Ternary phase diagrams and experimental investigation of the particle formation kinetics for the CO$_2$-NH$_3$-H$_2$O system

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Motivation: The Chilled Ammonia Process (CAP)

- **Aqueous ammonia** as solvent
  - ✔ globally available, low cost
  - ✔ no toxic degradation products
  - ✔ highly competitive energy penalty

![Diagram of the Chilled Ammonia Process (CAP)]
Motivation: The Chilled Ammonia Process (CAP)

- **Aqueous ammonia** as solvent
  - globally available, low cost
  - no toxic degradation products
  - highly competitive energy penalty
Strategic project objectives

Study the formation of solids in the CO$_2$-NH$_3$-H$_2$O system in order to

a) enable high CO$_2$ concentrations while avoiding solid formation in the absorber in the current CAP
Strategic project objectives

Study the formation of solids in the CO$_2$-NH$_3$-H$_2$O system in order to

a) enable high CO$_2$ concentrations while **avoiding solid formation** in the absorber in the current CAP

b) **integrate solid formation** into a next generation CAP
Outline

- Thermodynamics
  - The system CO$_2$-NH$_3$-H$_2$O
  - Ternary phase diagrams
- Experimental
  - Methodology
  - Identification of solids by Raman
- Process simulations
  - Process model
  - Comparison of standard CAP & crystallizer-CAP
Thermodynamics of the CO$_2$-NH$_3$-H$_2$O system

\[
\begin{align*}
\text{Vapor} \\
\text{Aqueous} \\
\text{Solid}
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2 & \quad \text{H}_2\text{O} & \quad \text{NH}_3 \\
\downarrow & \quad \downarrow & \quad \downarrow \\
\text{CO}_2 & \quad \text{H}_2\text{O} & \quad \text{NH}_3 \\
\leftrightarrow & \quad \leftrightarrow & \quad \leftrightarrow \\
\text{CO}_2 + \text{H}_2\text{O} & \quad \Leftrightarrow \quad \text{HCO}_3^- + \text{H}^+ \\
\text{HCO}_3^- & \quad \Leftrightarrow \quad \text{CO}_3^{2-} + \text{H}^+ \\
\text{NH}_3 + \text{H}^+ & \quad \Leftrightarrow \quad \text{NH}_4^+ \\
\text{NH}_3 + \text{HCO}_3^- & \quad \Leftrightarrow \quad \text{NH}_2\text{COO}^- + \text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{NH}_4\text{HCO}_3 & \quad (\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O} \\
(\text{NH}_4)_2\text{CO}_3 \cdot 2\text{NH}_4\text{HCO}_3 & \quad \text{NH}_2\text{COONH}_4
\end{align*}
\]
Thermodynamics of the CO₂-NH₃-H₂O system

Vapor

\[ \begin{align*}
\text{CO}_2 & \quad \text{H}_2\text{O} & \quad \text{NH}_3 \\
\Downarrow & \quad \Downarrow & \quad \Downarrow \\
\text{CO}_2 & \quad \text{H}_2\text{O} & \quad \text{NH}_3
\end{align*} \]

Aqueous

\[ \begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \\
\text{HCO}_3^- & \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \\
\text{NH}_3 + \text{H}^+ & \rightleftharpoons \text{NH}_4^+ \\
\text{NH}_3 + \text{HCO}_3^- & \rightleftharpoons \text{NH}_2\text{COO}^- + \text{H}_2\text{O}
\end{align*} \]

Solid

\[ \begin{align*}
\text{NH}_4\text{HCO}_3 & \quad (\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O} \\
(\text{NH}_4)_2\text{CO}_3 \cdot 2\text{NH}_4\text{HCO}_3 & \quad \text{NH}_2\text{COONH}_4
\end{align*} \]

SRK - EOS for gas phase fugacities

VLE

Extended UNIQUAC for activities

SLE

Pure solids, activity = 1

Thermodynamic model: Darde et al., Ind Eng Chem Res 49 (2010) 12663-74
Solid properties: Jänecke, Z Elektrochem 35 (1929) 9:716-28
Ternary phase diagram

BC: ammonium bicarbonate
NH₄HCO₃

SC: ammonium sesqui-carbonate
(NH₄)₂CO₃ • 2NH₄HCO₃

CB: ammonium carbonate
(NH₄)₂CO₃ • H₂O

CM: ammonium carbamate
NH₂COONH₄

10°C, 1 bar
Ternary phase diagram – Stoichiometry

\[
(NH_4)_2CO_3 \cdot H_2O \leftrightarrow NH_2COONH_4 + 2H_2O
\]

10°C, 1 bar
Ternary phase diagram – Stoichiometry

BC: ammonium bicarbonate

SC: ammonium sesqui-carbonate

CB: ammonium carbonate

CM: ammonium carbamate

<table>
<thead>
<tr>
<th>Solid</th>
<th>Molar ratio CO₂/NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bicarbonate</td>
<td>1/1</td>
</tr>
<tr>
<td>Sesqui-carbonate</td>
<td>3/4</td>
</tr>
<tr>
<td>Carbonate</td>
<td>1/2</td>
</tr>
<tr>
<td>Carbamate</td>
<td>1/2</td>
</tr>
</tbody>
</table>

10°C, 1 bar
Ternary phase diagram – Stoichiometry

BC: ammonium bicarbonate
\( \text{NH}_4\text{HCO}_3 \)

SC: ammonium sesqui-carbonate
\((\text{NH}_4)_2\text{CO}_3 \cdot 2\text{NH}_4\text{HCO}_3\)

CB: ammonium carbonate
\((\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}\)

CM: ammonium carbamate
\(\text{NH}_2\text{COONH}_4\)

\((\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow 2\text{NH}_4\text{HCO}_3\)

\(10^\circ \text{C, 1 bar}\)
Ternary phase diagram – Stoichiometry

<table>
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<tr>
<th>Solid</th>
<th>Molar ratio CO₂/NH₃</th>
<th>Mass fraction of CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bicarbonate</td>
<td>1/1</td>
<td>0.55</td>
</tr>
<tr>
<td>Sesqui-carbonate</td>
<td>3/4</td>
<td>0.52</td>
</tr>
<tr>
<td>Carbonate</td>
<td>1/2</td>
<td>0.39</td>
</tr>
</tbody>
</table>

10°C, 1 bar
Ternary phase diagram applied to the CAP

- BC: ammonium bicarbonate \( \text{NH}_4\text{HCO}_3 \)
- SC: ammonium sesqui-carbonate \( (\text{NH}_4)_2\text{CO}_3 \cdot 2\text{NH}_4\text{HCO}_3 \)
- CB: ammonium carbonate \( (\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O} \)
- CM: ammonium carbamate \( \text{NH}_2\text{COONH}_4 \)

The diagram illustrates the ternary phase behavior at 1 bar, with the vertices representing pure components and the phases at various compositions and temperatures.
Ternary phase diagram applied to the CAP

BC: ammonium bicarbonate \(\text{NH}_4\text{HCO}_3\)

SC: ammonium sesqui-carbonate \((\text{NH}_4\text{)}_2\text{CO}_3 \cdot 2\text{NH}_4\text{HCO}_3\)

CB: ammonium carbonate \((\text{NH}_4\text{)}_2\text{CO}_3 \cdot \text{H}_2\text{O}\)

CM: ammonium carbamate \(\text{NH}_2\text{COONH}_4\)

\(\text{CO}_2\) \(\text{NH}_3\) \(\text{H}_2\text{O}\)

Temperature and composition diagram with different regions indicating stability of compounds at 1 bar.

Diagram includes phase boundaries and composition points for different temperatures (10°C, 20°C, 30°C, 40°C).
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Experimental investigation of crystallization kinetics

Setup
- closed batch system
- minimized gas volume
- ATR-FTIR for concentration
- FBRM to detect nucleation
- Raman for identification of solids
Cooling crystallization experiments
Experimental – Metastable zone width

[2] Veiga et al., 14th International Symposium on Industrial Crystallization (ISIC) 1999
Outline

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- Process simulations
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Process simulations

- A) Standard CAP (solid-free)

Black et al. (2013), US 2013/0028807 A1
Process simulations

- B) Crystallizer-CAP

Black et al. (2013), US 2013/0028807 A1
Process simulations – Methods

- Implementation of Extended UNIQUAC model in Aspen Plus \([1,2]\)
- Absorber
  - Radfrac
  - 30/50 stages
- Desorber
  - Radfrac
  - 10 equilibrium stages
  - 10 bar
- Crystallizer
  - CSTR
  - equilibrium-based
- benchmarked against simulations published by Thomsen group \([1,2]\)

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Same specifications for both processes

Absorber
- Flue gas inlet conditions
- Lean stream conditions
- CO₂ capture rate (~90%)
- NH₃ slip before ammonia recovery

Desorber
- Pressure
- Vapor fraction of feed
- CO₂ purity

General parameters
- ΔT for heat exchange (3°C)
- Utilities:
  - cooling water at 15°C,
  - chilling water at 2°C
Simulation results - Comparison

Stream to regeneration

Solid density (wt.-%)  
14%

CO₂ loading (mol CO₂/mol NH₃)  
+ 27%

Mass flow (kg/s)  
- 40%
Simulation results - Comparison

Stream to regeneration

- Solid density (wt.-%): 14%
- CO₂ loading (mol CO₂/mol NH₃): +27%
- Mass flow (kg/s): -40%

Energy penalty «key players»

- Pump power (MWₑᵢ): -49%
Simulation results - Comparison

**Stream to regeneration**
- Solid density (wt.-%) 14%
- CO₂ loading (mol CO₂/mol NH₃) + 27%
- Mass flow (kg/s) - 40%

**Energy penalty «key players»**
- Pump power (MWₑ) - 49%
- Reboiler duty (MWₜₜ) - 20%
Simulation results - Comparison

Stream to regeneration

- **Solid density (wt.-%)**: 14%
- **CO₂ loading (mol CO₂/mol NH₃)**: +27%
- **Mass flow (kg/s)**: -40%

Energy penalty «key players»

- **Pump power (MWₑ)**: -49%
- **Reboiler duty (MWₜₑ)**: -20%
- **Chilling duty (MWₜₑ)**: +200%
Comparison on the basis of electric energy

Pump power 
(MW$_{el}$) $\rightarrow$ Pump efficiency 
$\eta_P = 0.75$ $\rightarrow$ $\dot{W}_{el} = \frac{\dot{W}_{el}^{ideal}}{0.75}$
Comparison on the basis of electric energy

Pump power
\( (\text{MW}_{el}) \) \quad \rightarrow \quad \text{Pump efficiency} \quad \eta_p = 0.75 \quad \rightarrow \quad \dot{W}_{el} = \frac{\dot{W}_{el}^{\text{ideal}}}{0.75}

Reboiler duty
\( (\text{MW}_{th}) \)

\( \Delta P_{Gen} \) due to steam bleeding

European Benchmarking Task Force (2011) CAESAR Project, No. 213206
Comparison on the basis of electric energy
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\( (\text{MW}_{el}) \)

Pump efficiency
\( \eta_p = 0.75 \)

\( \dot{W}_{el} = \frac{\dot{W}_{el}^\text{ideal}}{0.75} \)

Reboiler duty
\( (\text{MW}_{\text{th}}) \)

\( \Delta P_{\text{Gen}} \) due to steam bleeding

\( \dot{W}_{el} = P_{\text{Gen}}^0 - P_{\text{Gen}}^w/\text{bleed} \)

Chilling duty
\( (\text{MW}_{\text{th}}) \)

Coefficient of performance (COP)
\[
\text{COP}_{\text{ideal}} = \frac{T_c}{T_h - T_c} = \frac{275 \text{ K}}{(298 - 275) \text{ K}} = 12.0
\]

\[
\text{COP} = 0.6 \times \text{COP}_{\text{ideal}} = 7.2
\]

European Benchmarking Task Force (2011) CAESAR Project, No. 213206
Comparison on the basis of electric energy

Equivalent electric penalty for "key players" (%)

Standard CAP

- Pump: 10%
- Reboiler: 81%
- Chilling: 9%
Comparison based on energy penalty

Equivalent electric penalty for "key players" (%)

Standard CAP
- Pump: 10%
- Reboiler: 81%
- Chilling: 9%

Crystallizer CAP
- Pump: 6%
- Reboiler: 67%
- Chilling: 27%
Comparison based on energy penalty

- Both processes not fully optimized
- Potential for heat integration for solid-mode
Conclusions

- Ternary phase diagrams as a tool for the design of a solid-mode CAP

- Experimental investigation of solid formation in the CO$_2$-NH$_3$-H$_2$O system
  - Setup and analytical concept
  - On-line identification of solids by RAMAN

- Process simulation of solid-mode CAP
  - Significant reduction of the reboiler duty (approx. 20%)
  - Slight reduction of overall energy penalty (based on «key players»)
  - Potential for further reduction with heat integration
  - Increase of complexity and CAPEX for absorption section (low pressure)
  - Decrease of size and CAPEX for regeneration section (high pressure)