Modeling Ammonia Absorption of CO\textsubscript{2}

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Modeling CO₂ Absorption with Ammonia

- Basis for Process and Model
- Types of OLI Models Used
- Results
- Conclusions
Basis for Process and Model

• Process Basis
  ▪ Stable solvent
  ▪ Non-foaming solvent
  ▪ High loading capacity solvent
  ▪ High solvent regeneration pressure
  ▪ Low CO2 compression energy
  ▪ Unique gas-liquid contacting device

• Model Basis
  ▪ Ammonia chemistry complex
  ▪ Products unstable
  ▪ Difficult to prepare standard solutions
Absorption & Regeneration

Routes

**Minor route:** Ammonium carbonate

\[
2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2 \quad \leftrightarrow \quad (\text{NH}_4)_2\text{CO}_3
\]

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

**Major route:** Ammonium carbamate

\[
2\text{NH}_3 + \text{CO}_2 \quad \leftrightarrow \quad (\text{NH}_3)_2\text{CO}_2
\]

\[
(\text{NH}_3)_2\text{CO}_2 + 2\text{H}_2\text{O} + \text{CO}_2 \quad \leftrightarrow \quad 2\text{NH}_4\text{HCO}_3
\]
Models Used

• Bench Scale Stirred Tank Reactor
  • DynaChem: Gas and liquid phase composition

• Analyzers Calibration – Chemical species
  • Stream Analyzer
  • DynaChem

• Equilibrium Model – Pressure versus Temperature
  • Stream Analyzer

• Steady State Commercial Process Modeling
  • ESP
  • OLIPRO
Stirred Tank Reactor

- Split-ring assembly
- Heating jacket
- Guide rail for heater
- Fixed head
- Reactor vessel
- Pneumatic lift
Stirred Tank Reactor
Stirred Tank Reactor Dynamic Model

Unit 1
Raw Gas

Absorber
Unit 2

Treated Gas

V3

CL3

TC

Cooler

Unit 3

Rich Solvent

V4

V7

Regenerator
Unit 4

Unit 6

Unit 5

Heater

Condensate

CO2

1

2

3

4

5

6

7

8

9

10

11

12

13

Solvent

Gas

Thermal Energy

Electrical Signal
Measured versus Predicted CO$_2$ Capture Efficiencies and $R$ values

![Graph showing measured versus predicted CO$_2$ capture efficiencies and $R$ values.](image)

- **Axes:**
  - X-axis: Time, mins

- **Lines:**
  - Model Eff.
  - Exp Eff
  - Model $R$
  - Exp $R$
  - NH4HCO3PPT

- **Annotations:**
  - R and ABC Crystals, wt%

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This graph illustrates the comparison between measured and predicted CO$_2$ capture efficiencies and $R$ values over time, with markers for different substances and conditions.
Measured versus Predicted Ammonia Slip
Liquor Composition Predicted by OLI Model

Molar Ratio, R, (NH$_3$/CO$_2$)

Chemical Species, g mols
- Aqueous ammonia
- Bicarbonate ions
- Ammonium ions
- Carbamate ions
- ABC crystals

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Nuclear Magnetic Resonance Analysis

- **Left-hand peak allows direct determination of ammonium carbamate.**
- **Right-hand peak determines combination of ammonium carbonate and bicarbonate.**
- **Greater the horizontal separation of peaks the greater the bicarbonate content.**

Frequency shift
Measured vs. Predicted Ammonium Carbamate

\[ y = 0.988x \]

\[ R^2 = 0.9947 \]
Measured vs. Predicted Ammonium Carbonate

\[ y = 1.7339x \]

\[ R^2 = 0.9911 \]
Measured versus Predicted Ammonium Bicarbonate

\[ y = 0.9622x \]

\[ R^2 = 0.9906 \]
Comparing NMR Data and OLI Model

Comparison of NMR Data and OLI Model

- OLI Model Prediction, Wt% vs. NMR Measurement, Wt %
- Different compounds (Bicarbonate, Carbonate, Carbamate) indicated by different markers
- Perfect Agreement line drawn for reference
Raman Spectra Basics

- Raman spectroscopy uses vibrational and rotational energy to identify and quantify molecules.
- Peak wave numbers identify the compound.
- Intensity of the energy or the peak heights determine the concentration of the compound.
Raman Spectral Correlation to Carbamate

Correlation ($R^2$) = 0.9777

5 Factors
Raman Spectral Correlation to Bicarbonate

Correlation ($R^2$) = 0.985
5 Factors
Equilibrium Pressure vs. Temperature
ESP Model for CO2 Capture with Ammonia

- **LS** = Lean Solvent
- **RS** = Rich Solvent
- **SV** = Syngas Vapor
- **SC** = Syngas Cool

**NH3 Valve**
- NH3
- A-NH3
- NH3 CNTL

**MIX 104**
- MIX 102
- RS1
- RS2
- E-102

**RSH**
- RS3
- RS4

**V-100**
- Rich Solvent 6

**Lean Cooler**
- LRH

**LRH**
- Lean Rich Heat Exchanger

**Lean Solvent**
- Lean Solvent

**RCGH**
- Raw Syngas
- Clean Syngas H

**Raw SC**
- Clean Syngas M

**E-6**
- Condensate 1

**Regen**
- Final Acid Gas

**FSPLIT**
- FSPLIT = Flow Splitter

**V-102**
- Clean Syngas 3

**Clean Syngas 2**

**Clean Syngas 1**

**Clean Syngas**

**C+4 CNTL**

**A-NH3**

**A-H2O**

**H2O Valve**

**Lean Rich Heat Exchanger (LRH)**

**H2O CNTL**

**Lean Solvent (LS)**

**Rich Solvent (RS)**

**Syngas Vapor (SV)**

**Syngas Cool (SC)**

**Raw & Clean Gas Heat Exchanger (RCGH)**

**Clean Syngas Mix (CSM)**

**Clean Syngas (CS)**

**Raw Syngas (RS)**

**Rich Solvent Heat Exchanger (RSH)**
Conclusion

• Using a bench scale stirred tank reactor we successfully validated the OLI Mixed Solvent Electrolyte (MSE) data and established that the reaction between $\text{CO}_2$ and ammonia is equilibrium controlled.

• MSE and ESP will be used to model and establish the economic viability of the steady state commercial process for $\text{CO}_2$ capture with ammonia.