Thermodynamic Modeling of MEA-based CO2 Capture Process with Uncertainty Quantification and Validation with Steady-State Data from a Pilot Plant

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AIChE Annual Meeting 2015
CCSI | For Accelerating Technology Development

Rapidly synthesize optimized processes to identify promising concepts

Better understand internal behavior to reduce time for troubleshooting

Quantify sources and effects of uncertainty to guide testing & reach larger scales faster

Stabilize the cost during commercial deployment

National Labs

Academia

Carnegie Mellon

PRINCETON UNIVERSITY

West Virginia University

Boston University

The University of Texas at Austin

Industry

ADA

ALSTOM

B&W

GE

SOUTHERN COMPANY

FLUOR

PHILLIPS 66

AMERICAN ELECTRIC POWER

ExxonMobil

AIR PRODUCTS

EASTMAN

aspentech

ANSYS

Schneider Electric

PSE

U.S. DEPARTMENT OF ENERGY
Outline

• Scope of Work
• Submodel Development
  – Thermodynamic and kinetic models
  – Mass transfer and hydraulic models
• Model Validation
• Conclusions
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Gold Standard Solvent Model

• Gold Standard model for comparing different proposals for advanced solvent-based capture technologies
  – Open source
  – Validated framework
  – Well documented
  – Uncertainties quantified
• Aqueous monoethanolamine (MEA) used as baseline
  – Industry standard
  – Extensive amount of data available
• Applicability to novel solvents
Deficiencies in Existing Absorber Models

ProTreat-Optimized Gas Treating, Inc.; CO2SIM-NTNU/SINTEF
CHEMASIM-BASF SE; AspenRatesep-modified by IFP

Luo et al., “Comparison and validation of simulation codes against sixteen sets of data from four different pilot plants”, Energy Procedia, 1249-1256, 2009

Deficiencies in Existing Regenerator Models

Luo et al., “Comparison and validation of simulation codes against sixteen sets of data from four different pilot plants”, Energy Procedia, 1249-1256, 2009
How to Develop Gold Standard Model

- Property models
  - Valid for absorber and stripper operating conditions
- Hydraulic and mass transfer models
  - Developed simultaneously with relevant properties models using both WWC and packing data
- Uncertainty quantification
- Steady State Validation
- Dynamic Validation*

* Anderson Soares Chinen
  687g Dynamic Model Development and Validation of a MEA-Based CO₂ Capture System
  11/9/2015
  2:36 p.m.
  Salon D (Marriott)
Overall Approach

- Properties Models
- Process Models
- Kinetic Models
- Process Simulation
- % CO₂ Capture
- Energy Requirement
- Other Key Variables
Stochastic Modeling Methodology

Sample from Prior Parameter Distribution
\[ \theta = \theta_j \quad (j = 1,2, \ldots, N) \]

Predictor Variables (M Observations)
\[ x = x_i \quad (i = 1,2, \ldots, M) \]

Mathematical Model (M \times N observations)
\[ \varphi_{ij} = F(x_i, \theta_j) \]
\[ (i = 1,2, \ldots, M; j = 1,2, \ldots, N) \]

Response Surface Model
\[ \varphi \sim F^*(x, \theta) \]

Bayesian Inference
\[ \pi(\theta | Z) \propto P(\theta) L(Z | \theta) \]

Posterior Parameter Distributions
\[ \theta^* \]

Experimental Data with Uncertainty
\[ Z = \{Z_i(x_i), i = 1,2, \ldots, M\} \]
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Reactive System Thermodynamic Framework

**Vapor-Liquid Equilibrium**

\[ \hat{f}_i^V = \hat{f}_i^L \rightarrow \hat{\phi}_i y_i P = \gamma_i^* x_i H_i \] (for solutes)

**Activity Coefficient**

\[ \ln(\gamma_i) = \left. \frac{1}{RT} \frac{\partial(nG^e)}{\partial n_i} \right|_{T,P,n_{j \neq i}} \]

\[ \gamma_i^* = \lim_{x_i \to 0} \gamma_i \]

**Reaction Equilibrium Constant**

\[ \Delta G_{rxn} = -RT\ln(K) \]

**Enthalpy Equations**

**Excess Enthalpy**

\[ H^e = -RT^2 \sum x_i \left( \frac{\partial \ln \gamma_i}{\partial T} \right) \]

**Heat Capacity**

\[ H_m^l(T + \Delta T) - H_m^l(T) = \int_T^{T+\Delta T} C_p,m^l dT \]

**Heat of Absorption**

\[ \Delta H_{abs} = \frac{n_{final} H_{final} - n_{initial} H_{initial} - n_{CO_2} H_{CO_2}}{n_{CO_2}} \]
MEA System Reaction Kinetics

Reaction 1
2MEA + CO₂ ⇌ MEA⁺ + MEACOO⁻

\[ r_1^f = 8.5616 \times 10^{10} \exp \left( - \frac{3963.9}{8.314} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) a_{\text{MEA}}^2 a_{\text{CO₂}} \]

\[ r_1^r = 24800 \exp \left( - \frac{59600}{8.314} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) a_{\text{MEACOO}^-} a_{\text{MEA}^+} \]

Reaction 2
MEA + H₂O + CO₂ ⇌ MEA⁺ + HCO₃⁻

\[ r_2^f = 22991.13 \exp \left( - \frac{49000}{8.314} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) a_{\text{MEA}} a_{\text{CO₂}} \]

\[ r_2^r = 18.35 \exp \left( - \frac{96230}{8.314} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right) \frac{a_{\text{HCO₃}^-} a_{\text{MEA}^+}}{a_{\text{H₂O}}} \]

**MEA System Reaction Kinetics - New**

**Reaction 1**

\[ 2\text{MEA} + \text{CO}_2 \leftrightarrow \text{MEA}^+ + \text{MEACOO}^- \]

**Reaction 2**

\[ \text{MEA} + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{MEA}^+ + \text{HCO}_3^- \]

\[
r_1 = 8.5616 \times 10^{10} \exp\left(-\frac{3963.9}{8.314} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right) a_{\text{MEA}}^2 a_{\text{CO}_2} \left(1 - \frac{a_{\text{MEA}} a_{\text{MEACOO}^-}}{K_1 a_{\text{MEA}}^2 a_{\text{CO}_2}}\right)
\]

\[
r_2 = 22991.13 \exp\left(-\frac{49000}{8.314} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right) a_{\text{MEA}} a_{\text{CO}_2} \left(1 - \frac{a_{\text{MEA}} a_{\text{HCO}_3^-}}{K_2 a_{\text{MEA}} a_{\text{CO}_2} a_{\text{H}_2\text{O}}}\right)
\]

\[
K_1 = \frac{\gamma_{\text{MEA}}^+ x_{\text{MEA}}^+ \gamma_{\text{MEACOO}^-} x_{\text{MEACOO}^-}}{(\gamma_{\text{MEA}}^* x_{\text{MEA}})^2 \gamma_{\text{CO}_2}^* x_{\text{CO}_2}}_{\text{eq}}
\]

\[
K_2 = \frac{\gamma_{\text{MEA}}^+ x_{\text{MEA}}^+ \gamma_{\text{HCO}_3^-} x_{\text{HCO}_3^-}}{\gamma_{\text{MEA}}^* x_{\text{MEA}}^* \gamma_{\text{CO}_2}^* x_{\text{CO}_2} \gamma_{\text{H}_2\text{O}}^* x_{\text{H}_2\text{O}}}_{\text{eq}}
\]
## VLE Ternary Data

<table>
<thead>
<tr>
<th>Data Source</th>
<th>Number of Data</th>
<th>Temperature (°C)</th>
<th>CO₂ loading (mol CO₂/mol MEA)</th>
<th>MEA weight percent</th>
<th>CO₂ partial pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aronu et al.</td>
<td>138</td>
<td>40-80</td>
<td>0.017-0.565</td>
<td>15-60</td>
<td>0.007-19</td>
</tr>
<tr>
<td>Hilliard</td>
<td>55</td>
<td>40-60</td>
<td>0.114-0.591</td>
<td>17-40</td>
<td>0.005-50</td>
</tr>
<tr>
<td>Jou et al.</td>
<td>46</td>
<td>25-120</td>
<td>0.003-0.589</td>
<td>30</td>
<td>0.0015-822</td>
</tr>
<tr>
<td>Dugas</td>
<td>50</td>
<td>40-100</td>
<td>0.231-0.500</td>
<td>30-45</td>
<td>0.01-29</td>
</tr>
<tr>
<td>Lee et al.</td>
<td>155</td>
<td>25-120</td>
<td>0.065-0.600</td>
<td>6.5-32</td>
<td>0.1-1000</td>
</tr>
<tr>
<td>Xu</td>
<td>36</td>
<td>100-130</td>
<td>0.313-0.520</td>
<td>30</td>
<td>12-1000</td>
</tr>
<tr>
<td>Ma’mun et al.</td>
<td>19</td>
<td>120</td>
<td>0.155-0.418</td>
<td>30</td>
<td>7-192</td>
</tr>
</tbody>
</table>

Aronu et al., Chem Eng Sci, 2011;66:6393-6406

Hilliard MD, Ph.D. Dissertation, UT Austin, 2008

Jou et al., Can J Chem Eng, 1995;73:140-147

Dugas RE, Ph.D. Dissertation, UT Austin, 2009

Lee et al., J Appl Chem Biotechn, 1976;26:541-549

Xu Q, Ph.D. Dissertation, UT Austin, 2011

Ma’mun et al., J Chem Eng Data, 2005;50:630-634
Ternary VLE Model Fit (30 wt%)
Binary VLE Model Fit

Txy Diagrams (data from Cai et al.)

P = 101.33 kPa

P = 66.66 kPa

Pxy Diagrams (data from Tochigi et al.)

T = 363.15 kPa

Cai et al., J Chem Eng Data, 1996; 41: 1101-1103
Tochigi et al., J Chem Eng Data, 1999; 44: 588-590
Heat of Absorption Comparison

Data from: Kim et al., Energy Procedia, 2014; 63: 1446-1455
VLE Model Uncertainty Quantification

CO₂ Partial Pressure for 80°C and 30 wt% MEA

Prior Distribution

Posterior Distribution

Sample of 5000 drawn from each distribution

* Model

* Data
Outline

• Scope of Work
• **Submodel Development**
  – Thermodynamic and kinetic models
  – Mass transfer and hydraulic models
• Model Validation
• Conclusions
Integrated Mass Transfer Model Development

Usual approach: Sequential regression

FOQUS capability: Simultaneous regression

FOQUS can run multiple simulations and optimize an unique model for mass transfer and interfacial area

Experimental data from: Tobiesen et al., AIChE Journal, 2007;53:846-865
Mass Transfer and Hydraulic Model Results

• Final model form for hydraulics and mass transfer:
  – Pressure drop: Billet and Schultes (1999)
  – Holdup: Tsai (2011)
  – Interfacial area: Tsai et al. (2012)

• Model parameters regressed for Mellapak Plus™ 252Y

![Pressure drop comparison (Pa/m)](image)

Experimental Data from: Tsai RE, Ph.D. Dissertation, UT Austin, 2010
Outline

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• Model Validation
• Conclusions
CCSI team conducted tests at NCCC
### NCCC vs Other Pilot Plants

<table>
<thead>
<tr>
<th>Source of Flue Gas</th>
<th>Absorber</th>
<th>Regenerator</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diameter (cm)</td>
<td>Height (m)</td>
</tr>
<tr>
<td>UT, Austin</td>
<td>42.7</td>
<td>6.1</td>
</tr>
<tr>
<td>NTNU/SINTEF</td>
<td>15.0</td>
<td>4.4</td>
</tr>
<tr>
<td>ITC, Regina</td>
<td>33.0</td>
<td>7.1</td>
</tr>
<tr>
<td>ITT, Stuttgart</td>
<td>12.5</td>
<td>4.2</td>
</tr>
<tr>
<td>Esbjerg CASTOR</td>
<td>110.0</td>
<td>17.0</td>
</tr>
<tr>
<td>NCCC (PSTU)</td>
<td>64.1</td>
<td>18.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CO₂ Capacity (tpd)</th>
<th>Source of Flue Gas</th>
<th>Diameter (cm)</th>
<th>Height (m)</th>
<th>Diameter (cm)</th>
<th>Height (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UT, Austin</td>
<td>Non-coal</td>
<td>42.7</td>
<td>6.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NTNU/SINTEF</td>
<td>Non-coal</td>
<td>15.0</td>
<td>4.4</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>7.1</td>
<td></td>
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<tr>
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<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Esbjerg CASTOR</td>
<td>Coal</td>
<td>110.0</td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCCC (PSTU)</td>
<td>Coal</td>
<td>64.1</td>
<td>18.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
NCCC Steady State Testing

- Runs selected from test matrix developed by CCSI team
- Total of 23 tests performed
- Range of variables/operating conditions

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorber Inlet Flue Gas Flow (kg/hr)</td>
<td>1320-2900</td>
</tr>
<tr>
<td>Lean Solvent Flowrate (kg/hr)</td>
<td>3175-11800</td>
</tr>
<tr>
<td>Absorber L/G ratio (molar)</td>
<td>1.7-10.4</td>
</tr>
<tr>
<td>Reboiler Duty (kW)</td>
<td>166-677</td>
</tr>
<tr>
<td>Lean Solvent Loading (mol CO₂/mol MEA)</td>
<td>0.045-0.287</td>
</tr>
<tr>
<td>Rich Solvent Loading (mol CO₂/mol MEA)</td>
<td>0.198-0.343</td>
</tr>
<tr>
<td>Inlet Flue Gas CO₂ Volume %</td>
<td>9-11</td>
</tr>
<tr>
<td>Number of Beds in Absorber</td>
<td>1-3</td>
</tr>
<tr>
<td>Presence of Intercooling in Absorber</td>
<td>Yes/No</td>
</tr>
</tbody>
</table>
Uncertainty of the Measurement Techniques

- **Dynamic Test Runs**: Gas Chromatography (GC) for Amine Concentration and Bench Equivalence Point (EQP) Base Titration (CO₂ Concentration)
- **Steady State Runs**: Online EQP Acid Titration (Amine Concentration) and Online EQP Base Titration (CO₂ Concentration)

- Analysis Techniques Repeatability Evaluation
- Analysis Techniques Uncertainty Evaluation

### Critical Model Parameters:

<table>
<thead>
<tr>
<th>Portion of Campaign</th>
<th>Dynamic</th>
<th>Steady State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine Concentration (wt% MEA Nominal)</td>
<td>4.9%</td>
<td>7.3%</td>
</tr>
<tr>
<td>CO₂ Loading (mol CO₂ / mol MEA)</td>
<td>7.4%</td>
<td>10.7%</td>
</tr>
</tbody>
</table>

![Bland-Altman Plot: Online CO₂ Concentration](image)
Steady State Absorber Validation

Percent Deviation Between Data and Model Values (Summary)

<table>
<thead>
<tr>
<th></th>
<th>Data CO₂ Capture-Liquid vs. Gas Discrepancy</th>
<th>CO₂ Capture-Gas Side</th>
<th>CO₂ Capture-Liquid Side</th>
<th>Rich Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>9.19</td>
<td>8.09</td>
<td>10.84</td>
<td>7.36</td>
</tr>
<tr>
<td>Average</td>
<td>3.62</td>
<td>2.69</td>
<td>3.97</td>
<td>2.69</td>
</tr>
</tbody>
</table>
Steady State Absorber Validation

No parameter tuned

Sample Temperature Profiles

Case K3

Relative column positions of 0 and 1 correspond to top and bottom of column, respectively

<table>
<thead>
<tr>
<th>Case</th>
<th>L/G (mass)</th>
<th>Beds/Intercooling</th>
<th>Lean Loading (mol CO₂/mol MEA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K3</td>
<td>1.41</td>
<td>3/Yes</td>
<td>0.091</td>
</tr>
<tr>
<td>K6</td>
<td>3.02</td>
<td>3/Yes</td>
<td>0.347</td>
</tr>
<tr>
<td>K20</td>
<td>2.38</td>
<td>1/No</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Case K6

Case K20
Steady State Regenerator Validation

Lean Loading Comparison

Lean Solvent Temperature Comparison

Percent Deviation Between Data and Model Values (Summary)

<table>
<thead>
<tr>
<th></th>
<th>Lean Loading</th>
<th>Lean Solvent Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>16.53</td>
<td>1.14</td>
</tr>
<tr>
<td>Average</td>
<td>6.39</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Steady State Regenerator Validation

No parameter tuned

Sample Temperature Profiles

Case K1

Case K9

Case K10

<table>
<thead>
<tr>
<th>Case</th>
<th>Rich Solvent Flow (kg/hr)</th>
<th>Reboiler Duty (kW)</th>
<th>Rich Loading (mol CO$_2$/mol MEA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>7242</td>
<td>430.61</td>
<td>0.384</td>
</tr>
<tr>
<td>K9</td>
<td>3337</td>
<td>165.74</td>
<td>0.474</td>
</tr>
<tr>
<td>K10</td>
<td>3358</td>
<td>670.62</td>
<td>0.477</td>
</tr>
</tbody>
</table>
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Conclusions

• Developed complete process model of MEA carbon capture system
  – Includes consistent thermodynamic framework
• Model adequately predicts performance of NCCC absorber and stripper
  – Model parameters not adjusted to improve fit of model to plant data
• Future work
  – Complete uncertainty quantification of full process model
  – Apply methodology to novel solvent systems
Acknowledgements

This research was conducted through the Carbon Capture Simulation Initiative (CCSI), funded through the U.S. DOE Office of Fossil Energy.

A portion of this work was conducted as part of the National Energy Technology Laboratory’s Regional University Alliance (NETL-RUA), a collaborative initiative of the NETL; this technical effort was performed under the RES contract DE-FE0004000.

The authors would like to thank Prof. Gary T. Rochelle from The University of Texas at Austin for sharing the Phoenix model. The authors sincerely acknowledge valuable discussions with Prof. Rochelle and Brent Sherman from The University of Texas at Austin

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