Modelling CO_2 chemical absorption using the CESAR1 solvent

Diego Morlando, Hanna K. Knuutila

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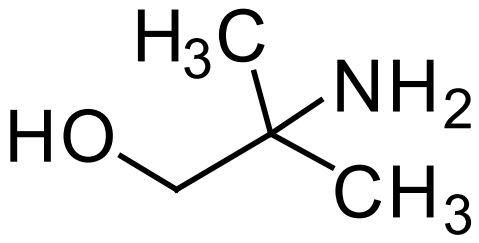
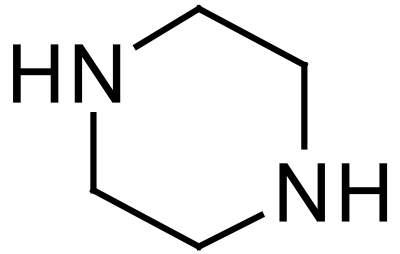
The CESAR1 Blend

Blend of a sterically-hindered primary amine and a cyclic secondary diamine.



2-amino-2-methyl-1-propanol
(AMP)
3 M



Piperazine
(PZ)
1.5 M

We found some experimental gaps

Review

Available data and knowledge gaps of the CESAR1 solvent system

Diego Morlando [a], Vanja Buvik [b], Asmira Delic [b], Ardi Hartono [a], Hallvard F. Svendsen [a], Hanne M. Kvamsdal [b], Eirik F. da Silva [b], Hanna K. Knuutila [a]

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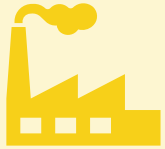
Some important gaps…

- CO_2 solubility data at high temperature were missing (>120◦C).
- Liquid Speciation data for the CESAR1 blend were missing.
- CO_2 Henry's Constant data for the CESAR1 blend were missing.
- There was a lack of physical properties data at the CESAR1 concentration.

- An open-access pilot plant scale validated model in Aspen Plus was missing.

- Pilot Plant data at high flue gas concentration (>15 % were missing) and mostly focused at 90% Capture Rate.



We filled some of these gaps

Journal of Chemical & Engineering Data > Vol 70/Issue 1 > Article

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THERMOPHYSICAL AND THERMOCHEMICAL PROPERTIES | November 8, 2024

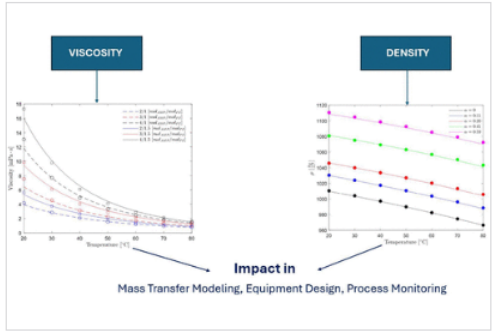
Density and Viscosity of CO_2-Loaded Aqueous 2-Amino-2-methyl-1-propanol (AMP) and Piperazine (PZ) Mixtures

Diego Morlando, Ardi Hartono, and Hanna K. Knuutila*

Open PDF | Supporting Information (1)

Abstract

Densities and viscosities of aqueous 2-amino-2-methyl-1-propanol (AMP)/piperazine (PZ) solutions with and without CO_2 are measured from 20 to 80 °C at ambient pressure. Redlich–Kister-based correlations are proposed for the excess molar volumes and viscosity deviation of the binary and ternary mixtures. Empirical correlations are developed to quantitatively describe the effect of CO_2 on the density and viscosity of the aqueous AMP/PZ solutions. The experimental data and correlations developed can be used in the design and simulation of AMP/PZ-based CO_2 capture absorption plants.



Subjects

Amines | Mixtures | Solution Chemistry | Solutions | Viscosity

ELSEVIER

Carbon Capture Science & Technology

Volume 16, September 2025, 100458

Full Length Article

Thermodynamic data for CO_2 absorption in aqueous 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) solutions: CO_2 solubility, N_2O solubility, heat of absorption of CO_2, pH and liquid speciation

Diego Morlando, Ardi Hartono, Hanna K. Knuutila

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Outline of this work

Development of an e-NRTL framework for AMP/PZ/H_2O/CO_2 solutions

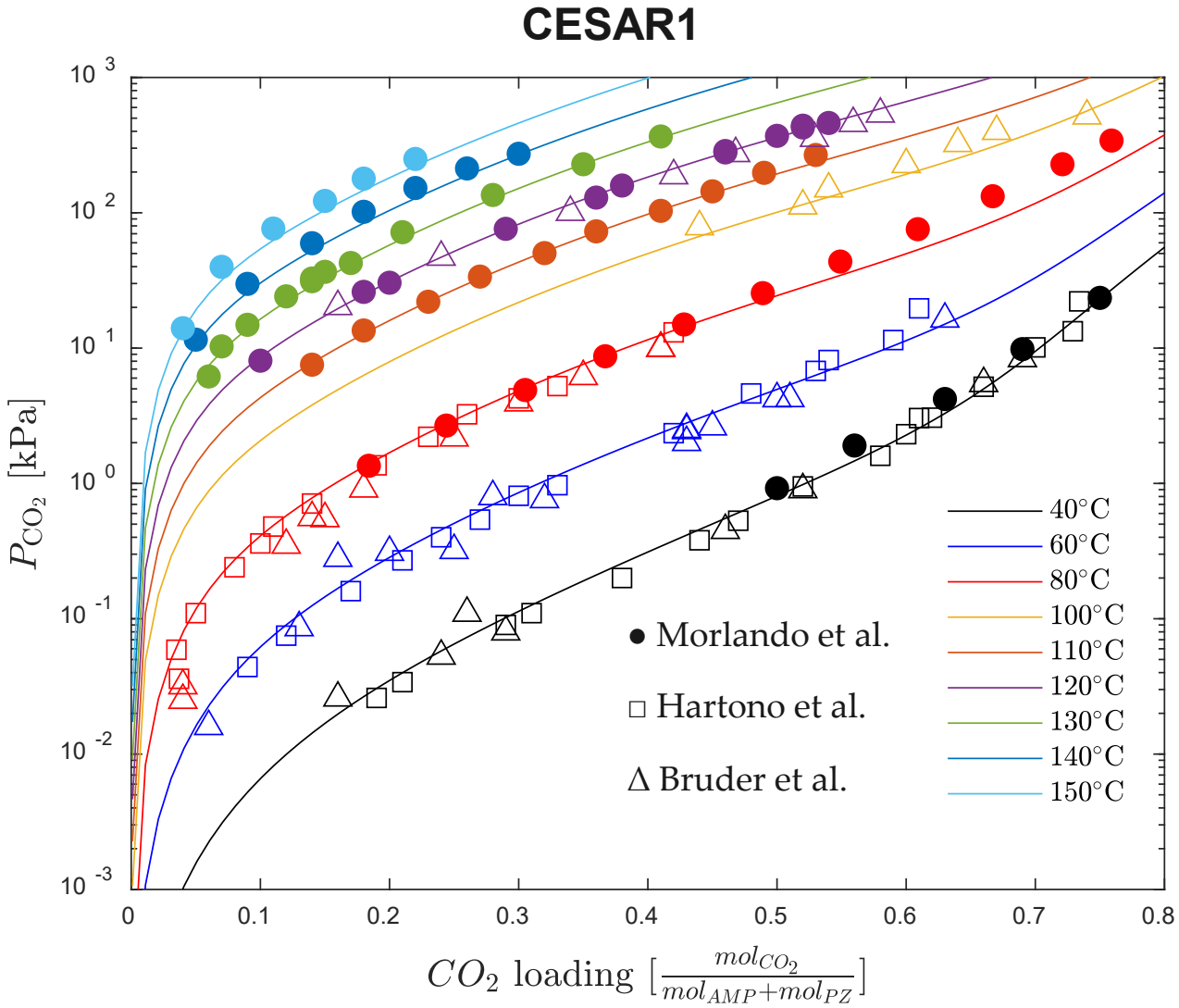
CO_2 absorption kinetics and mass transfer modeling

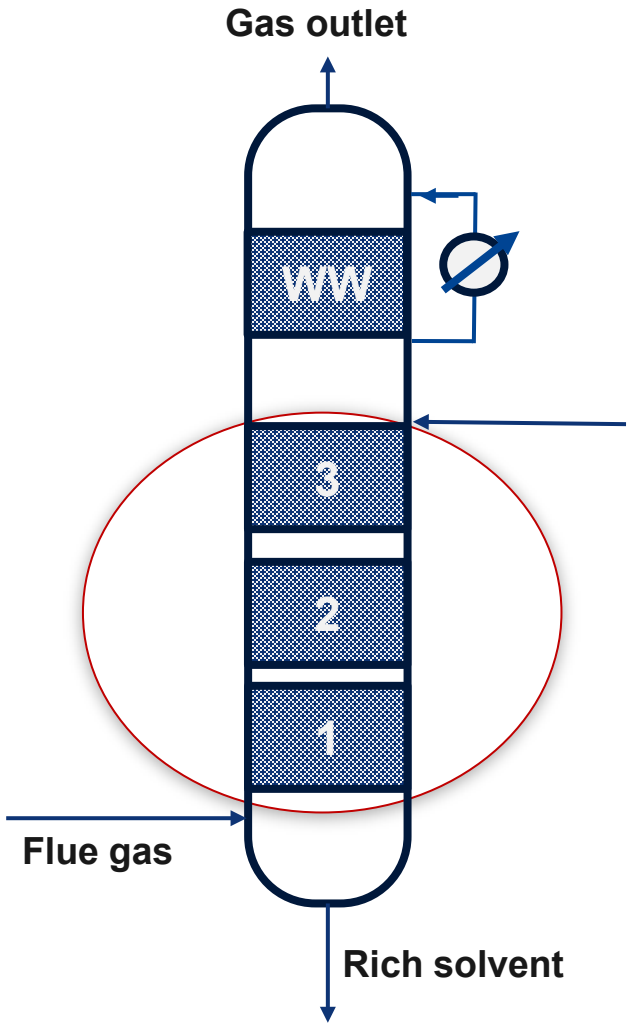
Process model

Validation on Pilot Plant Data

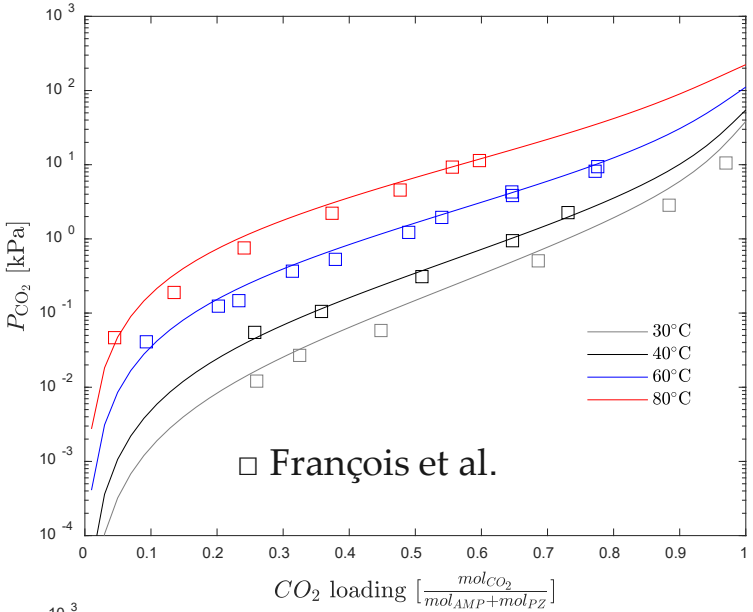
Conclusions

Predicting the driving force in the Absorber and Desorber

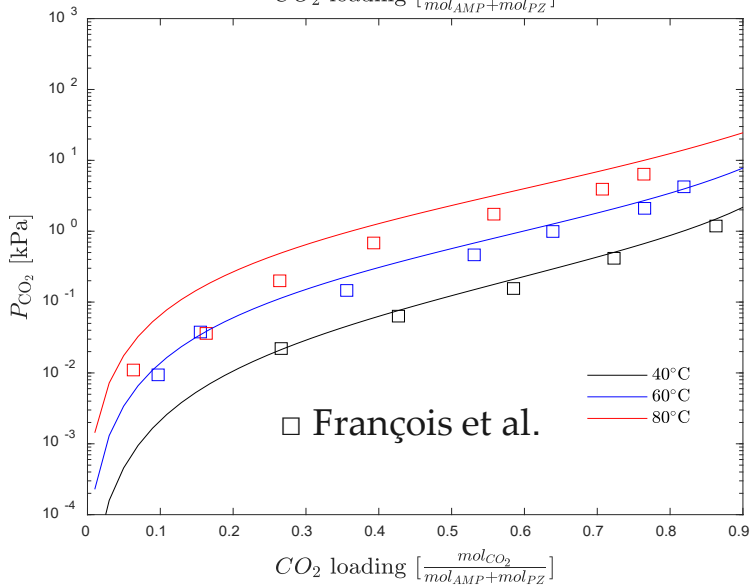




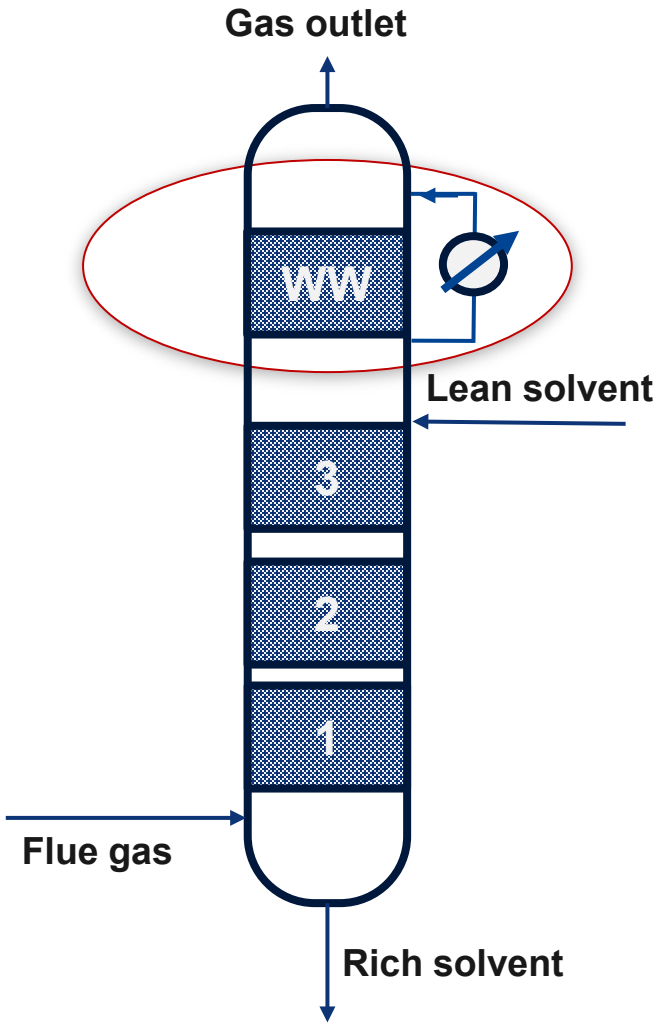
Predicting the driving force at water wash



10 times diluted CESAR1

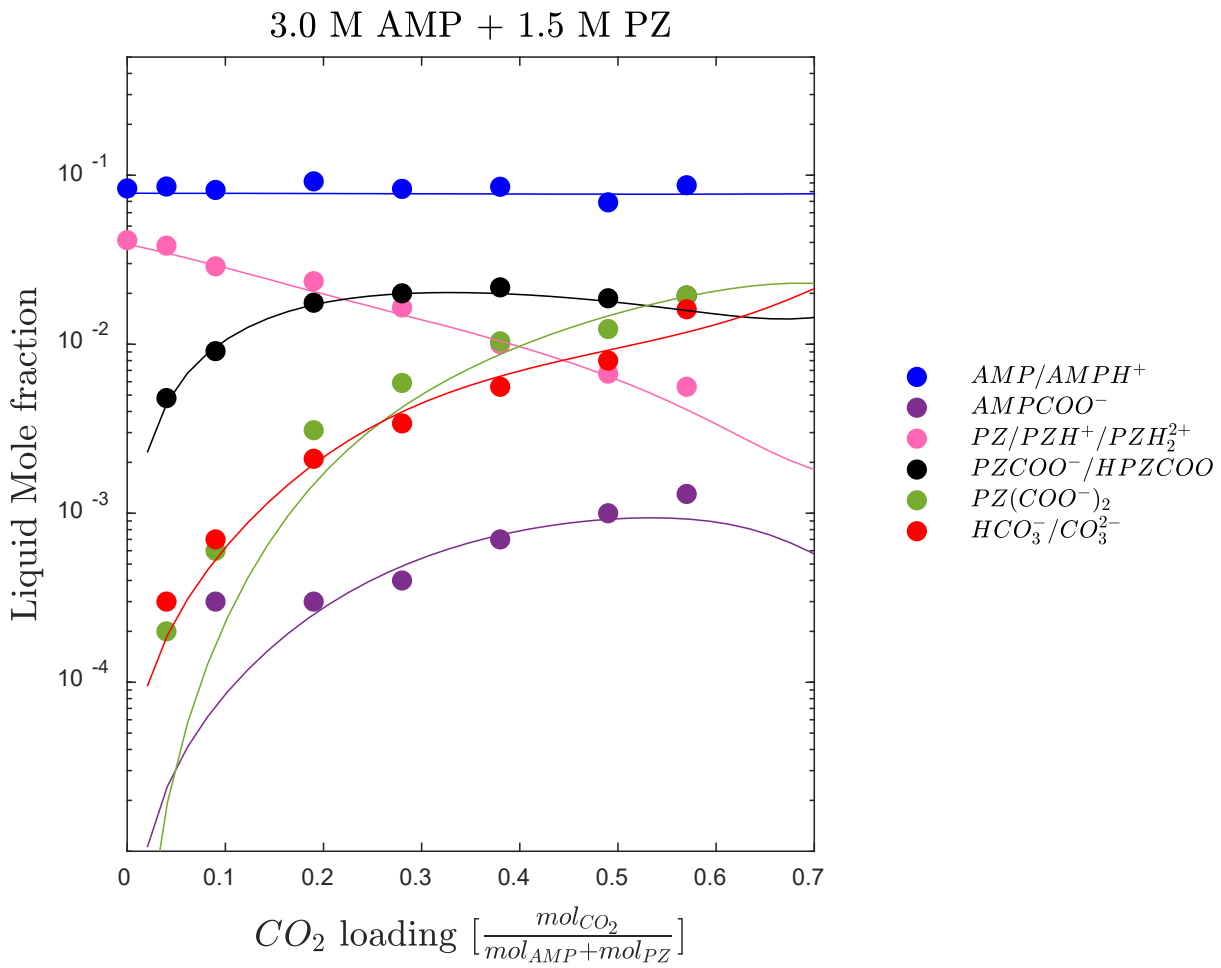


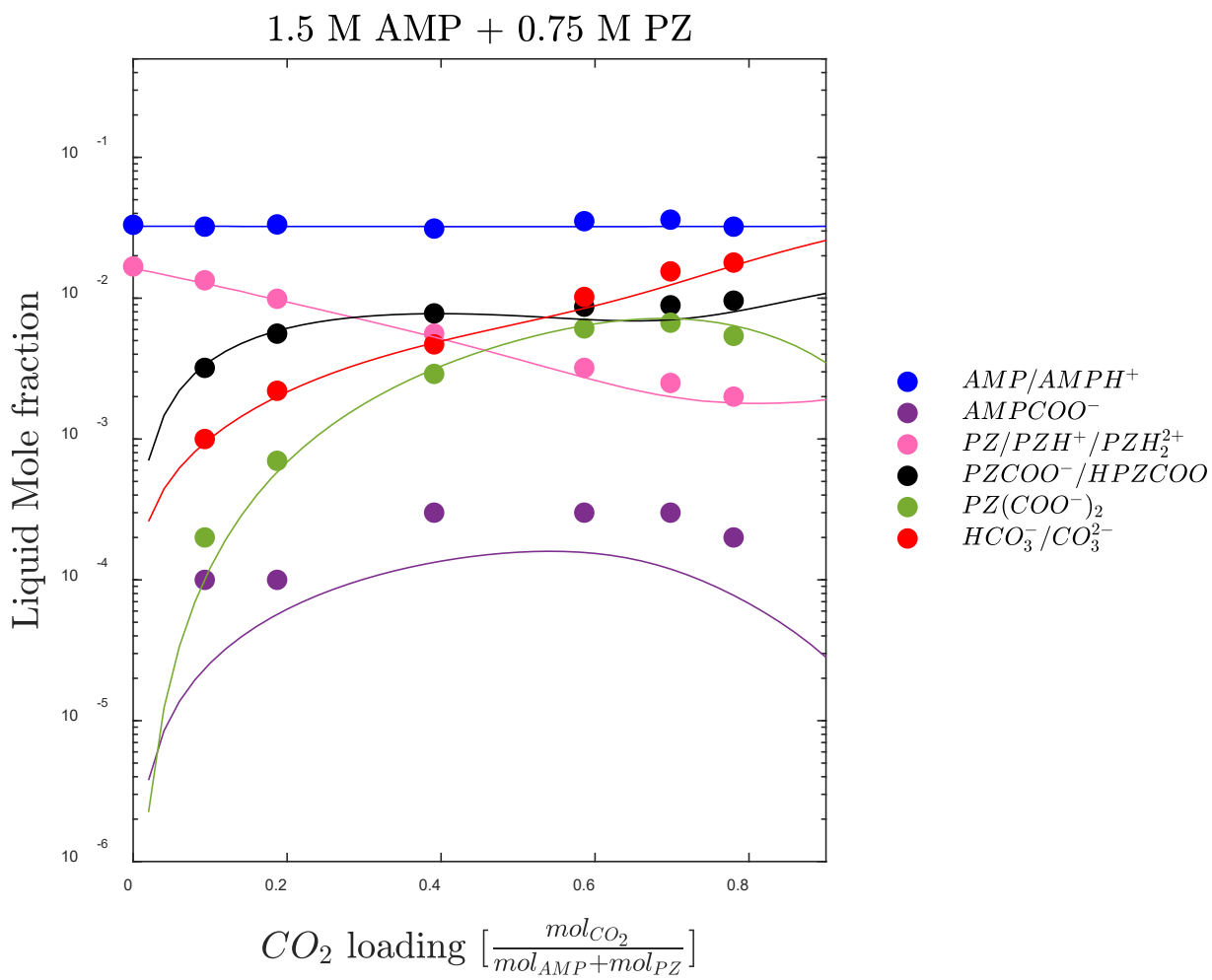
50 times diluted CESAR1



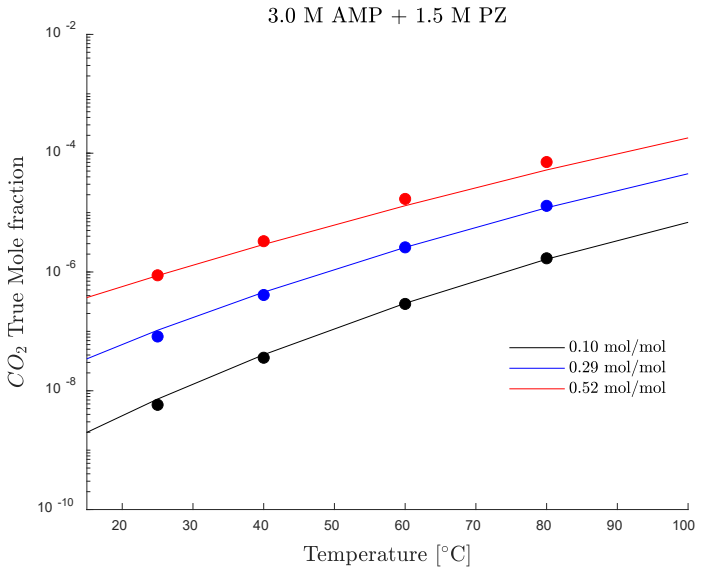
François et al.: https://doi.org/10.1016/j.rineng.2024.102163

Liquid Speciation





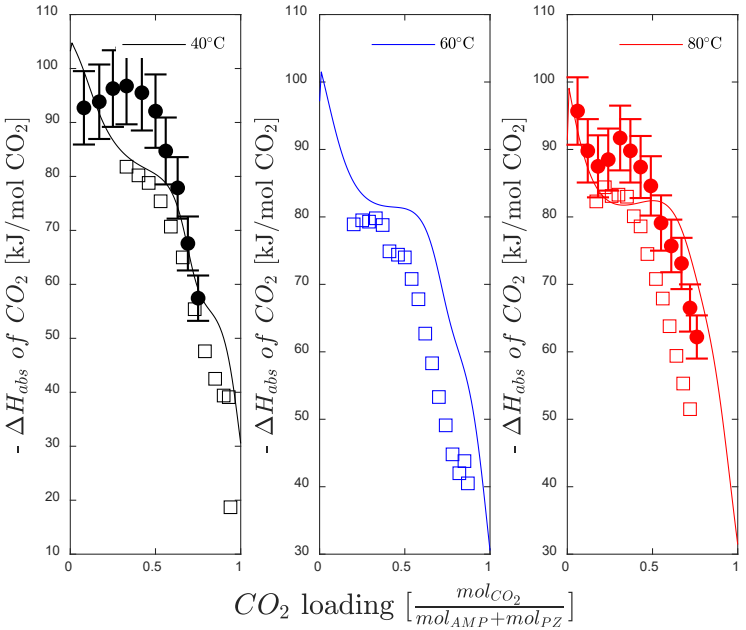
Heat of absorption and Liquid free CO_2 concentration



- Morlando et al.

$$H_{CO_2}^{app}(\alpha, T) = H_{N_2O}^{app}(\alpha, T) \cdot \frac{H_{CO_2}^{water}(\alpha, T)}{H_{N_2O}^{water}(\alpha, T)}$$

$$x_{CO_2}^{free,exp} = \frac{P_{CO_2}^{mod}}{H_{CO_2}^{app}(\alpha, T)}$$



- Morlando et al.
- □ Hartono et al.

CALORIMETRIC MEASUREMENTS FOR THE HEAT OF ABSORPTION OF CO_2.

Kinetics Modeling

Reactions	Concentration basis	Pre-exponential factor	E $\left[\frac{J}{kmol}\right]$	Sources
$CO_2 + OH^- \rightarrow HCO_3^-$	Activity	$1.33 \cdot 10^{17}$	$5.55 \cdot 10^7$	Pinsent et al.
$HCO_3^- \rightarrow CO_2 + OH^-$	Activity	$6.63 \cdot 10^{16}$	$1.07 \cdot 10^8$	This work
$AMP + CO_2 + H_2O \rightarrow AMPCOO^- + H_3O^+$	Activity	$1.38 \cdot 10^{10}$	$2.04 \cdot 10^7$	Jamal et al.
$AMPCOO^- + H_3O^+ \rightarrow AMP + CO_2 + H_2O$	Activity	$6.14 \cdot 10^{24}$	$6.17 \cdot 10^7$	This work
$PZ + CO_2 + H_2O \rightarrow PZCOO^- + H_3O^+$	Activity	$3.99 \cdot 10^{10}$	$2.53 \cdot 10^6$	Samanta et al.
$PZCOO^- + H_3O^+ \rightarrow PZ + CO_2 + H_2O$	Activity	$1.26 \cdot 10^{24}$	$6.17 \cdot 10^7$	This work
$PZCOO^- + CO_2 + H_2O \rightarrow PZ(COO^-)_2 + H_3O^+$	Activity	$3.21 \cdot 10^{14}$	$3.52 \cdot 10^7$	Samanta et al.
$PZ(COO^-)_2 + H_3O^+ \rightarrow PZCOO^- + CO_2 + H_2O$	Activity	$8.52 \cdot 10^{17}$	$1.05 \cdot 10^7$	This work

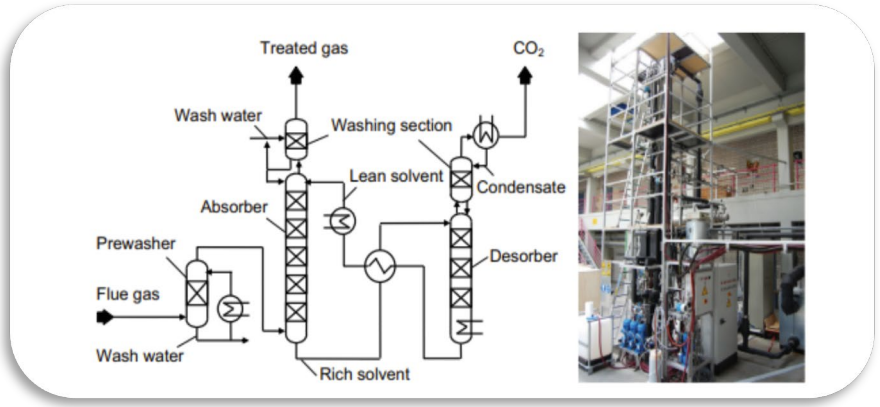
Kinetics of CO_2 absorption data have been retrieved from the open literature.

The reactions have been converted to activity based.

The reverse reactions have been obtained to be compliant to the equilibrium model developed in this work.

$$K_{eq} = \frac{k_d}{k_i} = \prod a_i^{v_i}$$

Pilot Plant Validation



Kaiserslautern Pilot Plant

Tiller Pilot Plant

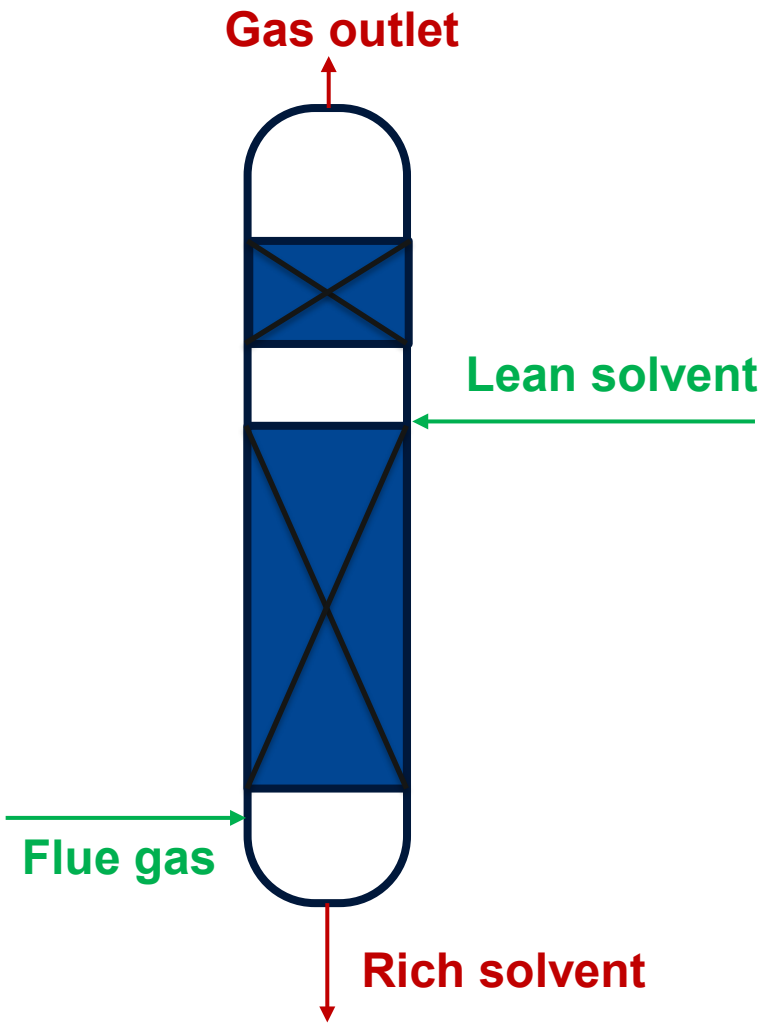
TCM

Pilot Plant Validation

	Kaiserslautern	*Tiller*	*TCM*
CO_2 Concentration Flue gas wet [vol%]	5 and 10%	2, 10 and 17 %	3-3.5 %
CO_2 Capture [%]	69-92 %	77-98 %	90-98
CO_2 Lean Loading [mol/mol]	0.011-0.224	0.026-0.31	0.064-0.236
CO_2 Rich Loading [mol/mol]	0.40-0.60	0.47-0.65	0.42-0.61
Absorber Packing Height [m]	4.25	19.4	12-24

Validation: 36 Cases on Single Units.

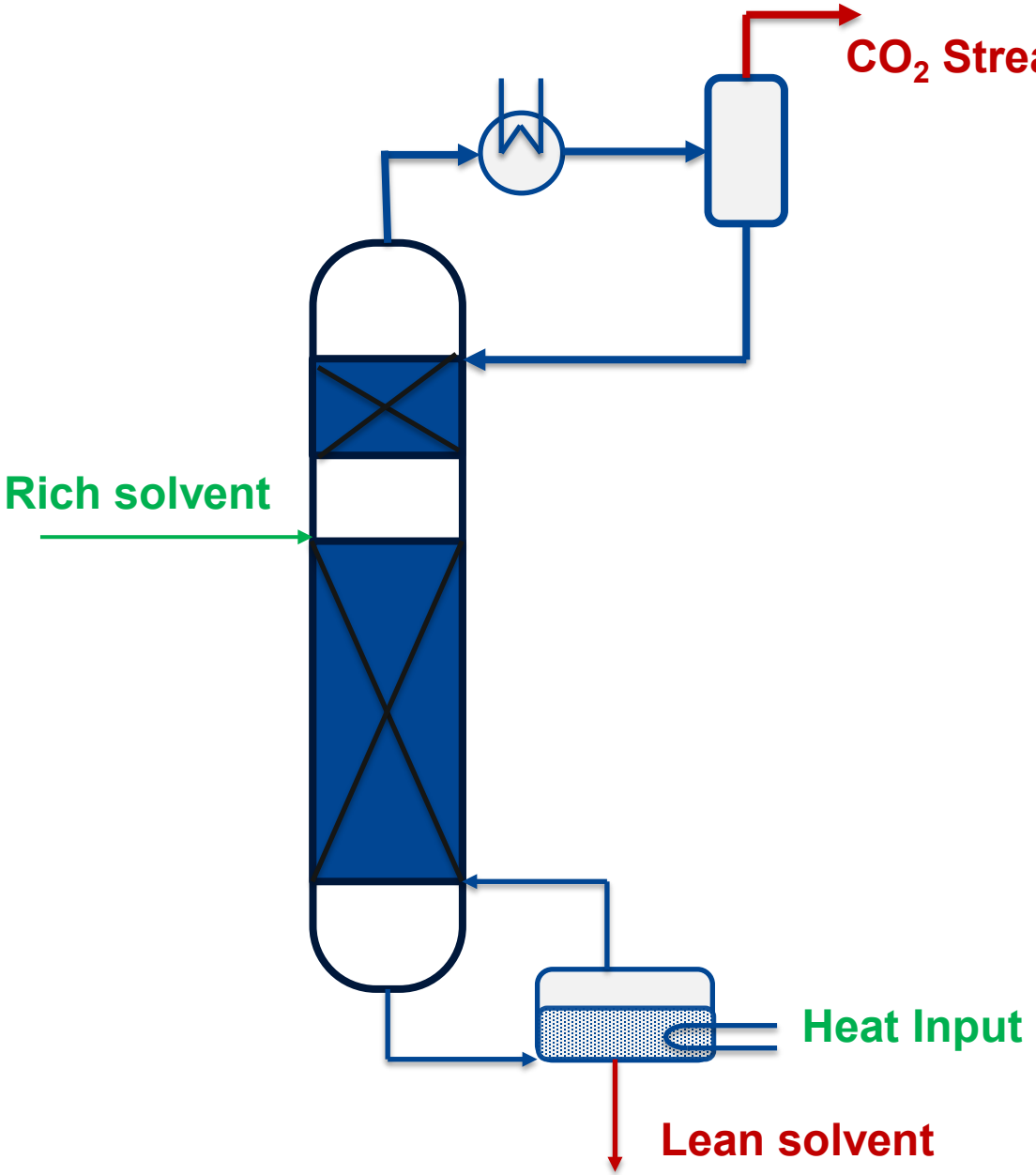
Absorber Validation



INPUT: Lean stream, Flue gas

OUTPUT: Gas stream leaving the absorber, Rich stream, Temperature Profiles.

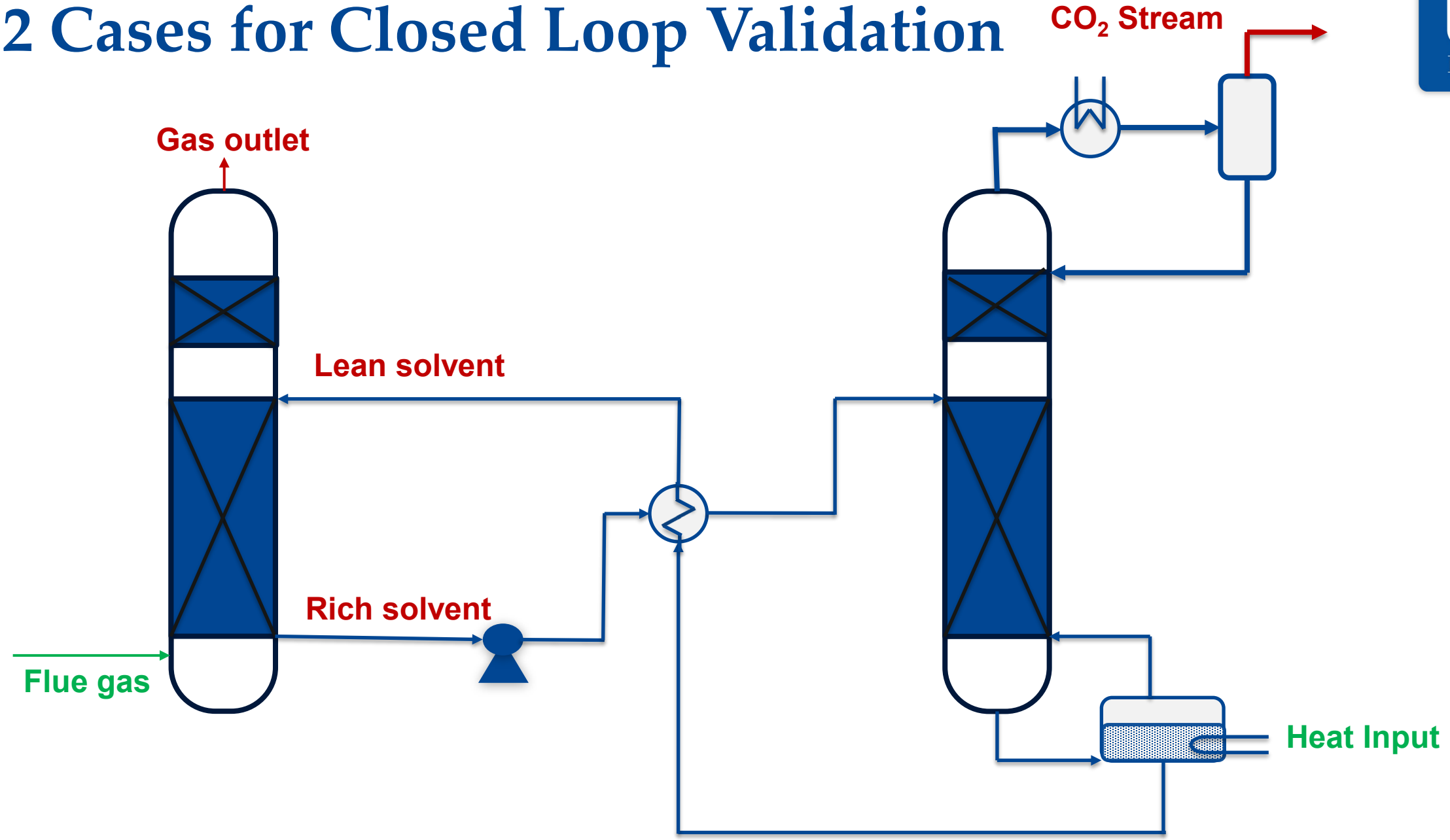
Desorber Validation



INPUT: Rich Solvent, Reboiler Duty

OUTPUT: Lean stream, CO_2 product stream, Temperature Profiles.

12 Cases for Closed Loop Validation



Validation: Some Error Metrics

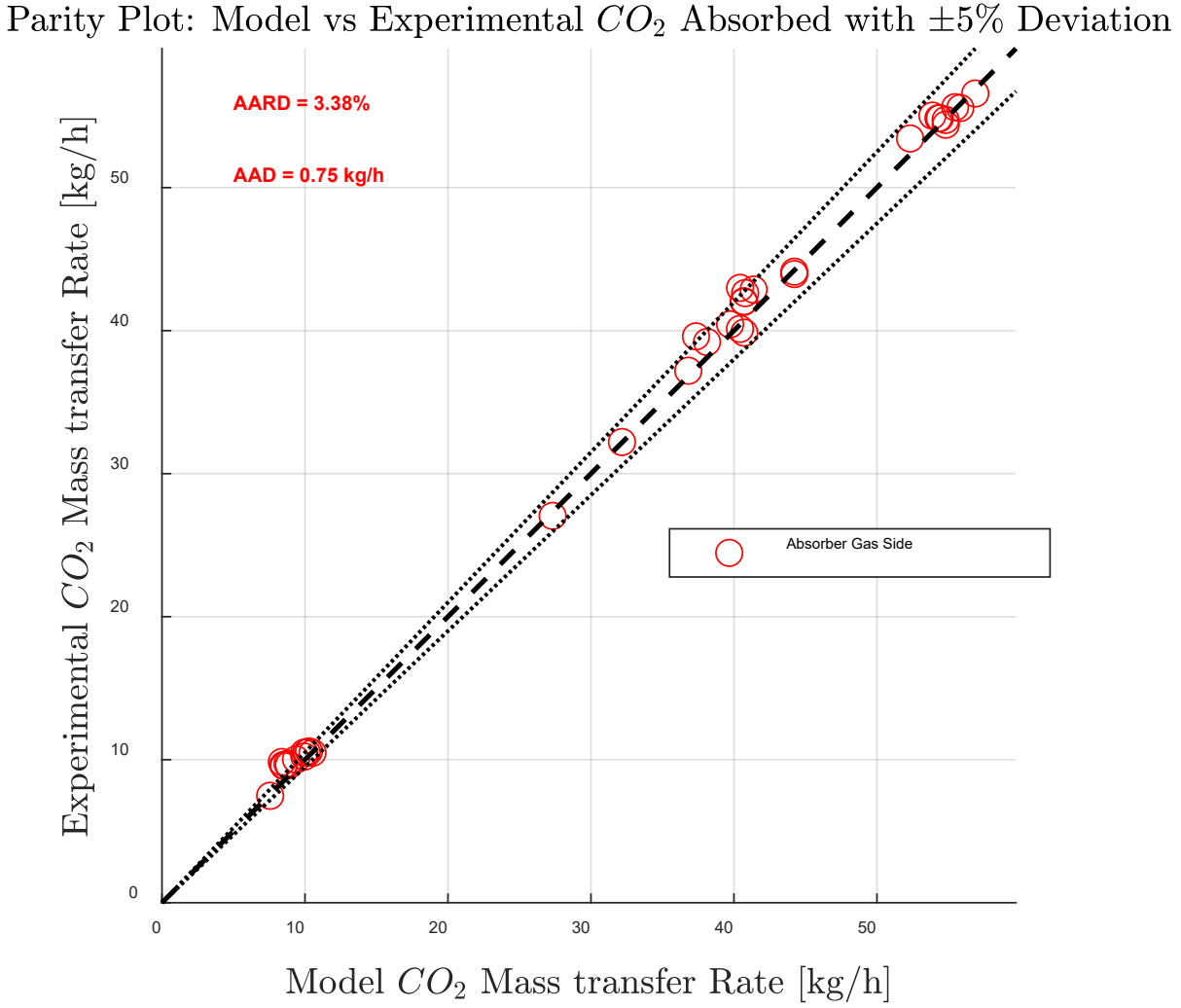
$$AD\ (Average\ Deviation) = \sum_{i}^{N} \frac{y_{model} - y_{exp}}{N}$$

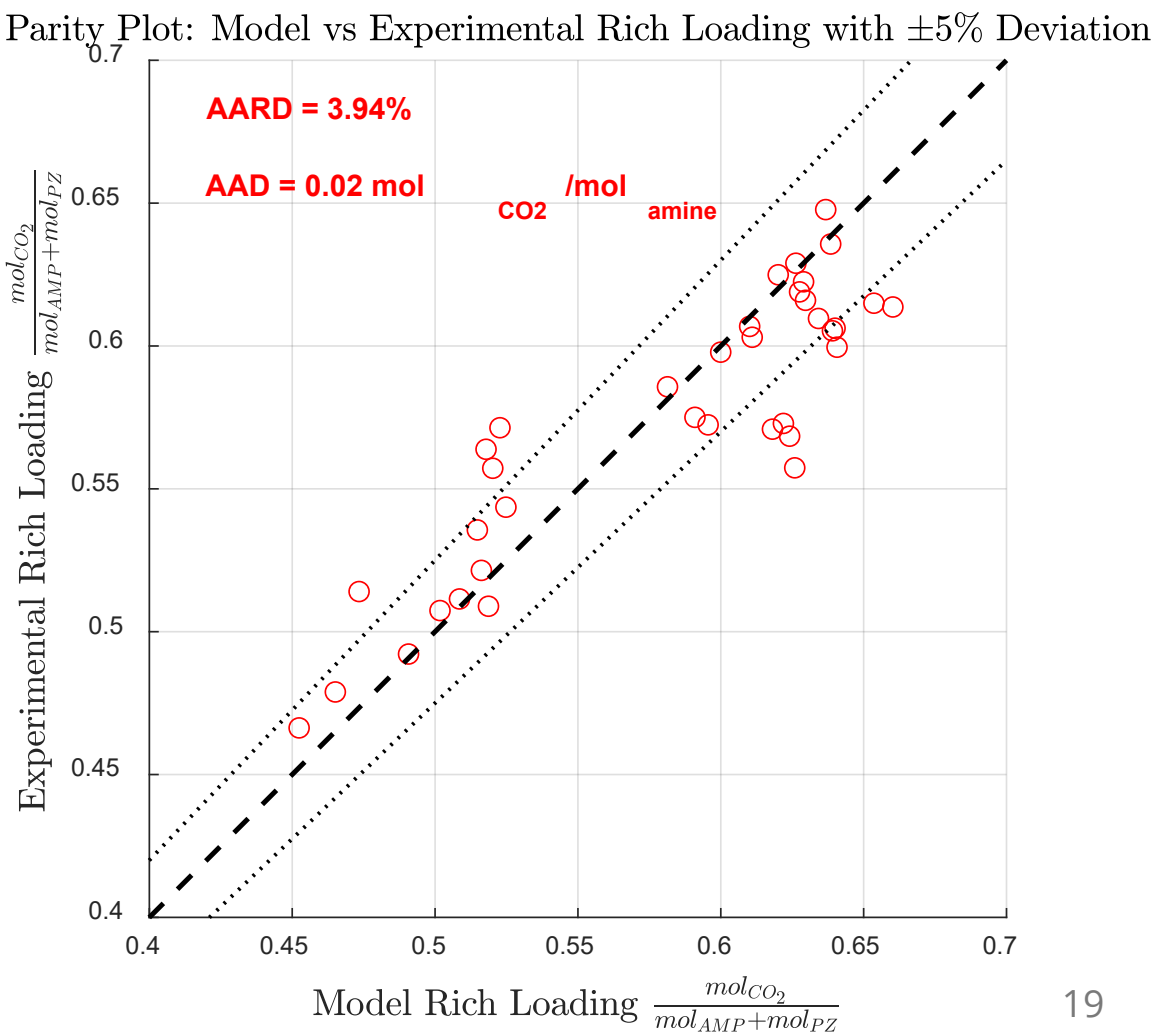
$$AAD(Absolute\ Average\ Deviation) = \sum_{i}^{N} \frac{|y_{model} - y_{exp}|}{N}$$

$$ARD(Average\ Relative\ Deviation) = \frac{\sum_{i}^{N} \frac{y_{model} - y_{exp}}{y_{exp}}}{N} \cdot 100$$

$$AARD(Absolute\ Average\ Relative\ Deviation = \frac{\sum_{i}^{N} \frac{|y_{model} - y_{exp}|}{y_{exp}}}{N} \cdot 100$$

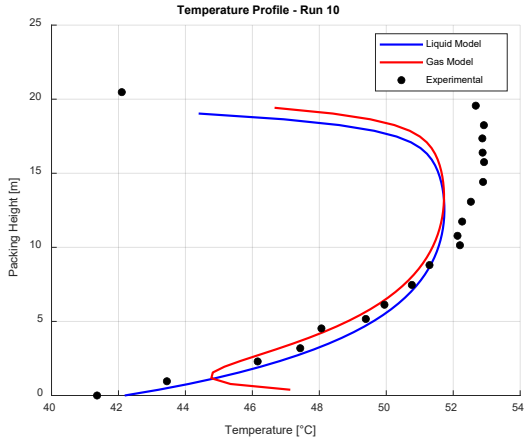
Absorber Validation: CO_2 Rich Loading and Mass transfer Rate [kg/h]

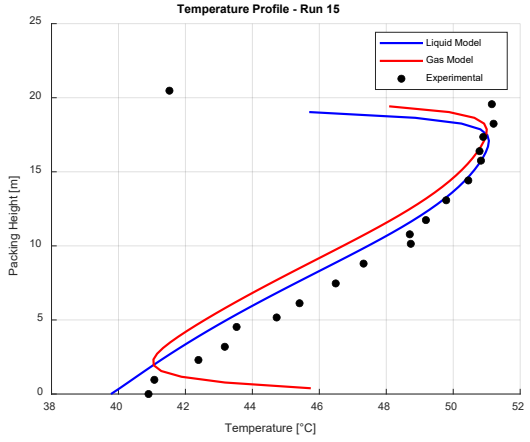




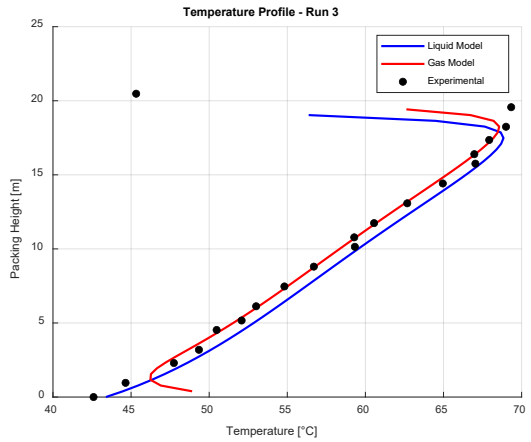
Absorber Validation: Temperature Profile

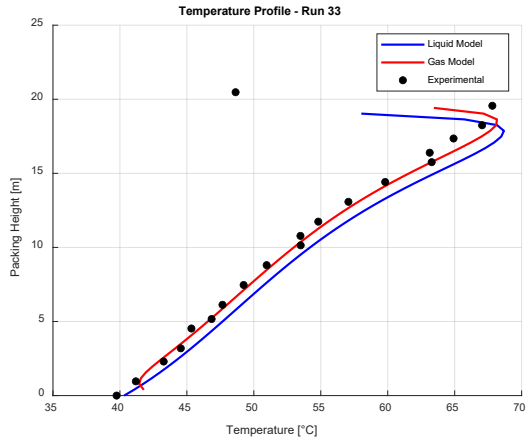
2-3 % CO_2



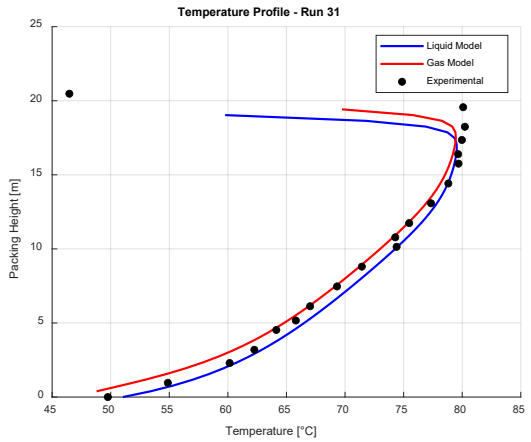


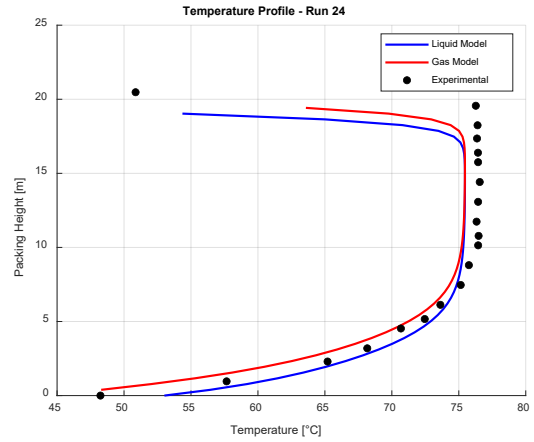
10 % CO_2



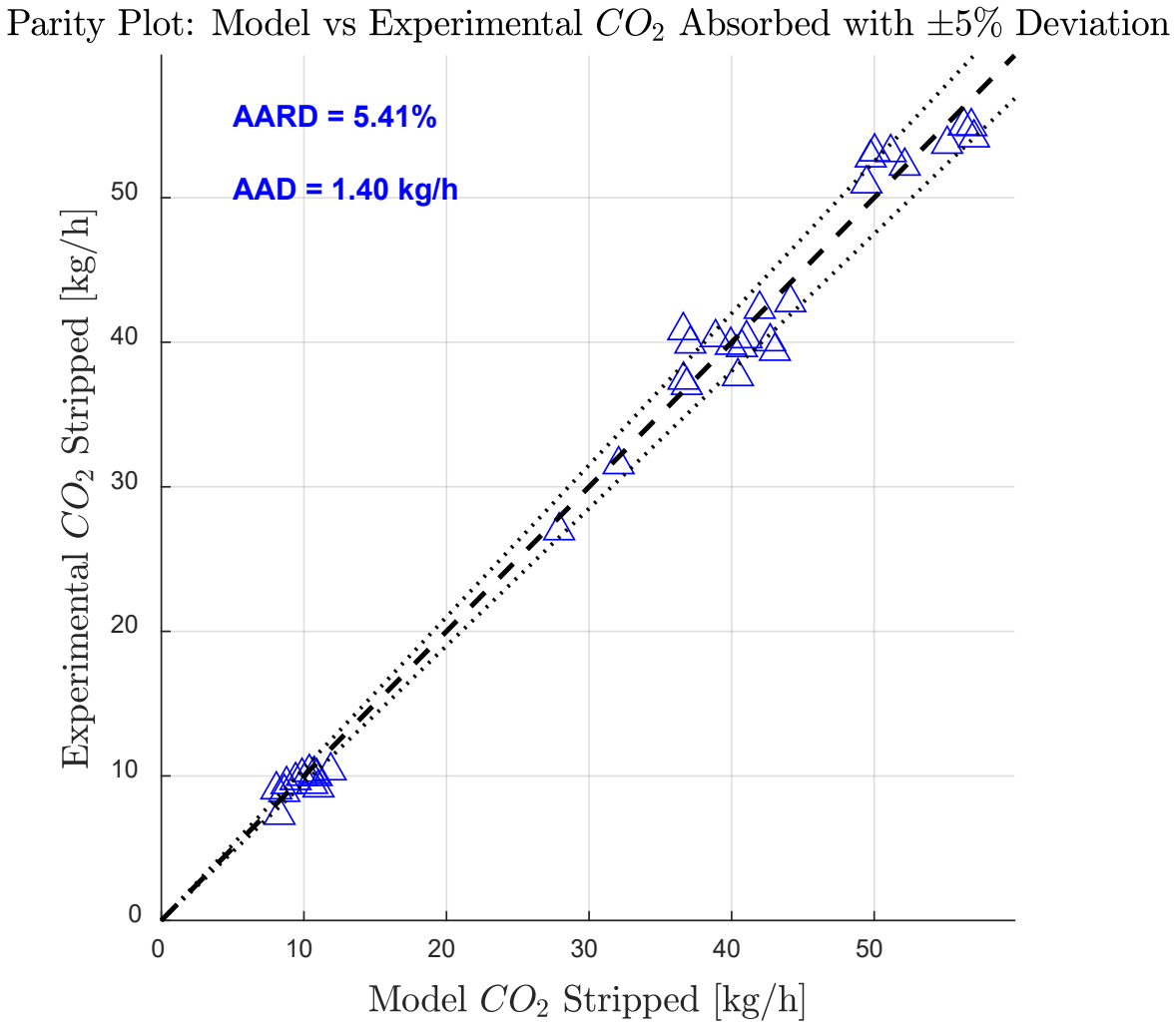


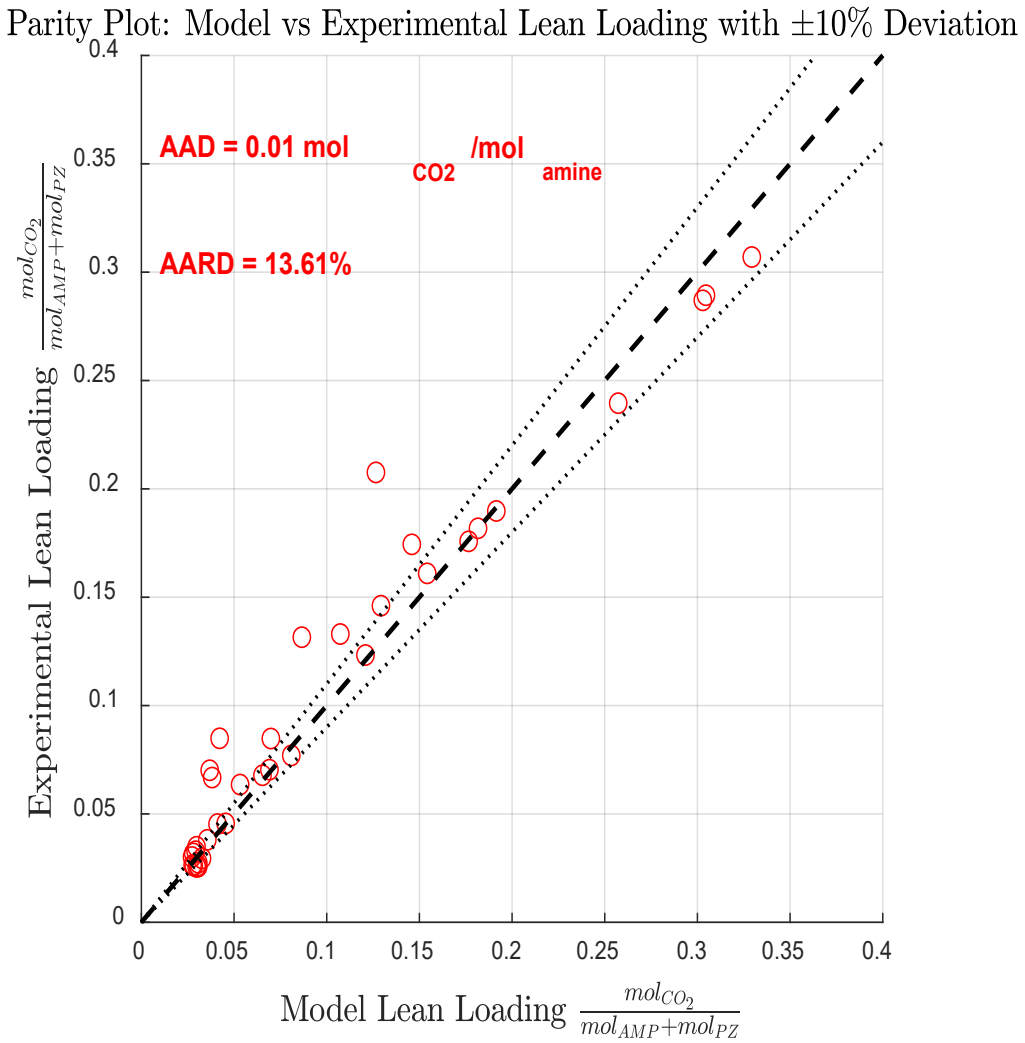
17 % CO_2



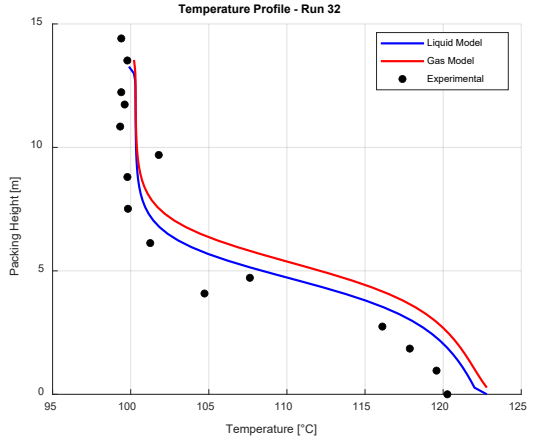


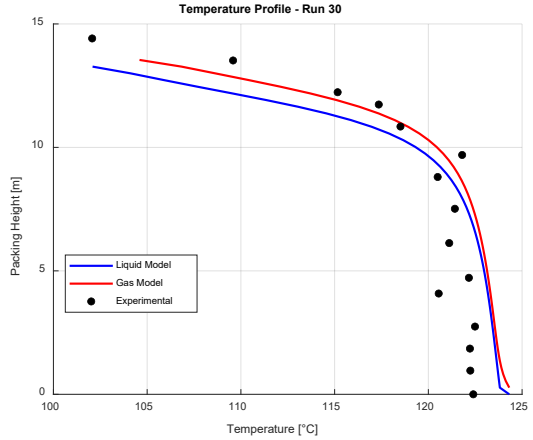
Desorber Validation: CO_2 Lean Loading and Mass transfer Rate [kg/h]

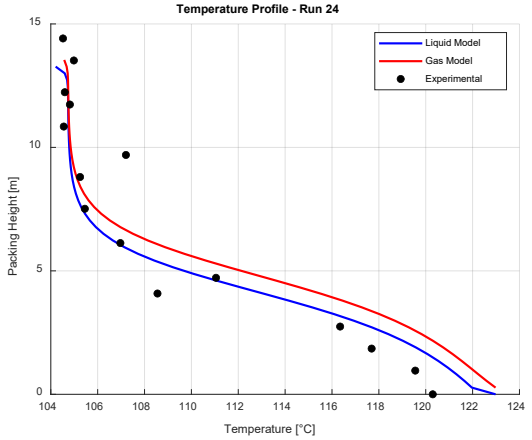


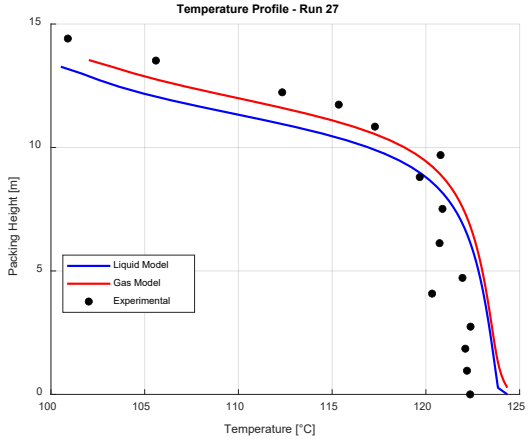


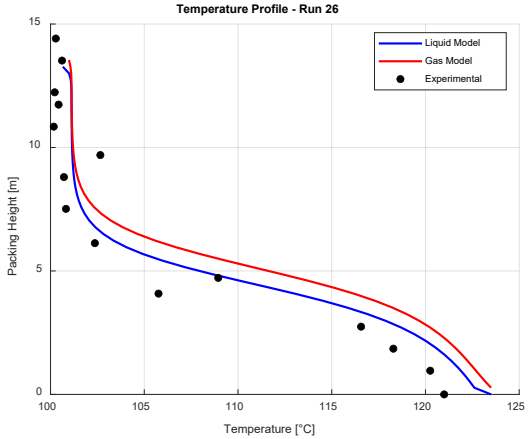
Desorber Validation: Temperature Profile

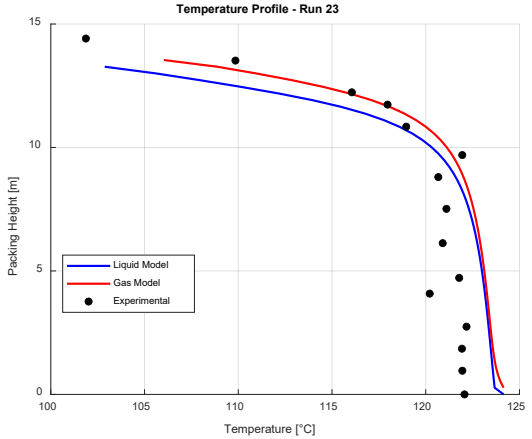






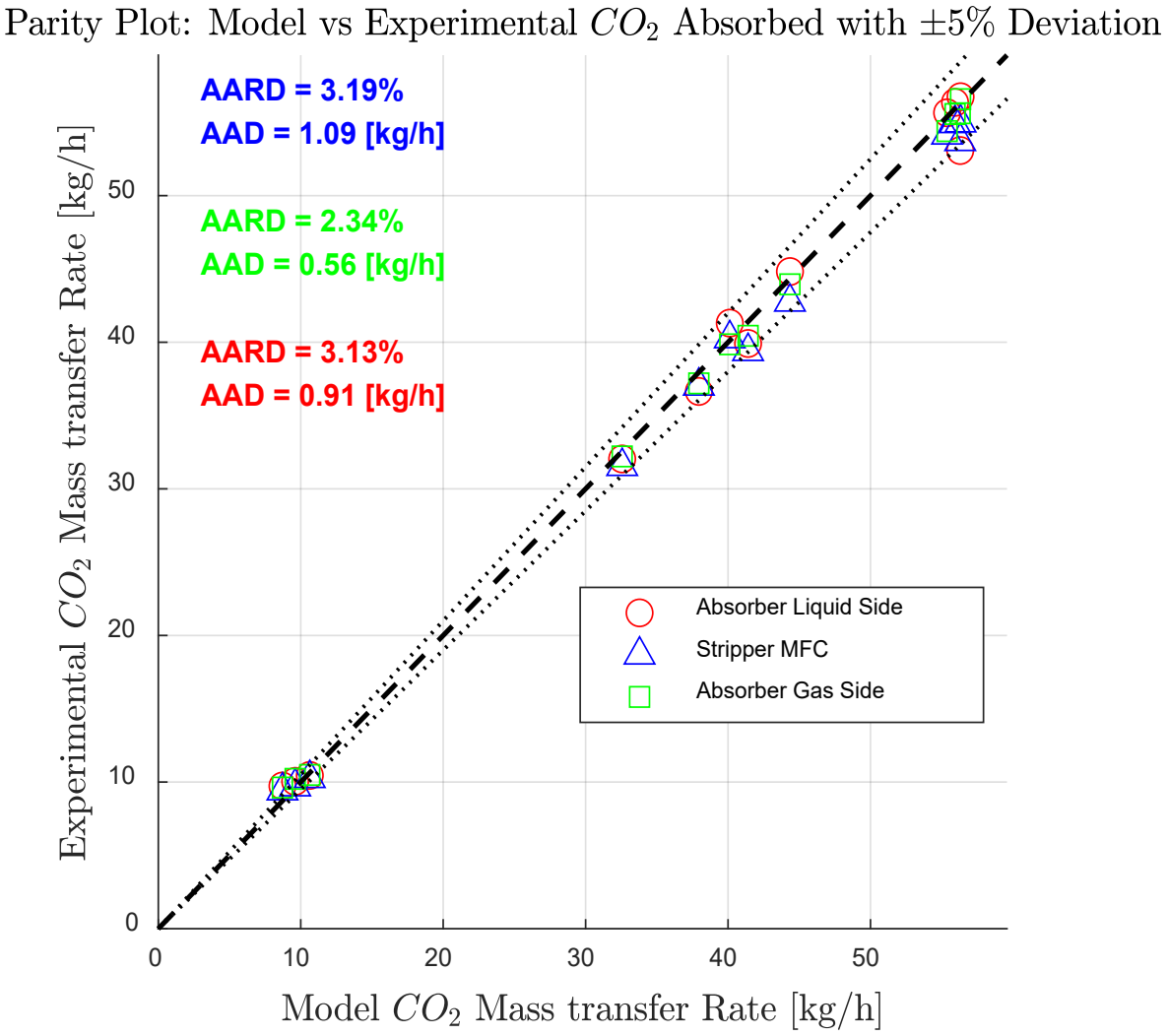






The model predicts well the temperature profile in the desorber and the breakthrough of steam.

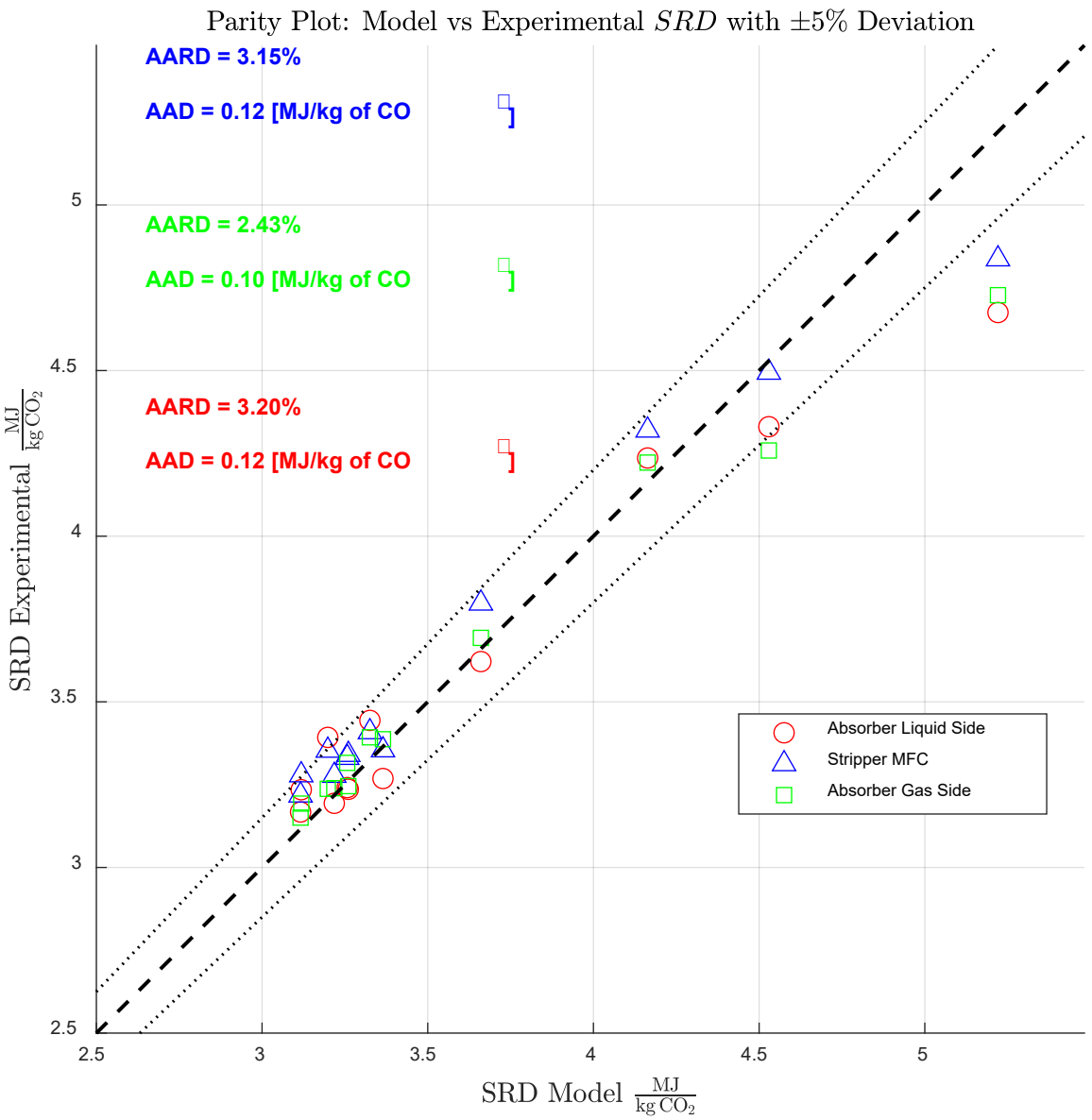
Full Plant Validation: Mass transfer Rate



The model predicts the mass transfer rate [kg/h] with the following error metrics:

Model-Exp	AD [kg/h]	AAD [kg/h]	ARD [%]	AARD [%]
Gas Analyses	0.26	0.56	-0.31	2.34
Liquid Analyses	0.21	0.91	-0.33	3.13
CO_2 Product	0.94	1.09	1.78	3.19

Full Plant Validation: Energy Requirement



The model predicts the specific reboiler duty [MJ/kg of CO_2] with the following error metrics:

Model-Exp	AD [MJ/kg of CO_2]	AAD [MJ/kg of CO_2]	ARD [%]	AARD [%]
Gas Analyses	0.030	0.10	0.62	2.43
Liquid Analyses	0.033	0.12	0.69	3.20
CO_2 Product	-0.048	0.12	-1.47	3.15

Conclusions

- A new e-NRTL model for AMP/PZ/H_2O/CO_2 has been developed in Aspen Plus v14.
- The thermodynamic framework predicts well the CO_2 solubility over a large range of CO_2 partial pressure, temperature and AMP/PZ concentration.
- The model predicts well other thermodynamic properties such as: liquid speciation, free CO_2 concentration and heat of absorption.
- The model predicts well the absorber and desorber operation as separated units with errors < 5%.
- The model was validated in a closed-loop simulation on 12 cases from Tiller. The SRD is predicted within an absolute average deviation of 0.12 MJ/kg of CO_2 and AARD of 3.2 %.
- The process model will be shared and further details on the methodology and the framework are available in an accepted open-access publication titled: ***Development of a validated rate-based model for CO_2 absorption in aqueous 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) blends using Aspen Plus.***

Acknowledgement

This research has received funding from the European Union's Horizon research and innovation programme under grant agreement No. 101096521

Thank you for your attention

Diego Morlando - NTNU

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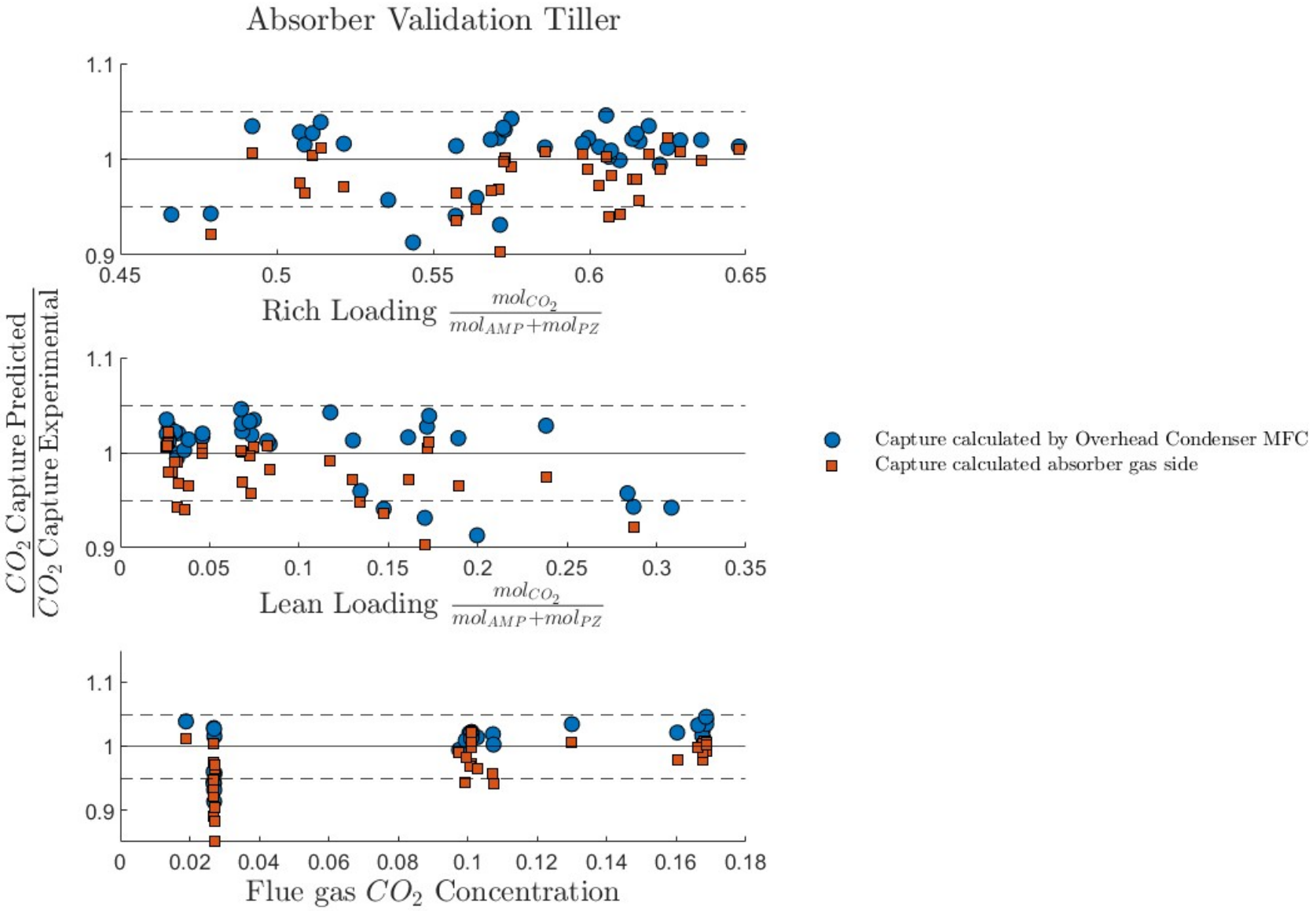
Supplementary Slides

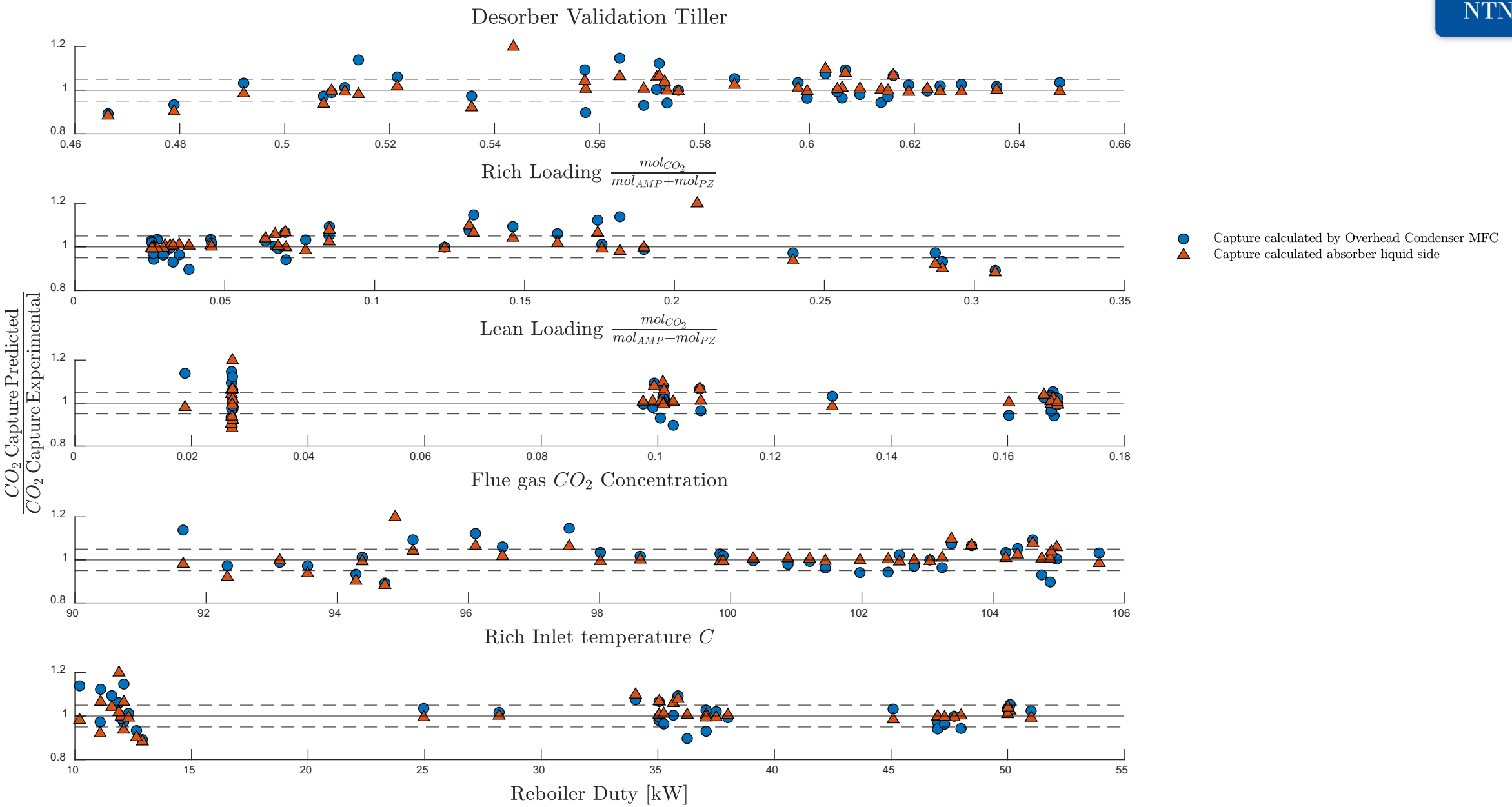
Rate-based Modeling Specification

Features	Specification
Calculation Type	Rate-Based
Number of stages	50
Mass transfer coefficient model	Brf-85
Interfacial area model	Brf-85
Interfacial area factor	1
Heat transfer coefficient model	Chilton and Colburn Analogy
Holdup correlation	Billet-93
Flow Model	Mixed
Reaction film resistance	Discretized film reactions for liquid phase, Consider film for vapor phase
Reaction condition factor	0.5
Transfer condition factor	0.5

Absorber Validation: Residual Plot

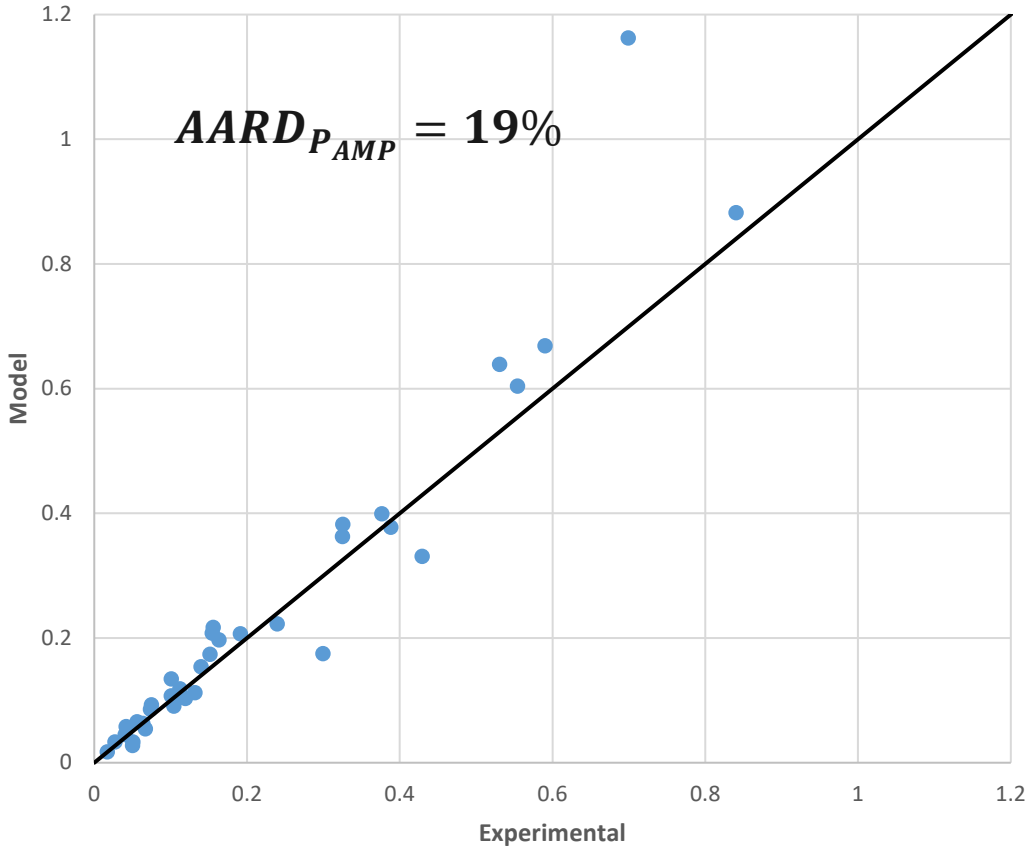


Desorber Validation: Residual Plot

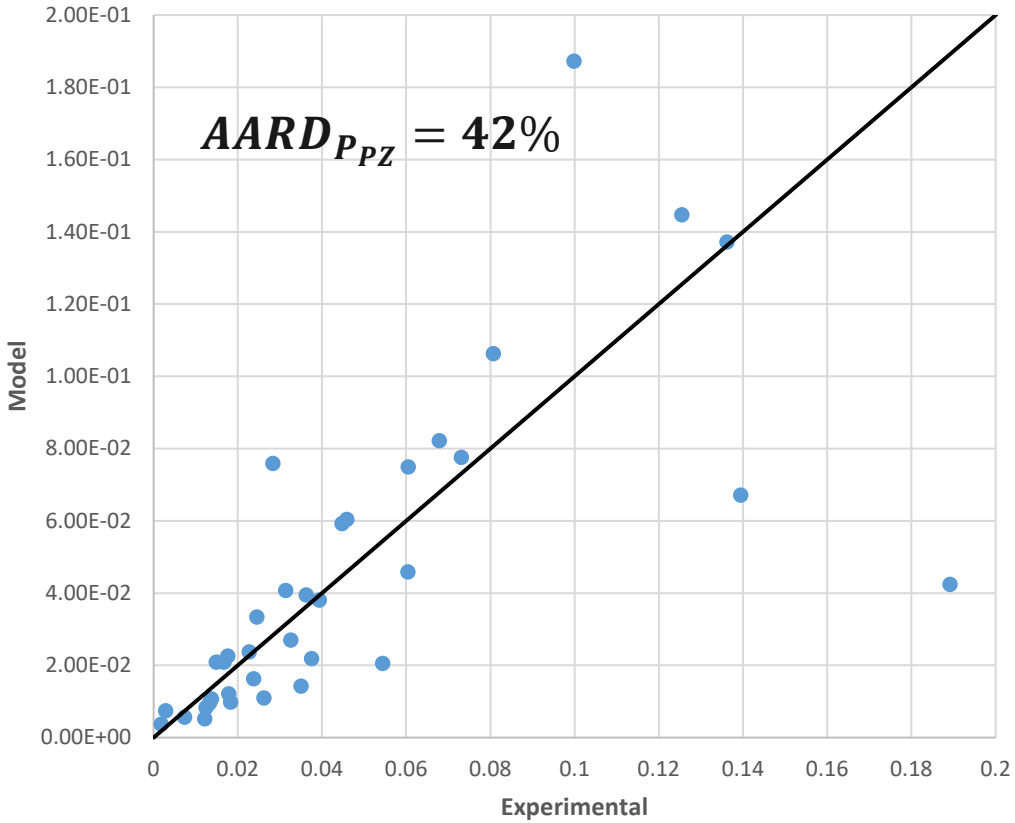


Volatility

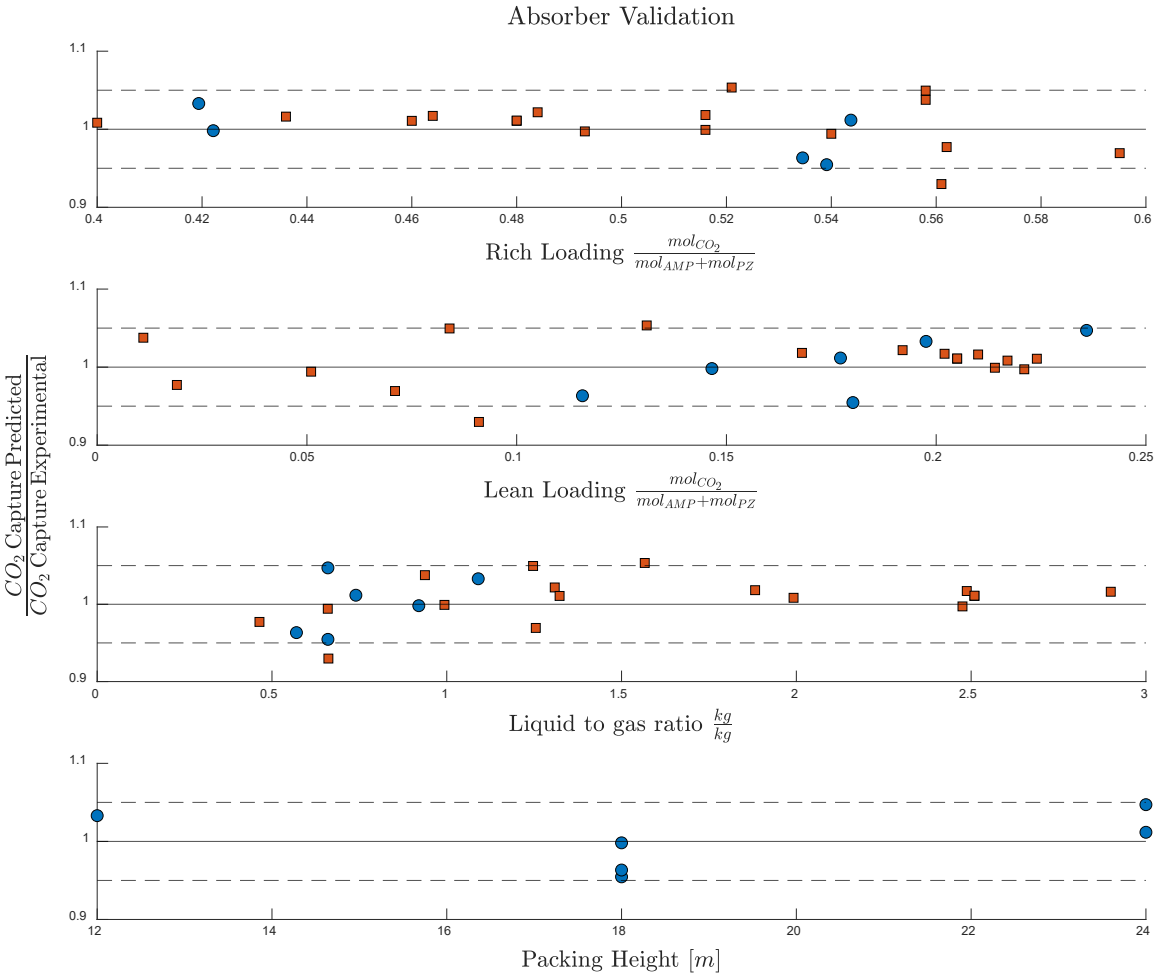
Partial pressure of AMP [kPa] Hartono et al. Dataset



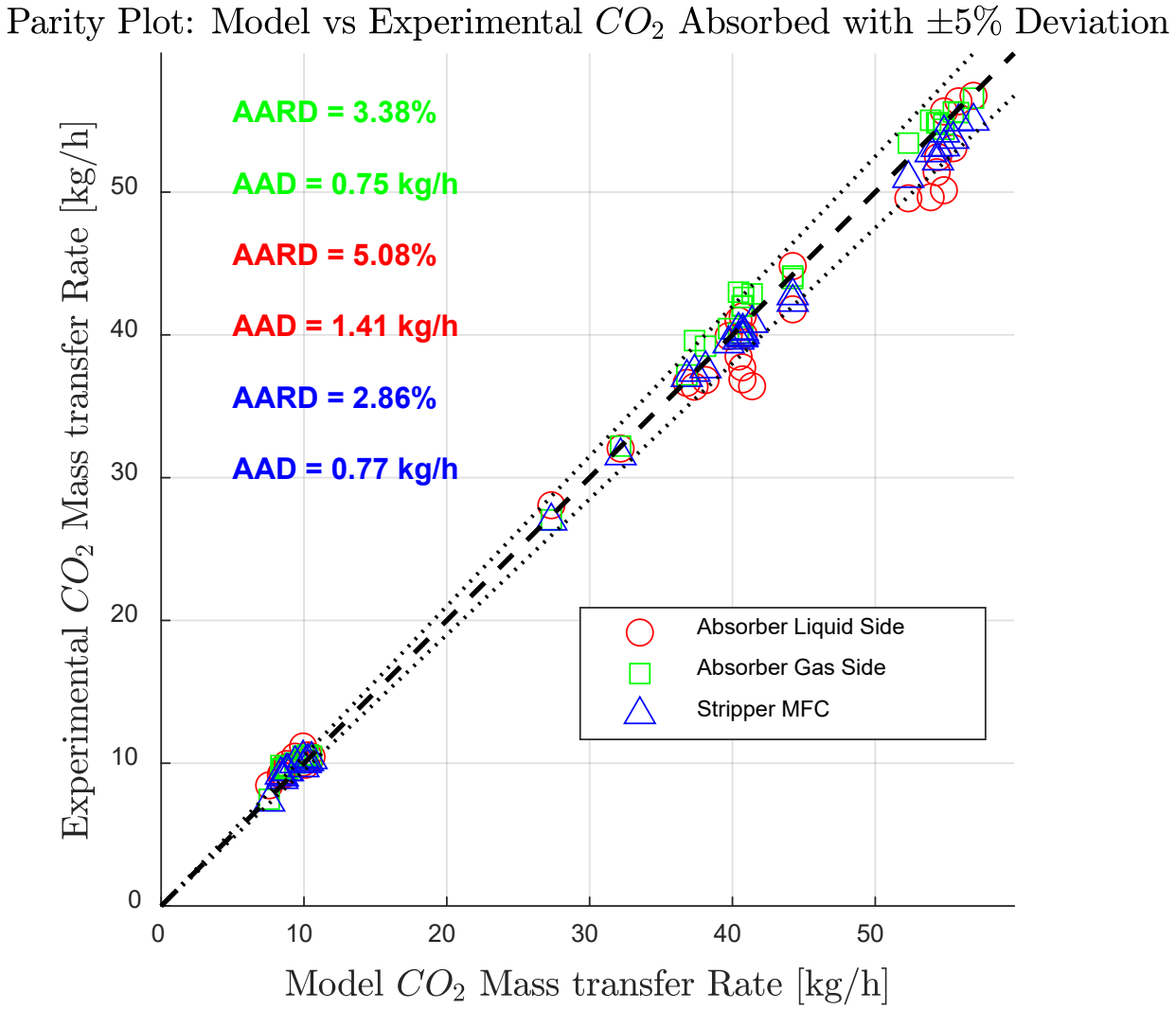
Partial pressure of PZ [kPa] Hartono et al. Dataset



Absorber Validation: TCM and Mangalapally



Absorber Validation: Tiller Absorber



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