Accurate Screening of Candidate Solvents by the Wetted Wall Column

Xi Chen, Ross Dugas, Fred Closmann, Shan Zhou, Gary T. Rochelle

The University of Texas at Austin

12th MEETING of the INTERNATIONAL POST-COMBUSTION CO₂ CAPTURE NETWORK
Sep 29, 2009
Regina, Canada
Outline

• Background
  • Research needs
  • Literature review

• Apparatus
  • Wetted Wall Column (WWC)

• Results:
  • CO$_2$ solubility, CO$_2$ capacity, Heat of absorption
  • Absorption/Desorption Rates

• Conclusions
Research Needs

• Previous amine capacity & kinetics studies:
  – Low amine concentration (< 3 M)
  – Zero or very lean CO₂ loading
  – Narrow temperature range (25~60 °C)

• Typical industrial conditions for CO₂ capture
  – Absorber: 40-60 °C
  – Stripper: 80-120 °C
  – 12% CO₂ in flue gas at 1atm and 90% removal: CO₂-loaded amine solvent ($P_{\text{CO₂,lean}}^*=0.5 \text{ kPa}$ and $P_{\text{CO₂,rich}}^*=5 \text{ kPa}$)

• Previous amine screening efforts
  – Simple gas sparging: Absorption rate affected by solution property (density, viscosity & surface tension etc.)
  – CO₂ capacity for industrial conditions not available
Why WWC for Screening?

• More representative of commercial packing than laminar jet or stirred cell.
• More accurate VLE and mass transfer rate in loaded solution.
• Adequate for design of absorber and stripper.
# Previous work with WWC

<table>
<thead>
<tr>
<th>Literature</th>
<th>Solvents</th>
<th>$[\text{Amine}]_{\text{max}}$ (molality)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dugas 2009</td>
<td>MEA/PZ</td>
<td>13</td>
</tr>
<tr>
<td>Cullinane 2005</td>
<td>$K^+$/ PZ</td>
<td>4</td>
</tr>
<tr>
<td>Al-Juaied 2004</td>
<td>DGA / Morpholine</td>
<td>18</td>
</tr>
<tr>
<td>Bishnoi 2000</td>
<td>MDEA/PZ</td>
<td>8</td>
</tr>
<tr>
<td>Pacheco 1998</td>
<td>MDEA/ DGA</td>
<td>12</td>
</tr>
<tr>
<td>Mashewa 1995</td>
<td>MDEA/DEA</td>
<td>9</td>
</tr>
</tbody>
</table>
## Scope of this work

<table>
<thead>
<tr>
<th>Type</th>
<th>Amine</th>
<th>Conc. (m)</th>
<th>Viscosity@ 40°C &amp; $P*_{CO2}$ =5kPa (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary Amines</strong></td>
<td>Ethanolamine (MEA)</td>
<td>7</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Ethylenediamine (EDA)</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Diglycolamine® (DGA®)</td>
<td>10</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Piperazine &amp; derivatives</strong></td>
<td>Piperazine (PZ)</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>N-(2-hydroxyethyl)piperazine (HEP)</td>
<td>7.7</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>1-(2-Aminoethyl)piperazine (AEP)</td>
<td>6</td>
<td>23</td>
</tr>
<tr>
<td><strong>Hindered Amines</strong></td>
<td>2-amino-2-methyl-1-propanol (AMP)</td>
<td>4.8</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>2-piperidineethanol (2-PE)</td>
<td>8</td>
<td>24</td>
</tr>
<tr>
<td><strong>Promoted Tertiary Amine</strong></td>
<td>Methyldiethanolamine (MDEA)/Piperazine (PZ)</td>
<td>7/2</td>
<td>8</td>
</tr>
</tbody>
</table>
Wetted Wall Column

Diagram of a wetted wall column with components labeled:
- Needle Valve
- Bypass Valve
- Condenser
- CO₂ Analyzer (IR)
- WWC (Wetted Wall Column)
- Septum
- Pump
- Solution Reservoir
- Flow Controllers
- Saturator
- Temp. Bath
- Gas IN
- Gas OUT
- Liq IN
- Liq OUT
\[ R_1 = \frac{1}{k_g} \quad R_2 = \frac{H_{CO_2}}{Ek_l^0} \quad R_3 = \frac{1}{k_{l,PROD}^0} \frac{\partial P_{CO_2}^*}{\partial [CO_2]_T} \]
\[
\frac{1}{K_G} = \frac{1}{k_g} + \frac{H_{CO_2}}{E k^0_l} + \frac{1}{k^0_{l,PR} \partial [CO_2]_T} = \frac{1}{k_g} + \frac{1}{k'_g}
\]

\[
N_{CO_2} = K_g (P_{CO_2,g} - P_{CO_2,l})
\]

\[
= k'_g (P_{CO_2,i} - P_{CO_2,l})
\]

\[
\Rightarrow k'_g = \frac{N_{CO_2}}{P_{CO_2,i} - P_{CO_2,l}}
\]

\[
\approx \sqrt{D_{CO_2} k_2 [Am]_b} \frac{1}{H_{CO_2}}
\]
10m DGA® @ 60°C, 
CO₂ ldg = 0.4 mol/mol alka

Flux (mol/(s*cm²))

Driving force (P_{CO₂, g} - P^*_{CO₂, l}) (Pa)

Equilibrium point (P_{CO₂}^* = 2670 Pa)
PIPERAZINE DERIVATIVES
CO$_2$ Solubility

7.7 m HEP

\[ \ln P = a + \frac{b}{T} + c \cdot \alpha + d \cdot \alpha / T + e \cdot \alpha^2 \]

![Graph showing the relationship between CO$_2$ solubility and temperature.](image)

- Capacity = 0.68 mol CO$_2$/kg (H$_2$O+HEP)

Temperature and pressure values are plotted for 40, 60, 80, and 100°C, showing the solubility of CO$_2$ in different conditions.
6m AEP

\[
\Delta H_{abs} = -R \frac{d(\ln P)}{d(1/T)}
\]

- Heat of absorption (kJ/mol)
- CO₂ Loading (mol/mol alkalinity)
- P* (kPa)

Graph showing the relationship between CO₂ loading and the heat of absorption at various temperatures (40°C, 60°C, 80°C, 100°C) with corresponding P* values.
HINDERED AMINE
8m 2-PE

\[
\begin{align*}
\text{H} & \quad \text{N} \\
\text{\textbf{P}E} & \quad \text{\textbf{N}} \\
\text{\textbf{H}} & \quad \text{\textbf{O}} \text{H}
\end{align*}
\]

![Graph showing the relationship between CO₂ Loading (mol/mol alkalinity) and P* (kPa) at different temperatures (40, 60, 80, and 100 °C). The graph includes data points and lines for PZ@40 °C (Hilliard & Dugas) and PZ@100 °C. The CO₂ Loading ranges from 0.01 to 1.23 mol CO₂/kg Solv., and P* ranges from 0.01 kPa to 100 kPa.](image)

- 100 °C
- PZ@100 °C
- 80 °C
- 60 °C
- 40 °C
- PZ@40 °C (Hilliard & Dugas)

- 1.23 mol CO₂/kg Solv.
PRIMARY AMINE
PROMOTED TERTIARY AMINE
7m MDEA/2m PZ

\[
\begin{align*}
\text{HO-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_3 \\
\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{NH} & \quad \text{NH}
\end{align*}
\]

\[
\begin{align*}
P@100 \ ^\circ \text{C} & \quad 100 \ ^\circ \text{C} \\
P@80 \ ^\circ \text{C} & \quad 80 \ ^\circ \text{C} \\
P@60 \ ^\circ \text{C} & \quad 60 \ ^\circ \text{C} \\
P@40 \ ^\circ \text{C} & \quad 40 \ ^\circ \text{C}
\end{align*}
\]

\[
\begin{align*}
0.71 \ \text{mol CO}_2/\text{kg Solv.}
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2 \text{ Loading (mol/mol alkalinity)}
\end{align*}
\]

\[
\begin{align*}
P* \ (\text{kPa})
\end{align*}
\]
CO₂ Capacity for 5kPa Rich Solution

CO₂ capacity (mol/kg (water+amine))

Lean Partial Pressure of CO₂ (Pa)

8m PZ
8m 2-PE
7m MEA
7.7m HEP
Enthalpy of CO₂ Absorption

Enthalpy of CO₂ absorption (kJ/mol) vs CO₂ Loading (mol/mol alkalinity).

Lines represent different solvents:
- 7m MEA
- 4.8m AMP
- 7.7m HEP
- 8m 2-PE
- 12m EDA
- 8m PZ
- 7m MDEA/2m PZ
$k'_{g} \approx \sqrt{k_2 [Am] D_{CO2}} \over H_{CO2}$
Absorption/Desorption rates for 7.7m HEP

\[ k'_g = \frac{N_{CO_2}}{P_{CO_2,i} - P_{CO_2,b}} \]

- 7 m MEA@40°C
- 8 m PZ@40°C
- HEP@100°C
- HEP@80°C
- HEP@60°C
- HEP@40°C

\[ \text{kg} \] (mol/s·Pa·m²)
8m 2-PE

[Graph showing the relationship between $k_g^*$ (mol/s·Pa·m²) and $P^*_\text{CO}_2$ @ 40°C (kPa) for different temperatures: 40°C, 60°C, 80°C, and 100°C. The graph includes data points for 7 m MEA@40°C and 8 m PZ@40°C.]
12m EDA

![Graph showing the relationship between $k_g$ (mol/s·Pa·m²) and $P^{*}_{CO_2 @ 40C}$ (kPa) for different temperatures and solutions.](image)

- 80°C: 8 m PZ@40°C
- 100°C: 7 m MEA@40°C
- 40°C: 60°C

Solutions:
- H₂N
- NH₂
### Apparent second order reaction rate of amine with CO$_2$

<table>
<thead>
<tr>
<th>Amine</th>
<th>$k_2$ (m$^3$/mol·s)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZ</td>
<td>54</td>
<td>(Bishnoi and Rochelle 2000)</td>
</tr>
<tr>
<td>AEP</td>
<td>30</td>
<td>(Bishnoi 2000)</td>
</tr>
<tr>
<td>HEP</td>
<td>12</td>
<td>(Bishnoi 2000)</td>
</tr>
<tr>
<td>EDA</td>
<td>8.8</td>
<td>(Sada et al. 1977)</td>
</tr>
<tr>
<td>MEA</td>
<td>5.9</td>
<td>(Blauwhoff et al. 1984)</td>
</tr>
<tr>
<td>DGA</td>
<td>5.1</td>
<td>(Pacheco 1998)</td>
</tr>
<tr>
<td>AMP</td>
<td>0.7</td>
<td>(Saha and Bandyopadhyay 1995)</td>
</tr>
<tr>
<td>2-PE</td>
<td>0.6</td>
<td>(Xu et al. 1993)</td>
</tr>
<tr>
<td>MDEA</td>
<td>0.005</td>
<td>(Versteeg and Van Swaaij 1988)</td>
</tr>
</tbody>
</table>
Conclusions

Fast solvents

<table>
<thead>
<tr>
<th>Amine</th>
<th>Conc (m)</th>
<th>CO$<em>2$ Capacity@$P</em>{CO2,lean}=0.5$kPa (mol/kg (water+amine))</th>
<th>$k'<em>g$ @$P</em>{CO2}=5$kPa ($\times10^7$mol/s·Pa·m$^2$)</th>
<th>$\Delta H_{abs}@P_{CO2}=1.5$kPa (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDEA/PZ</td>
<td>7/2</td>
<td>0.71</td>
<td>5.7</td>
<td>67</td>
</tr>
<tr>
<td>PZ</td>
<td>8</td>
<td>0.79</td>
<td>5.3</td>
<td>70</td>
</tr>
<tr>
<td>MEA</td>
<td>7</td>
<td>0.47</td>
<td>3.1</td>
<td>82</td>
</tr>
<tr>
<td>MEA</td>
<td>11</td>
<td>0.52</td>
<td>2.5</td>
<td>84</td>
</tr>
</tbody>
</table>
## Slow solvents

<table>
<thead>
<tr>
<th>Amine</th>
<th>Conc. (m)</th>
<th>CO₂ Capacity@ P&lt;sub&gt;CO₂,lean&lt;/sub&gt;=0.5kPa (mol/kg (water+amine))</th>
<th>k&lt;sub&gt;g'&lt;/sub&gt; @ P&lt;sub&gt;CO₂&lt;/sub&gt;=5kPa (×10&lt;sup&gt;7&lt;/sup&gt;mol/s·Pa·m&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>ΔH&lt;sub&gt;abs&lt;/sub&gt;@ P&lt;sub&gt;CO₂&lt;/sub&gt;=1.5kPa (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>7</td>
<td>0.47</td>
<td>3.1</td>
<td>82</td>
</tr>
<tr>
<td>HEP</td>
<td>7.7</td>
<td>0.68</td>
<td>2.9</td>
<td>69</td>
</tr>
<tr>
<td>DGA&lt;sup&gt;®&lt;/sup&gt;</td>
<td>10</td>
<td>0.38</td>
<td>2.4</td>
<td>81</td>
</tr>
<tr>
<td>AEP</td>
<td>6</td>
<td>0.66</td>
<td>2.3</td>
<td>72</td>
</tr>
<tr>
<td>2-PE</td>
<td>8</td>
<td>1.23</td>
<td>2</td>
<td>73</td>
</tr>
<tr>
<td>AMP</td>
<td>4.8</td>
<td>0.96</td>
<td>1.7</td>
<td>73</td>
</tr>
<tr>
<td>EDA</td>
<td>12</td>
<td>0.78</td>
<td>1.6</td>
<td>80</td>
</tr>
</tbody>
</table>
Acknowledgement

• Luminant Carbon Management Program
• Industrial Associates Program for CO$_2$ Capture by Aqueous Absorption
Accurate Screening of Candidate Solvents by the Wetted Wall Column

Questions?

Xi Chen
xi@che.utexas.edu