CCSI
Carbon Capture Simulation Initiative

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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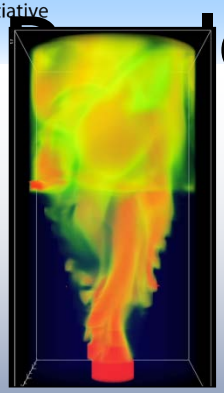
CCSI For Accelerating Technology Development

Carbon Capture Simulation Initiative



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

Berkeley Lab
Pacific Northwest National Laboratory
NETL
Los Alamos National Laboratory EST. 1943
Lawrence Livermore National Laboratory

Academia

Carnegie Mellon
Princeton University
West Virginia University
Boston University
The University of Texas at Austin

Industry

ADA Environmental Solutions
Alstom
B&W
GE
EPRI Electric Power Research Institute
Fluor
Phillips 66
AEP American Electric Power
Southern California Edison An Edison International Company San Onofre Nuclear Generating Station
Southern Company
ExxonMobil
Chevron
URS
Air Products
Eastman
aspentech
ANSYS
Schneider Electric
PSE

Outline

- Scope of Work
- Submodel Development
  - Thermodynamic and kinetic models
  - Mass transfer and hydraulic models
- Model Validation
- Conclusions

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- **Scope of Work**
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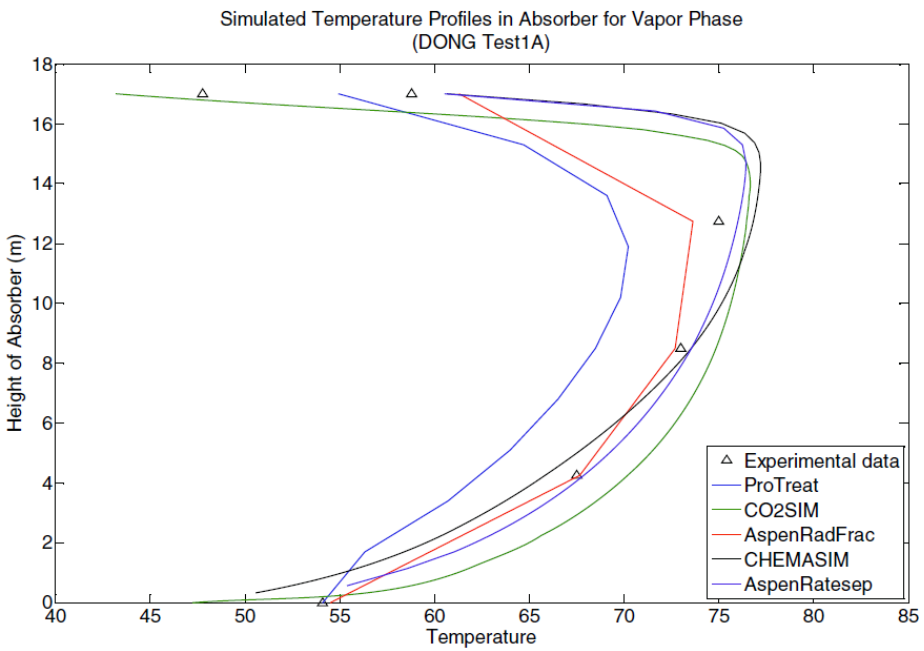
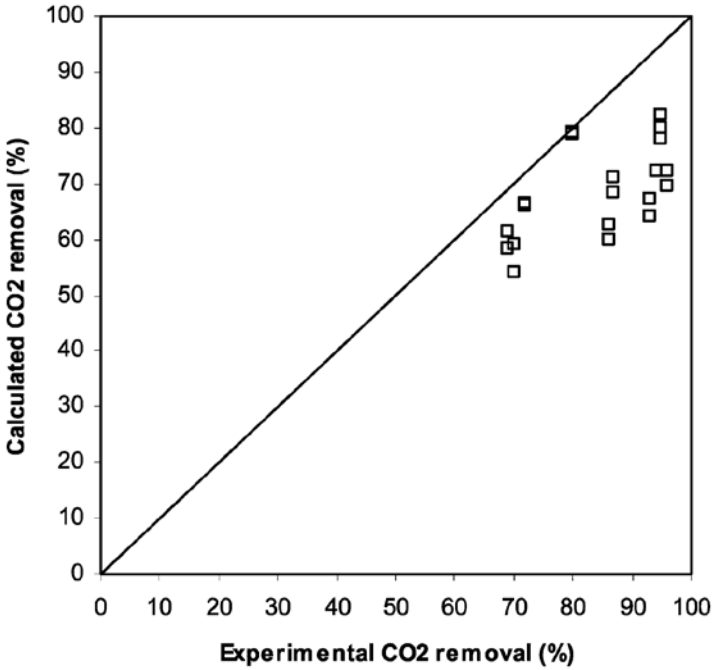
Gold Standard Solvent Model

- 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



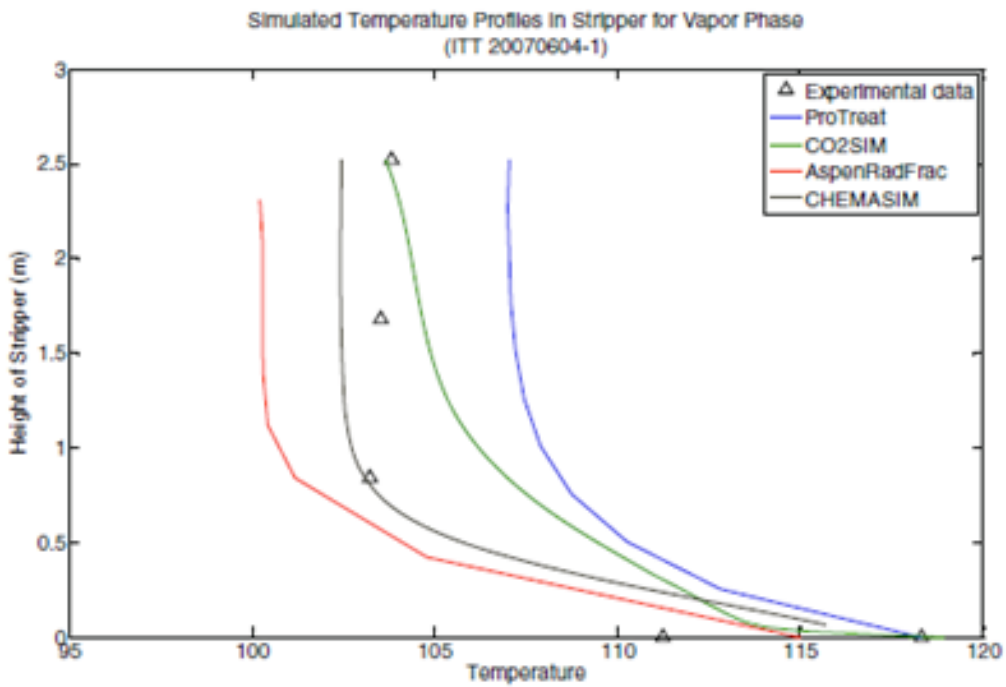


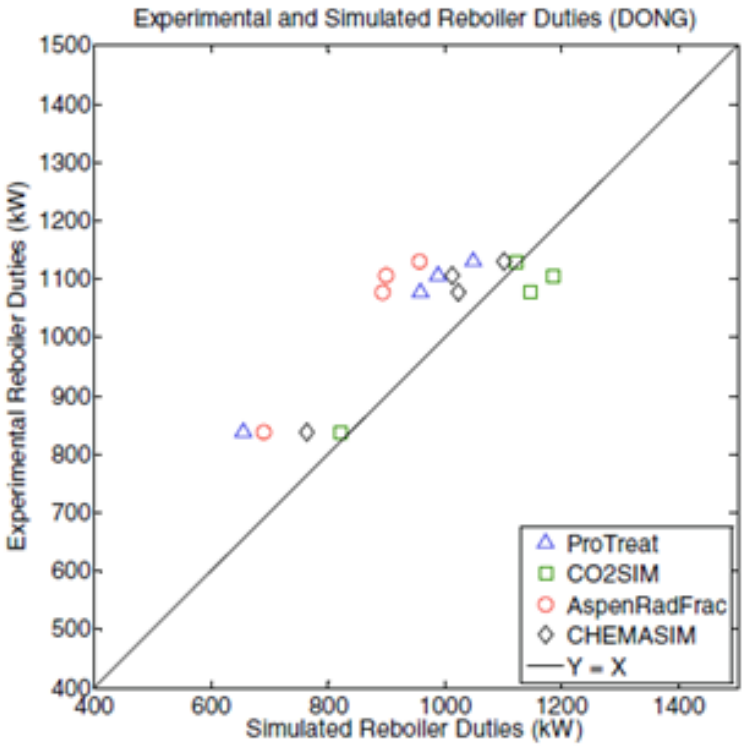
ProTreat-Optimized Gas Treating, Inc.; CO2SIM-NTNU/SINTEF CHEMASIM-BASF SE; AspenRatesep-modified by IFP

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

Zhang, et al., Rate-Based Process Modeling Study of CO_2 Capture with Aqueous Monoethanolamine Solution, Ind. Eng. Chem Res., 48, 9233-9246, 2009

Deficiencies in Existing Regenerator Models





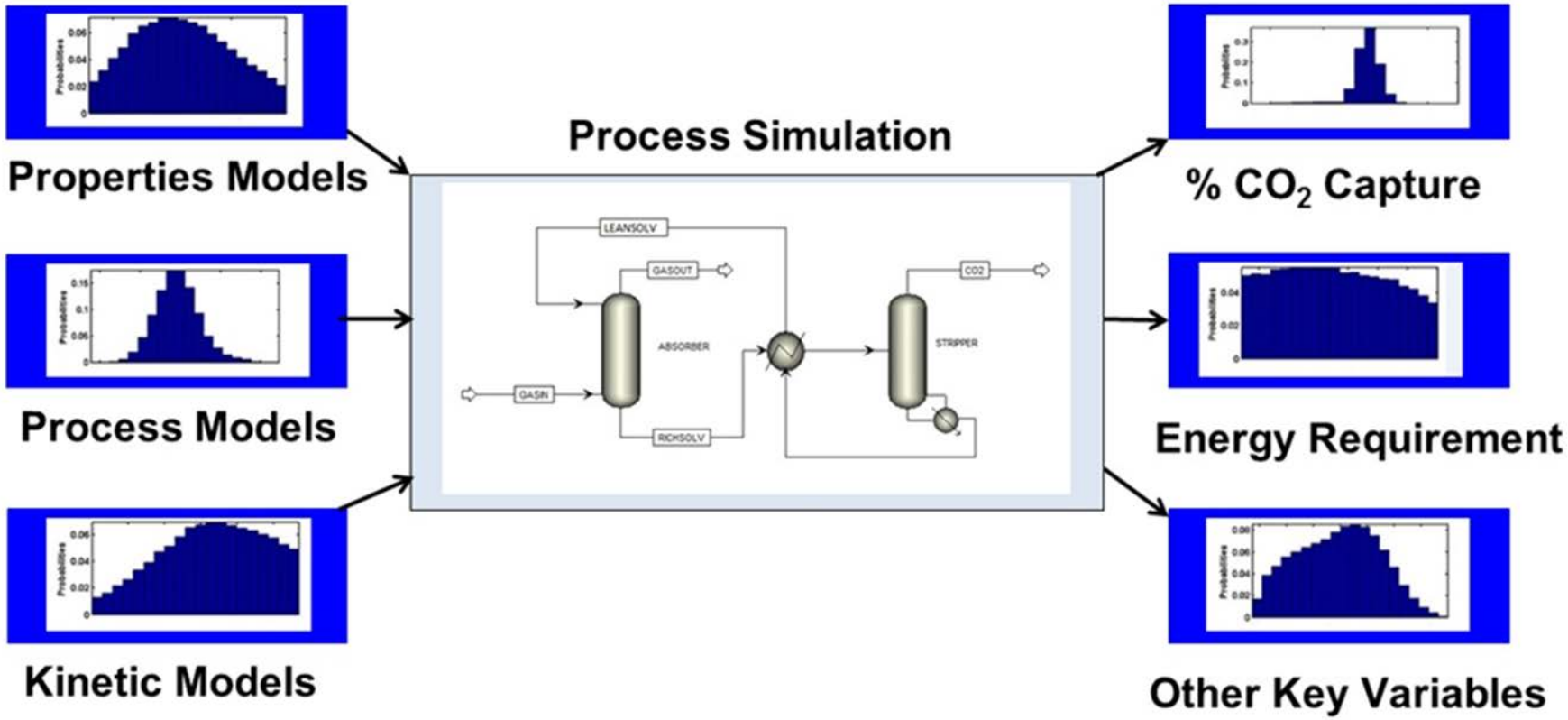
Luo et al., "Comparison and validation of simulation codes against sixteen sets of data from four different pilot plants", Energy Procedia, 1249-1256, 2009

How to Develop Gold Standard Model

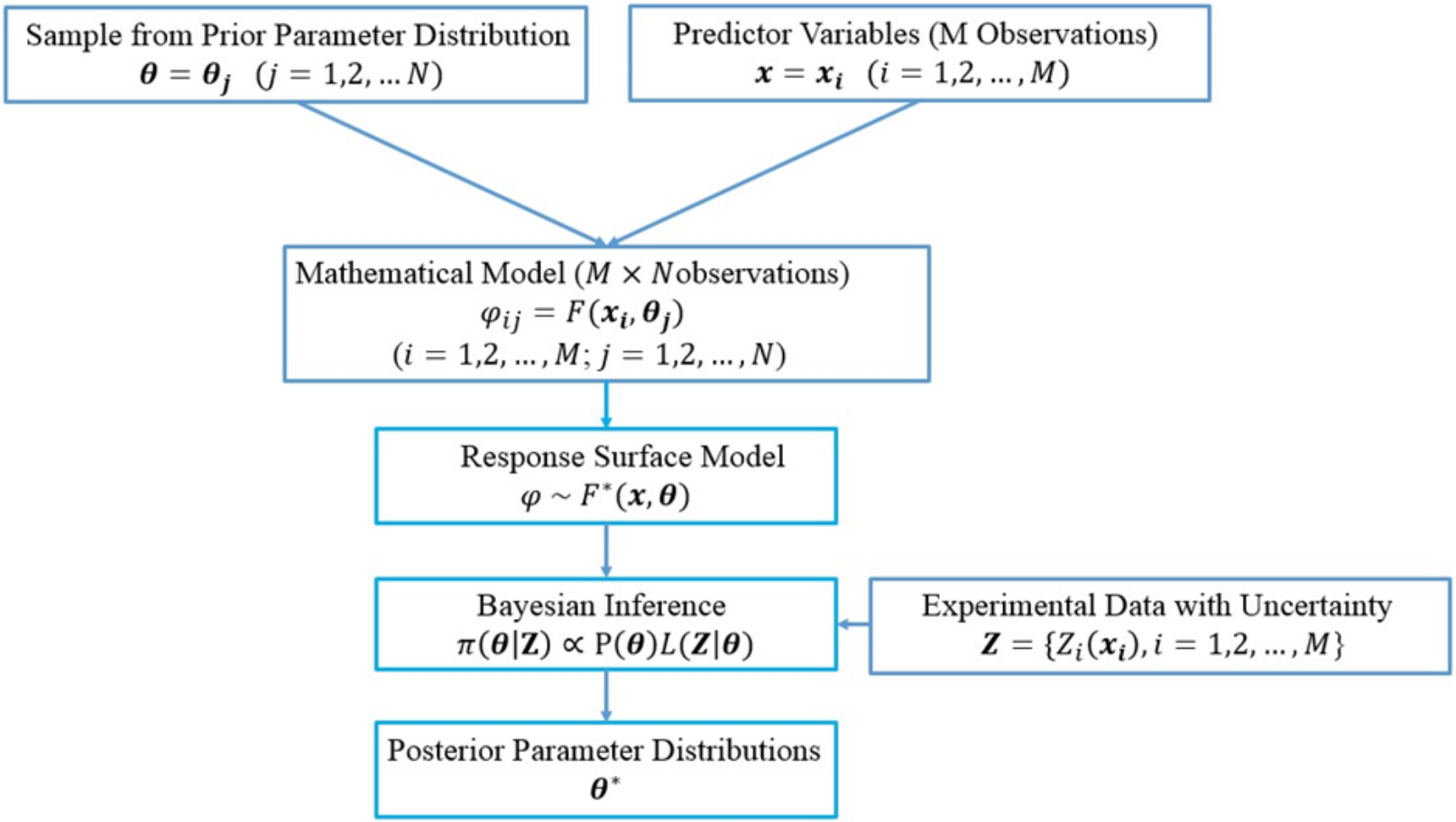
- Property models
  - Valid for absorber and stripper operating conditions
- Hydraulic and mass transfer models
  - Developed simultaneously with relevant properties models using both WWC and packing data
- Uncertainty quantification
- Steady State Validation
- Dynamic Validation*

* **Anderson Soares Chinen**
687g Dynamic Model Development and Validation of a MEA-Based CO_2 Capture System
11/9/2015
2:36 p.m.
Salon D (Marriott)

Overall Approach



Stochastic Modeling Methodology



Outline

- Scope of Work
- **Submodel Development**
  - **Thermodynamic and kinetic models**
  - Mass transfer and hydraulic models
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Reactive System Thermodynamic Framework

Vapor-Liquid Equilibrium

$$\hat{f}_i^V = \hat{f}_i^L \longrightarrow \hat{\varphi}_i y_i P = \gamma_i^* x_i H_i$$ *(for solutes)*

Activity Coefficient

$$ln(\gamma_i) = \frac{1}{RT}\frac{\partial(nG^{ex})}{\partial n_i}\bigg|_{T,P,n_{j\neq i}}$$

$$\gamma_i^* = \frac{\gamma_i}{\lim\limits_{x_i\to 0}\gamma_i}$$

Reaction Equilibrium Constant

$$\Delta G_{rxn} = -RTln(K)$$

Enthalpy Equations

Excess Enthalpy

$$H^{ex} = -RT^2\sum_i x_i\left(\frac{\partial \ln\gamma_i}{\partial T}\right)\bigg|_{P,x}$$

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 $2MEA + CO_2 \leftrightarrow MEA^+ + MEACOO^-$

Reaction 2 $MEA + H_2O + CO_2 \leftrightarrow MEA^+ + HCO_3^-$

$$r_1^f = 8.5616 \times 10^{10} \exp\left(-\frac{3963.9}{8.314}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right) a_{MEA}^2 a_{CO_2}$$

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

$$r_2^f = 22991.13 \exp\left(-\frac{49000}{8.314}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right) a_{MEA} a_{CO_2}$$

$$r_2^r = 18.35 \exp\left(-\frac{96230}{8.314}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \frac{a_{HCO_3^-} a_{MEA^+}}{a_{H_2O}}$$

Model from: Hilliard MD , Ph.D. Dissertation, UT Austin, 2008

MEA System Reaction Kinetics - New

Reaction 1 $2MEA + CO_2 \leftrightarrow MEA^+ + MEACOO^-$

Reaction 2 $MEA + H_2O + CO_2 \leftrightarrow MEA^+ + HCO_3^-$

$$r_1 = 8.5616 \times 10^{10} \exp\left(-\frac{3963.9}{8.314}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right) a_{MEA}^2 a_{CO_2} \left(1 - \frac{a_{MEA^+} a_{MEACOO^-}}{K_1 a_{MEA}^2 a_{CO_2}}\right)$$

$$r_2 = 22991.13 \exp\left(-\frac{49000}{8.314}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right) a_{MEA} a_{CO_2} \left(1 - \frac{a_{MEA^+} a_{HCO_3^-}}{K_2 a_{MEA} a_{CO_2} a_{H_2O}}\right)$$

$$K_1 = \left.\frac{\gamma_{MEA^+} x_{MEA^+} \gamma_{MEACOO^-} x_{MEACOO^-}}{(\gamma_{MEA}^* x_{MEA})^2 \gamma_{CO_2}^* x_{CO_2}}\right|_{eq} \qquad K_2 = \left.\frac{\gamma_{MEA^+} x_{MEA^+} \gamma_{HCO_3^-} x_{HCO_3^-}}{\gamma_{MEA}^* x_{MEA} \gamma_{CO_2}^* x_{CO_2} \gamma_{H_2O} x_{H_2O}}\right|_{eq}$$

VLE Ternary Data

Data Source	Number of Data	Temperature (°C)	CO_2 loading (mol CO_2/mol MEA)	MEA weight percent	CO_2 partial pressure (kPa)
Aronu et al.	138	40-80	0.017-0.565	15-60	0.007-19
Hilliard	55	40-60	0.114-0.591	17-40	0.005-50
Jou et al.	46	25-120	0.003-0.589	30	0.0015-822
Dugas	50	40-100	0.231-0.500	30-45	0.01-29
Lee et al.	155	25-120	0.065-0.600	6.5-32	0.1-1000
Xu	36	100-130	0.313-0.520	30	12-1000
Ma'mun et al.	19	120	0.155-0.418	30	7-192

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

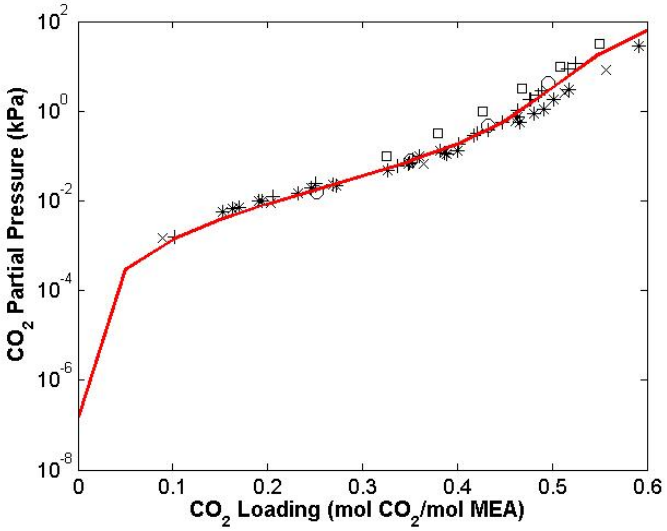
Lee et al., J Appl Chem Biotechn, 1976;26:541-549

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

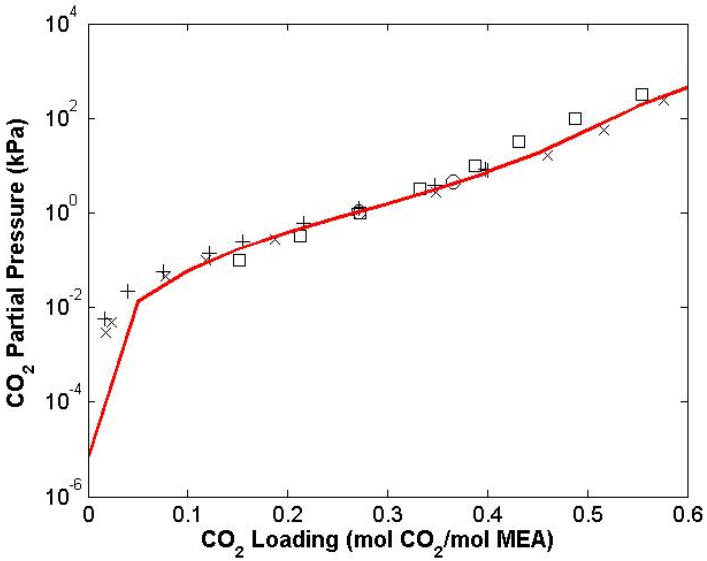
Ma'mun et al.,J Chem Eng Data, 2005;50:630-634

Ternary VLE Model Fit (30 wt%)

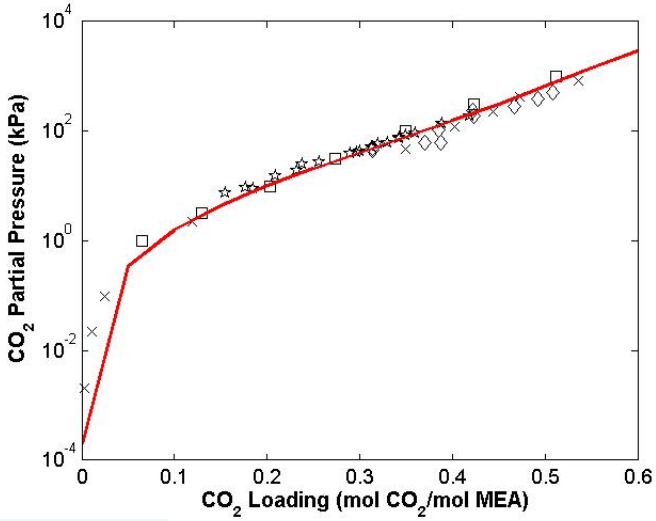
40°C



80°C



120°C



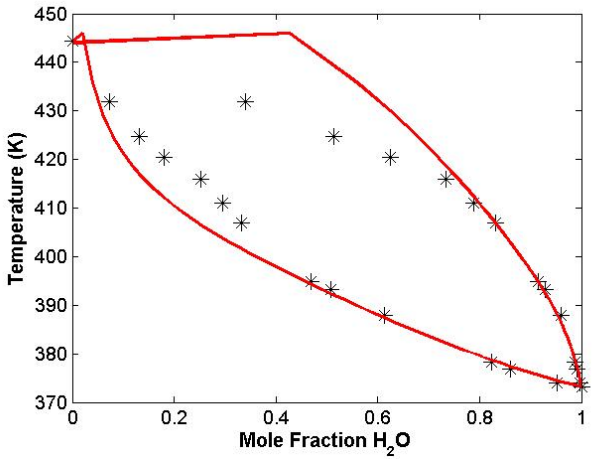
Data

- + Aronu et al.
- ✳ Hilliard
- × Jou et al.
- ○ Dugas
- □ Lee et al.
- ◇ Xu
- ☆ Ma'mun et al.

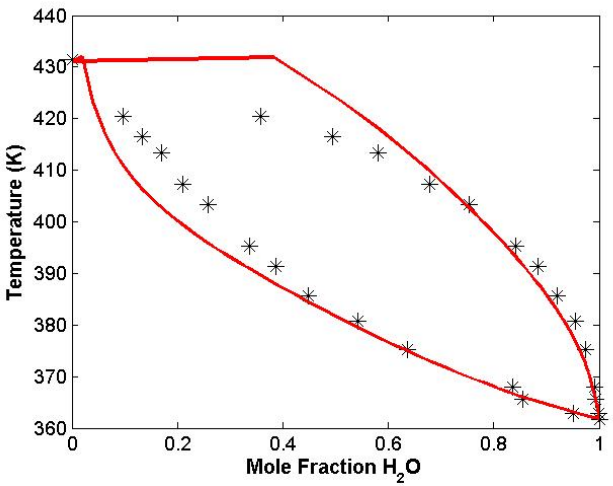
Binary VLE Model Fit

Txy Diagrams (data from Cai et al.)

P = 101.33 kPa

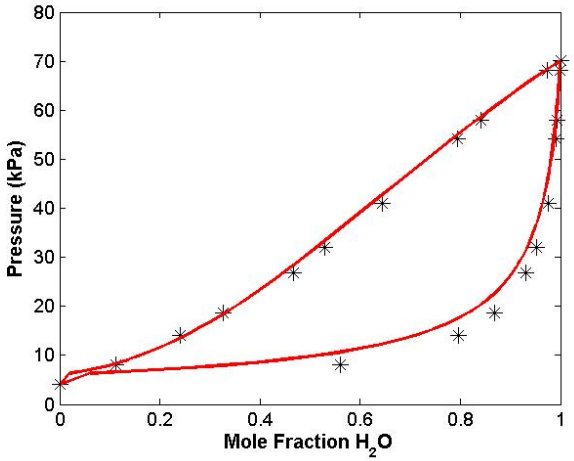


P = 66.66 kPa



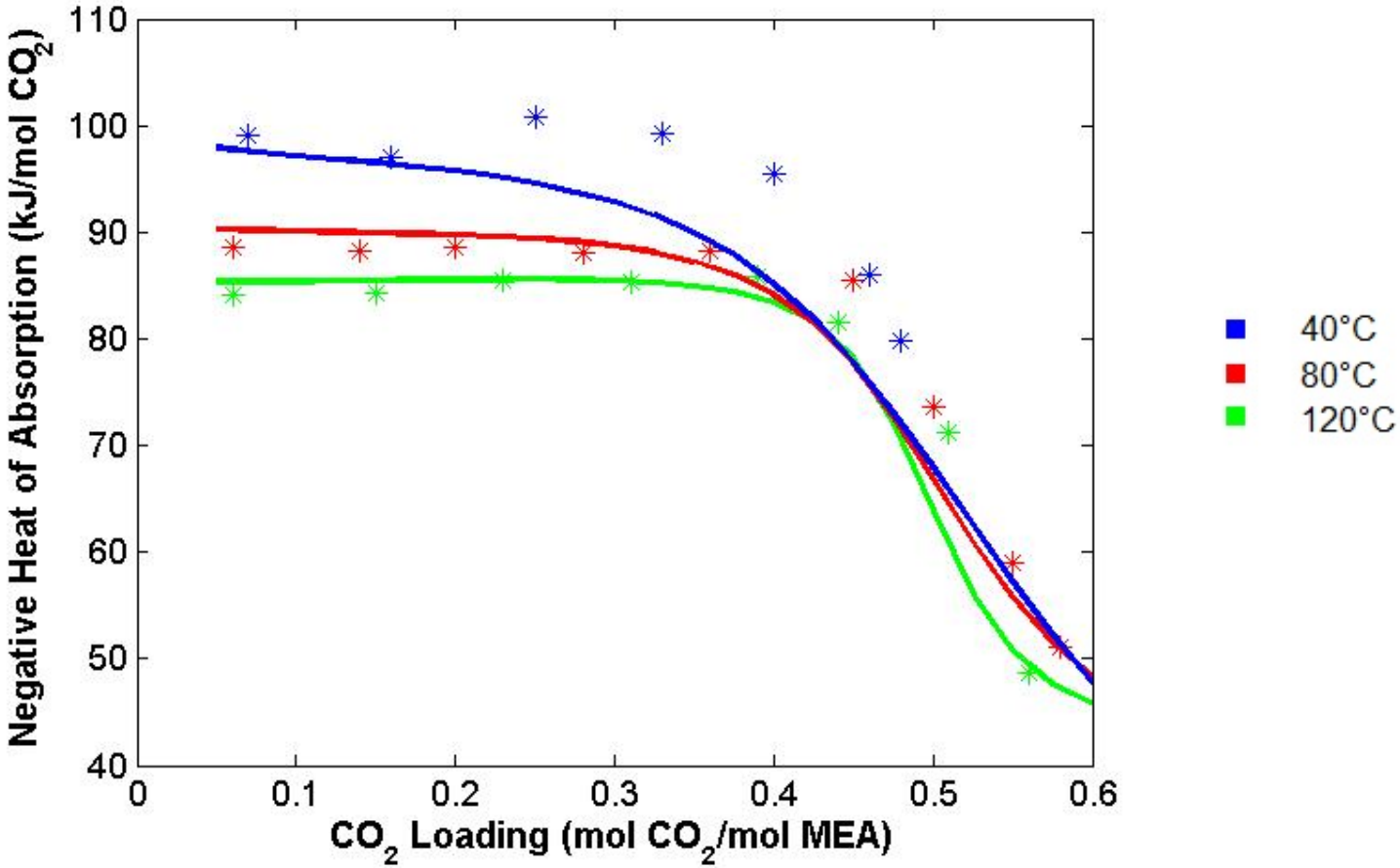
Pxy Diagrams (data from Tochigi et al.)

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

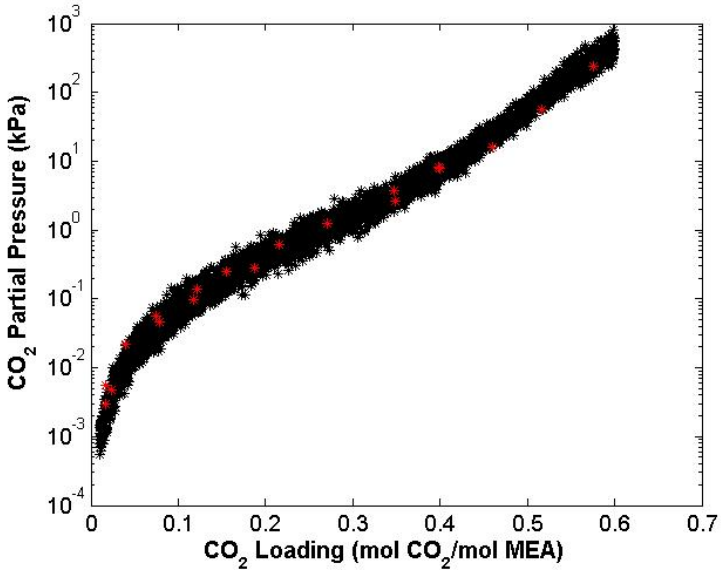


Data from: Kim et al., Energy Procedia,2014;63:1446-1455

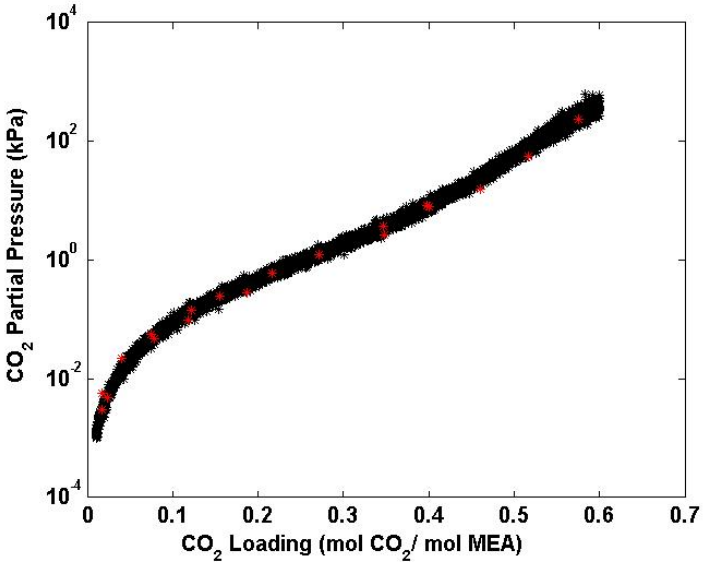
VLE Model Uncertainty Quantification

CO_2 Partial Pressure for 80°C and 30 wt% MEA

Prior Distribution



Posterior Distribution



✳ Model
✳ Data

Sample of 5000 drawn from each distribution

Outline

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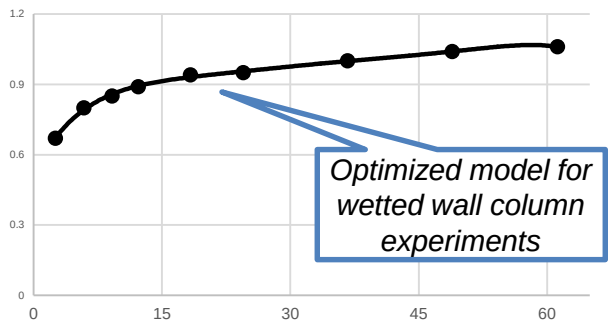
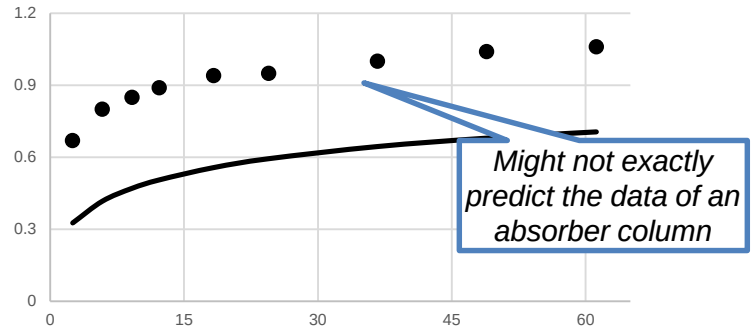
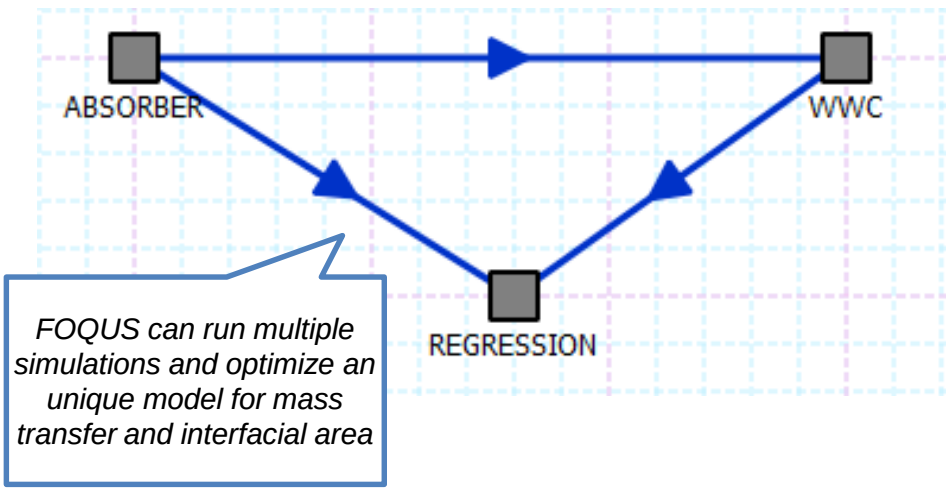
Integrated Mass Transfer Model Development

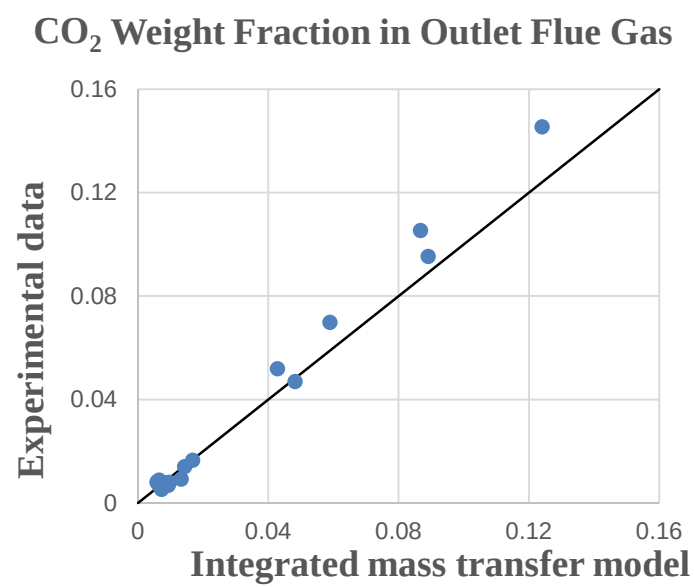
Usual approach: Sequential regression





FOQUS capability: Simultaneous regression

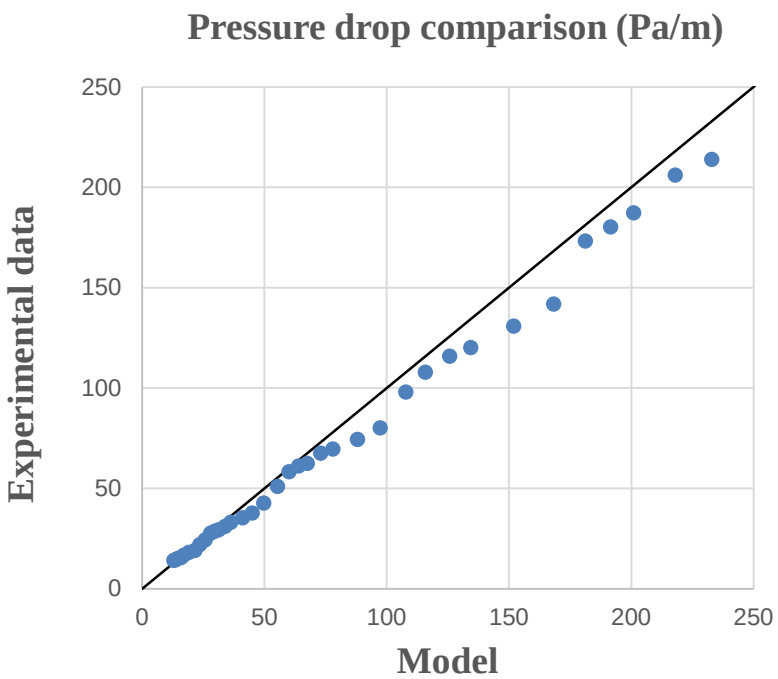




Experimental data from: Tobiesen et al., AIChE Journal, 2007;53:846-865

Mass Transfer and Hydraulic Model Results

- Final model form for hydraulics and mass transfer:
  - Pressure drop: Billet and Schultes (1999)
  - Holdup: Tsai (2011)
  - Mass transfer coefficients: Billet and Schultes (1993)
  - Interfacial area: Tsai et al. (2012)
- Model parameters regressed for Mellapak Plus™ 252Y



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

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CCSI team conducted tests at NCCC

NCCC vs Other Pilot Plants

	CO_2 Capacity (tpd)	Source of Flue Gas	Absorber		Regenerator	
			Diameter (cm)	Height (m)	Diameter (cm)	Height (m)
UT, Austin	3.0	Non-coal	42.7	6.1	42.7	6.1
NTNU/ SINTEF	0.3	Non-coal	15.0	4.4	10.0	3.9
ITC, Regina	1.0	Non-coal	33.0	7.1	33.0	10.0
ITT, Stuttgart	0.3	Non-coal	12.5	4.2	12.5	2.5
Esbjerg CASTOR	24.0	Coal	110.0	17.0	110.0	10.0
NCCC (PSTU)	10.0	Coal	64.1	18.5	59.1	12.1

NCCC Steady State Testing

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

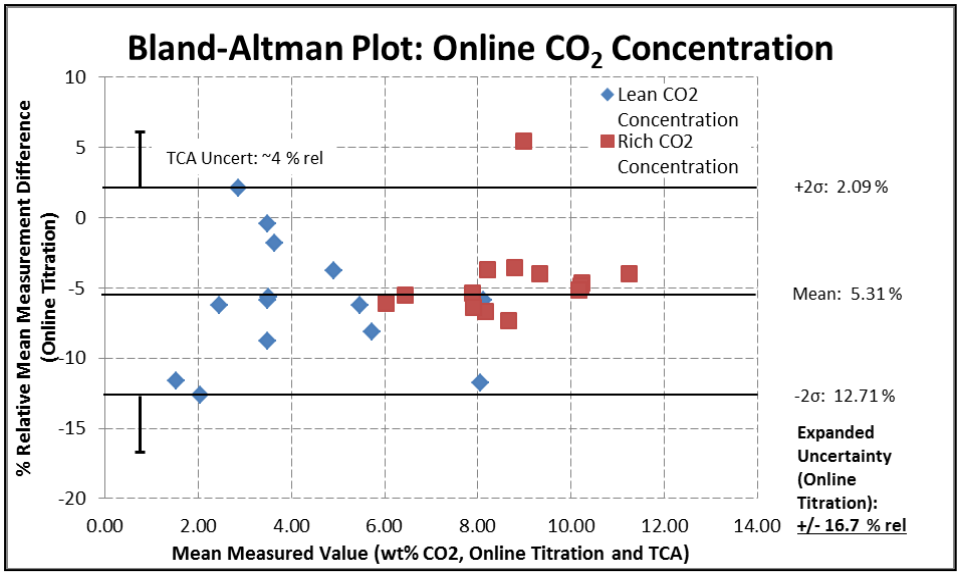
Variable	Range
Absorber Inlet Flue Gas Flow (kg/hr)	1320-2900
Lean Solvent Flowrate (kg/hr)	3175-11800
Absorber L/G ratio (molar)	1.7-10.4
Reboiler Duty (kW)	166-677
Lean Solvent Loading (mol CO_2/mol MEA)	0.045-0.287
Rich Solvent Loading (mol CO_2/mol MEA)	0.198-0.343
Inlet Flue Gas CO_2 Volume %	9-11
Number of Beds in Absorber	1-3
Presence of Intercooling in Absorber	Yes/No

Uncertainty of the Measurement Techniques

- ***Dynamic Test Runs**: Gas Chromatography (GC) for Amine Concentration and Bench Equivalence Point (EQP) Base Titration (CO_2 Concentration)*
- ***Steady State Runs**: Online EQP Acid Titration (Amine Concentration) and Online EQP Base Titration (CO_2 Concentration)*

➢ *Analysis Techniques Repeatability Evaluation*

➢ *Analysis Techniques Uncertainty Evaluation*

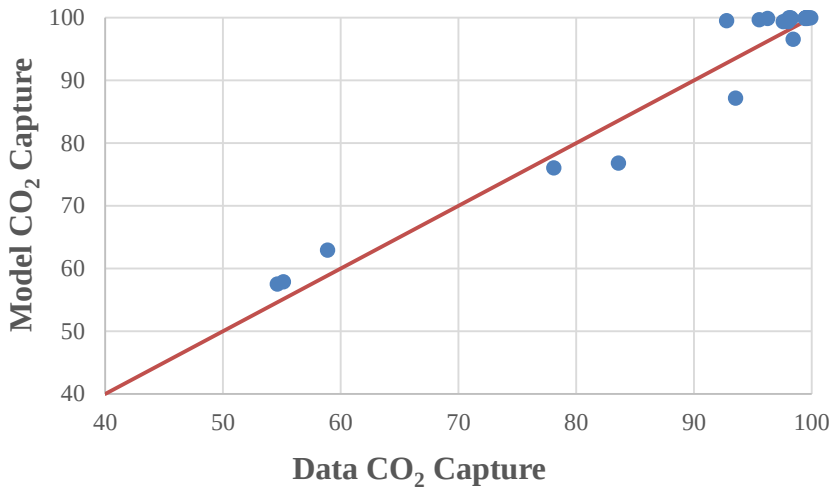


Critical Model Parameters:

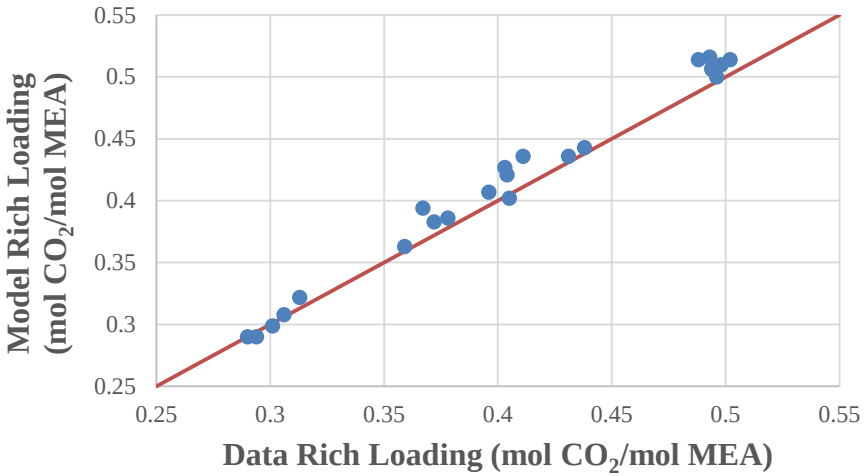
Portion of Campaign	Dynamic	Steady State
Amine Concentration (wt% MEA Nominal) % rel expanded uncertainty (k=2)	4.9%	7.3%
CO_2 Loading (mol CO_2 / mol MEA) % rel expanded uncertainty (k=2)	7.4%	10.7%

Steady State Absorber Validation

CO_2 Capture Prediction



Rich Loading Comparison



Percent Deviation Between Data and Model Values (Summary)

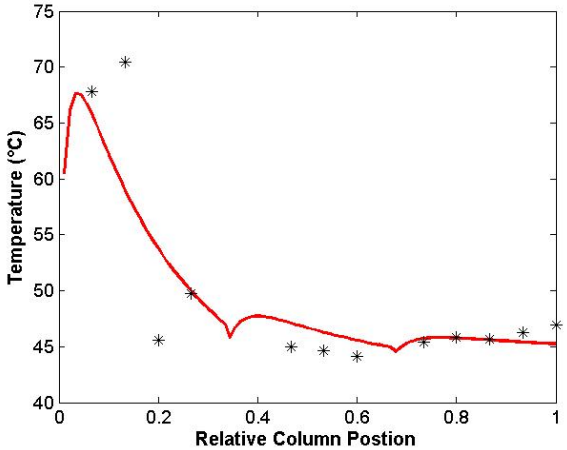
	Data CO_2 Capture-Liquid vs. Gas Discrepancy	CO_2 Capture-Gas Side	CO_2 Capture-Liquid Side	Rich Loading
Maximum	**9.19**	**8.09**	**10.84**	**7.36**
Average	**3.62**	**2.69**	**3.97**	**2.69**

Steady State Absorber Validation

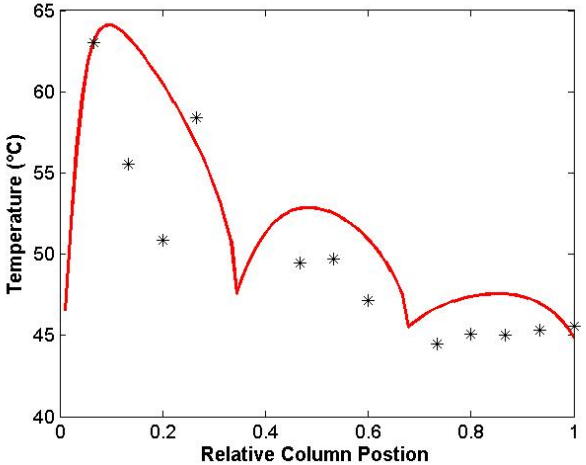
No parameter tuned

Sample Temperature Profiles

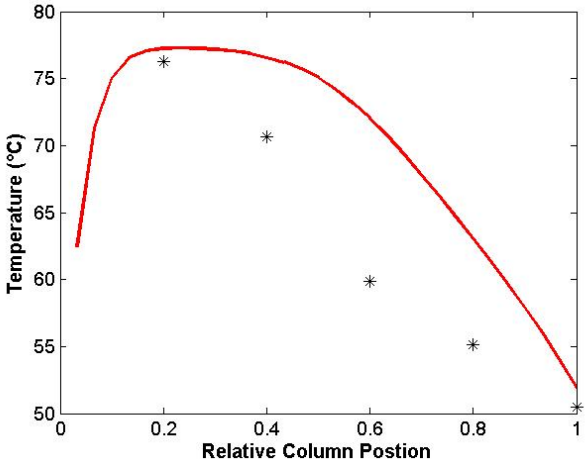
Case K3



Case K6



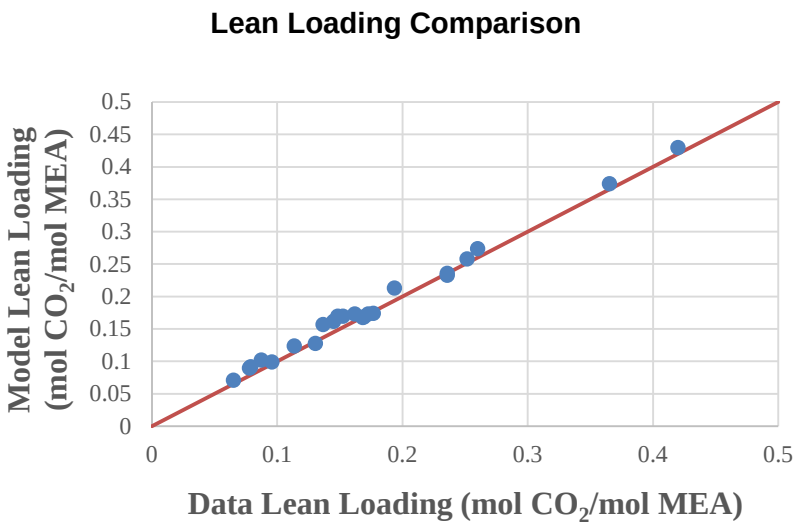
Case K20

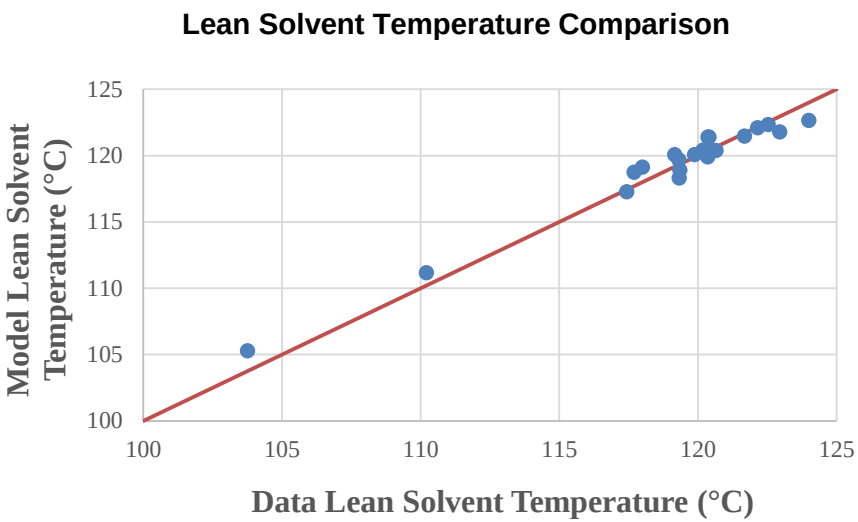


Relative column positions of 0 and 1 correspond to top and bottom of column, respectively

Case	L/G (mass)	Beds/Intercooling	Lean Loading (mol CO_2/mol MEA)
K3	1.41	3/Yes	0.091
K6	3.02	3/Yes	0.347
K20	2.38	1/No	0.075

Steady State Regenerator Validation





Percent Deviation Between Data and Model Values (Summary)

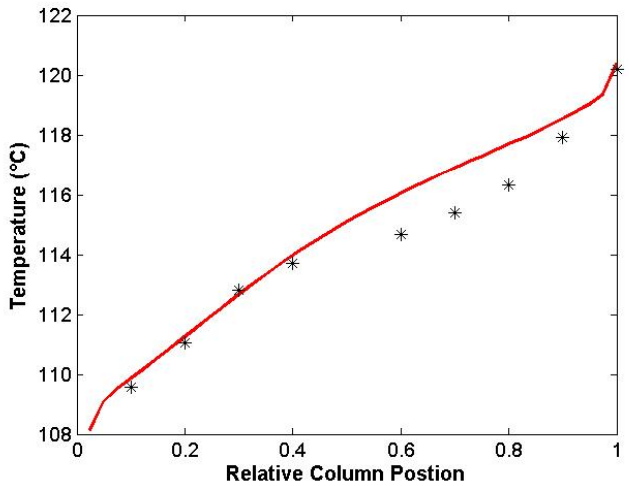
	Lean Loading	Lean Solvent Temperature
Maximum	16.53	1.14
Average	6.39	0.48

Steady State Regenerator Validation

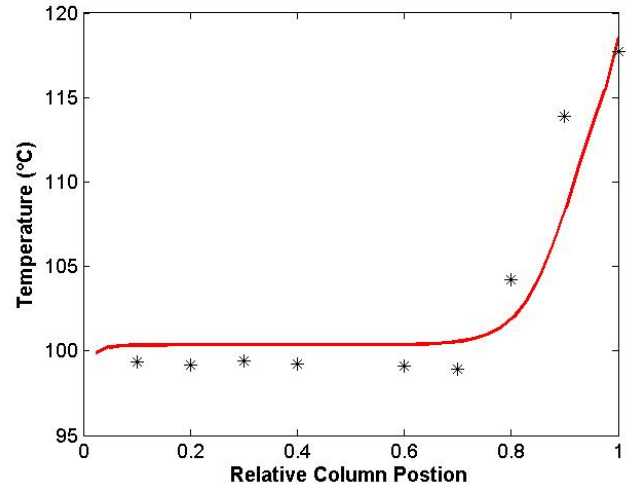
No parameter tuned

Sample Temperature Profiles

Case K1

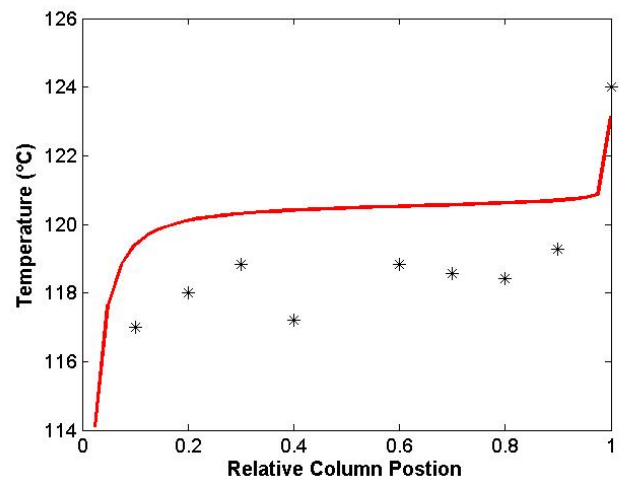


Case K9



Case	Rich Solvent Flow (kg/hr)	Reboiler Duty (kW)	Rich Loading (mol CO_2/mol MEA)
K1	7242	430.61	0.384
K9	3337	165.74	0.474
K10	3358	670.62	0.477

Case K10



Outline

- Scope of Work
- Submodel Development
  - Thermodynamic and kinetic models
  - Mass transfer and hydraulic models
- Model Validation
- **Conclusions**

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

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