

# CCSI

Carbon Capture Simulation Initiative

## Predictive Models of Carbon Capture Systems and their Validation Using Bench Scale and Pilot Scale Data

Joshua C. Morgan<sup>a</sup>, Anderson Soares Chinen<sup>a</sup>, Benjamin Omell<sup>b</sup>,  
David C. Miller<sup>b</sup>, Sarah Genovese<sup>c</sup>, Debangsu Bhattacharyya<sup>a</sup>

<sup>a</sup> *Department of Chemical Engineering, West Virginia University, Morgantown, WV 26506, USA*

<sup>b</sup> *National Energy Technology Laboratory, 626 Cochrans Mill Rd, Pittsburgh, PA 15236, USA*

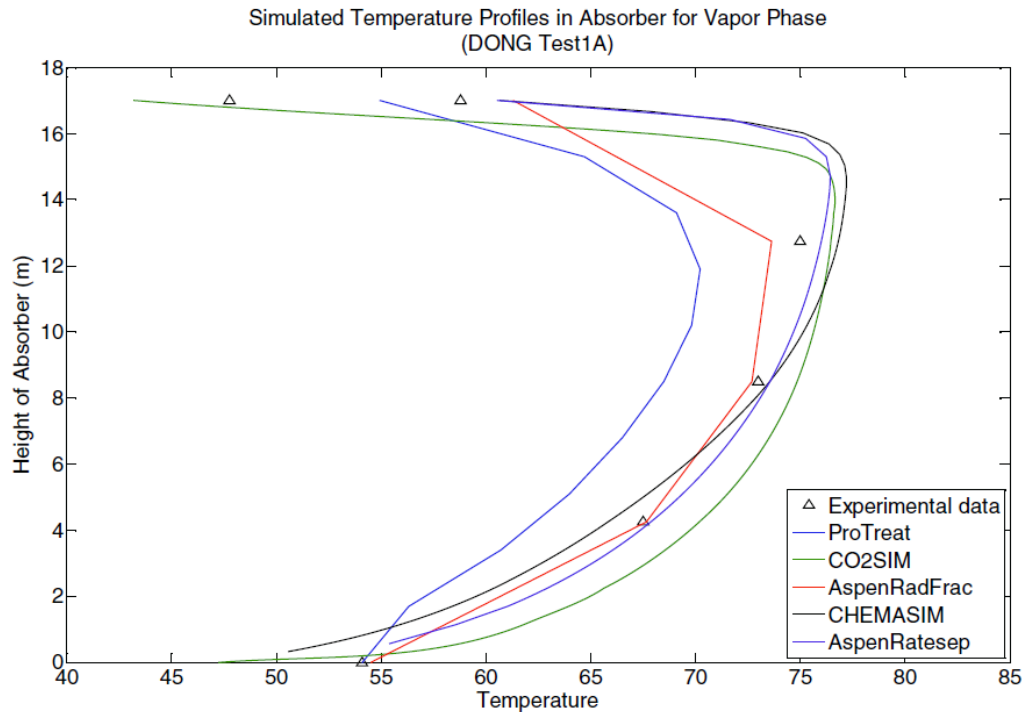
<sup>c</sup> *GE Global Research, One Research Circle, Niskayuna, NY 12309, USA* <sup>e</sup>

**CO<sub>2</sub> Summit II: Technologies and Opportunities**  
**Santa Ana Pueblo, New Mexico**  
**April 10-14, 2016**

# Motivations Behind CCSI Solvent System Process Models

- Development of a **Gold Standard** model for comparing different proposals for advanced solvent-based capture technologies
  - Open source
  - Validated framework
  - Well documented
  - Uncertainties quantified
  - Can be leveraged for scaleup studies
- Aqueous monoethanolamine (MEA) used as baseline
  - Industry standard
  - Extensive amount of data available
- Steady-state validation
- Dynamic validation

# Deficiencies in Existing Steady State Models



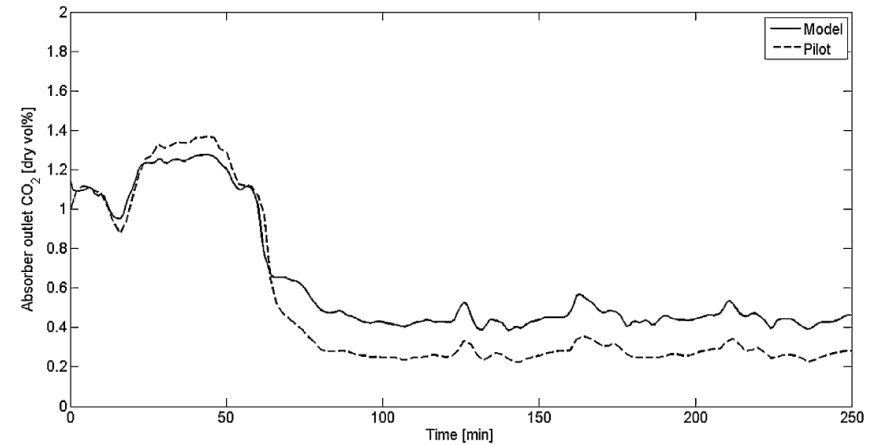
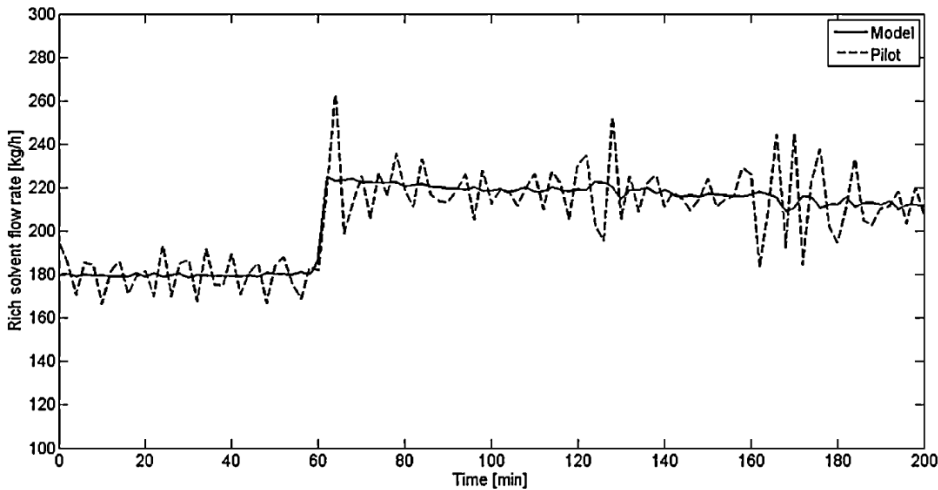
- Limited data from large scale pilot plants
- Limited variability in operating conditions and hardware (such as no of beds, intercoolers) while collecting experimental data
- Discrepancy in temperature profile and solvent loading estimation

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 Dynamic Models

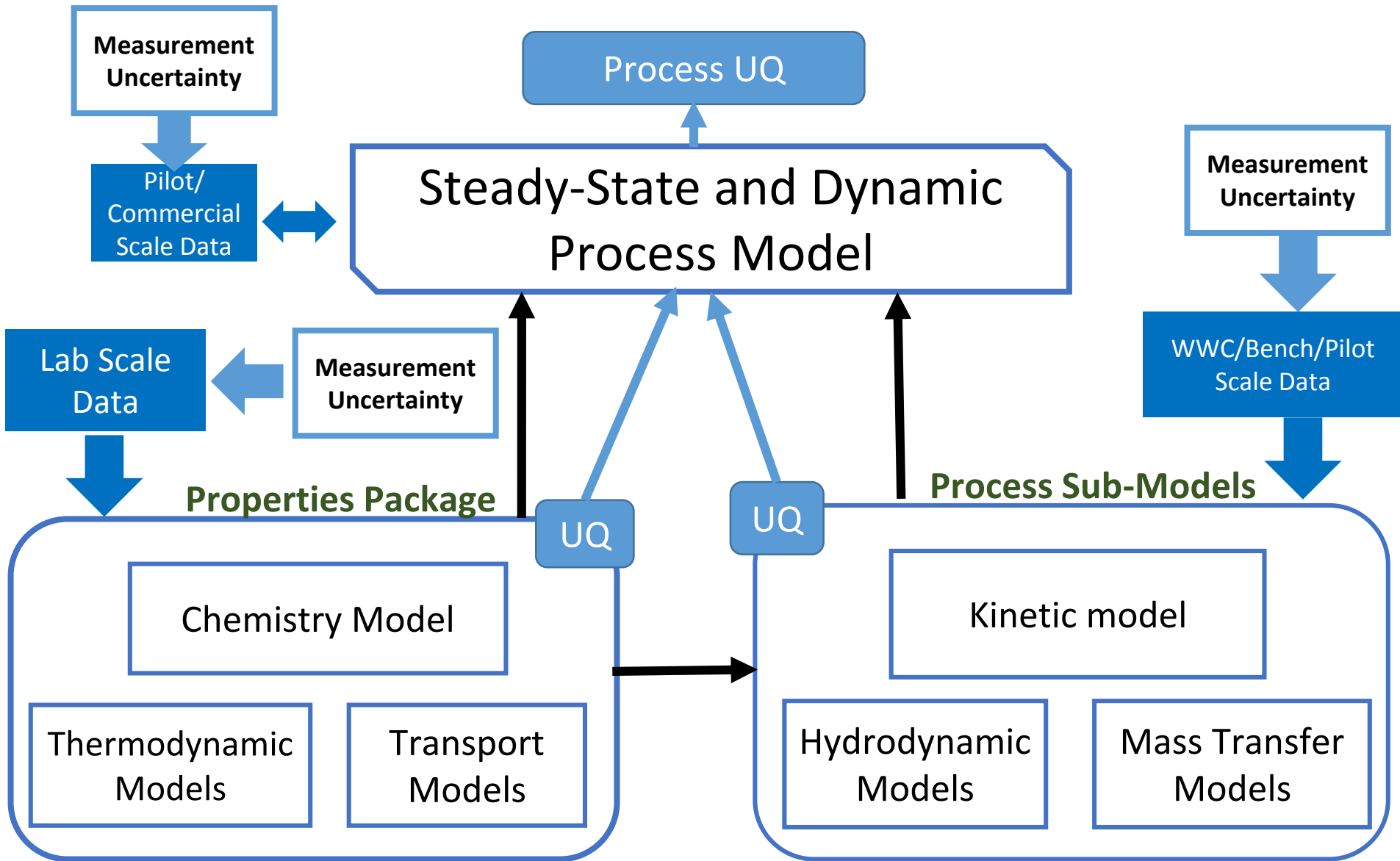
## Dynamic Response due to Step Change in Lean Solvent Flowrate\*



- Little work done so far
- Usually single step tests are done without maintaining persistence of excitation
- Mass and energy balance errors and noise in the data are either neglected or manually removed

*Enaasen Flø et al., Dynamic Model Validation of Post-Combustion CO<sub>2</sub> absorption Process, International Journal of Greenhouse Gas Control, 41, 127-141, 2015*

# How did we develop the gold standard model?



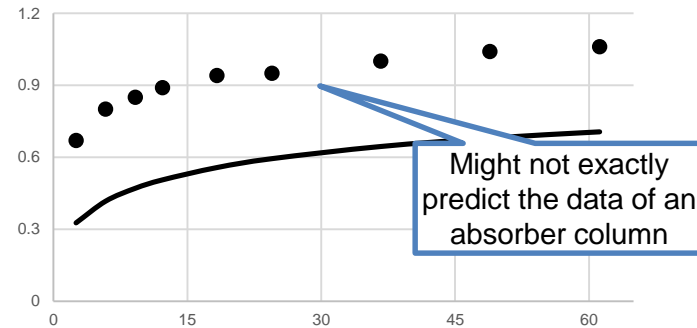
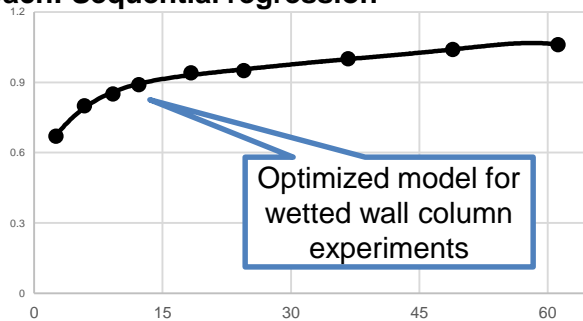
# Physical Property Model Development

- Independent property models
  - Viscosity
  - Density/Molar Volume
  - Surface Tension
- Thermodynamic framework
  - Electrolyte-NRTL
    - Binary MEA-H<sub>2</sub>O system
    - Ternary MEA-H<sub>2</sub>O-CO<sub>2</sub> system
  - Vapor-Liquid Equilibrium
  - Heat Capacity
  - Heat of Absorption
  - Reaction Kinetics
    - Consistency with reaction equilibrium constants

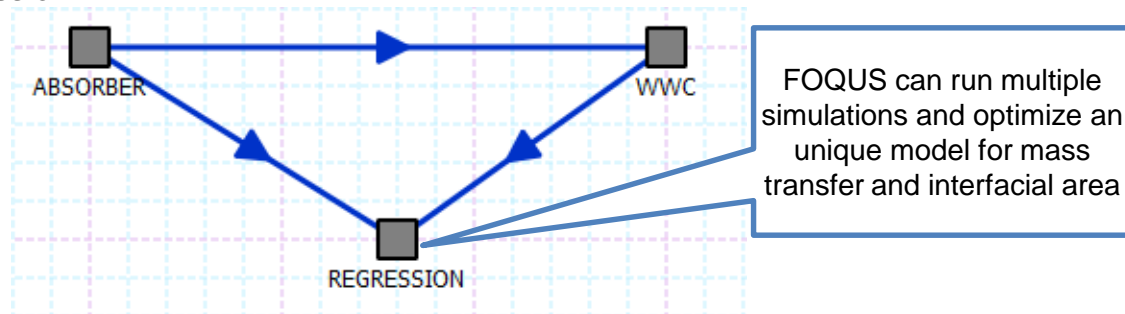
# Integrated Mass Transfer Model Development

- Properties (diffusivity, viscosity, surface tension), interfacial area, mass transfer coefficients, and reaction kinetics all affect mass transfer
- Use data from both wetted wall column and packed column
- Simultaneous regression not possible in Aspen Plus
  - solution can be sub-optimal
- FOQUS enables simultaneous regression of multiple models

Usual approach: Sequential regression



FOQUS capability: Simultaneous regression



# Validation with the Pilot Plant Data: State-of-the-Art in the Open Literature

## Steady-State

- Existing data in the literature do not encompass wide variations in operating conditions
  - Solvent flowrate, flue gas flowrate and composition, lean loading, no. of beds, and presence/absence of intercooler

## Dynamic

- Existing test runs do not ensure persistence of excitation nor the variability in operating conditions to capture the nonlinearities
  - Steps in all important manipulated and disturbance variables
  - Magnitude and directionality of steps
  - Conditions at which steps are introduced
- Existing dynamic test runs do not record/report transients in all key output variables (e.g. liquid sample analysis)

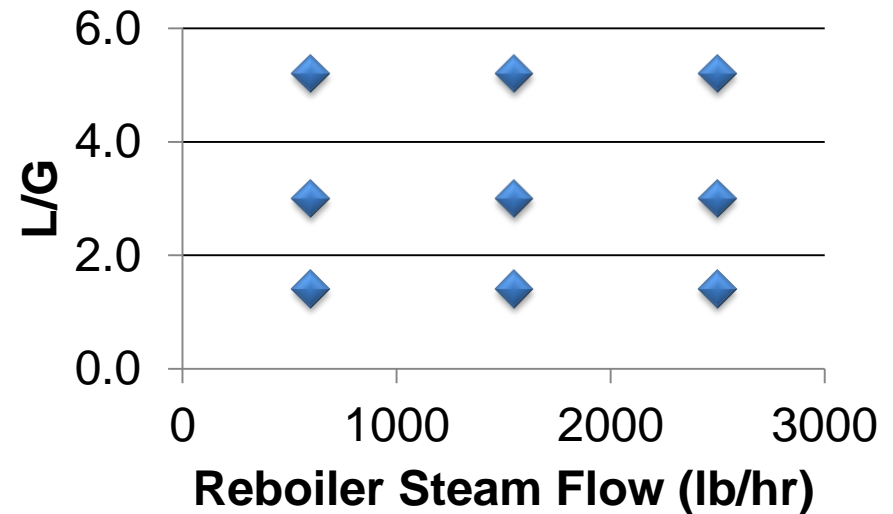


# Validation of Model with Pilot Plant Data



Operating Conditions	Range
Solvent Flow (lb/hr)	7,000-26,000
Inlet Flue Gas (lb/hr)	5,000-6,500
Reboiler Steam Flow (lb/hr)	600-2,500
Inlet FG CO <sub>2</sub> vol%	9-11%
# of beds	1-3
Intercooler	no - yes

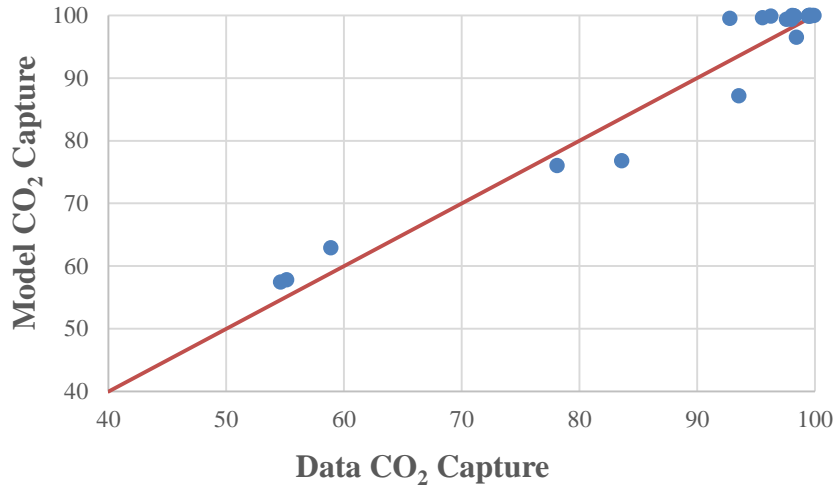
**Steady-State Test Matrix**



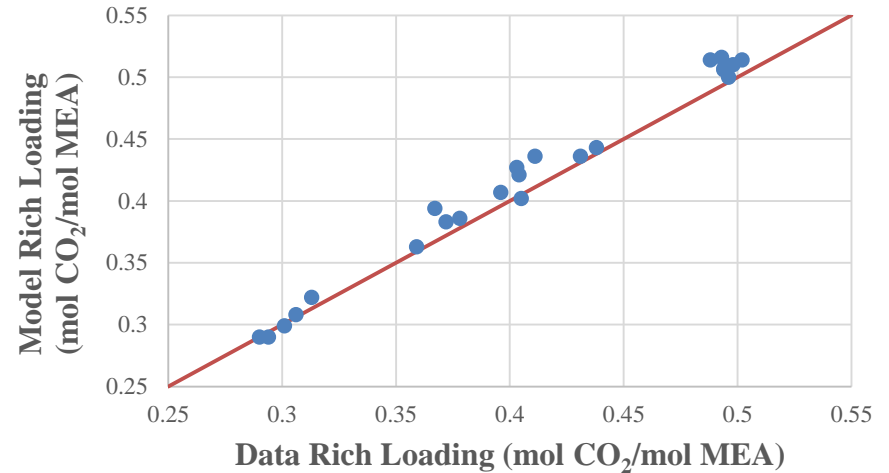
# Steady State Absorber Validation

No parameter tuned

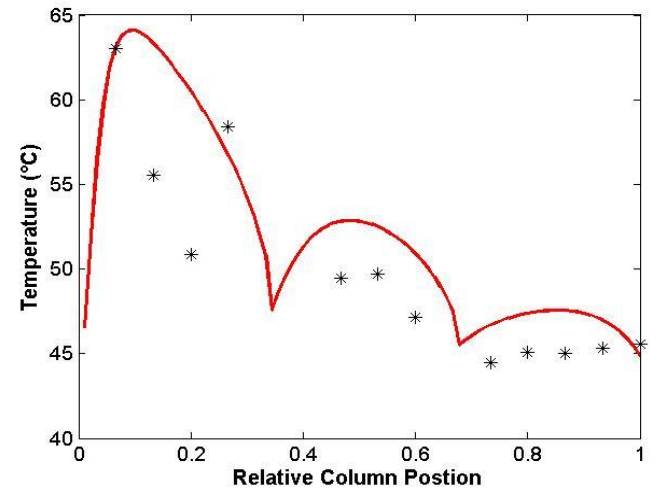
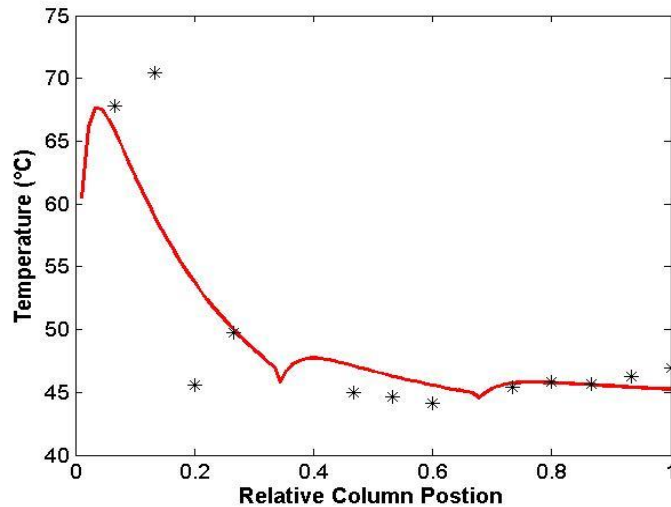
### CO<sub>2</sub> Capture Prediction



### Rich Loading Comparison



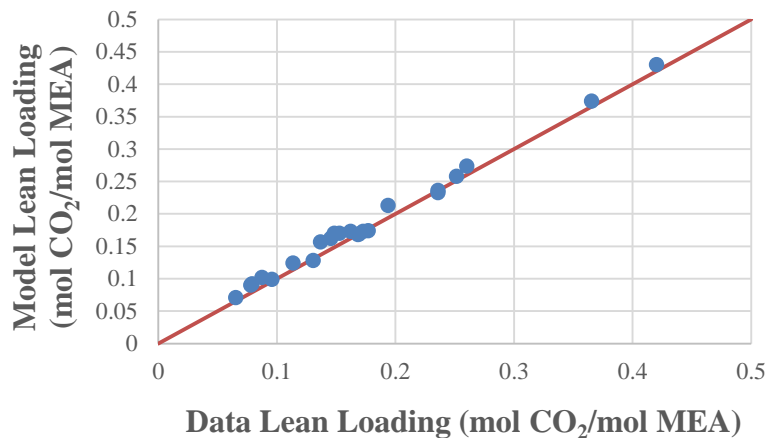
### Sample Temperature Profiles



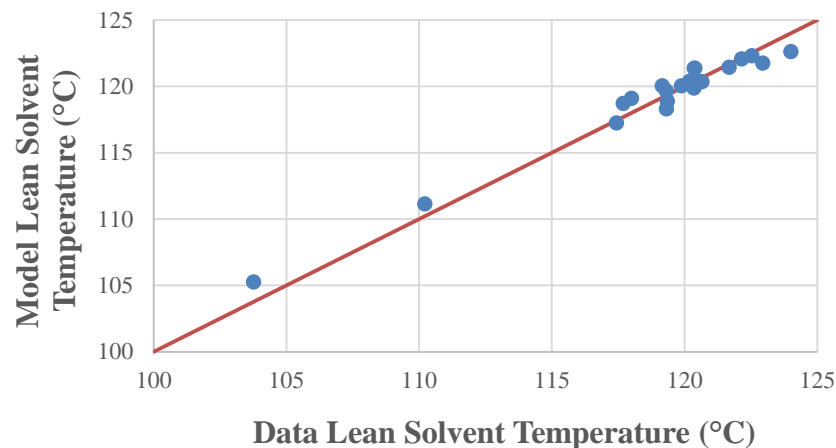
# Steady State Regenerator Validation

No parameter tuned

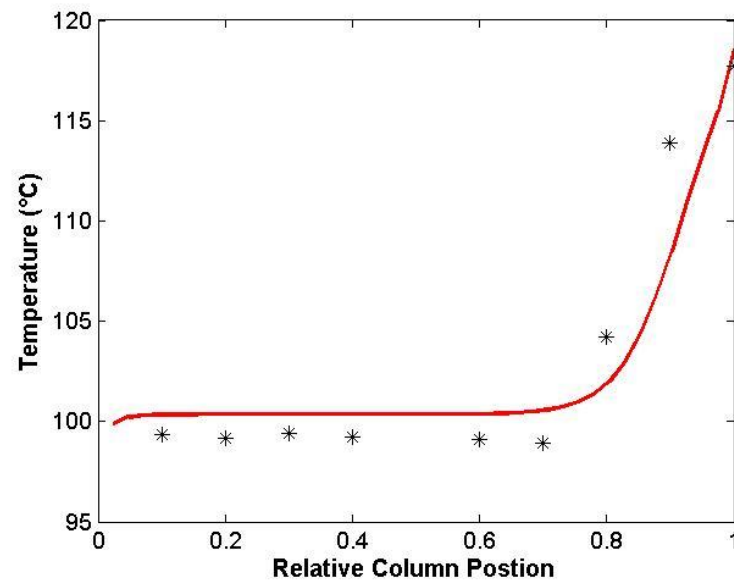
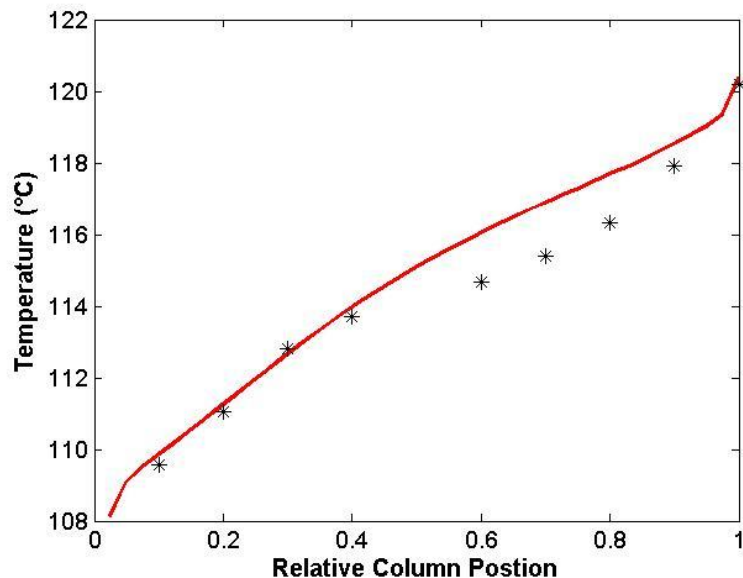
### Lean Loading Comparison



### Lean Solvent Temperature Comparison



## Sample Temperature Profiles



# Dynamic Data Reconciliation

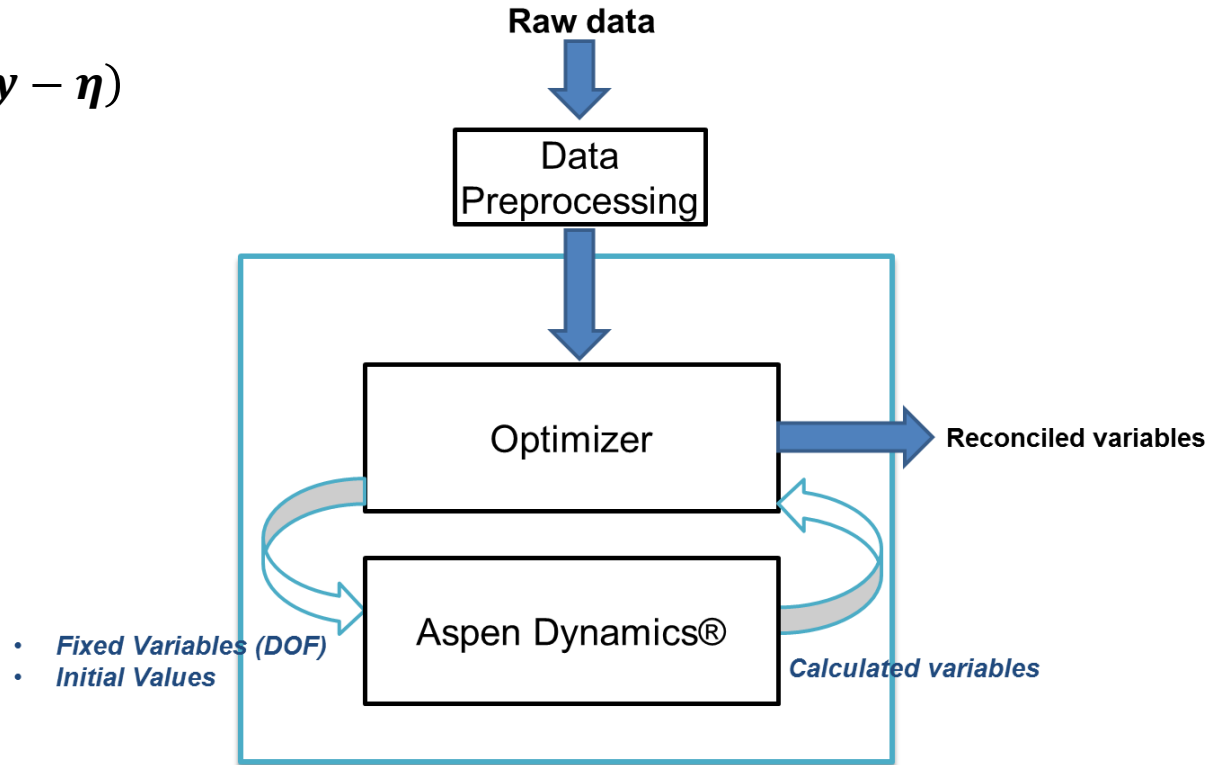
- Measurement noise, sensor bias, and unmeasured data
- Data reconciliation guarantees mass and energy conservation in the dynamic data

$$\min (\mathbf{y} - \boldsymbol{\eta})' \boldsymbol{\Sigma}^{-1} (\mathbf{y} - \boldsymbol{\eta})$$

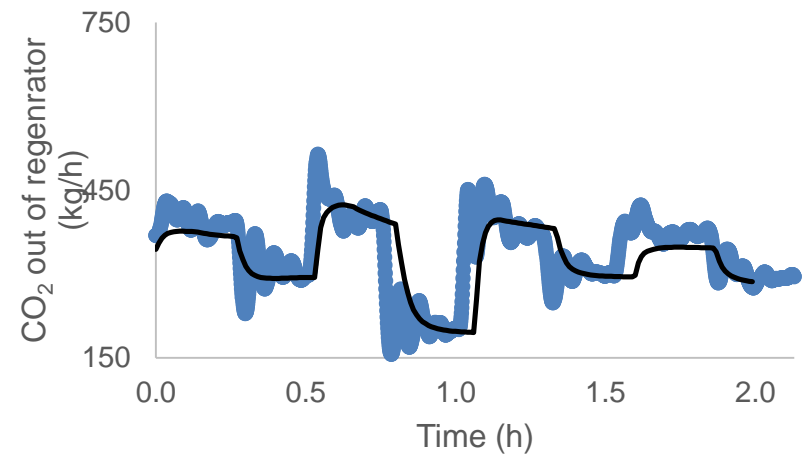
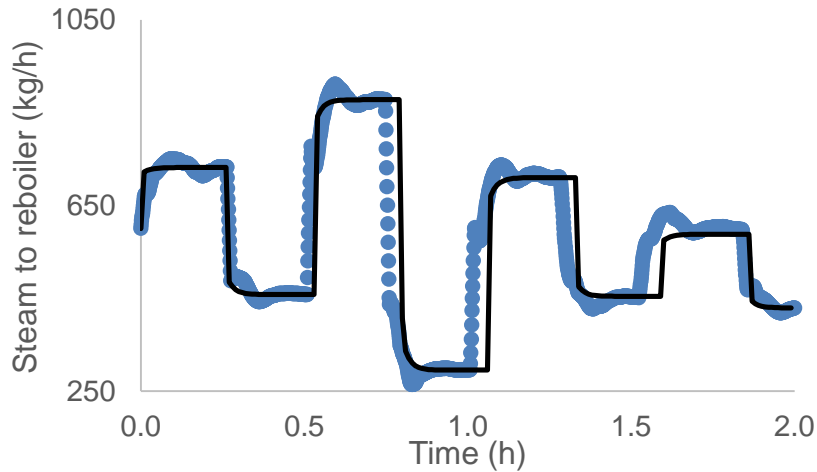
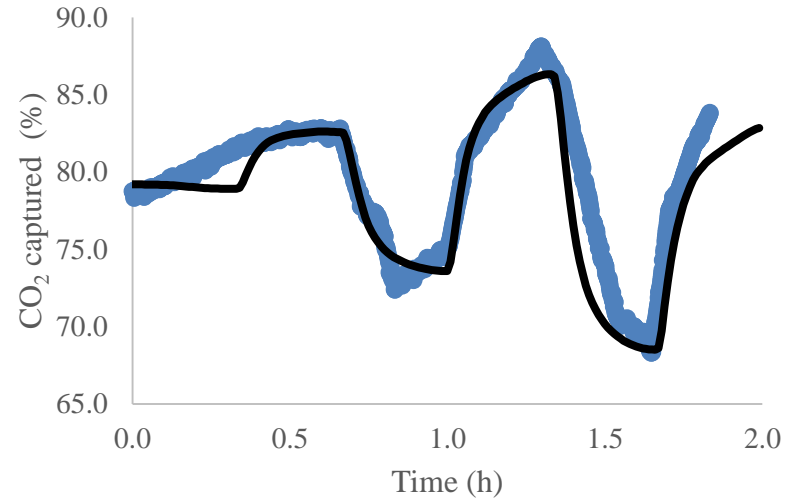
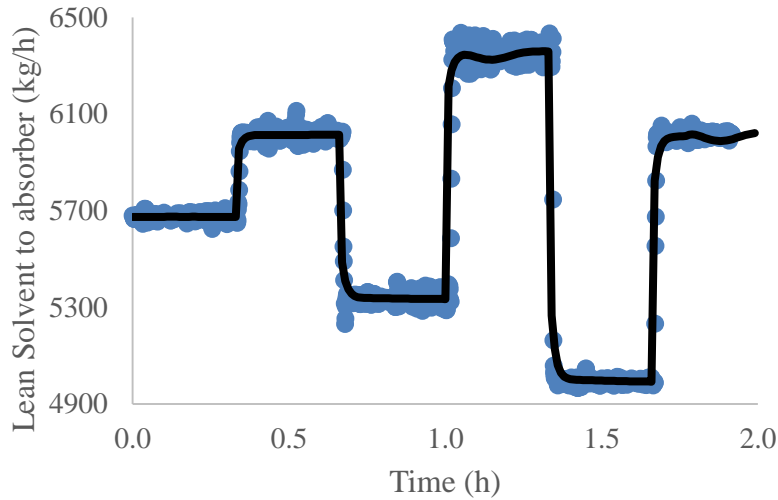
**s.t.**

$$\dot{\boldsymbol{\eta}} = \mathbf{f}(\boldsymbol{\eta}, \mathbf{u}, \boldsymbol{\theta})$$

$$\mathbf{g}(\boldsymbol{\eta}, \mathbf{u}, \boldsymbol{\theta}) \leq \mathbf{0}$$



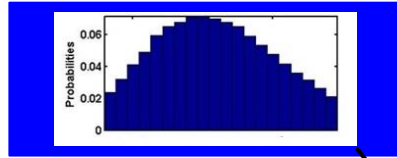
# Absorber Validation with DDR



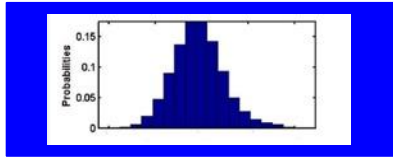
• Data

— Model

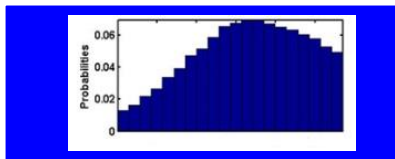
# Propagate input uncertainties to quantify the uncertainty in predictions



Uncertainty in Properties Models

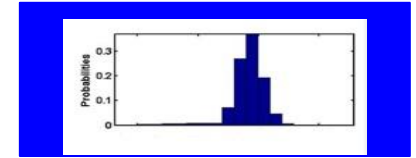
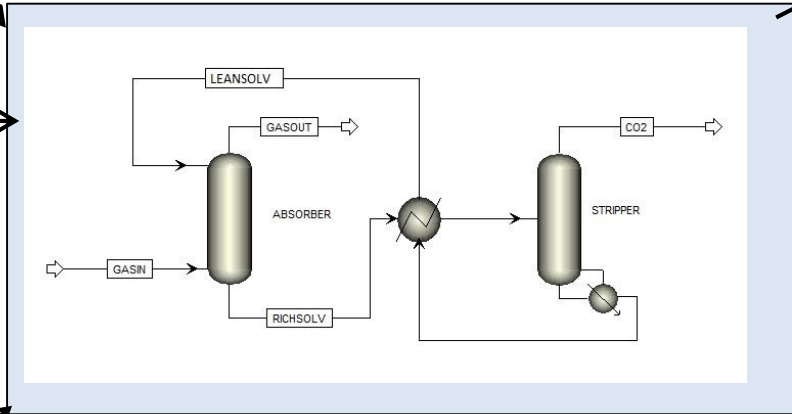


Uncertainty in Hydraulic Models, Mass and Heat Transfer Models



Uncertainty in Kinetic Models

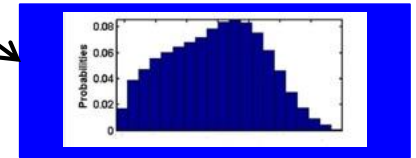
## Process Simulation



Uncertainty in % CO<sub>2</sub> Capture



Uncertainty in Energy Requirement



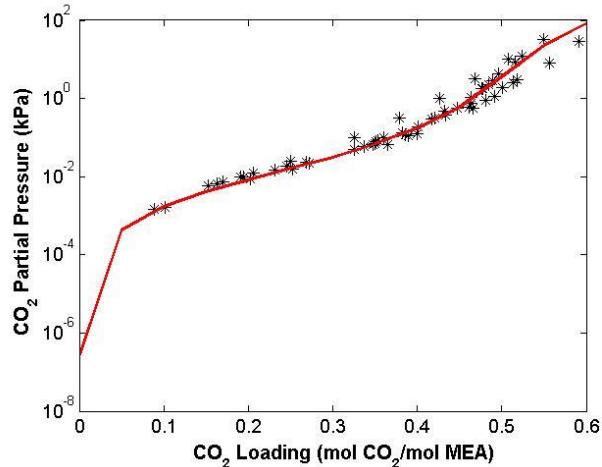
Uncertainty in Estimation of Other Key Variables

# Uncertainty Quantification of Process models

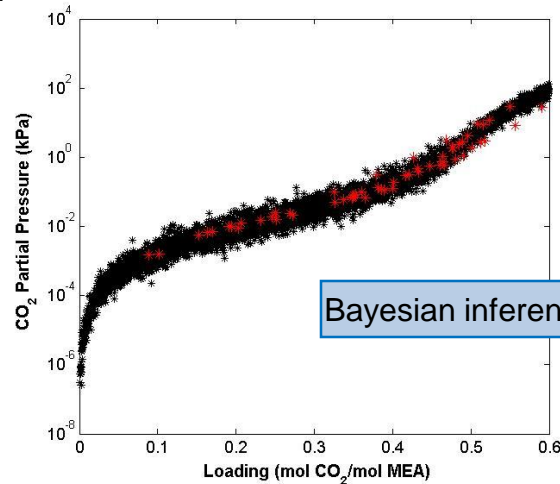
## VLE Data/Model Comparison at 40°C

\* Model  
\* Data

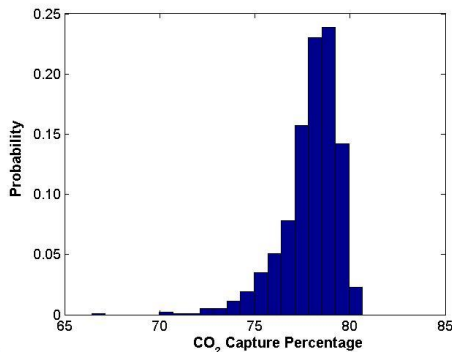
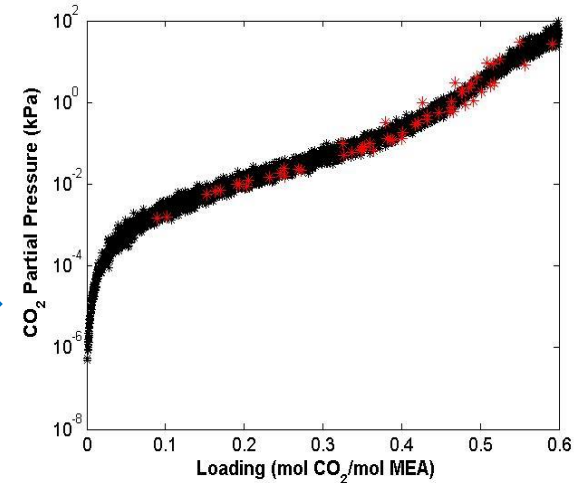
### Deterministic Model



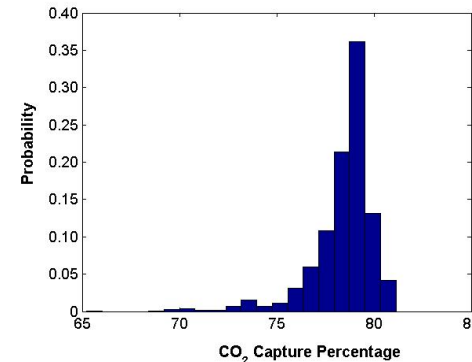
### Stochastic Model (Prior Parameter Distribution)



### Posterior Parameter Distribution

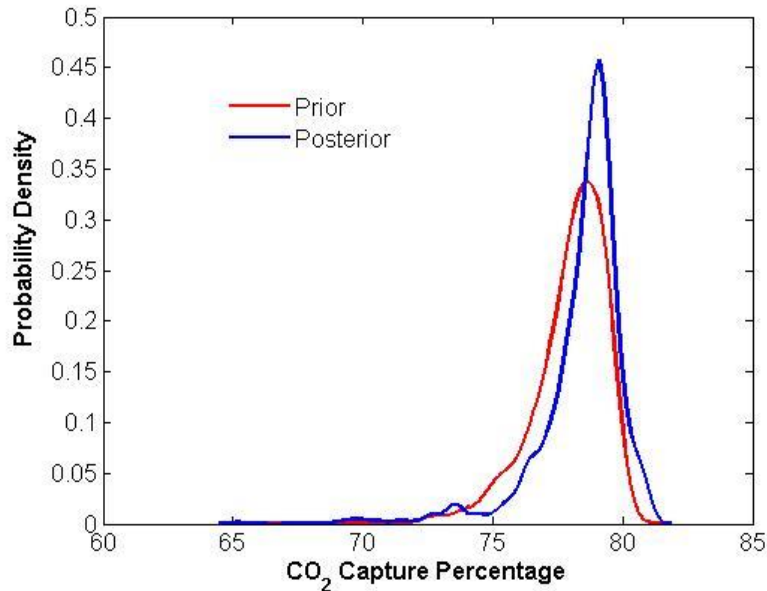


Process Model



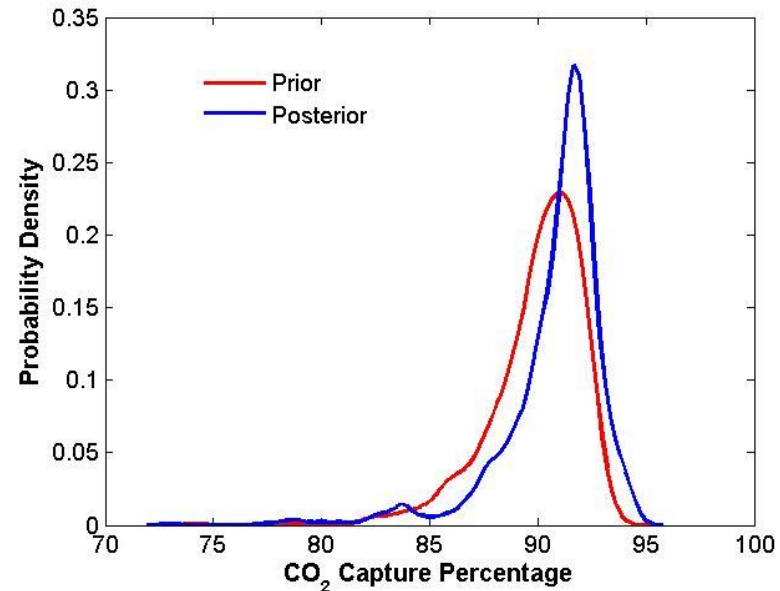
Process Model

# Absorber Uncertainty Quantification



## Case 1

Liquid Flowrate: 3000 kg/hr  
Vapor Flowrate: 680 kg/hr  
Lean Loading: 0.35 mol CO<sub>2</sub>/MEA

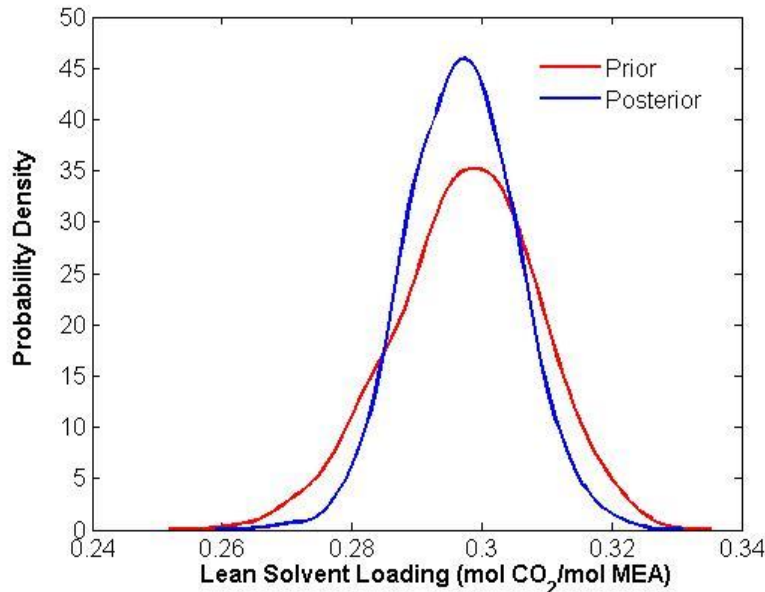


## Case 2

Liquid Flowrate: 3600 kg/hr  
Vapor Flowrate: 680 kg/hr  
Lean Loading: 0.35 mol CO<sub>2</sub>/MEA

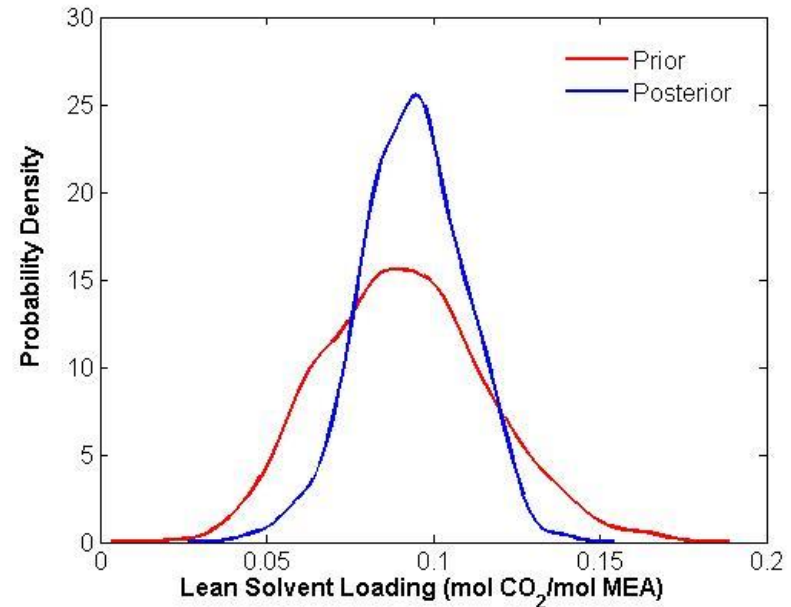


# Stripper Uncertainty Quantification



## Case 1

Solvent Flowrate: 3100 kg/hr  
Reboiler Duty: 140 kW  
Rich Loading: 0.5 mol CO<sub>2</sub>/MEA



## Case 2

Solvent Flowrate: 3100 kg/hr  
Reboiler Duty: 400 kW  
Rich Loading: 0.3 mol CO<sub>2</sub>/MEA

# High-Viscosity Solvent

- A novel solvent designed by GE is being investigated by the CCSI team. Some features of this solvent are:
  - High-viscosity and its strong dependence on the CO<sub>2</sub> loading
  - Low vapor-pressure
  - Higher degradation temperature leading to high-pressure operation of the desorber thus reducing the CO<sub>2</sub> compression penalty
- Experimental data including VLE and heat of absorption data were obtained for developing thermodynamic and transport properties model.
- Experiments were also conducted at a bench-scale system as well as on a wetted wall column apparatus. The experimental data were utilized to develop models for the interfacial area, mass transfer coefficients and holdup, that are directly affected by the viscosity.

# Viscosity Model

## Andrade Model in Aspen Plus

$$\ln(\mu_{mix}) = \sum_i w_i \ln(\mu_i) + \sum_i \sum_j (k_{ij} w_i w_j + m_{ij} w_i^2 w_j^2)$$

$$k_{ij} = a_{ij} + \frac{b_{ij}}{T}$$

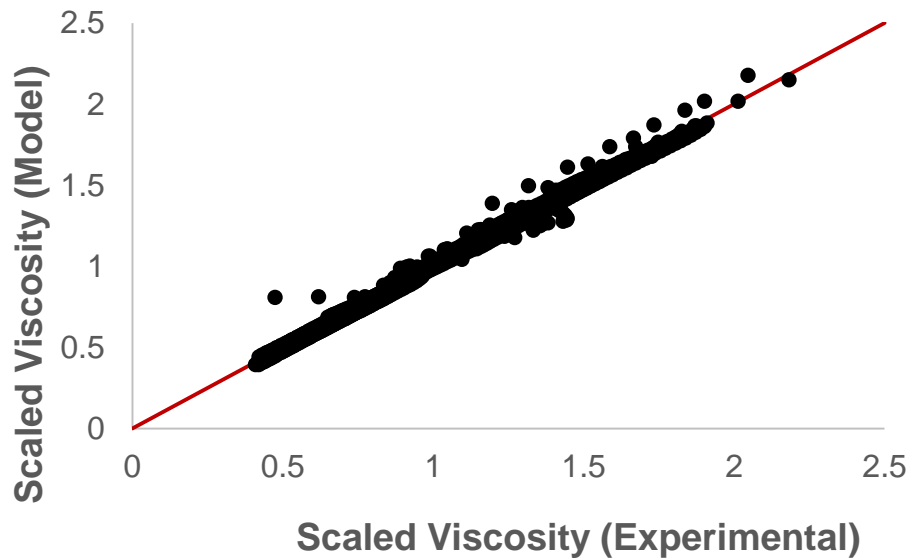
$$m_{ij} = c_{ij} + \frac{d_{ij}}{T}$$

$$\ln(\mu_i) = a_i + \frac{b_i}{T} + c_i \ln(T)$$

## Akaike Information Criterion (Parameter Selection)

$$AIC = N \ln\left(\frac{SSE}{N}\right) + 2k$$

**k** = Number of Parameters  
**N** = Number of Data  
**SSE** = Sum of Square Error



\* Data and Model predictions given in terms of  $\ln(\mu_{mix})$ .

# Thermodynamic Framework

Physical Equilibrium

$$P_{CO_2} = H_{CO_2} x_{CO_2} \gamma_{CO_2}$$

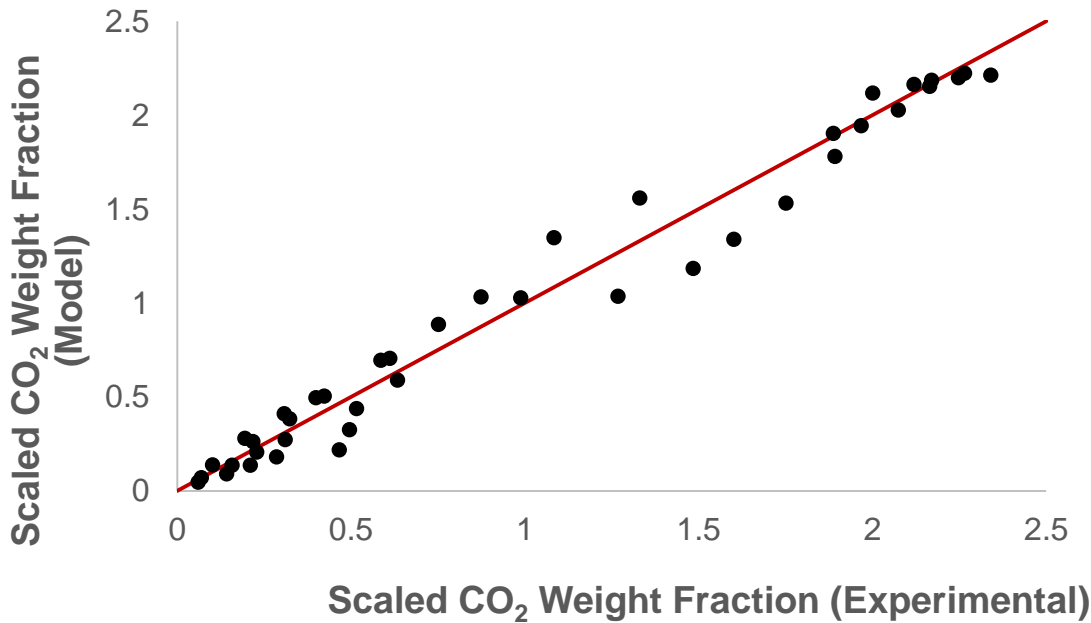
Chemical Equilibrium

$$K_{eq} = \frac{[Prod]}{[React][CO_2]}$$

Model parameters calibrated to optimize fit to VLE data:

$$H_{CO_2} = \exp\left(H_1 + \frac{H_2}{T}\right)$$

$$K_{eq} = \exp\left(K_1 + \frac{K_2}{T}\right)$$



# Model Validation Using Bench Scale Data

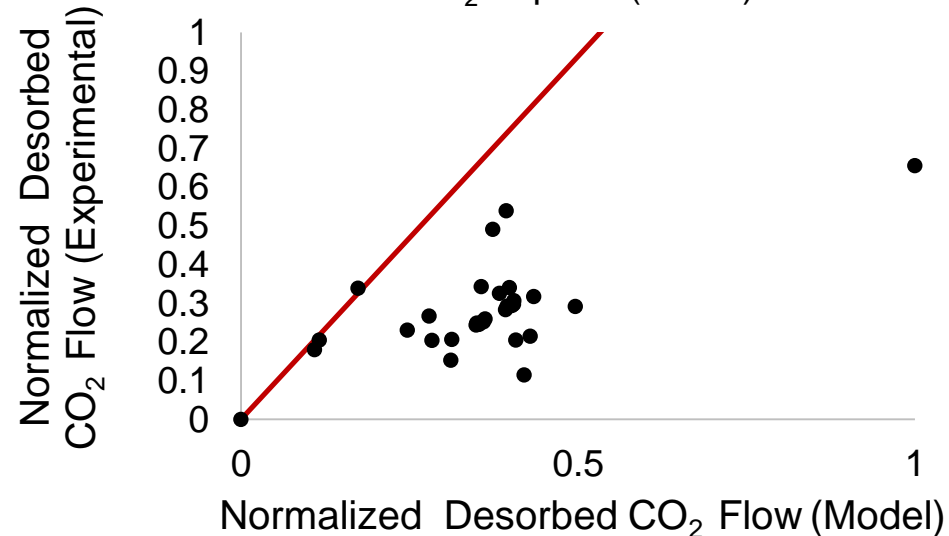
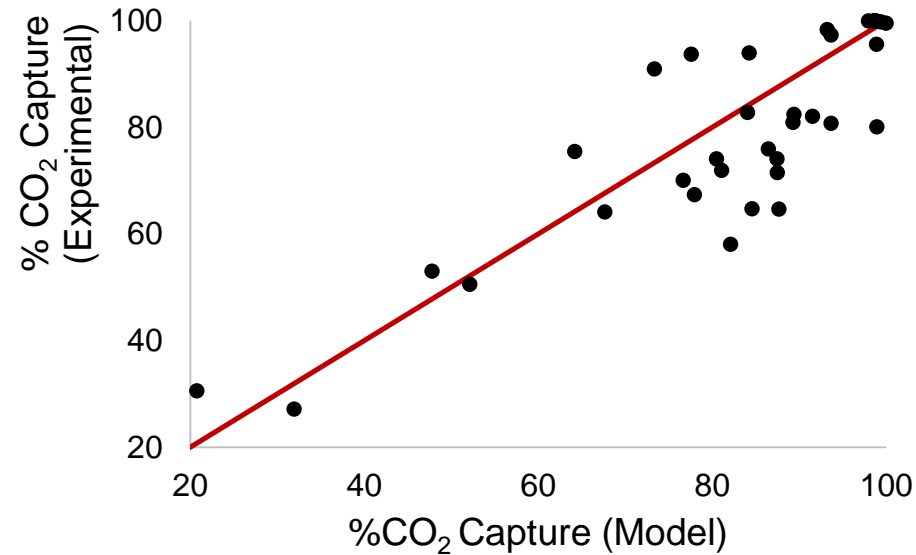
- Rate-based Aspen Plus™ model
  - Mass transfer coefficients: Modified Billet and Schultes model<sup>1</sup> (1993)
  - Interfacial area: Modified Tsai Model (2010)
  - Holdup: Modified Billet and Schultes model (1999)
- The pre-exponential factor and activation energy of the forward reaction were regressed

$$r_{CO_2} = k_f \left( [CO_2][Reac] - \frac{1}{K_{eq}} [Prod] \right)$$

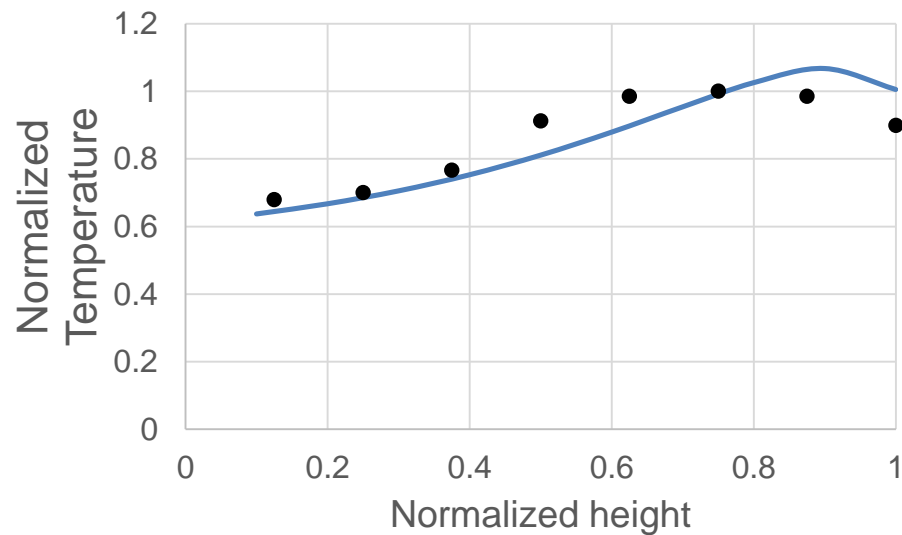
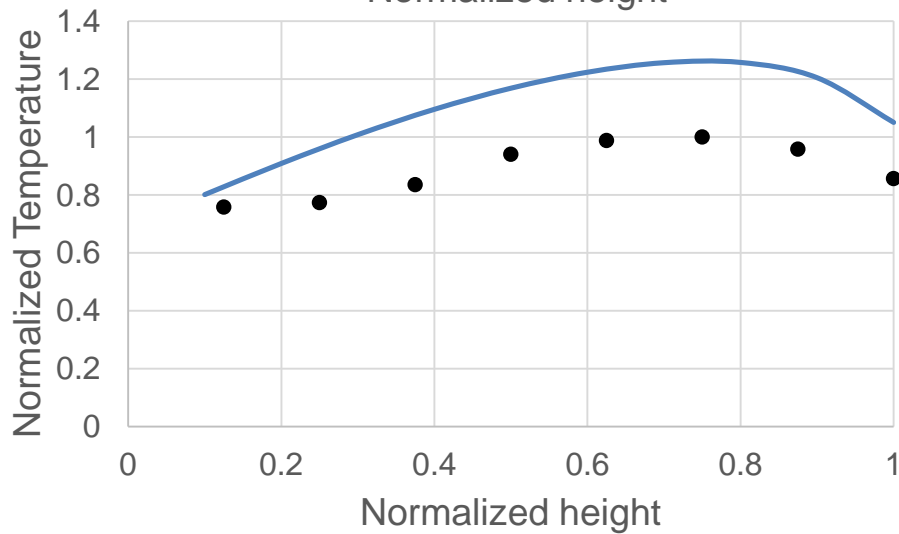
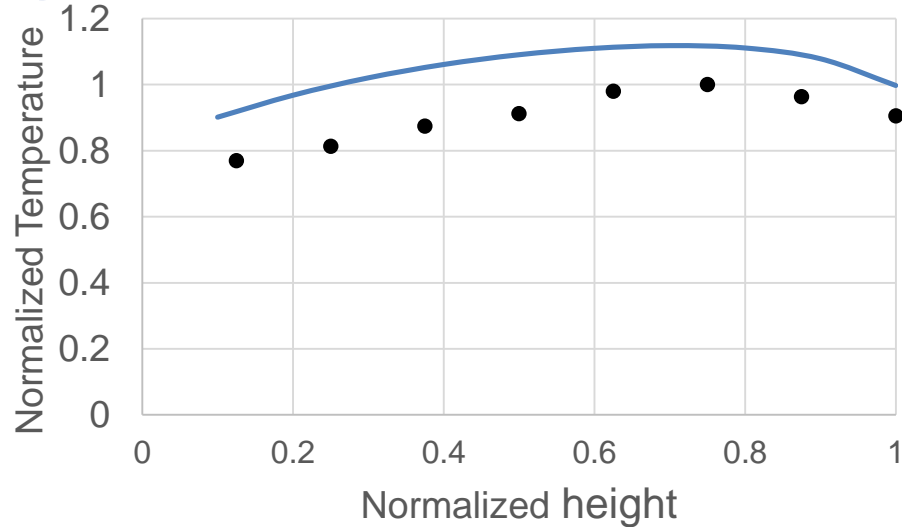
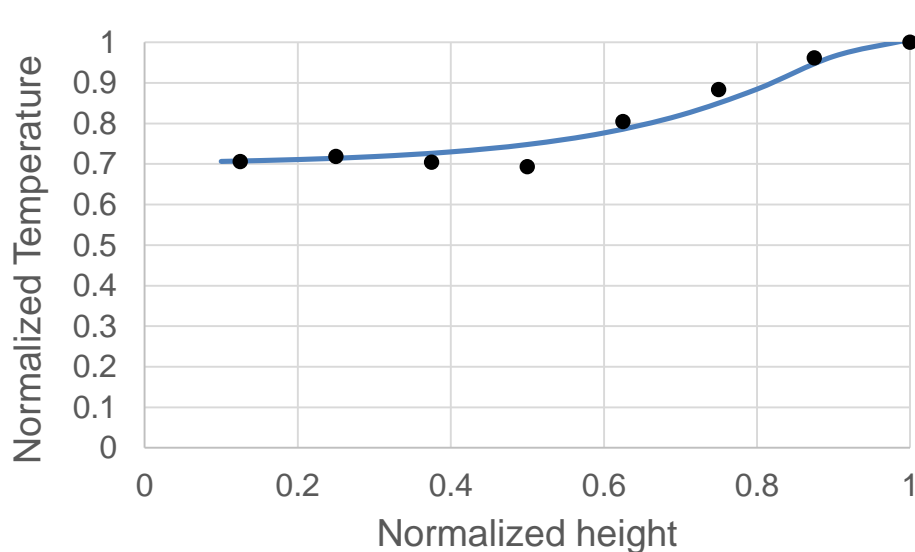
<sup>1</sup>Billet R, Schultes M. Predicting Mass Transfer in Packed Columns. Chem. Eng. Technol. 1993;16(1):1-9.

<sup>2</sup>Tsai R.E. Mass Transfer Area of Structured Packing. Ph.D. Dissertation, UT, Austin, 2010

<sup>3</sup>Billet R, Schultes M. Prediction of Mass Transfer Columns with Dumped and Arranged Packings: Updated Summary of the Calculation Method of Billet and Schultes. Chem. Eng. Res. Des. 1999; 77(A6): 498-504.



# Model Validation Using Bench Scale Data



• Experimental — Model

# Conclusions

- Developed validated modeling framework with UQ capabilities for a **gold standard** model that is capable of accurate estimation in wide operating range both under steady-state and dynamic conditions
- Developed dynamic model validation protocol
- Model predicted the experimental data for the scaleup case satisfactorily
- Demonstrated how synergistic coupling between experimental protocol and modeling methodology be mutually beneficial and informative- highly useful for scale up

**Acknowledgement.** 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 information, data, or work presented herein was funded in part by the National Energy Technology Laboratory (NETL), U.S. Department of Energy, under Award Numbers DE-FE0013755 and DE-FE0007502.

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.

**Disclaimer.** The information, data, or work presented herein was funded in part by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.



# Thank You