CCSI²
Carbon Capture Simulation for Industry Impact

RTI – Gen 2 Non-Aqueous Solvent

Joshua Morgan
National Energy Technology Laboratory (NETL)

Advanced PSE+ Stakeholder Summit – CCSI² Breakout

October 12, 2023

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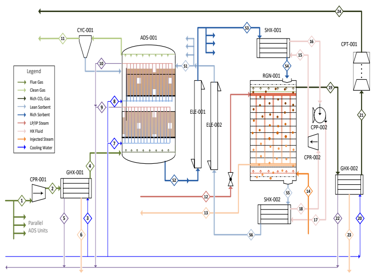
CCSI² – Modeling, Optimization and Technical Risk Reduction

CCSI²
Carbon Capture Simulation for Industry Impact

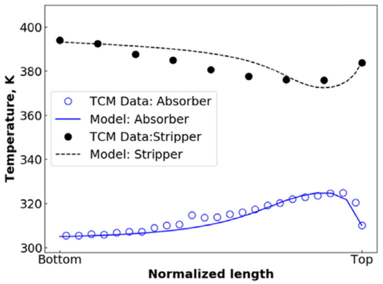
Multi-lab modeling initiative to support carbon capture technology development

National Energy Technology Laboratory · Berkeley Lab · Lawrence Livermore National Laboratory · Los Alamos National Laboratory · Pacific Northwest National Laboratory · Oak Ridge National Laboratory · Carnegie Mellon · West Virginia University · University of Notre Dame · The University of Texas at Austin · UT · University of Pittsburgh

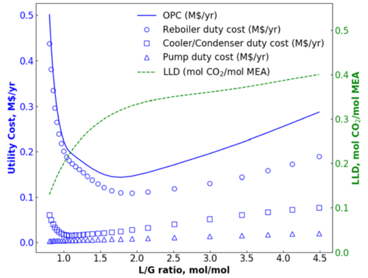
High Fidelity Process Modeling



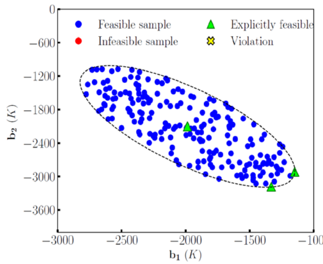
Model Validation



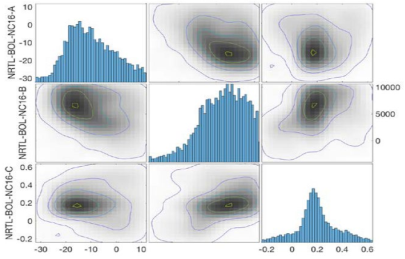
Process Optimization



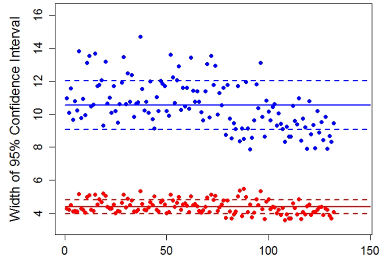
Robust Design

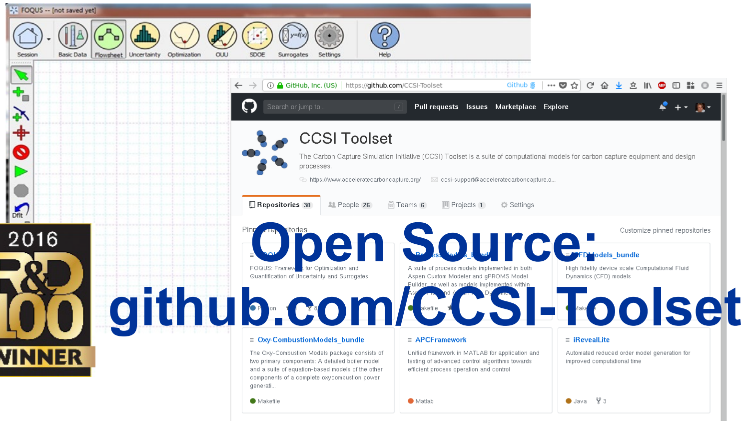


Uncertainty Quantification



Maximizing Learning





2016 R&D 100 WINNER

Open Source:
github.com/CCSI-Toolset

IDAES
Institute for the Design of Advanced Energy Systems

Open Source:
github.com/IDAES/idaes-pse

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Presentation Overview

- Background on CCSI^2/RTI collaboration
- Previous work – evaluation of NAS solvent at TCM
- Current work scope – CCSI^2 support of GEN2NAS system
  - Project goals and work plan
  - Process modeling efforts
- Summary and conclusions

RTI – SLB – CCSI² Collaboration

Non-Aqueous Solvent (NAS) technology:

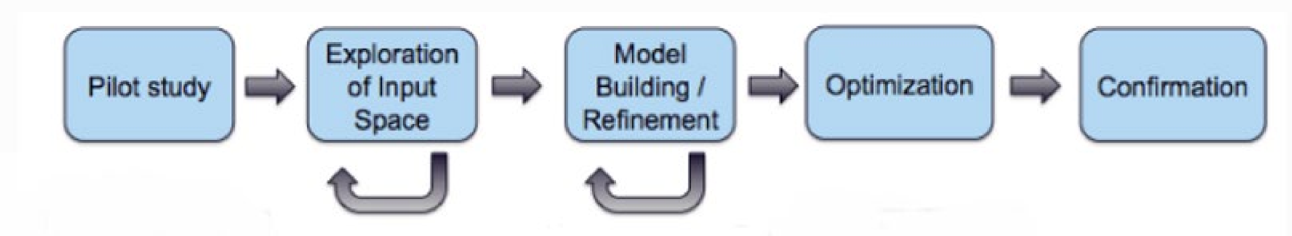
- Class of solvent-based CO_2 capture technologies developed by RTI and demonstrated at multiple scales from lab to large pilot in series of projects (2010 – present)
- Projected to have improved solvent regeneration energy requirement over baseline MEA process (~ 40%)
- Partnered with SLB (*formerly Schlumberger*) in 2022 to accelerate the industrialization of the NAS technology

CCSI²:

- Initiated collaboration with RTI in 2019 focused on process modeling and supporting test campaign at TCM through design of experiments (DoE)
- TCM test campaign completed in 2022 – incorporating experimental designs for testing with natural gas and coal-based flue gas sources
- Currently supporting new project for process modeling of GEN2NAS system

Sequential Design of Experiments (SDoE)

- **<u>Design of experiments (DOE)</u>** is a powerful tool for accelerating learning by targeting maximally useful input combinations to match experiment goals
- **<u>Sequential design of experiments (SDoE)</u>** allows for incorporation of information from an experiment as it is being run, by updating selection criteria based on new information
- Specific algorithms can be tailored to match experimental goals. Options available in the CCSI Toolset include:
  - Uniform Space Filling (USF)
  - Non-Uniform Space Filling (NUSF)
  - Input-Response Space Filling (IRSF)
  - Robust Optimality-Based Design of Experiments (ODoE)
- Recommended to run experiments in phases to take advantage of SDoE capabilities and customize test designs to meet expected project outcomes



<u>Detailed discussion on SDoE</u>:

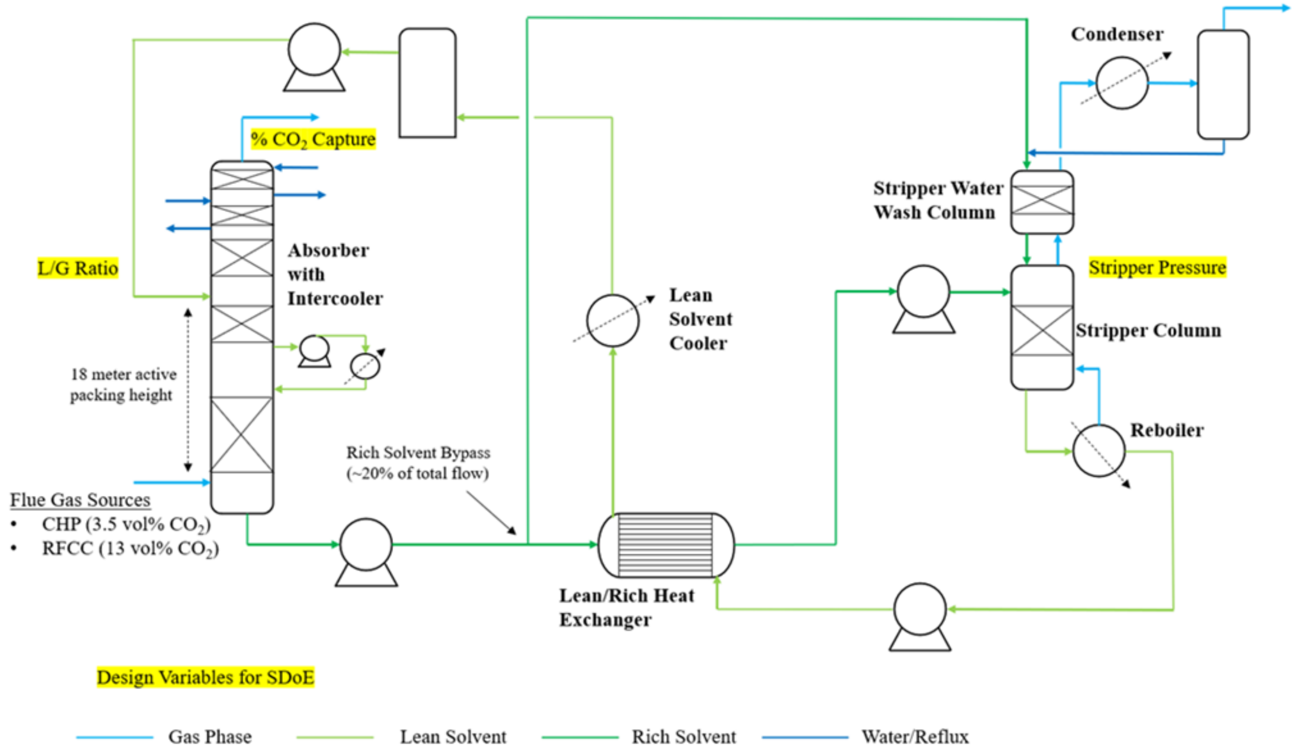
Technical Risk Reduction: Sequential Design of Experiments and Uncertainty Quantification (Abby Nachtsheim – LANL)
Thursday (8/31/2023) @ 9:30 AM during Point Source Carbon Capture Breakout Session

TCM Test Campaign for RTI NAS Solvent

- Leveraged SDoE to guide NAS test campaign at TCM → focused on demonstrating high levels of CO_2 capture with low solvent emissions and regeneration energy requirement

- CCSI[2] team contributed separate designed experiments for gas-fired combined heat and power (CHP) [3.7 vol% CO_2] and residual fluidized catalytic cracker (RFCC) [13.5 vol% CO_2] flue gas sources

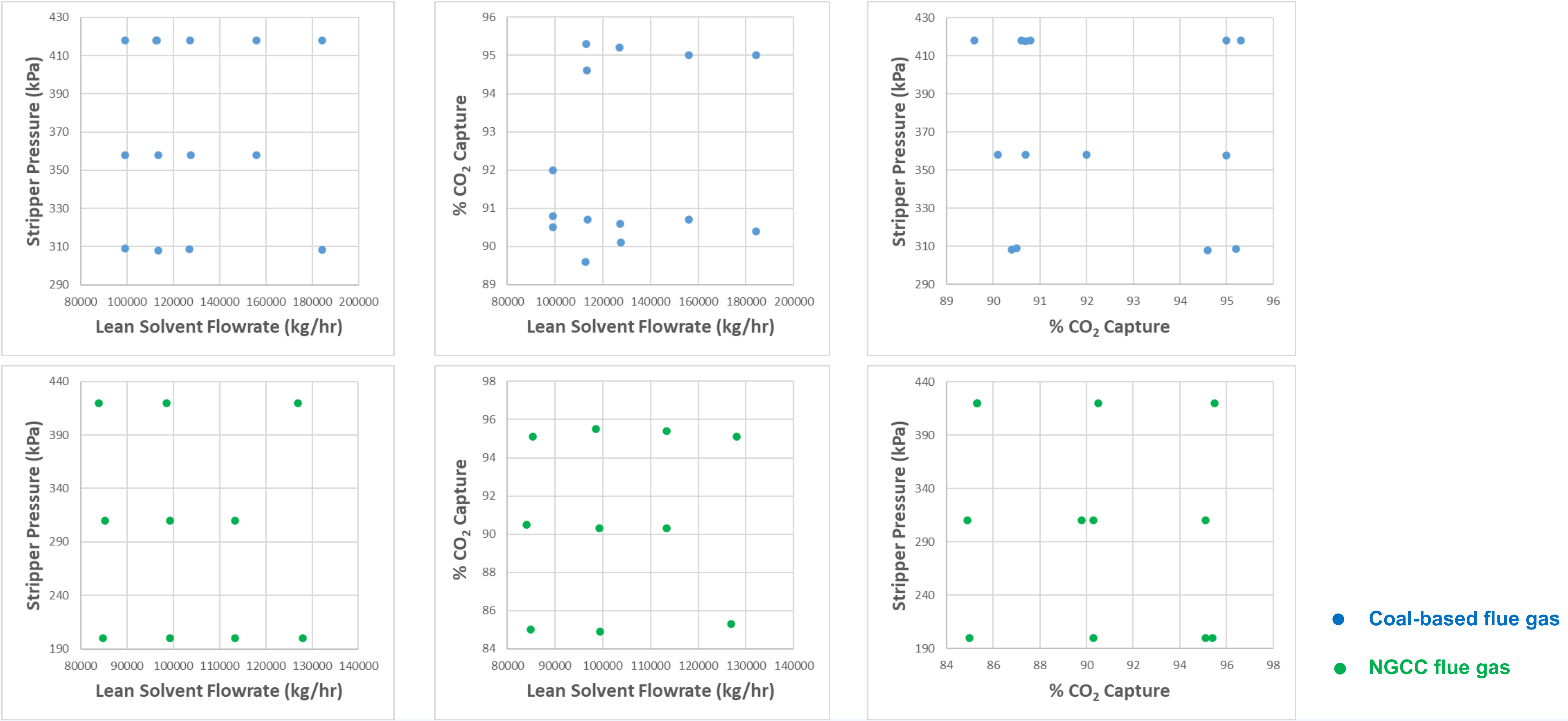
- Each designed experiment includes a series of test matrices with 12-22 proposed operating conditions for flexibility in design size



<u>Design factors</u>:
CO_2 Capture: 85 – 95%
Absorber L/G Ratio: 2.5 – 6.5 kg/kg
Stripper Pressure: 0.9 – 3.2 barg

SDoE Results – Data Collection at TCM

Data sets generated for SDoE demonstrate good coverage of operation space:



SDoE Results – Data Collection at TCM

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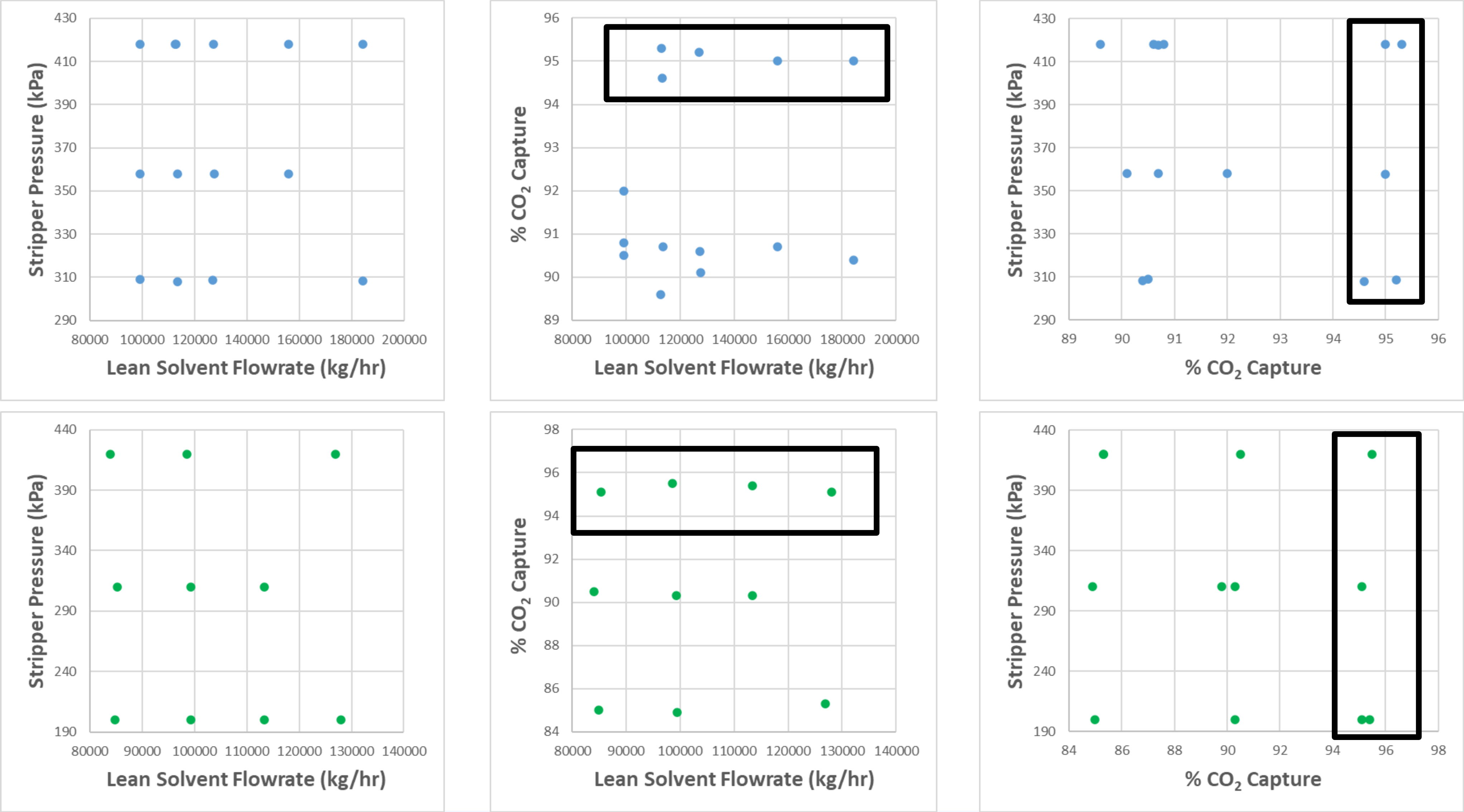


Characterization of parameter interactions through DoE → demonstrates multiple pathways to high capture levels based on the trade-off between solvent circulation and CO_2 capacity

- Coal-based flue gas
- NGCC flue gas

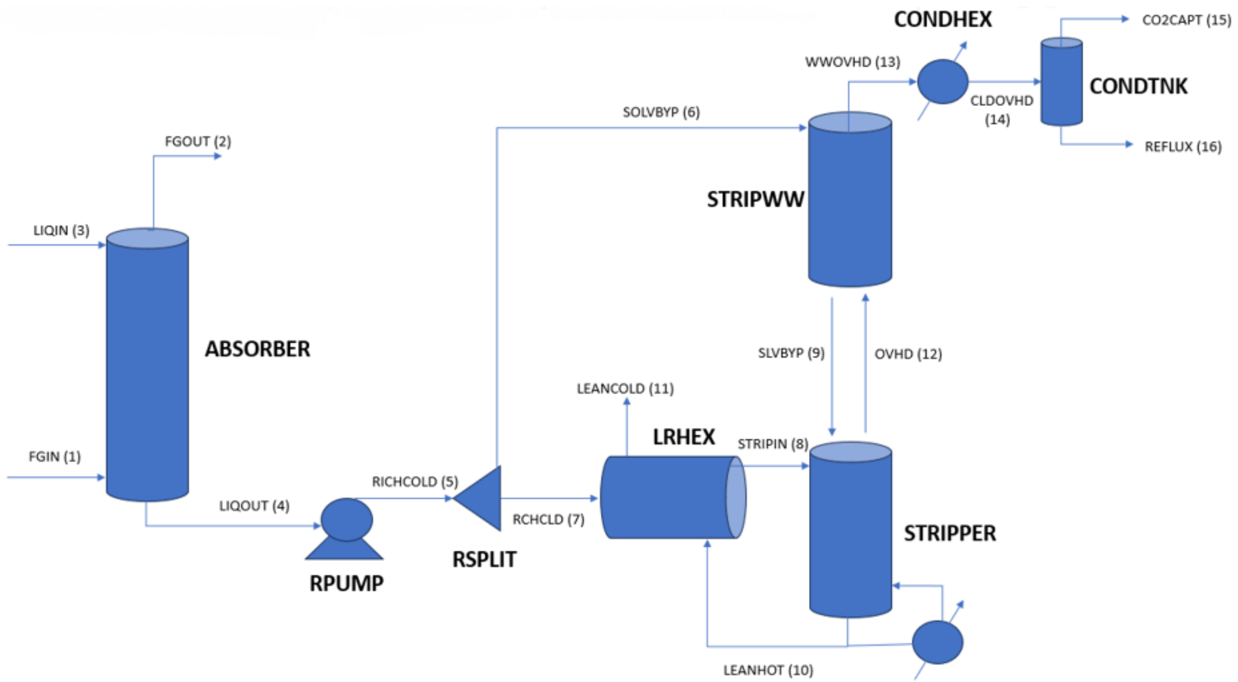
CCSI² Support of GEN2NAS Project

- RTI in process of developing GEN2NAS solvent system. Current plan is to identify two promising formulations (from a candidate set of around ~ 65) and collect relevant data for each:
  - Physical properties (density, viscosity, VLE)
  - Bench-scale performance data (e.g., CO_2 capture)
- CCSI² scope of work includes:
  - Quantification of effect of solvent properties (e.g., viscosity) on process equipment design
  - Support model development of GEN2NAS system – including property models, thermodynamics, mass transfer/interfacial area and implement uncertainty quantification for model parameters

CCSI^2 Support of GEN2NAS Project – Challenges and Opportunities

- Effective execution of project scope requires *improvement in model robustness* and ability to generalize to solvents with *variable physical properties*
  - Uncertainty quantification (UQ) tools can be leveraged to account for variations in physical properties → model robustness is essential
- Process data collected from TCM are currently being leveraged to assess quality of existing models and identify potential improvements and formulate UQ problems

Preliminary TCM Model



Base Case Simulation

Inlet Flue Gas

Temperature (°C)	40
Pressure (kPa)	110
Mass Flowrate (kg/hr)	28380
Mole Fractions	
H_2O	0.0703
CO_2	0.0370
N_2	0.7720
O_2	0.1207

Lean Solvent

Temperature (°C)	35
Pressure (kPa)	150
Mass Flowrate (kg/hr)	115000
Loading (mol/mol Amine)	
CO_2	0.100
H2O	0.917
Inert	0.315

Preliminary TCM Model

Absorber Model

- Packing height of 18 meter (2 beds) without intercooling
- Packing discretized with 30 stages
- For quantification of relative importance of various submodels on process performance, modeled at three levels of increasing fidelity (and thus computational complexity):
  (A) Equilibrium column
  (B) Rate-based column without kinetics
  (C) Rate-based column with kinetics

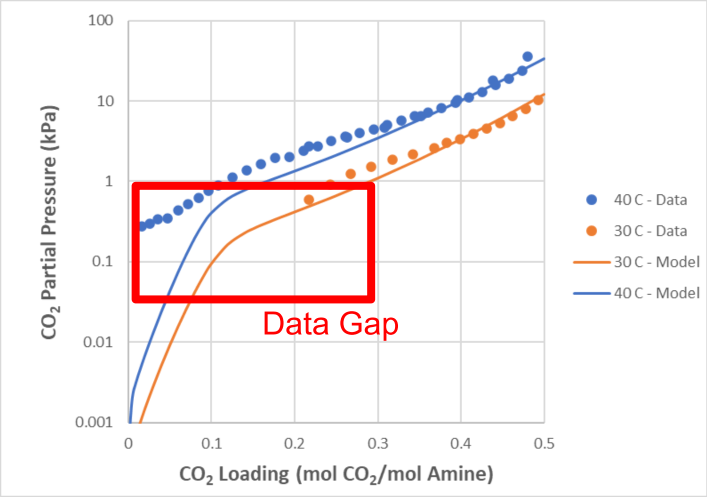
Stripper Model

- Bypass of 20% of rich solvent from lean/rich heat exchanger
- Modeled as equilibrium column with 5 computational stages

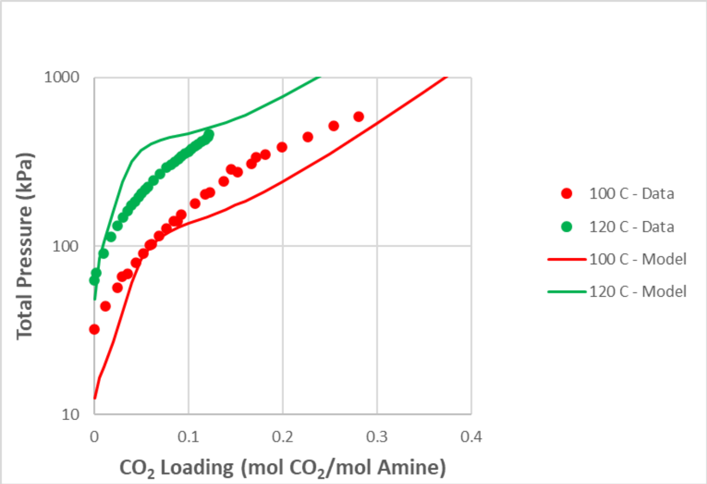
Preliminary Process Model - Thermodynamics

Vapor-Liquid Equilibria

Absorber Region

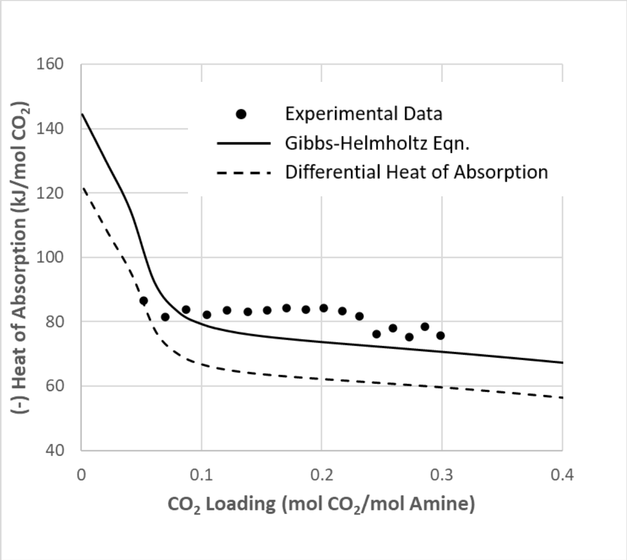


Stripper Region



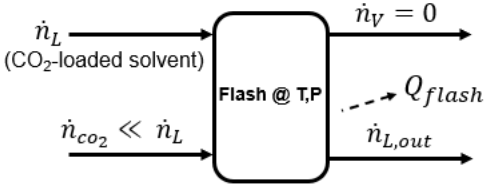
Heat of Absorption

Fit @ 100°C:



- Heat of absorption not directly defined in Aspen Plus as physical property. Two options for including in thermodynamic model regression:
  - Differential heat of absorption – requires user subroutine
  - Gibbs-Helmholtz equation – use temperature perturbation on CO_2 partial pressure (*method used in this work*)
- With internally consistent thermodynamic framework, these methods should produce comparable results
- Inconsistency noted here is not unique to this system

Differential Heat of Absorption:



$$\Delta H_{co_2-abs} \approx \frac{Q_{flash}}{\dot{n}_{co_2}}$$

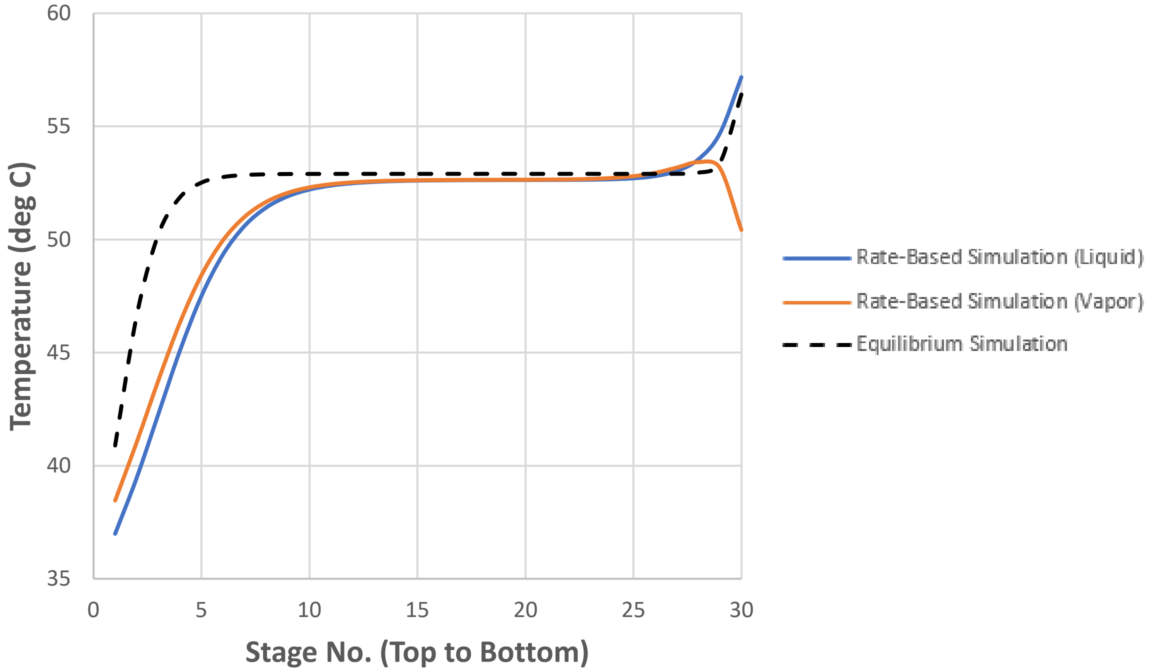
Gibbs-Helmholtz Equation:

$$\Delta H_{co_2-abs} \approx -R \left(\frac{\partial \ln(f_{co_2})}{\partial \left(\frac{1}{T}\right)} \right) \Bigg|_{\sigma,\{x_0\}}$$

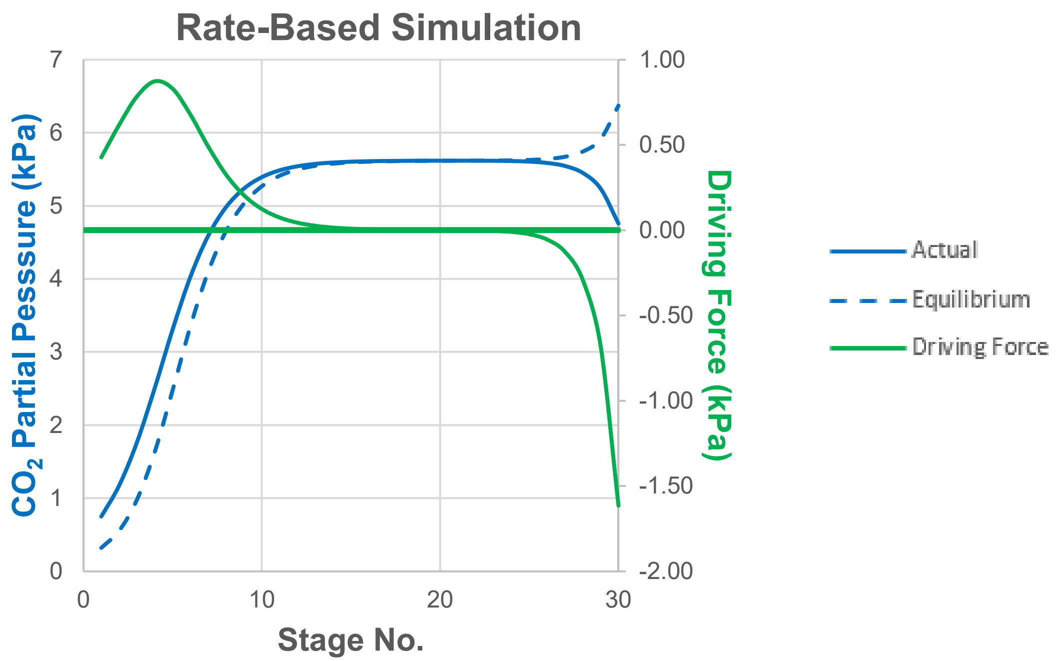
Preliminary TCM Model – Absorber Results

	% Capture	Rbr. Duty (MW)	SRD (MJ/kg CO_2)
(A) Equilibrium Absorber	78.15	1.386	3.92
(B) Rate-Based Absorber	81.97	1.400	3.77

Temperature Profiles



CO_2 Driving Force Profiles



Conclusion – effect of switching from equilibrium to rate-based simulation appears to be minimal → may not be practical to calibrate mass transfer/interfacial area parameters to fit plant data

CCSI[2]
Carbon Capture Simulation for Industry Impact

Preliminary TCM Model – Absorber Results

Chemical Reactions

$2\ H_2O \leftrightarrow H_3O^+ + OH^-$
$Amine + H_3O^+ \leftrightarrow AmineH^+ + H_2O$
$2\ Amine + CO_2 \leftrightarrow AmineH^+ + AmineCO^-$

Kinetically controlled reaction

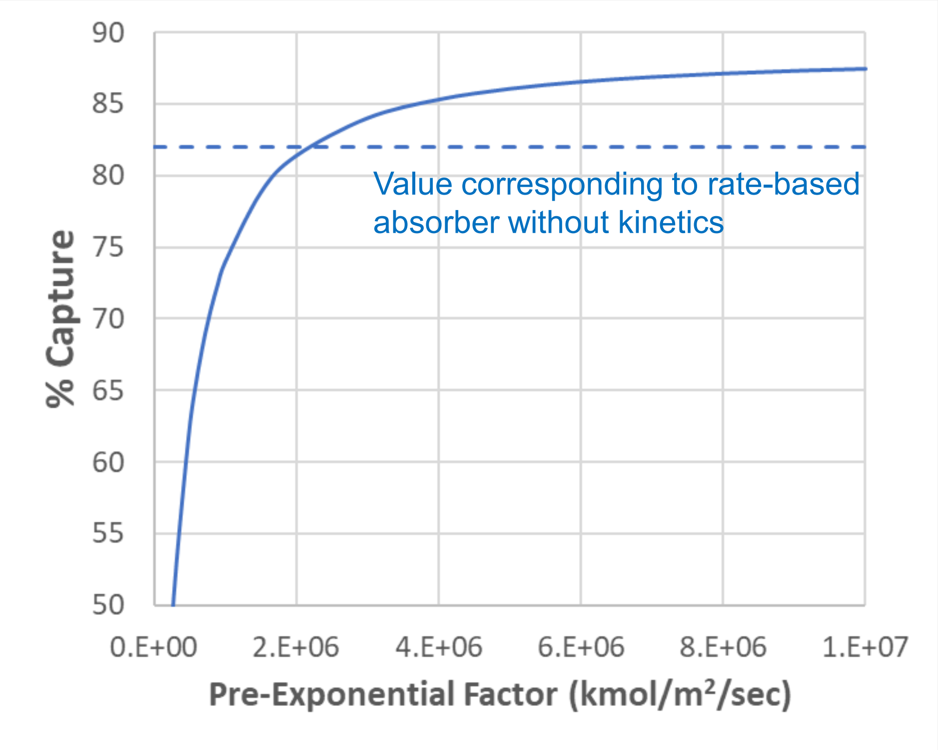
Kinetics implemented with user subroutine:

$$r_f = k_f a_{Amine}^2 a_{CO_2} \qquad r_{rev} = \frac{k_f}{K_{eq}} a_{AmineH^+} a_{AmineCO^-}$$

$$k_f = \mathbf{k_{0f}} \exp\left(\frac{-\mathbf{E_f}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \qquad K_{eq} = \left.\frac{a_{AmineH^+} a_{AmineCO^-}}{a_{Amine}^2 a_{CO_2}}\right|_{eq}$$

Fitting parameter

Parameter	Value
k_{0f} (kmol/m²/sec)	Analyzed in sensitivity analysis
E_f (J/mol)	50000

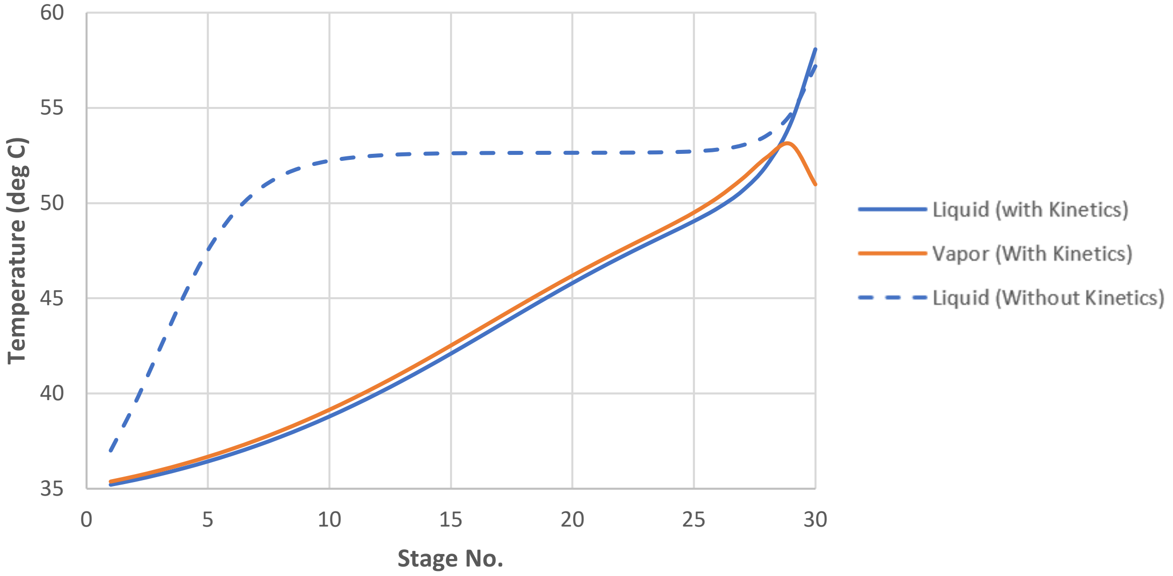


Preliminary TCM Model – Absorber Results

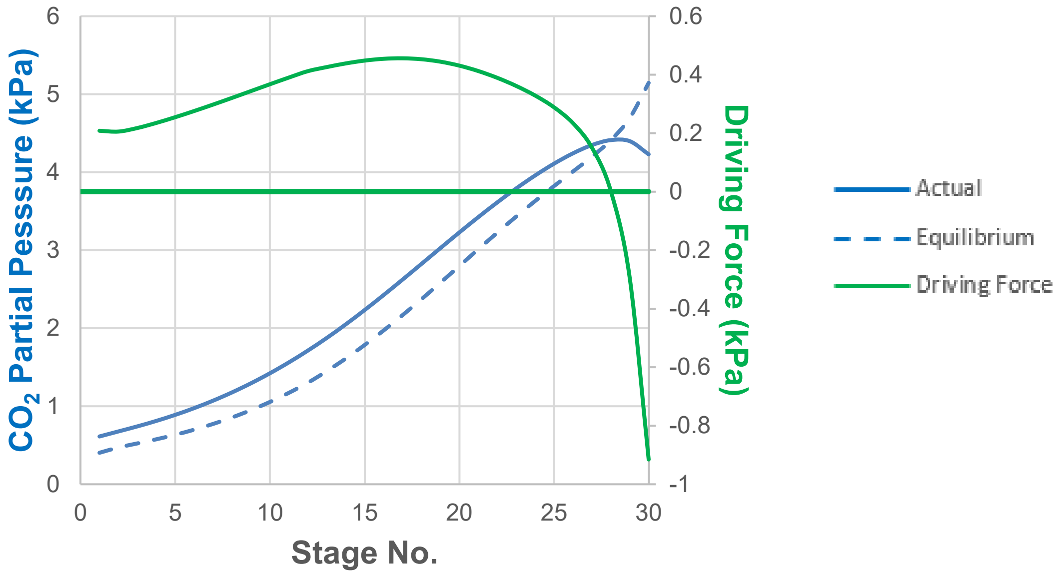
	% Capture	Rbr. Duty (MW)	SRD (MJ/kg CO_2)
(A) Equilibrium Absorber	78.15	1.386	3.92
(B) Rate-Based Absorber	81.97	1.400	3.77
(C) Rate-Based Absorber with Kinetics (*)	85.33	1.411	3.65

(*) uses fixed pre-exponential factor of 4e6 kmol/m^2/s

Temperature Profiles



CO_2 Driving Force Profiles

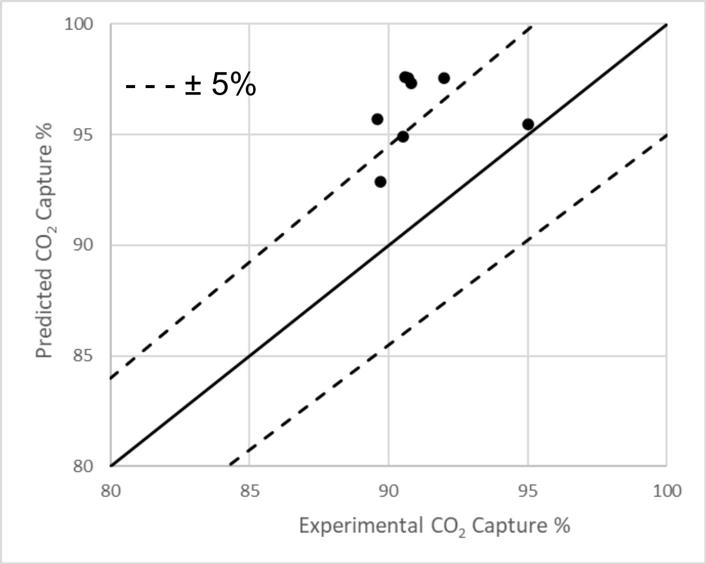


Conclusion – kinetic parameters can be tuned to adjust column performance in light of experimental data → computationally complex

TCM Model Validation: Coal-Based Flue Gas

Absorber Section

- Equilibrium model used for initial approximation
- Discrepancies can be investigated through UQ problems associated with thermodynamics, kinetics, and possibly mass transfer/interfacial area (if improvements in robustness can be realized)

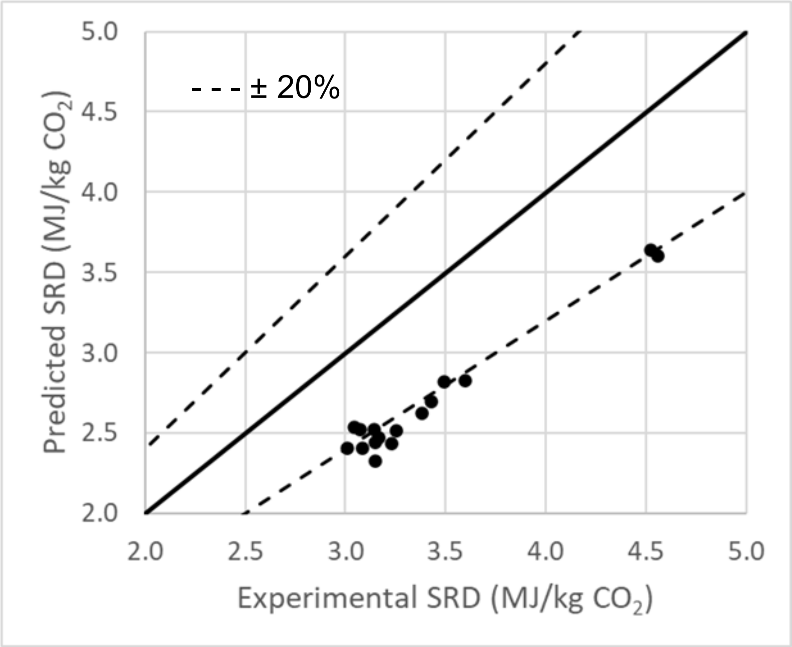


Includes only points for which converged simulation was obtained. Robustness issues primarily associated with solvent intercooling

Average error of ~ 5.5% (overprediction) for CO_2 capture percent

Stripper Section

- Modeled stripper section as standalone process with CO_2 capture constrained based on experimental data
- Stripper inlet temperature fixed to experimental value by adjusting lean/rich heat exchanger coefficient



$$SRD = \frac{Q_{reb}}{\dot{m}_{CO_2-captured}}$$

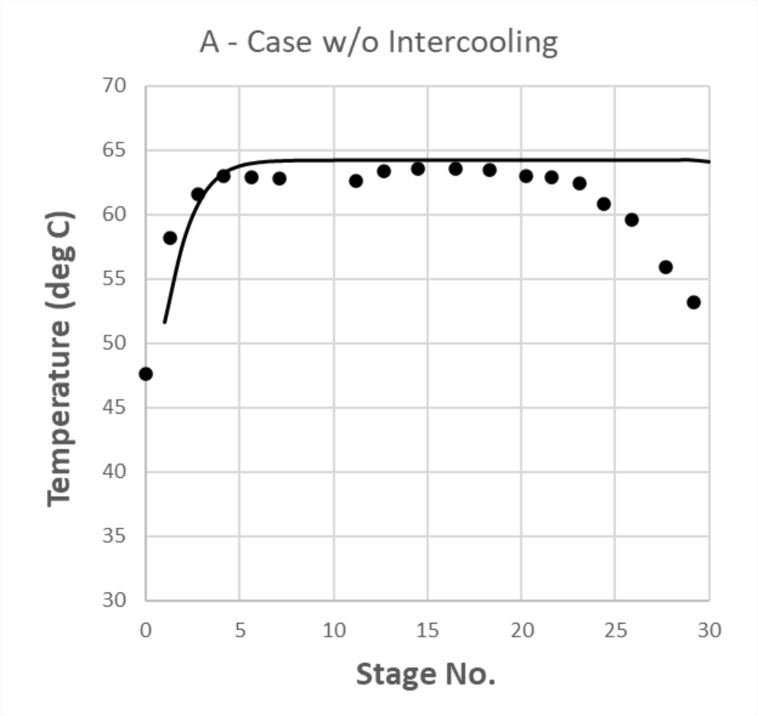
Identified bias in which the model consistently underpredicts heat of absorption by 20% - can attribute in part to heat of absorption calculation

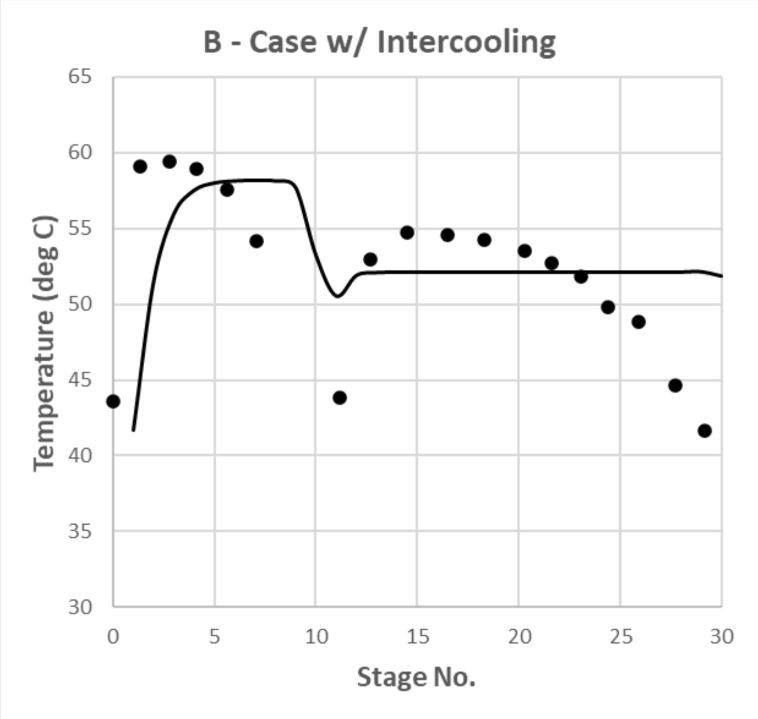
Model Validation - Absorber

- Closer look at results for some representative cases:

Case	Lean CO_2 Loading (mol CO_2/mol Amine)	FG – CO_2 vol%	L/G (kg/kg)	Intercooler Duty (MW)	% Capture - Experimental	% Capture - Predicted
A	0.0441	9.56	6.6	0	89.7	92.9
B	0.0484	13.21	3.5	1.44	92.0	97.6

Temperature Profiles:





Summary and Conclusions

- CCSI[2] collaborated with RTI for design of experimental test campaign for evaluating NAS solvent at TCM using SDoE methodology
  - Resulted in rich data set with characterization of variable interactions within multi-dimensional input space → essential for rigorous model validation and scale-up
  - Demonstrated high capture levels with reduced SRD in comparison with aqueous MEA
- Current CCSI[2] research direction is focused on evaluating and refining TCM process models in preparation for support of GEN2NAS project

Acknowledgements

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* NETL Support Contractor
** Subcontractor to SLB

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Disclaimer

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Carbon Capture Simulation for Industry Impact

For more information

Joshua.Morgan@netl.doe.gov

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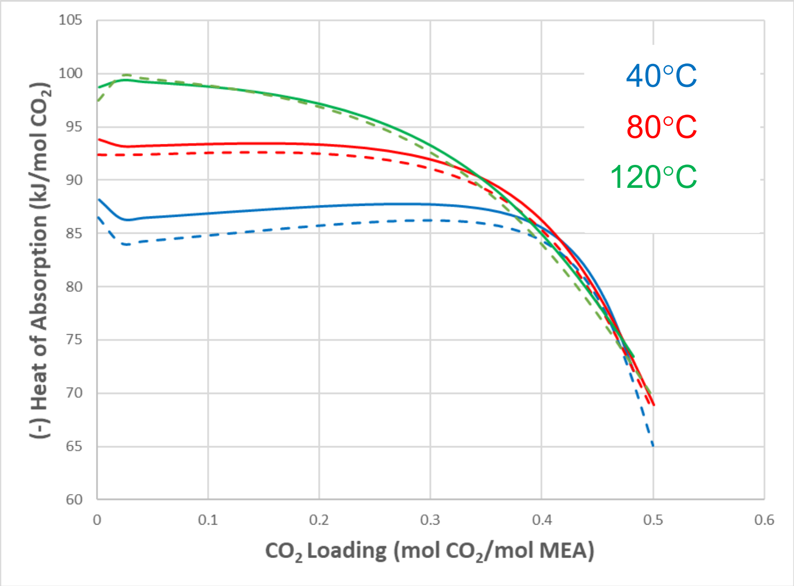
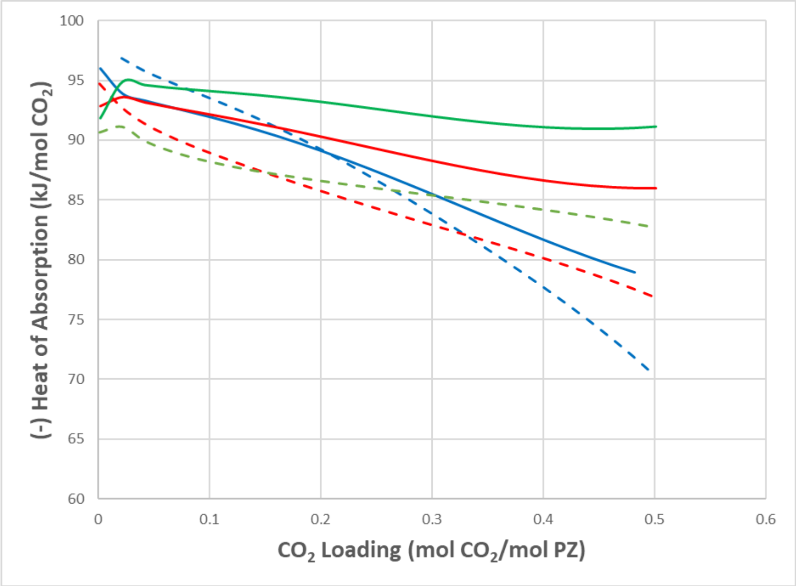
Backup Slides

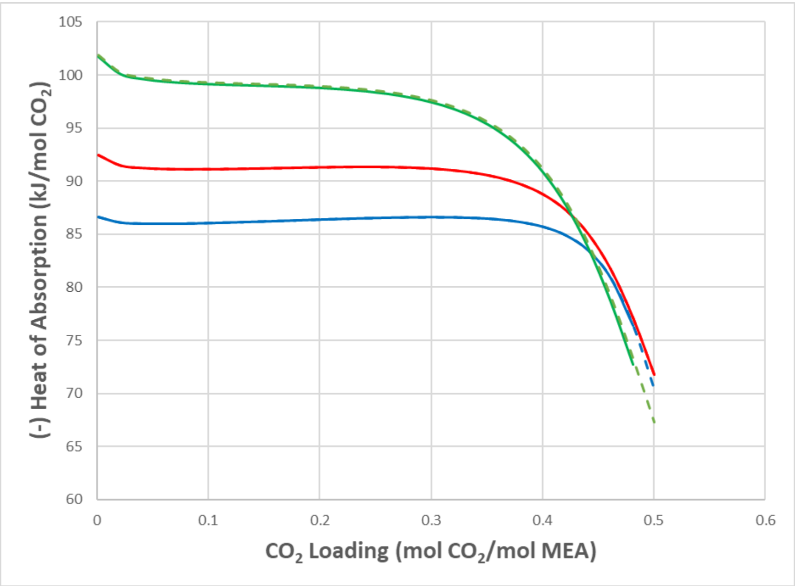
Heat of Absorption Calculation Inconsistency – Other Models



MEA model distributed with Aspen Tech software (ENRTL-RK thermodynamic method)



PZ model distributed with Aspen Tech software (ENRTL-RK thermodynamic method)



MEA model developed by CCSI team – Akaike information criterion (AIC) used to regress parameters to fit thermodynamic data - *does not include electrolyte pair parameters*
(ELECNRTL thermodynamic method)

—— Differential Heat of Absorption

– – – Gibbs-Helmholtz Equation