>
<td>0.380</td>
</tr>
<tr>
<td>4.81</td>
<td>7.1</td>
<td>0.316</td>
<td>0.380</td>
</tr>
<tr>
<td>4.95</td>
<td>6.8</td>
<td>0.274</td>
<td>0.360</td>
</tr>
<tr>
<td>4.88</td>
<td>5.5</td>
<td>0.257</td>
<td>0.360</td>
</tr>
<tr>
<td>4.64</td>
<td>4.8</td>
<td>0.262</td>
<td>0.380</td>
</tr>
</tbody>
</table>

Independent streams of PZ, CO₂ and water were created in the model and mixed to generate the reported solvent conditions. Nitrogen, oxygen, water and CO₂ streams were mixed to generate the inlet gas conditions. The model accuracy and quality of the data were evaluated using the parameter estimation tool in Aspen Plus® RateSep™. This tool adjusts experimental data and results to close material and energy balances and match CO₂ removal. The level of necessary adjustment is an indicator of the quality of the data and the accuracy of the model. Table 3 shows the range of adjustment of the variables and parameters required to close material and energy balances. The interfacial area factor was the only manipulated model parameter. It corrected the effective interfacial area calculated using the correlation by Tsai et al[9].

The interfacial area was reduced 2% to fit the data. To close the material balance, rich and lean loadings were adjusted no more than 0.03 and no less than 0.01. Removal fraction was increased by 0.008 to 0.03. CO₂ gas outlet gas concentrations were matched to less than 4% deviation. Temperatures were adequately represented with exception of a couple of outliers. Figures 3 and 4 show the temperature profile for two runs in the PZ campaign. The temperature bulge was correctly located. Its location depends on the values for the L/G. Higher solvent flow rates move the bulge towards the bottom of the column (figure 4) and reduce its temperature.
Table 3 Pilot plant reconciliation results. 6.10 m absorber packing, 0.427 m diameter.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Specified standard deviation</th>
<th>Reconciled variation range</th>
<th>Variable</th>
<th>Specified standard deviation</th>
<th>Reconciled variation range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area Factor</td>
<td>±1.0</td>
<td>Not applicable</td>
<td>T (°C)</td>
<td>±3</td>
<td>0.2 to 9.5</td>
</tr>
<tr>
<td>Inlet liquid flow (kg/s)</td>
<td></td>
<td></td>
<td>Inlet Gas</td>
<td>±3</td>
<td>-6.6 to -3.1</td>
</tr>
<tr>
<td>PZ</td>
<td>5%</td>
<td>-4.0% to 2.6%</td>
<td>Inlet Solvent</td>
<td>±3</td>
<td>-0.19 to 2.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>5%</td>
<td>-2.9% to 3.9</td>
<td>Outlet Gas</td>
<td>±3</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>5%</td>
<td>-2.6% to 3.2%</td>
<td>Z/Z_Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lean ldg (mol CO₂/mol alkalinity)</td>
<td>±0.03</td>
<td>0.0004 to 0.03</td>
<td>0.14</td>
<td>±3</td>
<td>3.0 to 10.7</td>
</tr>
<tr>
<td>Rich ldg (mol CO₂/mol alkalinity)</td>
<td></td>
<td></td>
<td>0.34</td>
<td>±3</td>
<td>2.3 to 15.6</td>
</tr>
<tr>
<td>Gas mol flow (kmol/s)</td>
<td></td>
<td></td>
<td>0.50</td>
<td>±3</td>
<td>0.3 to 5.8</td>
</tr>
<tr>
<td>CO₂</td>
<td>5%</td>
<td>-0.2% to 8.9%</td>
<td>0.64</td>
<td>±3</td>
<td>-2.4 to 6.4</td>
</tr>
<tr>
<td>H₂O</td>
<td>5%</td>
<td>0.0% to 0.2%</td>
<td>0.72</td>
<td>±3</td>
<td>-5.9 to 2.0</td>
</tr>
<tr>
<td>N₂</td>
<td>5%</td>
<td>-3.5% to 0.04%</td>
<td>0.84</td>
<td>±3</td>
<td>-17.8 to -1.2</td>
</tr>
<tr>
<td>O₂</td>
<td>5%</td>
<td>-0.9% to 0.01%</td>
<td>0.90</td>
<td>±3</td>
<td>-19.3 to -0.5</td>
</tr>
<tr>
<td>Y_out</td>
<td>5%</td>
<td>-0.0005 to 0.0006</td>
<td>1.06***</td>
<td>±3</td>
<td>-2.5 to 0.02</td>
</tr>
<tr>
<td>Removal fraction</td>
<td>5%</td>
<td>0.008 to 0.02</td>
<td>1.08***</td>
<td>±3</td>
<td>-3.8 to -1.3</td>
</tr>
</tbody>
</table>

* Lean loading was not specified directly. It was entered as individual streams of PZ, CO₂ and water.
** Z/Z_Total = 1 is the bottom of the column.
*** Z/Z_Total greater than 1 refers to thermocouples located below the packing bed.

Figure 3. Liquid temperature and CO₂ mass transfer profiles for L/G = 4.5 mol/mol, 7.5 m PZ. Lean loading = 0.29. Points are pilot plant temperature data. Intercooling was placed at Z/Z_Total=0.5 and specified to reach 40°C. It increased CO₂ removal from 69.8% to 80.4%.

5. Performance analysis

The validated model predicted the expected performance of the absorber as a function of lean loading and L/G. (Figure 5). An additional analysis introduced an intercooling heat stream in the middle of the column (Z/Z_Total=0.5) to set stage temperature to 40°C. Results show that intercooling offers a benefit for all studied cases by increasing rich loading and removal. However, the benefit is negligible for conditions with low lean loading and high L/G. This result is similar to that observed by Plaza et al. for K₂CO₃/PZ [12]. Following the 90% and 80% removal curves on figure 5 it is possible to define the critical L/G region for this system. As in Plaza et al. [12] the critical L/G is located at the discontinuity observed for rich loading at constant removal. Figures 3 and 4 show the resulting profiles. Figure 3 is located near the...
critical L/G so the CO$_2$ mass transfer approaches a pinch at the temperature bulge location ($Z/Z_{Total}$ ≈ 0.5). Intercooling breaks the pinch and reduces the magnitude of the bulge. Figure 4 is a high L/G case. The bulge has a lower magnitude and is not located near the mass transfer pinch.

Figure 4  Liquid Temperature and CO$_2$ mass transfer profiles for L/G = 6.8, 7.6 m PZ. Lean loading = 0.28 rich loading= 0.35. Points are temperature pilot plant data CO$_2$ removal 93.2%.

Figure 5. Effect of solvent lean loading on rich loading for 6.1 m Mellapak 2X. diameter 0.427 m, 8 m PZ. $y_{CO2} = 0.12$. Inlet gas and liquid T = 40° C. Constant gas flow rate = 0.165 actual m$^3$/s.

Table 4 is summarizes conditions for 90% removal using concentrated PZ. It combines pilot plant results with the intercooling analysis. The stripper heat rates are based on pilot plant conditions for a stripper at 138 kPa. The equivalent work is calculated following the methodology by Van Wagener[11] and assuming final product CO$_2$ compression to 15 MPa.
Table 4. Conditions to obtain 90% CO2 removal using concentrated PZ. Absorber with 6.1 m of Mellapak 2X and 0.427 m diameter. Intercooling of liquid to 40°C

<table>
<thead>
<tr>
<th>PZ concentration (m)</th>
<th>L/G (mol L/mol G)</th>
<th>Loading (mol CO2/mol alkalinity)</th>
<th>Steam heat rate (kJ/mol CO2)</th>
<th>Equivalent work (kJ/mol CO2)</th>
<th>Intercooling?</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>4.9</td>
<td>Lean 0.266; Rich 0.360</td>
<td>148</td>
<td>37.4</td>
<td>NO</td>
</tr>
<tr>
<td>8**</td>
<td>5.4</td>
<td>Lean 0.272; Rich 0.361</td>
<td>148</td>
<td>40.1</td>
<td>NO</td>
</tr>
<tr>
<td>8</td>
<td>5.9</td>
<td>Lean 0.294; Rich 0.374</td>
<td>136</td>
<td>35.6</td>
<td>YES</td>
</tr>
<tr>
<td>8***</td>
<td>6.7</td>
<td>Lean 0.320; Rich 0.389</td>
<td>137</td>
<td>33.6</td>
<td>YES</td>
</tr>
</tbody>
</table>

*Equivalent work obtained calculated using pilot plant conditions and the method by Van Wagener[11] assuming final compression to 15 MPa. For the intercooled systems values were extrapolated taking into account rich and lean loadings.

**Reported CO2 removal for this case is 87.7%.

***Conditions for this run require 9 m of packing height.

Plaza et al.[12] proposed an approximation of the critical L/G for the absorption of CO2 that required the heat of absorption of the solvent and heat capacity values for gas and liquid:

$$
\left( \frac{L}{G} \right)_c = \left(1 + (1 - R)Y_{CO2}^{CO2} + Y_{H2O}^{H2O}\right) \left( \frac{C_{Pout}}{C_{Pin}} \right) + \frac{\left(Y_{b}^{CO2} - (1 - R)Y_{in}^{CO2}\right) h_{abs}|_{T_b} + \left(Y_{out}^{H2O} - Y_{b}^{H2O}\right) h_{vap}|_{T_b}}{C_{Pin}(T_{in}^L - T_b)}
$$

(10)

where: \((L/G)_c\) is the critical ratio of liquid to inert gas species;

\(Y_{H2O}^{H2O}, Y_{CO2}^{CO2}\) are the fractions of water and carbon dioxide respectively to inert species in the gas stream \(n_{CO2}/G_i, n_{H2O}/G_i\).

R is the specified removal.

Using this relation to predict the critical L/G and the methodology in Plaza et al.[12] for the analyzed system gave similar results to the observed in Figure 5. The critical L/G for 8m PZ was predicted at 4.2 (mol L/mol G) for 90% removal and 4.4 (mol L/mol G) for 80%. The temperature bulge magnitude was also predicted within 5% of the value observed in Figure 3 (65°C)

6. Conclusions

- Pilot plant results show that it is possible to obtain 90% removal using 6.1 m of Mellapak 2X packing and concentrated PZ. The developed model is capable of predicting the necessary conditions to reach 90% removal using intercooling. (Table 4). Intercooling is capable of reducing the equivalent work by 11% since it allows the absorber to operate at higher loading values that translate in a reduction in stripper energy requirements. An additional 3 m of packing in absorber can reduce the equivalent work to 33.6 kJ/mol CO2 which is almost 18% less than the reported value for the pilot plant for 9 m MEA by Van Wagener.[11]

- Reconciled pilot plant results demonstrate that the model is capable of simulating absorber operation. Loadings and removal fraction were matched (less than 0.03 difference). Temperature profiles were adequately traced and the temperature bulge location was closely approximated. The interfacial area factor used was equal to 0.98 showing and adequate prediction of the effective area using Tsai et al.[9].

- Intercooling is capable of increasing absorber removal by as much as 10% when the absorber is designed close to the critical L/G. The critical L/G region for this system is near 4 mol/mol as was observed in Figure 5 and in the profiles in Figure 3 where the mass transfer pinch is located close to the temperature bulge.

- This observed critical L/G (figure 5) was compared to the predicted value using the proposed equation by Plaza et al.[12] with satisfactory results. The equation predicted a value of 4.2 (mol/mol) for 90% and 4.4 (mol/mol) for 80% removal. The temperature bulge was also predicted within 5% for the critical L/G.

- The WWC model is capable of generating kinetic values for CO2 absorption using concentrated PZ. The reported laboratory CO2 flux data are matched with a ±20% deviation (Figure 2). Model results above 80 °C show a higher deviation from experimental data due to additional phenomena becoming predominant at these conditions, possibly the increase of diffusion effects of reactants and products.
Preliminary evaluation of the reported pilot plant data (Figure 1) shows that the $K_G$ is located within the expected values based on the laboratory results. This serves as a first validation of the data obtained.

7. Acknowledgements

This work was supported by the LSPower Pilot Plant Initiative and the Luminant Carbon Management Program. AspenTech provided Aspen Plus® with RateSep™. Special thanks to Dr. Frank Seibert and the staff at J.J Pickle Research Campus of The University of Texas at Austin for their operational support during the pilot plant campaign and to Stephanie Freeman for tabulating the pilot plant data.

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