Evaluation of Energy in Precipitating 2-Amino-2-methyl-1-propanol Carbonate Solvent Process for CO$_2$ Capture

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Requirements for PCCS and how to approach

- Novel amine
- Blend amines

Technologies
- Quantum chemistry
- Organic synthesis

Heat of reaction \( \downarrow \) (depend on substance)
- Non-ideal mixing \(^2\)
- Dissolution of gas into liquid
- Chemical reaction \( \Delta H_r \downarrow \)

Exploring solvent
- Novel amine
- Blend amines

Target

Heat of reaction \( Q_R \)

- Sensible heat \( \downarrow \)
- Heat of vaporization \( \downarrow \)

Flow rate \( \downarrow \)
- Absorption flux \( \uparrow \)

Temperature swing \( \downarrow \)

- Concentration & \( \Delta \)CO\(_2\) loading \( \uparrow \)
- Multi pressure stripping \(^3\)
- Rate of reactions
  - Fast: RN-COO\(^-\) H\(^+\) \( (pK_a) \)
  - H\(^+\) acceptor
    - R’N-H\(^+\) \( \leftrightarrow \) RN-H\(^+\)
  - pH \( \uparrow \) \( \rightarrow \) HCO\(_3^\) \( \uparrow \) (Low temp. stripping)

- Condensation
- Precipitate separation

Regeneration energy (GJ/t)

1) RITE, COURSE50 NEDO Project report(2006), 2) Kim, I. et. al., Chem. Eng. Sci. 64 (2009)2027-2038,
2-Amino-2-methyl-1-propanol (AMP)

M.W. 89.14 g/mol
B.P. 165.5 °C
M.P. 25.5 °C

- One of promising candidates
- Moderately, sterically hindered primary amine
- Lower corrosiveness
- Lower reaction rate (promoter: PZ etc.)

Unstable carbamate

Protonated AMP

$K_c = \frac{[\text{AMPCOO}^-]}{[\text{AMP}][\text{HCO}_3^-]} < 0.01$

VLE and absorption rate: AMP and MEA

1) Tong, D. et. al., Int. J. GHG Ctrl, 6 (2012)37-47
Experimental: Precipitation of AMP

AMP 50wt% (5.6M) at 40°C → getting whitely turbid by precipitation of salt

Chemical structure by Raman spectroscopy
Cation: Protonated AMP
Anion: Carbonate (1068 cm⁻¹)

\[
\text{CO}_3^{2-} + 2\text{AMPH}^+ \rightarrow (\text{AMPH})_2(\text{CO}_3)
\]

Reaction model in AMP-REA (ASPEN PLUS)*

\[
\begin{align*}
\text{AMPH}^+ + \text{H}_2\text{O} & \leftrightarrow \text{AMP} + \text{H}_3\text{O}^+ \\
2\text{H}_2\text{O} & \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \quad (\leftrightarrow \text{Equilibrium})
\end{align*}
\]

\[
\begin{align*}
\text{HCO}_3^- + \text{H}_2\text{O} & \leftrightarrow \text{H}_3\text{O}^+ + \text{CO}_3^{2-} \\
\text{CO}_2 + \text{OH}^- & \rightarrow \text{HCO}_3^- \\
\text{HCO}_3^- & \rightarrow \text{CO}_2 + \text{OH}^- \quad (\rightarrow \text{Kinetic})
\end{align*}
\]

\[
\begin{align*}
\text{AMP} + \text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{AMPCOO}^- + \text{H}_3\text{O}^+ \\
\text{AMPCOO}^- + \text{H}_3\text{O}^+ & \rightarrow \text{AMP} + \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]


Separation of concentrated carbonates reduces regeneration energy?
Advantage of Solid-Liquid phase separation process

Higher concentration:
- ✓ Absorption capacity ↗
- ✓ Sensible heat ↘

✓ Keeping higher pH & driving force
× Additional energy of phase change

Prior researches

Alstom\(^1\)  Ammonia bicarbonate
\[ \text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{NH}_4\text{HCO}_3 \downarrow \]
\[ 2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_3^{2-} \rightarrow (\text{NH}_4)^2\text{CO}_3 \]
\[ (\text{NH}_4)^2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{NH}_4\text{HCO}_3 \downarrow \]

Shell\(^2\)  Potassium bicarbonate
\[ \text{CO}_2 + \text{H}_2\text{O} + \text{CO}_3^{2-} \rightarrow 2\text{HCO}_3^- \]
\[ 2\text{HCO}_3^- + 2\text{K}^+ \rightarrow 2\text{KHCO}_3 \downarrow \]
Solid separation: 35°C
Stripper: 90°C, 1.1 bar

SINTEF\(^3\)  Potassium salt of sarcosine (KSAr)

Development of operating line of precipitation process

Operating line

CO₂ desorption / AMP regeneration

Temperature (°C)

<table>
<thead>
<tr>
<th>CO₂ absorption</th>
<th>Crystallization curve</th>
<th>Filtration</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°C 0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40°C 0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C, 0.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental condition

<table>
<thead>
<tr>
<th></th>
<th>T (°C)</th>
<th>P_{CO₂} (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorber</td>
<td>40～50</td>
<td>10</td>
</tr>
<tr>
<td>Stripper</td>
<td>90～120</td>
<td>10 ～ 100</td>
</tr>
</tbody>
</table>

VLE: Experimental apparatus

Gas Analyzer
Inlet gas sampling line
Outlet gas sample line
Back pressure regulator
Liquid sampling line
Low temp. circulator
Condenser
Heater
Slurry
Liquid
Crystallization
Buchner funnel & filter
Vacuum pump
Suction filtration

Experimental condition

Vacuum pump
Buchner funnel & filter
CO₂ absorption 90°C 0.34
CO₂ loading α (mol-CO₂/mol-amine)

Experimental condition

Fusion

Vacuum pump
Buchner funnel & filter
CO₂ absorption 90°C 0.34
CO₂ loading α (mol-CO₂/mol-amine)

Experimental condition

Fusion

Vacuum pump
Buchner funnel & filter
CO₂ absorption 90°C 0.34
CO₂ loading α (mol-CO₂/mol-amine)
Slurry separation and crystal recovery

### Condition of suction filtration

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtration Temp. (°C)</td>
<td>25~60 ±5</td>
</tr>
<tr>
<td>Filter diameter (μm)</td>
<td>8~10</td>
</tr>
<tr>
<td>Suction Pressure (kPa)</td>
<td>80</td>
</tr>
<tr>
<td>Suction time (min./g)</td>
<td>0.1</td>
</tr>
</tbody>
</table>

### Estimation of CO₂ recovery

**Equilibrium Slurry:** $T=40°C$, $p_{CO₂}=10kPa$

- **AMP=50wt% 100g**
  - AMP
  - H₂O
  - CO₂

**Liquid-Solid separation:** $T=40°C$, $p=0.2atm$

- Liquid
  - 55% (54%)
- Solid
  - 45% (35%)
- CO₂
  - 13.9g

**Analysis by TOC**

- 35%
- 54%
- 72%

**Crystal recovery from slurry**

- CO₂ loading $\alpha=0.56$ (max.)
- $\alpha=0.30$

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8/14
Conceptual PFD and operating line (AMP 50%)

Process flow diagram

- Water wash
- Absorber
- Gas inlet
- Cooler
- Gas outlet
- CO₂ lean liquid
- CO₂ semi-lean liquid
- Solid-liquid separator
- CO₂ rich slurry
- Absorber Stripper
- HEX
- CO₂ rich liquid
- CO₂ lean liquid
- Condenser
- CO₂ recovery
- Stripper
- Reboiler

Liquid phase
- Liquid
- Solid

Regeneration
- 6
- 5
- CO₂ rich liquid
- 55%
- 50wt%
- 40%

CO₂ absorption
- Lean inlet
- Rich outlet (Slurry)
- CO₂ rich slurry

Mixing
- 1
- 2
- 3
- 4

Phase separation
- 6
- 3
- 6

CO₂ loading α (mol-CO₂/mol-amine)

Temperature (℃)
- 0
- 20
- 40
- 60
- 80
- 100
- 120

Δα = Cycle capacity

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Equilibrium-based estimation of regeneration energy

Process flow diagram

Liquid Solid

Absorber Stripper

Gas inlet

Gas outlet

CO₂ rich liquid

CO₂ lean liquid

Q = Q_R + Q_H + Q_V + Q_F

<table>
<thead>
<tr>
<th>Heat</th>
<th>Formula</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolution</td>
<td>( Q_R = f(m_1, m_2, H_{abs}) )</td>
<td>DRC</td>
</tr>
<tr>
<td>Sensible</td>
<td>( Q_H = \left( \int_{T_1}^{T_2} C_{pS} dT + \int_{T_1}^{T_F} C_{pL} dT \right) \cdot \frac{W_{sol}}{W_{CO₂}} )</td>
<td>DRC, VLE</td>
</tr>
<tr>
<td>Vaporization</td>
<td>( Q_V = H_V \cdot \frac{W_{V}}{W_{CO₂}} )</td>
<td>VLE</td>
</tr>
<tr>
<td>Fusion</td>
<td>( Q_F = f(m_F, H_F) )</td>
<td>DRC, TG-DSC</td>
</tr>
</tbody>
</table>

*RITE, COURSE50 NEDO Project report (2006)
Measurement of heat of fusion

Heat of CO₂ absorption by DRC

Mass flow controllers
Buffer tank
Gas collection
Stirrer
DC Power
TCs
Syringe
Gas
Ball filter
Heater
High-response temperature measurement
DC Power
PC
TG-DSC

Precipitation +25~30kJ/mol
AMP 25wt% (Kim, 2011)
AMP 30wt%
AMP 50wt%

CO₂ loading α (mol-CO₂/mol-amine)

Heat flow (w/g)

Temperature °C (5°C/min.)

Relative weight %

CO₂ N₂
Stirrer
DC Power
TCs
Dummy heater
Buffer tank
Mass flow controllers

6mg crystal on a open Al-pan
Melting point peak=224 J/g

TG-DSC
α=0.00
α=0.51

R1 R2
Thermostatic controller
Operating condition of stripper

CO$_2$ rich liquid (derived from separated solid) kept a low CO$_2$ loading (0.15) at 110°C

✓ Lower $T_2 \rightarrow Q_H = \left( \int_{T_1}^{T_F} C_p S \, dT + \int_{T_F}^{T_2} C_p L \, dT \right) \cdot W_{sol}/W_{CO_2}$ decrease
✓ Higher $P_T \rightarrow Q_V = H_V \cdot W_V/W_{CO_2}$ decrease

Operating condition of stripper for CO$_2$ rich liquid (Solid with 45% moisture):
Reboiler temperature $T_2 =$110°C  Total pressure $P_T =$300kPa(abs.)
Result: regeneration energy estimation

<table>
<thead>
<tr>
<th>0.0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
<th>4.5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Regeneration energy (GJ/t-CO2)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEA 30wt%</td>
<td>AMP 30wt%</td>
<td>AMP 50wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.10</td>
<td>3.68</td>
<td>3.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MEA 30wt%</th>
<th>AMP 30wt%</th>
<th>AMP 50wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>4.91</td>
<td>3.37</td>
<td>6.17*</td>
</tr>
<tr>
<td>$P_T$ (kPa)</td>
<td>200</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>$T_2$ (°C)</td>
<td>120</td>
<td>120</td>
<td>110</td>
</tr>
<tr>
<td>$P_{H2O_2}$ (kPa)</td>
<td>198.5</td>
<td>198.5</td>
<td>143.3</td>
</tr>
<tr>
<td>$P_{CO2_2}$ (kPa)</td>
<td>1.5</td>
<td>1.5</td>
<td>156.7</td>
</tr>
<tr>
<td>$m_1$ mol-CO$_2$/mol-amine</td>
<td>0.52</td>
<td>0.6</td>
<td>0.65</td>
</tr>
<tr>
<td>$m_2$ amine</td>
<td>0.2</td>
<td>0.02</td>
<td>0.15</td>
</tr>
<tr>
<td>$H_R$ (kJ/mol-CO$_2$)</td>
<td>85</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>$H_v$ (kJ/kg)</td>
<td>2202</td>
<td>2202</td>
<td>2230</td>
</tr>
<tr>
<td>$C_p$ (kJ/kgK)</td>
<td>3.60</td>
<td>3.75</td>
<td>3.50</td>
</tr>
<tr>
<td>$\rho$ (kg/L)</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>$W_{CO2}/W_{sol}$ kg-CO$_2$/kg-amine</td>
<td>64.0</td>
<td>81.8</td>
<td>128.1</td>
</tr>
<tr>
<td>$W_v/W_{CO2}$ kg-H$_2$O/kg-CO$_2$</td>
<td>0.22</td>
<td>0.22</td>
<td>0.12</td>
</tr>
<tr>
<td>$Q_R$</td>
<td>1.93</td>
<td>1.82</td>
<td>1.82</td>
</tr>
<tr>
<td>$Q_H$</td>
<td>1.69</td>
<td>1.38</td>
<td>0.55</td>
</tr>
<tr>
<td>$Q_V$ GJ/t-CO$_2$</td>
<td>0.49</td>
<td>0.49</td>
<td>0.28</td>
</tr>
<tr>
<td>$Q_F$</td>
<td>(0.00)</td>
<td>(0.00)</td>
<td>0.57</td>
</tr>
<tr>
<td>$Q_{total}$</td>
<td>4.10</td>
<td>3.68</td>
<td>3.21</td>
</tr>
</tbody>
</table>

\[ Q_{total} = Q_R + Q_H + Q_V + Q_F \]

*Value of solid paste derived from 50% AMP
Conclusions

We proposed a precipitating 2-Amino-2-methyl-1-propanol (AMP) carbonate solvent process for CO₂ capture and estimated its regeneration energy by the equilibrium-based method using properties obtained by VLE and calorimetry.

- At 40°C and 10kPa CO₂, 50 wt% AMP precipitated in CO₂ loadings of more than 0.22 and equilibrium CO₂ loading of slurry was 0.56.
- Chemical structure of the crystal was identified as a salt of protonated AMP and carbonate by Raman spectroscopy.
- The precipitate solid obtained by simple suction filtration contained 35% moisture and 72% of absorbed CO₂.
- The precipitate solid completely melted at 70°C and was regenerated down to a CO₂ loading of 0.05 at 120°C and 100kPa CO₂.
- The regeneration energy using the precipitating AMP carbonate solvent process was estimated at 3.21 GJ/t-CO₂, and 18% of which requires only 70°C.