Uncertainty Quantification of Properties Models for an MEA System

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For Accelerating Technology Development

Identify promising concepts → Reduce the time for design & troubleshooting → Quantify the technical risk, to enable reaching larger scales, earlier → Stabilize the cost during commercial deployment

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Presentation Outline

• Research Objectives and Motivation
• Physical Property Model Development
  – Model choice
  – Deterministic modeling
  – Parameter screening
  – Stochastic modeling
• Results
  – Viscosity Model
  – Density Model
  – Surface Tension Model
Research Objectives

• Development of an algorithm for determining physical property models for solvent-based carbon capture with uncertainty quantification (UQ) capability
  – Consider monoethanolamine (MEA) as baseline solvent
  – Use Phoenix Model (University of Texas-Austin) as a starting point

• Validation of models with plant scale data
Model Development Overview

• Identify models that give physical properties as functions of solution conditions (e.g. temperature and composition)
• Deterministic modeling: Calibrate model parameters to fit available experimental data (best fit optimization)
• Parameter screening: Surface response analysis and sensitivity analysis
• Stochastic modeling: Use Bayesian inference to represent model parameters as probability distribution functions
Model Identification

• Use Phoenix model developed by Dr. Rochelle’s group at UT Austin as starting point for model choice
• Started with simple/independent properties (viscosity, density, surface tension)
  – Necessary for design and evaluation of separation equipment (e.g. flooding and mass transfer correlations)
• Solution physical properties given as functions of temperature and composition only
  – Composition represented by two independent variables (generally CO$_2$ loading and MEA weight fraction/percent)
Solution Chemistry

• Represented as ternary MEA-H₂O-CO₂ system in available models and process data

• Simplified electrolytic speciation:

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

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

– Does not consider presence of other ions (H⁺, OH⁻, CO₃²⁻) found to be in negligible concentration

• Electrolyte presence generates complexity in properties modeling (highly non-ideal solution)
Deterministic Modeling

• Function inputs (variables/parameters) and outputs are represented as single values

• General procedure
  – Gather as much relevant data as possible
  – Optimize model parameters to minimize sum of square error (SSE) between data values and model predictions
Parameter Screening

• Determine parameters to which the model is most sensitive
  – UQ necessary for parameters of high sensitivity
  – Parameters of low sensitivity may be eliminated from UQ analysis not only to avoid unnecessary computation, but also for computational tractability

• Response surface method: qualitative parameter screening

• Sensitivity calculation method: quantitative parameter screening
Response Surfaces

• Multivariate Adaptive Regression Splines (MARS) regression technique
  – Reduces mathematical model into non-parametric form that maintains capability of describing relationships between input and output variables
• Computationally inexpensive
• Generated using PSUADE software developed by LLNL
  – Input: Uniform distribution of model variables and parameter and associated output
  – Output: Response surface
• Parameter sensitivity determined by response surface shape
Sensitivity matrix calculation

- For generic physical property:
  \[ S_{ij} = \max \left| \frac{\partial}{\partial \hat{y}_i} \left( \frac{\partial \phi}{\partial x_j} \right) \right| \]
  \[ y_i = \bar{y}_i \hat{y}_i \]

- Subject to
  \[ \hat{y}_i^L \leq \hat{y}_i \leq \hat{y}_i^U \quad T^L \leq T \leq T^U \quad \alpha^L \leq \alpha \leq \alpha^U \quad X_{MEA}^L \leq X_{MEA} \leq X_{MEA}^U \]

- Normalized version
  \[ N_{ij} = \frac{S_{ij}}{\max_{i \in [1,n], j \in [1,m]} S_{ij}} \]

- Parameter sensitivity determined by value of \( N_{ij} \)
- Method may be more convenient than visualizing surface responses
Stochastic Modeling

- Function inputs and outputs are represented as PDFs
- Sources of uncertainty
  - Process variable measurements (input uncertainty)
  - Physical property measurements (output uncertainty)
  - Functional form of physical property models (model uncertainty)
- Bayesian inference may be used to quantify parametric uncertainty
  - Prior distributions of parameters are updated as additional information is acquired (sampling of experimental data)
  - Markov Chain Monte Carlo (MCMC) method using Gibbs sampling
Bayesian Inference

Sets of process variables (sample size M) → Prior distribution of parameters (sample size N) → Mathematical Model → Input vs. Output Observations (sample size M × N) → MARS → Response Surface → Bayesian Inference

Posterior Parameter Distributions

Experimental Data with Uncertainty
Viscosity Model

\[ \mu_{sln} = \mu_{H_2O}(T) \exp \left( \frac{(aX_{MEA}+b)T+cX_{MEA}+d)(\alpha(eX_{MEA}+fT+g)+1)X_{MEA}}{T^2} \right) \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Given Value</th>
<th>Calibrated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
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</tr>
<tr>
<td>b</td>
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<tr>
<td>c</td>
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</tr>
<tr>
<td>d</td>
<td>2373</td>
<td>1817</td>
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<tr>
<td>e</td>
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<td>0.00847</td>
</tr>
<tr>
<td>f</td>
<td>0.0093</td>
<td>0.0103</td>
</tr>
<tr>
<td>g</td>
<td>-2.2589</td>
<td>-2.3890</td>
</tr>
</tbody>
</table>
Viscosity Model/Data Comparison

$X_{MEA}=20$  $X_{MEA}=30$  $X_{MEA}=40$

**Legend**
- **Marker**
  - Data
  - Original model
  - New model

**Color**
- 298.15 K
- 313.15 K
- 323.15 K
- 343.15 K
- 363.15 K
Viscosity Model-Sensitivity Analysis

\[
\begin{align*}
\begin{bmatrix}
\frac{\partial}{\partial a} \left( \frac{\partial \mu}{\partial T} \right) & \frac{\partial}{\partial a} \left( \frac{\partial \mu}{\partial x_{MEA}} \right) & \frac{\partial}{\partial a} \left( \frac{\partial \mu}{\partial \alpha} \right) \\
\frac{\partial}{\partial b} \left( \frac{\partial \mu}{\partial T} \right) & \frac{\partial}{\partial b} \left( \frac{\partial \mu}{\partial x_{MEA}} \right) & \frac{\partial}{\partial b} \left( \frac{\partial \mu}{\partial \alpha} \right) \\
\frac{\partial}{\partial c} \left( \frac{\partial \mu}{\partial T} \right) & \frac{\partial}{\partial c} \left( \frac{\partial \mu}{\partial x_{MEA}} \right) & \frac{\partial}{\partial c} \left( \frac{\partial \mu}{\partial \alpha} \right) \\
\frac{\partial}{\partial \hat{c}} \left( \frac{\partial \mu}{\partial T} \right) & \frac{\partial}{\partial \hat{c}} \left( \frac{\partial \mu}{\partial x_{MEA}} \right) & \frac{\partial}{\partial \hat{c}} \left( \frac{\partial \mu}{\partial \alpha} \right) \\
\frac{\partial}{\partial \hat{f}} \left( \frac{\partial \mu}{\partial T} \right) & \frac{\partial}{\partial \hat{f}} \left( \frac{\partial \mu}{\partial x_{MEA}} \right) & \frac{\partial}{\partial \hat{f}} \left( \frac{\partial \mu}{\partial \alpha} \right) \\
\frac{\partial}{\partial \hat{g}} \left( \frac{\partial \mu}{\partial T} \right) & \frac{\partial}{\partial \hat{g}} \left( \frac{\partial \mu}{\partial x_{MEA}} \right) & \frac{\partial}{\partial \hat{g}} \left( \frac{\partial \mu}{\partial \alpha} \right)
\end{bmatrix} & = \\
\begin{bmatrix}
0.0022 & 0.0089 & 0.1566 \\
0.0019 & 0.0058 & 0.1329 \\
0.0034 & 0.0123 & 0.2176 \\
0.0048 & 0.0134 & 0.3063 \\
0.0009 & 0.0028 & 0.0827 \\
0.0090 & 0.0254 & 1.0000 \\
0.0074 & 0.0186 & 0.7246
\end{bmatrix}
\end{align*}
\]

- \( N = \max \)
Viscosity Model-Surface Response Analysis

Viscosity (mPa-s) vs. CO₂ Loading

f, c, e
Viscosity Model-Posterior Distributions from Bayesian Inference
Density Model

- Three sources of data available for parameter calibration

\[ \rho_{sln} = \frac{MW_{sln}}{X_{MEA}V_{MEA} + X_{H_2O}V_{H_2O} + X_{CO_2}V_{CO_2} + X_{MEA}X_{H_2O}V^* + X_{MEA}X_{H_2O}V^{**}} \]

- Solution molecular weight calculation takes electrolyte speciation into account in new model

- Five uncertain parameters
  - \( V_{CO_2} = a \)
  - \( V^* = b + cX_{MEA} \)
  - \( V^{**} = d + eX_{MEA} \)

<table>
<thead>
<tr>
<th>Baseline Parameter Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>c</td>
</tr>
<tr>
<td>d</td>
</tr>
<tr>
<td>e</td>
</tr>
</tbody>
</table>
Density Model/Data Comparison

- Results shown for one data source only

For each value of $r$:

- $r=0.2$
- $r=0.3$
- $r=0.4$

![Graphs showing solution density vs. CO$_2$ loading (mol CO$_2$/mol MEA) for different values of $r$.](image)

**Marker**
- *: data
- Dashed line: original model
- Solid line: new model

**Color**
- 303.15 K
- 313.15 K
- 323.15 K
- 333.15 K
Density Model-Sensitivity Analysis

\[
\begin{bmatrix}
\frac{\partial}{\partial \hat{a}} \left( \frac{\partial V}{\partial T} \right) & \frac{\partial}{\partial \hat{a}} \left( \frac{\partial V}{\partial r} \right) & \frac{\partial}{\partial \hat{a}} \left( \frac{\partial V}{\partial \alpha} \right) \\
\frac{\partial}{\partial \hat{b}} \left( \frac{\partial V}{\partial T} \right) & \frac{\partial}{\partial \hat{b}} \left( \frac{\partial V}{\partial r} \right) & \frac{\partial}{\partial \hat{b}} \left( \frac{\partial V}{\partial \alpha} \right) \\
\frac{\partial}{\partial \hat{c}} \left( \frac{\partial V}{\partial T} \right) & \frac{\partial}{\partial \hat{c}} \left( \frac{\partial V}{\partial r} \right) & \frac{\partial}{\partial \hat{c}} \left( \frac{\partial V}{\partial \alpha} \right) \\
\frac{\partial}{\partial \hat{d}} \left( \frac{\partial V}{\partial T} \right) & \frac{\partial}{\partial \hat{d}} \left( \frac{\partial V}{\partial r} \right) & \frac{\partial}{\partial \hat{d}} \left( \frac{\partial V}{\partial \alpha} \right) \\
\frac{\partial}{\partial \hat{e}} \left( \frac{\partial V}{\partial T} \right) & \frac{\partial}{\partial \hat{e}} \left( \frac{\partial V}{\partial r} \right) & \frac{\partial}{\partial \hat{e}} \left( \frac{\partial V}{\partial \alpha} \right)
\end{bmatrix}
\]

\[
\cdot \quad N = 0.1624 \quad 0.1092
\]

\[
= 0.1624 \quad 0.1092
\]

\[
0.0566 \quad 0.0067
\]

\[
0.0277 \quad 0.0022
\]

\[
1.000 \quad 0.3639
\]

\[
0.6199 \quad 0.1628
\]
Density Model-Posterior Distributions from Bayesian Inference
Surface Tension Model-Original Form

\[ \sigma_{mix} = \sigma_{H_2O} + \sum_{i=CO_2,MEA} \left( 1 + \frac{b_i x_i}{(1-a_i)(1+\sum_{j=CO_2,MEA} a_j x_j)} \right) \left( x_i (\sigma_i - \sigma_{H_2O}) \right) \]

- Parameters \( a_i \) and \( b_i \) regressed individually for data sets with given value of MEA weight fraction
- Cannot be used to represent solvents over a range of temperature and composition
New Surface Tension Model

- Continuous function of temperature, CO$_2$ loading ($\alpha$), and MEA weight fraction ($r$) on CO$_2$-free basis

\[
\sigma_{\text{mix}} = \sigma_{H_2O} + (\sigma_{CO_2} - \sigma_{H_2O})f(r, \alpha)x_{CO_2} + (\sigma_{MEA} - \sigma_{H_2O})g(r, \alpha)x_{MEA}
\]

\[
f(r, \alpha) = a + b\alpha + c\alpha^2 + dr + er^2
\]

\[
g(r, \alpha) = f + g\alpha + h\alpha^2 + ir + jr^2
\]

- Functionally similar to original model
- Preserves quality of fit between model and experimental data
## Surface Tension Model-Calibrated Parameter Values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2.4558</td>
<td>f</td>
<td>2.3122</td>
</tr>
<tr>
<td>b</td>
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<tr>
<td>c</td>
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<tr>
<td>e</td>
<td>10.2109</td>
<td>j</td>
<td>-12.0494</td>
</tr>
</tbody>
</table>
Surface Tension Model/Data Comparison

$r=0.2$

$r=0.3$

$r=0.4$

Marker

- data
- original model
- new model

Color

- 303.15 K
- 313.15 K
- 323.15 K
- 333.15 K
Surface Tension Model-Sensitivity Analysis

\[
\begin{bmatrix}
\frac{\partial}{\partial \alpha} \left( \frac{\partial \sigma}{\partial T} \right) & \frac{\partial}{\partial \alpha} \left( \frac{\partial \sigma}{\partial r} \right) & \frac{\partial}{\partial \alpha} \left( \frac{\partial \sigma}{\partial \alpha} \right) \\
\frac{\partial}{\partial b} \left( \frac{\partial \sigma}{\partial T} \right) & \frac{\partial}{\partial b} \left( \frac{\partial \sigma}{\partial r} \right) & \frac{\partial}{\partial b} \left( \frac{\partial \sigma}{\partial \alpha} \right) \\
\frac{\partial}{\partial c} \left( \frac{\partial \sigma}{\partial T} \right) & \frac{\partial}{\partial c} \left( \frac{\partial \sigma}{\partial r} \right) & \frac{\partial}{\partial c} \left( \frac{\partial \sigma}{\partial \alpha} \right) \\
\frac{\partial}{\partial d} \left( \frac{\partial \sigma}{\partial T} \right) & \frac{\partial}{\partial d} \left( \frac{\partial \sigma}{\partial r} \right) & \frac{\partial}{\partial d} \left( \frac{\partial \sigma}{\partial \alpha} \right) \\
\frac{\partial}{\partial e} \left( \frac{\partial \sigma}{\partial T} \right) & \frac{\partial}{\partial e} \left( \frac{\partial \sigma}{\partial r} \right) & \frac{\partial}{\partial e} \left( \frac{\partial \sigma}{\partial \alpha} \right) \\
\frac{\partial}{\partial f} \left( \frac{\partial \sigma}{\partial T} \right) & \frac{\partial}{\partial f} \left( \frac{\partial \sigma}{\partial r} \right) & \frac{\partial}{\partial f} \left( \frac{\partial \sigma}{\partial \alpha} \right) \\
\frac{\partial}{\partial g} \left( \frac{\partial \sigma}{\partial T} \right) & \frac{\partial}{\partial g} \left( \frac{\partial \sigma}{\partial r} \right) & \frac{\partial}{\partial g} \left( \frac{\partial \sigma}{\partial \alpha} \right) \\
\frac{\partial}{\partial h} \left( \frac{\partial \sigma}{\partial T} \right) & \frac{\partial}{\partial h} \left( \frac{\partial \sigma}{\partial r} \right) & \frac{\partial}{\partial h} \left( \frac{\partial \sigma}{\partial \alpha} \right) \\
\frac{\partial}{\partial i} \left( \frac{\partial \sigma}{\partial T} \right) & \frac{\partial}{\partial i} \left( \frac{\partial \sigma}{\partial r} \right) & \frac{\partial}{\partial i} \left( \frac{\partial \sigma}{\partial \alpha} \right) \\
\frac{\partial}{\partial j} \left( \frac{\partial \sigma}{\partial T} \right) & \frac{\partial}{\partial j} \left( \frac{\partial \sigma}{\partial r} \right) & \frac{\partial}{\partial j} \left( \frac{\partial \sigma}{\partial \alpha} \right)
\end{bmatrix}
\]

\[
N = \begin{bmatrix}
0.0008 & 0.6143 & 0.5005 \\
0.0002 & 0.1918 & 0.2771 \\
0.0003 & 0.2192 & 0.4816 \\
0.0007 & 0.8493 & 0.4594 \\
0.0005 & 1.0000 & 0.3330 \\
0.0001 & 0.3298 & 0.0158 \\
0.0001 & 0.2782 & 0.1865 \\
0.0000 & 0.0727 & 0.0875 \\
0.0001 & 0.5227 & 0.0148 \\
0.0001 & 0.6702 & 0.0126
\end{bmatrix}
\]
Surface Tension Model-Posterior Distributions from Bayesian Inference
Future Work

- Complete physical properties models/UQ for MEA
  - Vapor-liquid equilibrium
  - Heat capacity
  - Thermal conductivity
  - Diffusion coefficient
- Implement models in Aspen Plus® to allow for quantification of uncertainty in process variables (e.g. capture efficiency)
- Validate models with process data
  - UT-Austin Pilot Plant
  - National Carbon Capture Center (NCCC)
- Shift focus to high viscosity solvents
Thank you!

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