DOCCSS Support for PNNL CO2BOLs Solvents

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Introduction

Objective

Understanding transformational solvents

Predicting performance via multiscale modeling

Targeting optimal system design

Computational Tools:

- Uncertainty Quantification (UQ) analysis for full-scale process model
- Computational Fluid Dynamics (CFD) model for device-scale mass transfer
- Lost work analysis of water-lean solvent CO2BOL
Outline

• UQ analysis for full scale process model with CO2BOL

• CFD models for mass transfer of CO2BOL
  – Model description
  – Model validation
  – Preliminary results for CO2BOL

• Lost work analysis of water-lean solvent CO2BOL
Standard Practice: Least Squares Fit

Basic Data Model

Large Scale Model
Uncertainty Quantification

Basic Data Model

Large Scale Model
Procedure for using UQ methods

1. At Each Stage, Identify Relevant System Information and Ranges for Parameters/Inputs
2. Identify Prior Distributions for Model Parameters
3. Develop a “Space-Filling” Design to Train Surrogate Model
4. Run Model (Aspen) at Designed Parameter/Input Values Adjusting if Needed
5. UQ Analysis: Calibrate the Model to Data to Compute Parameter Distributions
6. Get Output Predictions with Uncertainty
7. Propagate Results to Full-Scale Model
UQ: Working with Novel Solvent Systems

- UQ Analysis is Done at Each Sub-Model as Well as Full-Scale Model
  - Divided into Sub-Models such as Thermodynamics, Viscosity, Mass Transfer, Kinetics, etc.
- UQ Requires Full Access to the Model
  - When Subroutines are Used, Parameters Need to be Aspen-Accessible
- Parameter Selection for CO₂BOLs*
  - >150 System-Specific Parameters Reduced to 41
- What do you Want to Learn?
  - Primary Objectives From UQ
    - Data Gaps
    - Uncertainty in Predictions of Carbon Capture or Energy Penalty
    - Accuracy of Model at Different Scales

*Further Details for CO₂BOLs Analysis at Tuesday Poster Session
• Begin With Parameter Distribution (Typically Uniform) and Determine New Distribution From Data
• Red Indicates High Likelihood of Parameter Value

Predictions (solid line) and 95% Uncertainty Bounds for Predictions (Dotted) Largely Covers PTx Data (Dots) for CO₂/BOL/NC16 System
Initial UQ Results for Full-Scale Model

Sub-Model Posterior Parameter Distributions

Propagation of Sub-Model Results to Full-Scale Model

Full-scale Model

Full-Scale Model CO₂ Capture Predictions

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CFD Models for Solvent Absorption in Packed Column

Objectives: Using CFD to
- Study the local hydrodynamics
- Directly model the mass transfer coefficients
- Directly model the mass transfer area

Methods:
- Multiphase flow using Volume of Fluid (VOF) method

Challenges:
- Multiscale & Multiphysics
- Extremely complex geometry

Counter-current flow

Rich Solvent

Lean Solvent

Random Rings

Purified Gas

Flue Gas

to Stripper

Multiscale

Layer height\(^2\): ~20cm

Corrugation height\(^2\): O(10 mm)

film thickness\(^2\): ~ O(0.1 mm)

Column\(^2\):
Φ ~10m
H ~30m
Model Description: Countercurrent Flow in Random Packing

Packed column
- Column diameter: 100 mm
- Column height: 200 mm
- Number of Pall rings: 160

Boundary conditions
- 13 solvent dripping inlets (10 mm diameter)
- No slip ring surface
- Prescribed gas flow rate at outlet

Design of pall ring
- Diameter: 16 mm
- Height: 16 mm
- Thickness: 0.5 mm
- Specific Area: 282 m^2/m^3
Model Validation: Hydrodynamics for Countercurrent Flow

### Solvent Properties (30% MEA)

#### Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density $\rho$ (kg/m$^3$)</td>
<td>1000</td>
</tr>
<tr>
<td>Viscosity $\mu$ (cP)</td>
<td>2.46</td>
</tr>
<tr>
<td>$D_{CO_2}[l]$ (m$^2$/s)</td>
<td>$1.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>$D_{CO_2}[g]$ (m$^2$/s)</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>Reaction Rate</td>
<td>5.96</td>
</tr>
<tr>
<td>Henry’s constant (Dimensionless)</td>
<td>1.228</td>
</tr>
<tr>
<td>Surface Tension (N/m)</td>
<td>0.065</td>
</tr>
<tr>
<td>Contact angle ($^\circ$)</td>
<td>40</td>
</tr>
</tbody>
</table>

**Computational cost**
- 96 cores on PNNL PIC HPC
- 7 CPU hours for every 1s solution

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Liquid Load: 40 m$^3$/m$^2$h  
Gas Load: 0.27 Pa$^{1/2}$
Model Validation: Hydrodynamics for Countercurrent Flow

### Solvent Properties (30% MEA)

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Liquid Load: 40 m$^3$/m$^2$h  Gas Load: 0.27 Pa$^{1/2}$
Model Validation: Mass Transfer Areas

Distinguish three areas
- Interface area (CFD)
- Wetted area (CFD)
- Effective mass transfer area (Exp.)

All areas are normalized by the packing Specific Area;

Correlation from column experiment (dash line):

\[ A = 1.16\eta \left( \frac{u_L g^{1/2} a_p^{-3/2}}{\rho_L / \sigma} \right)^{0.138} \]


For given size of Pall Ring (16mm):

\( \text{effective area} \approx \text{Interfacial area} > \text{wetted area} \)
Application to Structured Packed Column

**Mellapak 250.Y**

**Solvent (0.1M NaOH)**

**Physical Properties**

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<th>Value</th>
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</thead>
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<tr>
<td>Density $\rho$ (kg/m$^3$)</td>
<td>998</td>
</tr>
<tr>
<td>Viscosity $\mu$ (cP)</td>
<td>0.89</td>
</tr>
<tr>
<td>$D_{CO_2}$ [l] (m$^2$/s)</td>
<td>$1.0\times10^{-9}$</td>
</tr>
<tr>
<td>$D_{CO_2}$ [g] (m$^2$/s)</td>
<td>$1.0\times10^{-5}$</td>
</tr>
<tr>
<td>Surface Tension (N/m)</td>
<td>0.072</td>
</tr>
</tbody>
</table>

**Model**

**Hydrodynamics**

**Effective area**

$$a_e = \frac{u_g}{k'_g ZRT \ln \left( \frac{C_{CO_2, in}}{C_{CO_2, out}} \right)}$$

**Good Agreement**
Application to CO2BOL in Packed Column

Design of Column
- Column Diameter: 63 mm
- Column Height: 200 mm
- Number of packed rings: 2366

CO2BOL-2 water-lean solvent:
- Density: 1015 kg/m³
- Viscosity: 10.6 cP
- Surface tension: ~0.028 N/m
- Contact angle: ~10°

Raschig Ring Design
- Diameter: 6 mm
- Height: 6 mm
- Thickness: 0.5 mm
- Specific Area: 827 m²/m³
Application to CO2BOL in Packed Column

For small size of raschig ring (6mm):
\[ \text{effective area} \approx \text{Interfacial area} < \text{wetted area} \]
- Multiphase flow simulations for random/structure packings

- Validation with experiments (Song et. al. (2017))

- Interface/wetted areas directly from CFD
  Small rings $\Rightarrow$ large wetted area $\neq$ mass transfer area

- Affordable for a full-size bench-scale column

- Applications to CO2BOL or other solvents

- More detailed results in poster presentation (Tuesday)
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Estimate Energy Use for Any Solvent by Rigorous Thermo

- Energy use by:
  1. $Q_{\text{Reboiler}} + W_{\text{compression}}$
  Or 2. $W_{\text{min}} + W_{\text{lost}}$
    - $W_{\text{min}}$ by rigorous thermo
    - $W_{\text{lost}}$ by
      - standard estimate
      - Or by $\Delta G$ ($\text{Est}\Delta G$)

Useful to
  1. Estimate energy for new solvent
  2. Define operating conditions for new solvent
  3. Qualify estimates of energy use by other methods
  4. Evaluate potential of solvent classes such as water lean
Lost work in absorber = $W_{\text{actual}} - W_{\text{min}}$

\[
W_{\text{actual}} = -\frac{1}{\Delta n_{\text{CO}_2}} \int_{\text{bot}}^{\text{top}} RT \ln \left( \frac{P_{\text{CO}_2}^*}{1 \text{ bar}} \right) dn_{\text{CO}_2}
\]

\[
= RT \left( \frac{a}{2} \left( n_{\text{CO}_2,\text{lean}} + n_{\text{CO}_2,\text{rich}} \right) + b \right)
\]

\[
W_{\text{min}} = -\frac{RT \Delta S}{0.12 \times 0.9}
\]

\[
= -RT \Delta (x \ln x + (1-x) \ln x(1-x))/0.108
\]

Flue Gas Operating Line

Equilibrium for 5 m PZ (aq), 40 °C
\( \ln (P_{\text{CO}_2}) = a + b \times \text{loading} \)
Heat Exchanger lost work by Est\(\Delta G\) (Carnot)

- Simplify by assuming \(\Delta T_{\text{approach}} = \Delta T_{LM}\), constant

\[
W_{\text{lost}} = \sum \left(1 - \frac{T_C}{T_H}\right) Q = -\frac{mC_p}{\dot{n}_{CO2}} \int_{\text{in}}^{\text{out}} \frac{\Delta T_{LM}}{T_{\text{lean}}} dT = \frac{mC_p}{\dot{n}_{CO2}} \Delta T_{LM} \ln \frac{T_{\text{in,lean}}}{T_{\text{out,lean}}}
\]

- Total Cost = W$ \times W_{\text{lost}} + \text{Area$} \times Q/\Delta T_{LM}$

- \(\Delta T_{LM,\text{opt}}:\text{CAPEX:OPEX} \propto \mu^{0.175} k^{-0.325} C_p^{0.825} \Delta T_{crx}^{0.5}\)

- \(\Delta C_{\text{norm}} = \Delta C_{\text{Solv}} \left(\frac{\mu}{\mu_5 m_{PZ}}\right)^{-0.175} \left(\frac{k}{k_5 m_{PZ}}\right)^{0.325} \left(\frac{C_p}{C_{p,5mPZ}}\right)^{-0.825}\)

- Greater \(\Delta C_{\text{norm}} = \) lower HX cost and lower \(W_{\text{lost}}\)
# HX energy cost: normalized capacity

<table>
<thead>
<tr>
<th></th>
<th>$\mu$</th>
<th>$k$</th>
<th>$C_p$</th>
<th>$\Delta C_{cyc}$</th>
<th>$\Delta T_{opt}$</th>
<th>$\Delta C_{k,c_p,\mu}$</th>
<th>$\Delta C_{k,c_p,\mu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cP</td>
<td>W/mK</td>
<td>J/gK</td>
<td>$\text{mol CO}_2$</td>
<td>kg solvent</td>
<td>w/o $\Delta T_{crx}$</td>
<td>with $\Delta T_{crx}$</td>
</tr>
<tr>
<td>5 m PZ(aq)</td>
<td>4</td>
<td>0.41</td>
<td>3.6</td>
<td>0.95</td>
<td>5</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>7 m MEA (1 water/3 NMP)</td>
<td>16</td>
<td>0.28</td>
<td>2.8</td>
<td>0.85</td>
<td>7.5</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>1 CO2BOL/1 C16</td>
<td>20</td>
<td>0.14</td>
<td>2.2</td>
<td>0.72</td>
<td>7</td>
<td>0.58</td>
<td>0.68</td>
</tr>
<tr>
<td>1 CO2BOL/2 C16</td>
<td>20</td>
<td>0.14</td>
<td>2.4</td>
<td>0.59</td>
<td>7.1</td>
<td>0.44</td>
<td>0.61</td>
</tr>
</tbody>
</table>
### Lost work (kJ/mol CO₂ removed)

<table>
<thead>
<tr>
<th></th>
<th>5 m PZ</th>
<th>8 m PZ</th>
<th>Water lean</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solvent</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Stripper</strong></td>
<td>AFS</td>
<td>Simple</td>
<td>Simple</td>
</tr>
<tr>
<td><strong>Absorber</strong></td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>P*&lt;sub&gt;CO₂&lt;/sub&gt; at 40°C lean/rich (kPa)</td>
<td>0.1/5</td>
<td>0.1/5</td>
<td>0.1/5</td>
</tr>
<tr>
<td><strong>Heat exchanger</strong></td>
<td>4.1</td>
<td>4.2</td>
<td>4.5</td>
</tr>
<tr>
<td>Δ&lt;sub&gt;T&lt;/sub&gt;&lt;sub&gt;LM, opt&lt;/sub&gt;</td>
<td>5</td>
<td>5.8</td>
<td>7.2</td>
</tr>
<tr>
<td><strong>Condenser</strong></td>
<td>0.8</td>
<td>5.8</td>
<td>(0.8)</td>
</tr>
<tr>
<td><strong>Compressor</strong></td>
<td>2.3</td>
<td>2.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Stripper P (bar)</td>
<td>6.5</td>
<td>6.5</td>
<td>1.8</td>
</tr>
<tr>
<td><strong>Reboiler</strong></td>
<td>1.2</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Trim cooler, stripper, et al.</td>
<td>1.6</td>
<td>1.6</td>
<td>(1.6)</td>
</tr>
<tr>
<td><strong>Total W&lt;sub&gt;eq&lt;/sub&gt; = W&lt;sub&gt;lost&lt;/sub&gt; + W&lt;sub&gt;min&lt;/sub&gt;</strong></td>
<td>33.7</td>
<td>39.3</td>
<td>34.3</td>
</tr>
</tbody>
</table>

1. Water lean cases use CO2BOL properties
Conclusions

- $W_{eq}$ & $Q_{reb}$ for water lean solvent may compete with 2X aqueous.
- If normalized capacity is similar.
- If $W_{\text{lost,condenser}}$ is low as expected with little water.
- Normalized capacity determines heat exchanger CAPEX & OPEX.
- $CO_2$ solubility, $\mu$, $k_{\text{cond}}$, & $C_p$ all matter.

$$
\Delta C_{\text{norm}} = \Delta C_{\text{solv}}\left(\frac{\mu}{\mu_{\text{ref}}}\right)^{-0.175}\left(\frac{k}{k_{\text{ref}}}\right)^{0.325}\left(\frac{C_p}{C_{\text{ref}}}\right)^{-0.825}
$$

- Representative water lean solvents have lower $\Delta C_{\text{norm}}$ than 2X aqueous amine.
Acknowledgments

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NETL: Michael Matuszewski, Benjamin Omell, Joshua Morgan, Grigorios Panagakos
UT Austin: Gary Rochelle and Ye Yuan

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