Aspen Plus ENRTL Model for HS3 Blend, a Novel Solvent for CO_2 Capture

REALISE CCUS

PCCC-7
Pittsburgh, September, 25th – 28th

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Evaluating technology options to mitigate greenhouse gas emissions
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Post Combustion Capture Conference

Outlines

- Introduction to REALISE project
- Overview of the HS3 Aspen model
- Model validation
- Conclusions

REALISE Project

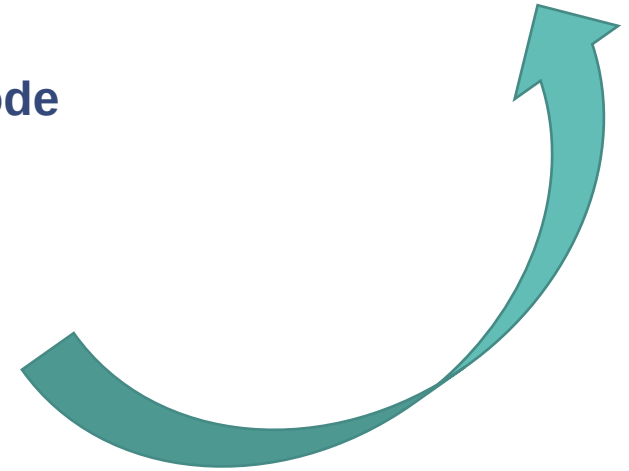
Innovation Action

SINTEF coordinator

Final TRL 7

Period: May 2020 – October 2023

Official webpage QR code



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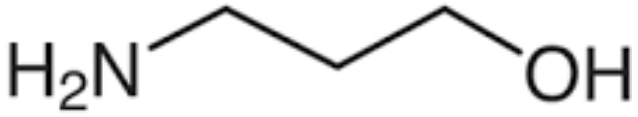
REALISE Project

Project Advisory Board

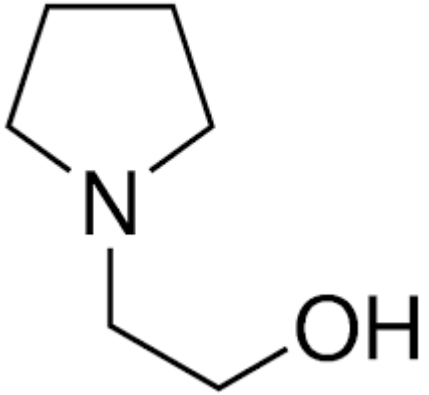
- Concawe – scientific division of the European Petroleum Refineries Association
- PetroIneos (UK)
- SARAS (Italy)
- TCM (Norway)
- Global CCS Institute (Australia)
- Science Foundation Ireland (Ireland)

HS3 solvent

- Blend of a primary amine and a tertiary amine studied in a previous EUH2020 project (HyPerCap) with promising energy savings



3-amino-1-propanol (AP)
(15% weight)

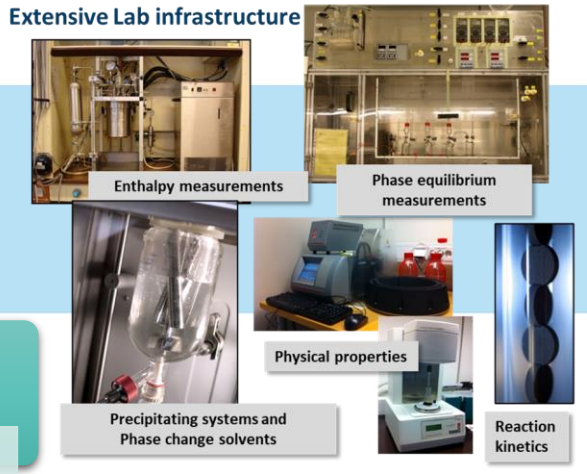


2-(1-hydroxyethyl)-pyrrolidine (PRLD)
(40% weight)

Introduction

- A new HS3 model has been implemented in Aspen Plus V11.0.
- The model includes:
  - Thermodynamics (VLE equilibrium);
  - Kinetics for global reactions;
  - Mass transfer limitations
- The model has been **tested and validated on Tiller pilot-scale exp data**

Model development



Physical properties definition
(vapor pressure, equilibrium constants, Henry…)

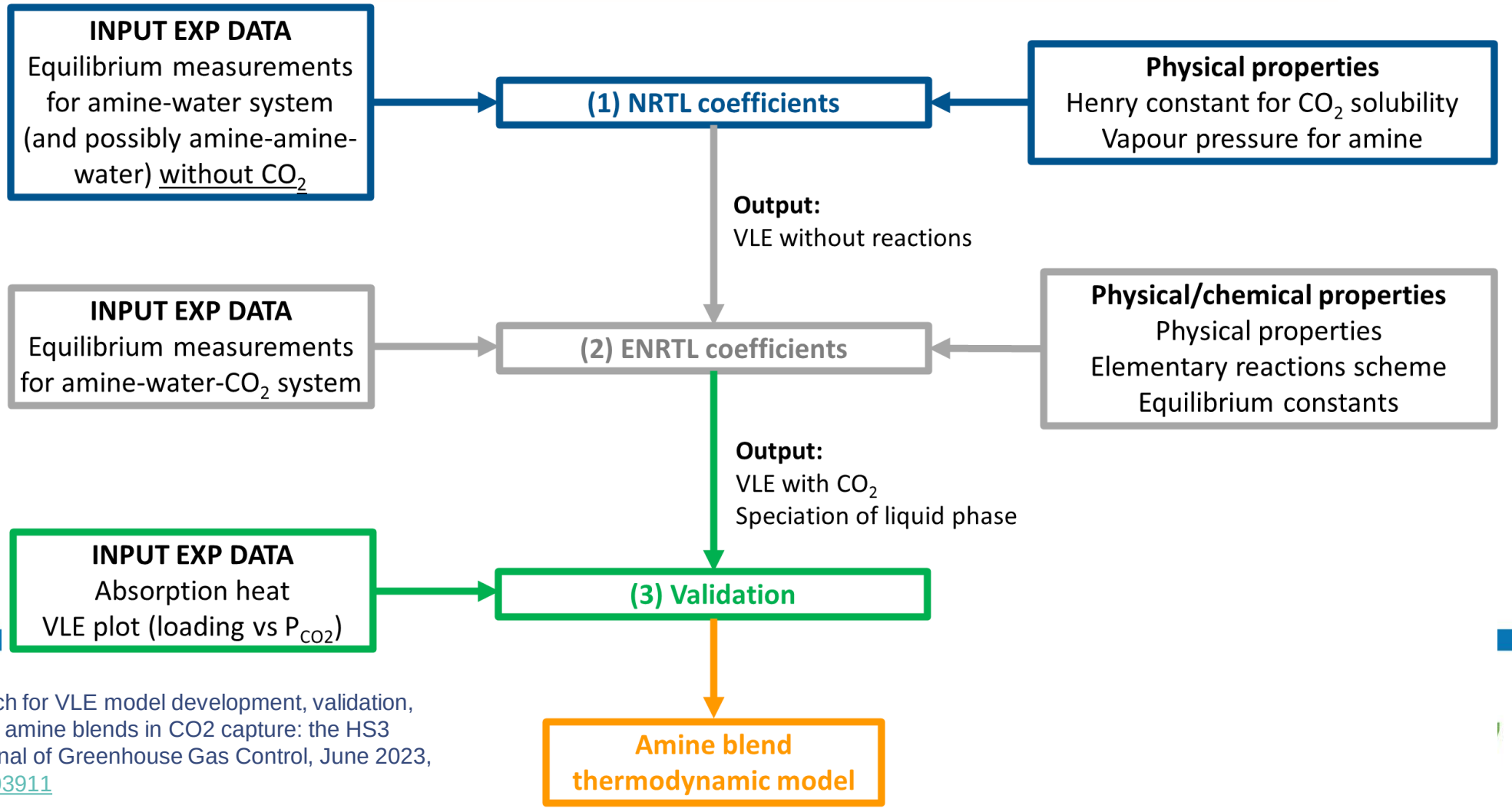
NRTL model

ENRTL activity model development

Mass transfer & kinetics

Validation on Tiller pilot plant

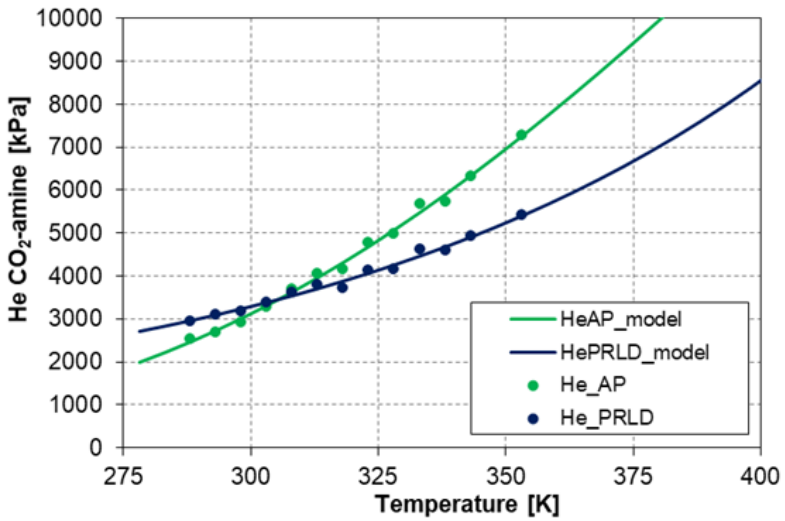
Thermodynamic framework development

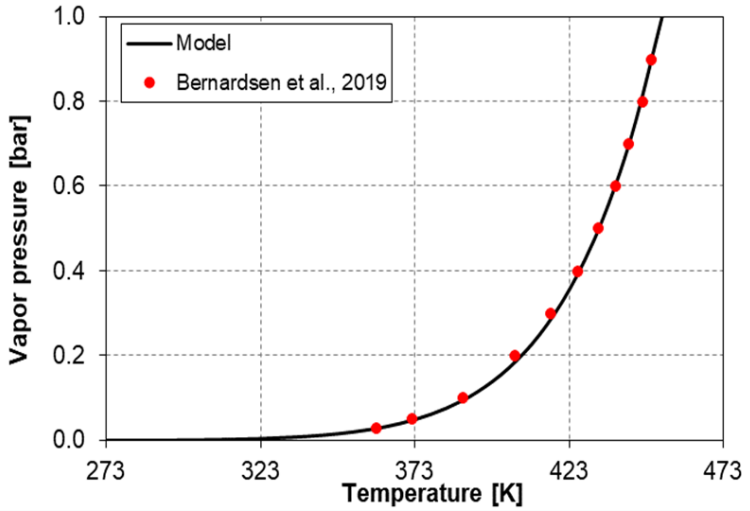


M. Gilardi, F. Bisotti et al., An approach for VLE model development, validation, and implementation in Aspen Plus for amine blends in CO2 capture: the HS3 solvent case study, International Journal of Greenhouse Gas Control, June 2023, https://doi.org/10.1016/j.ijggc.2023.103911

Physical properties fitted to experimental data

- Henry constant (using N_2O analogy) for both amines
- Amines vapour pressure
- Density
- Heat capacity of the liquid phase





A. Hartono, Vevelstad, S, Grimstvedt, A, Hovdahl, L, Wiig, M, Chikukwa, A, Hjarbo, K, Gjertsen, F, Tjessem, V, S. Hauger, *Realise D1.1 Solvent optimization: Experimental characterization of REALISE solvent*
I.M. Bernhardsen, A.A. Trollebø, C. Perinu, H.K. Knuutila, *Vapour-liquid equilibrium study of tertiary amines, single and in blend with 3-(methylamino)propylamine, for postcombustion CO2 capture*, Journal of Chemical Thermodynamics. 138 (2019) 211–228. https://doi.org/10.1016/j.jct.2019.06.017

NRTL coefficients (BINARY INTERACTION - NRTL)

Aspen Plus NRTL coefficient	Parameters	Component i	Component j	Value (SI units)	Source of experimental values
NRTL/1	A_{ij}	H_2O	AP	5.3843	(Bunevska, 2021)
NRTL/2	B_{ij}	H_2O	AP	-0.9199	
NRTL/1	A_{ji}	AP	H_2O	-989.213	
NRTL/2	B_{ji}	AP	H_2O	-440.101	
NRTL/3	$\alpha_{ij} = \alpha_{ji}$	H_2O	AP	0.2	
NRTL/1	A_{ij}	H_2O	PRLD	1.1755	(Bernhardsen et al., 2019)
NRTL/2	B_{ij}	H_2O	PRLD	-0.1156	
NRTL/1	A_{ji}	PRLD	H_2O	-1103.81	
NRTL/2	B_{ji}	PRLD	H_2O	1715.89	
NRTL/3	$\alpha_{ij} = \alpha_{ji}$	H_2O	PRLD	0.2	

8 Molecule-molecule interactions

Non-randomness coefficients fixed as in Chen et al.

I.M. Bernhardsen, A.A. Trollebø, C. Perinu, H.K. Knuutila, *Vapour-liquid equilibrium study of tertiary amines, single and in blend with 3-(methylamino)propylamine, for postcombustion CO2 capture*, Journal of Chemical Thermodynamics. 138 (2019) 211–228. https://doi.org/10.1016/j.jct.2019.06.017

T. Bunevska, *Characterization of a solvent for chemical absorption-based CO2 capture*, NTNU Thesis, 2021.

C. Chen, Y. Song, *Generalized electrolyte-NRTL model for mixed-solvent electrolyte systems*, AIChE Journal. 50 (2004) 1928–1941. https://doi.org/10.1002/aic.10151.

Electrolyte-NRTL model

ENRTL is an activity-based thermodynamic model

The activity accounts for:
- Long-range interactions
- **Short-range interactions**
- Born correction

Short-range interactions

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{n} x_j \cdot \tau_{ji} \cdot G_{ji}}{\sum_{k=1}^{n} x_k \cdot G_{ki}} + \sum_{j=1}^{n} \frac{x_j \cdot G_{ij}}{\sum_{k=1}^{n} x_k \cdot G_{kj}} \cdot \left(\tau_{ij} - \frac{\sum_{m=1}^{n} x_m \cdot \tau_{mj} \cdot G_{mj}}{\sum_{k=1}^{n} x_k \cdot G_{kj}} \right)$$

$$G_{ji} = \exp(-\alpha_{ij} \cdot \tau_{ij})$$

$$\tau_{ij} = A_{ij} + \frac{B_{ij}}{T[K]}$$

Renon, H., Prausnitz, J.M., 1969. *Estimation of Parameters for the NRTL Equation for Excess Gibbs Energies of Strongly Nonideal Liquid Mixtures*, Industrial & Engineering Chemistry Process Design and Development 8, 413–419. https://doi.org/10.1021/i260031a019
Renon, H., Prausnitz, J.M., 1968. *Local compositions in thermodynamic excess functions for liquid mixtures*, AIChE Journal 14, 135–144. https://doi.org/https://doi.org/10.1002/aic.690140124

ELECNRTL coefficients (ELECTROLYTE PAIR – GMELCC/GMELCD)

Molecule-ion interactions

- 24 **GMELCC** (temperature-independent parameters)
- 10 **GMELCD** (temperature-dependent parameters)

$$\frac{3n_M!}{n_M - 2} + 5n_M n_C n_A$$

n_M – number of molecules
n_C – number of cations
n_A – number of anions

HS3 solvent could be defined by 276 coefficients and 34 parameters allow to reduce by 88% the amount of adjusted parameters

ELECNRTL coefficient Aspen Plus name	Element i	Element j	Value (SI units)
GMELCC	H_2O	($PRLDH^+$,HCO_3^-)	13.6961
GMELCC	($PRLDH^+$,HCO_3^-)	H_2O	-5.4276
GMELCC	PRLD	($PRLDH^+$,HCO_3^-)	29.0442
GMELCC	($PRLDH^+$,HCO_3^-)	PRLD	8.7717
GMELCC	H_2O	(APH^+,HCO_3^-)	12.6182
GMELCC	(APH^+,HCO_3^-)	H_2O	-5.5317
GMELCC	H_2O	(APH^+,$APCOO^-$)	10.5229
GMELCC	(APH^+, $APCOO^-$)	H_2O	-6.9975
GMELCC	AP	(APH^+, HCO_3^-)	87.2557
GMELCC	(APH^+, HCO_3^-)	AP	60.3790
GMELCC	AP	(APH^+, $APCOO^-$)	20.7888
GMELCC	(APH^+, $APCOO^-$)	AP	34.8014
GMELCC	H_2O	($PRLDH^+$, $APCOO^-$)	10.9464
GMELCC	($PRLDH^+$, $APCOO^-$)	H_2O	-5.1289
GMELCC	AP	($PRLDH^+$, HCO_3^-)	52.3316
GMELCC	($PRLDH^+$, HCO_3^-)	AP	35.0286
GMELCC	AP	($PRLDH^+$, $APCOO^-$)	4.5923
GMELCC	($PRLDH^+$, $APCOO^-$)	AP	-1.3794
GMELCC	PRLD	($PRLDH^+$, $APCOO^-$)	12.5491
GMELCC	($PRLDH^+$, $APCOO^-$)	PRLD	2.8911
GMELCC	PRLD	(APH^+, HCO_3^-)	11.6230
GMELCC	(APH^+, HCO_3^-)	PRLD	0.1155
GMELCC	PRLD	(APH^+, $APCOO^-$)	7.4596
GMELCC	(APH^+, $APCOO^-$)	PRLD	19.9230
GMELCD	PRLD	($PRLDH^+$, HCO_3^-)	888.2463
GMELCD	($PRLDH^+$, HCO_3^-)	PRLD	8810.9267
GMELCD	AP	(APH^+, HCO_3^-)	1959.2531
GMELCD	(APH^+, HCO_3^-)	AP	1514.6851
GMELCD	AP	(APH^+, $APCOO^-$)	-259.7171
GMELCD	(APH^+, $APCOO^-$)	AP	432.8310
GMELCD	AP	($PRLDH^+$, $APCOO^-$)	530.2970
GMELCD	($PRLDH^+$, $APCOO^-$)	AP	-789.5392
GMELCD	PRLD	($PRLDH^+$, $APCOO^-$)	-2337.3930
GMELCD	($PRLDH^+$, $APCOO^-$)	PRLD	-66.6320

M. Gilardi, F. Bisotti et al., *An approach for VLE model development, validation, and implementation in Aspen Plus for amine blends in CO2 capture: the HS3 solvent case study*, International Journal of Greenhouse Gas Control, June 2023, https://doi.org/10.1016/j.ijggc.2023.103911

VLE

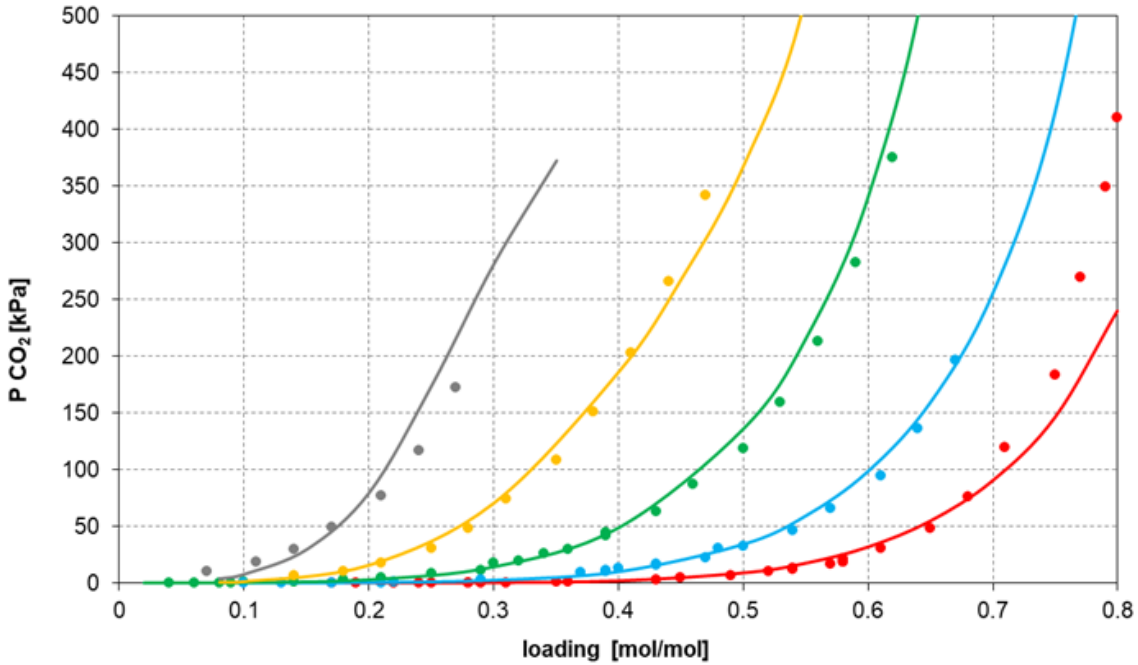
- Low number of parameters to guarantee model **smoothness** and **avoid overfitting**
- **Reliability** has been checked by two indexes:

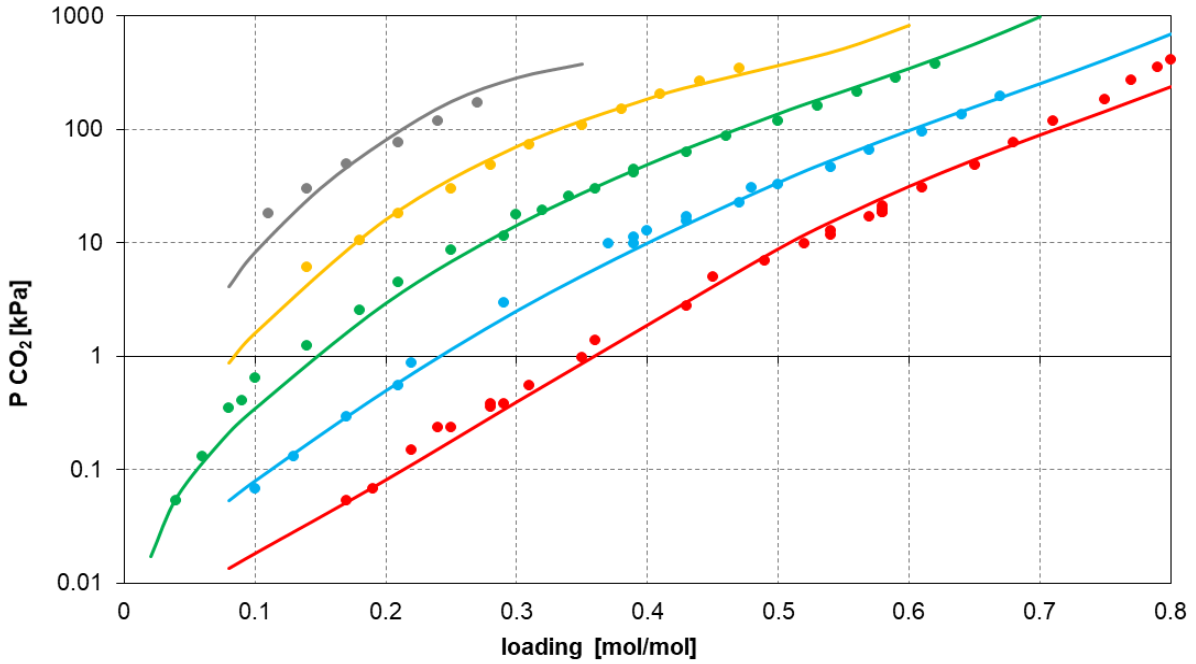
➢ **AARD - Average Absolute Relative deviation of CO_2 and H_2O partial pressures** (with respect to exp. data);
➢ **AAD - Average Absolute Deviations.**

$$\mathrm{AARD} = \frac{1}{n} \cdot \sum_{I=1}^{n} \left| \frac{z_{i,exp} - z_{i,mod}}{z_{i,exp}} \right|$$

$$\mathrm{AAD} = \sqrt{\sum_{i=1}^{n} \frac{\left(z_{i,exp} - z_{i,mod}\right)^2}{n}}$$

VLE (model accuracy)





		AARD [%]		AAD [kPa]	
Model	Data source	P_{CO2}	P_{H2O}	P_{CO2}	P_{H2O}
ELECNRTL	Hartono et al.	17.84	17.00	0.0712	0.0705

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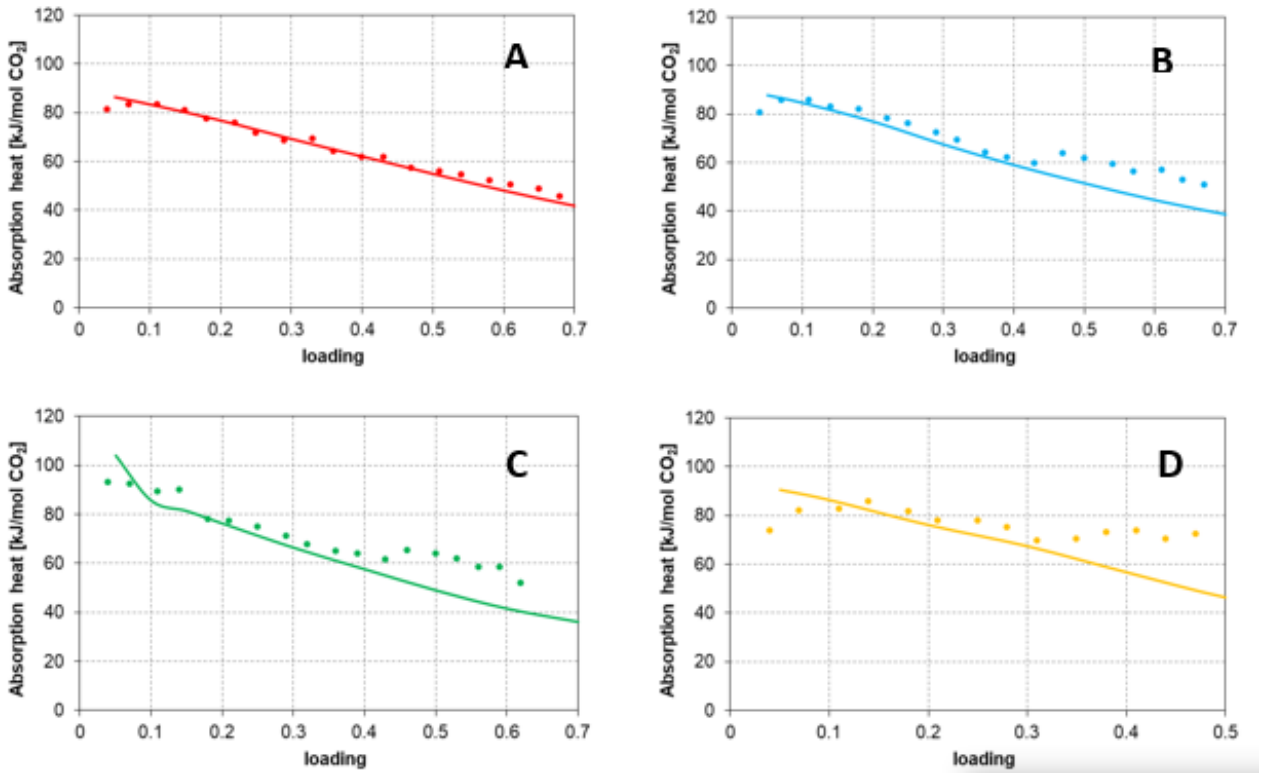
Heat of absorption



- Heat of formation of APH+, APCOO-, and PRLDH+ tuned on the experimental data

Hartono, Vevelstad, S, Grimstvedt, A, Hovdahl, L, Wiig, M, Chikukwa, A, Hjarbo, K, Gjertsen, F, Tjessem, V, S. Hauger, *Realise D1.1 Solvent optimization: Experimental characterization of REALISE solvent*

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Kinetics

- Arrhenius-type kinetics for global AP and PRLD reactions with CO2 has been taken from the literature.

AP	Penny and Ritter [1983]	Henni et al. [2008]
A [L/mol/s]	1,26E+12	6.6E+11
Eact [cal/mol]	11132.35	10838.7

$$AP + CO_2 + H_2O \rightarrow APCOO^- + H_3O^+$$

In accordance with other Aspen's framework for amine solvents, the kinetic is set **carbamate reaction** and the reverse kinetic is calculated using the **thermodynamic consistency** for the carbamate reaction

PRLD	Liu et al. [2017]
A [L/mol/s]	7.61E+8
Eact [cal/mol]	9783.99

$$PRLD + CO_2 + H_2O \rightarrow PRLDH^+ + HCO_3^-$$

D.E. Penny, T.J. Ritter, *Kinetic study of the reaction between carbon dioxide and primary amines*, J. Chem. Soc., Faraday Trans. 1. 79 (1983) 2103–2109. https://doi.org/10.1039/F19837902103

Henni, J. Li, P. Tontiwachwuthikul, *Reaction kinetics of CO2 in aqueous 1-amino2-propanol, 3-amino-1-propanol, and dimethylmonoethanolamine solutions in the temperature range of 298-313 K using the stopped-flow technique*, Industrial and Engineering Chemistry Research. 47 (2008) 2213–2220. https://doi.org/10.1021/ie070587r

H. Liu, M. Li, R. Idem, P. Tontiwachwuthikul, Z. Liang, *Analysis of solubility, absorption heat and kinetics of CO2 absorption into 1-(2-hydroxyethyl)pyrrolidine solvent*, Chemical Engineering Science. 162 (2017) 120–130. https://doi.org/10.1016/j.ces.2016.12.070

Mass transfer

- Diffusion coefficients of CO_2 into the solvent is calculated by the software using the Wilke-Chang method

$$D_i^l = 1.17282x10^{-16}\frac{(\varphi M)^{1/2}T}{\eta^l\left(V_{bi}^{*,l}\right)^{0.6}}$$

$$\varphi M = \frac{\sum_{j\neq i} x_j\varphi_j M_j}{\sum_{j\neq i} x_j}$$

Boiling-point molar volume

VISCOSITY OF THE LIQUID MIXTURE

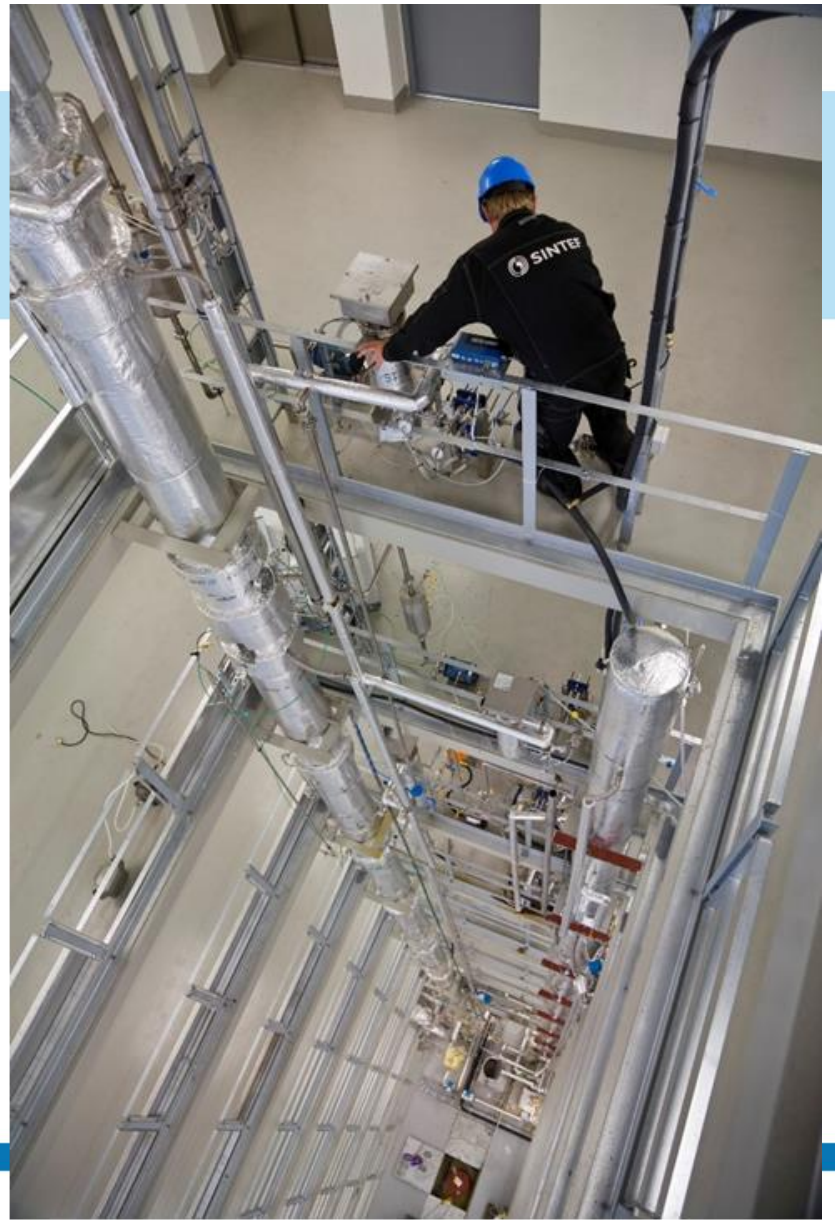
Mixture viscosity is calculated through the **Andrade model**

$$\ln \eta^l = \sum_{i=1}^{n} f_i \ln \eta_i^{*,l} + \sum_{i=1}^{n}\sum_{j=i+1}^{n}\left(k_{ij} f_i f_j + m_{ij} f_i^2 f_j^2\right)$$

Fitted to viscosity mixture exp data (Realise project)

Aspen Plus®, AspenONE™ V11.0 Documentation
Aspen Plus®, Aspen Plus® V11.0 Documentation, (2019)

Tiller Building



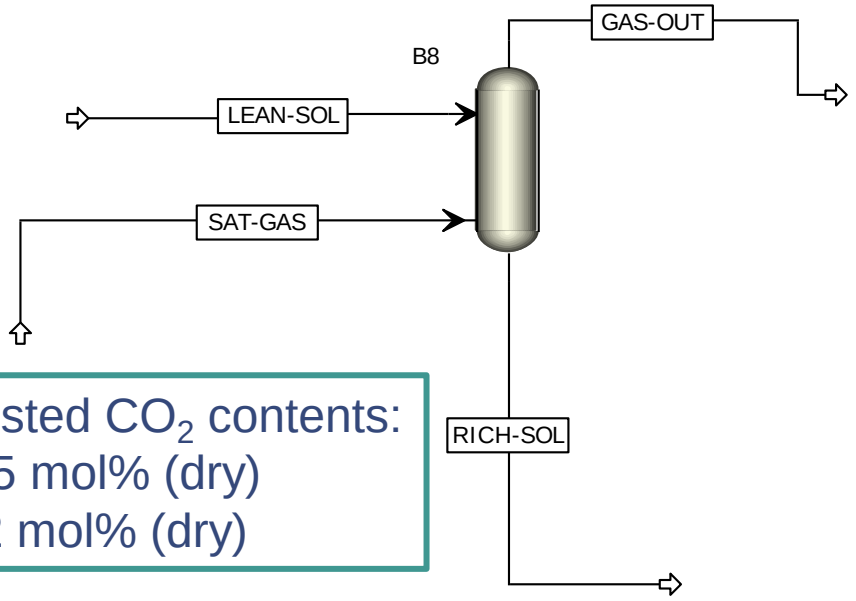
Tiller full height absorber and desorber

SINTEF Industry Tiller pilot plant

- Tiller CO_2-lab built 2010
- A **flexible full height** absorption laboratory infrastructure dedicated to pilot plant activities for CO_2 capture.
- Housed is a **400m² hall with adjacent analytical laboratory** and control room infrastructure.
- The hall has up to **30 meter roof-height** with good accessibility along the height from **11 floors in the tower**.
- Facility enables excellent conditions for controlled indoor pilot experiments.

QR code to SINTEF CO2Lab at Tiller

Model validation on Tiller data: open loop - absorber



Tested CO_2 contents:
5.5 mol% (dry)
12 mol% (dry)

- INPUT DATA (equal to exp data)

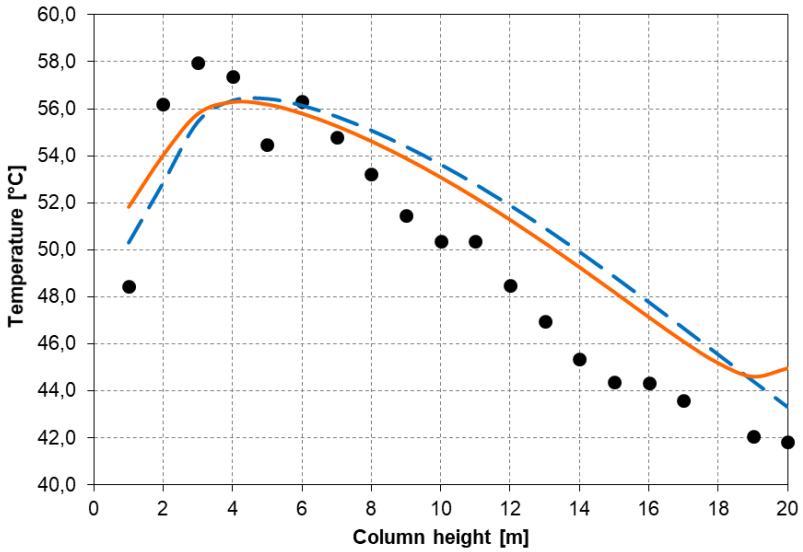
  - L and G flow, temperature, pressure
  - Gas composition (saturation conditions)
  - HS3 solvent composition
  - Lean loading
  - Column design (packing height, diameter)

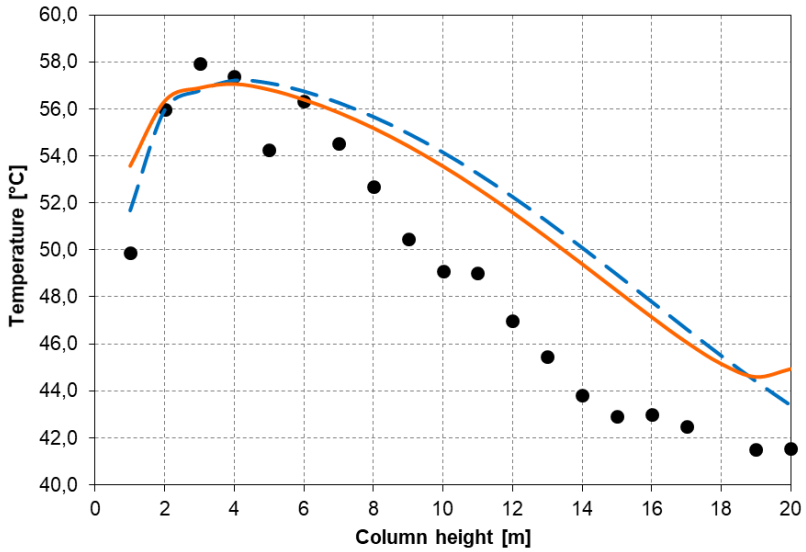
- OUTPUT (to compare)

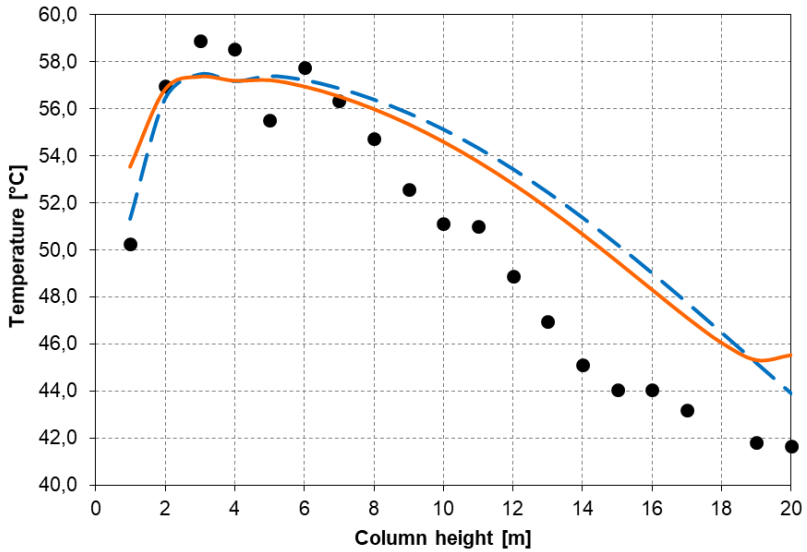
  - **Flow of captured CO_2**
  - % of CO_2 captured
  - **Temperature profile**
  - **Rich loading**

All 53 Tiller runs have been tested.

Results: absorber temperature profiles (5.5 mol%) - absorber



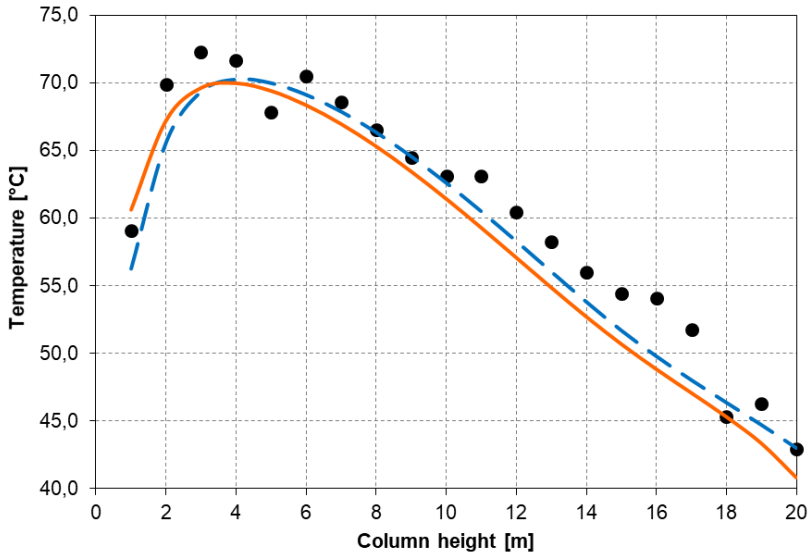


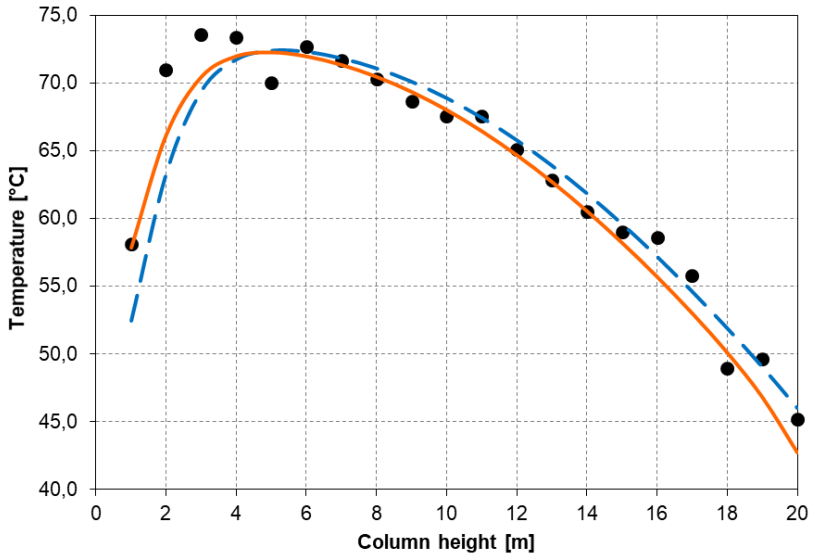


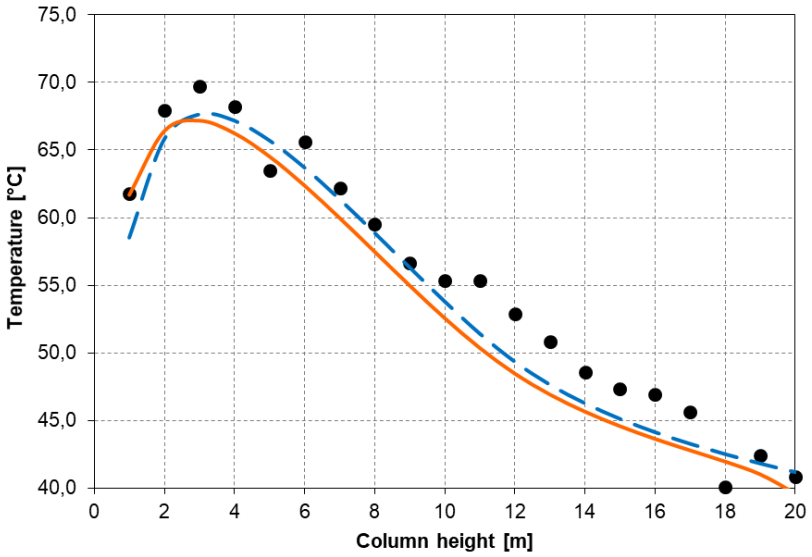
Vapour (orange solid)
Liquid (blue dashed)

	All runs	5.5% vol CO_2	12% vol CO_2
ARD%	2.41	6.37	-0.53
AARD%	3.67	5.37	1.66
Stand Dev [°C]	2.38	4.00	1.20

Results: absorber temperature profiles (12 mol%) - absorber







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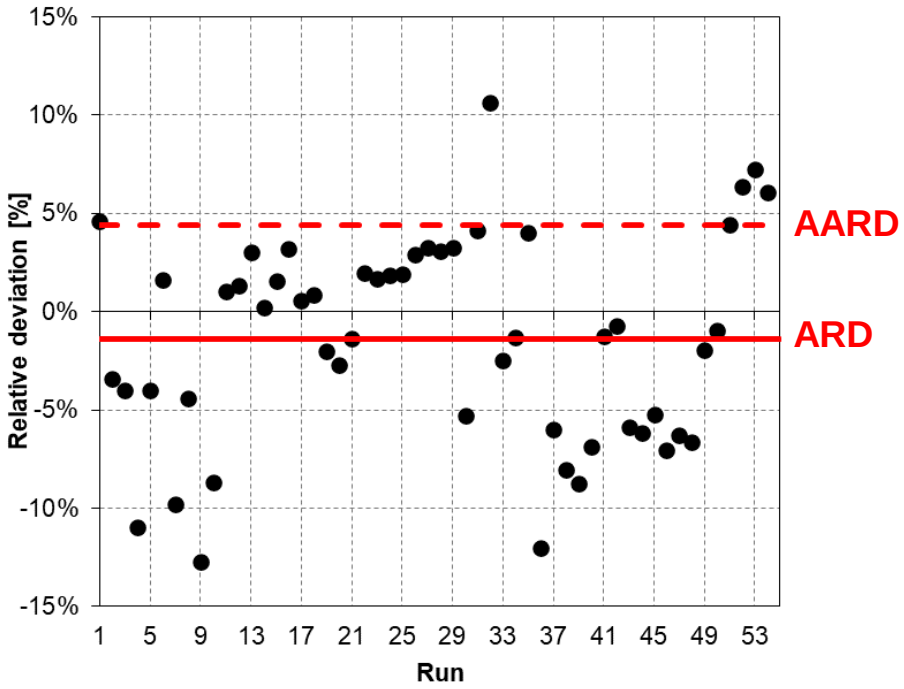
Stand Dev [°C]	2.38	4.00	1.20

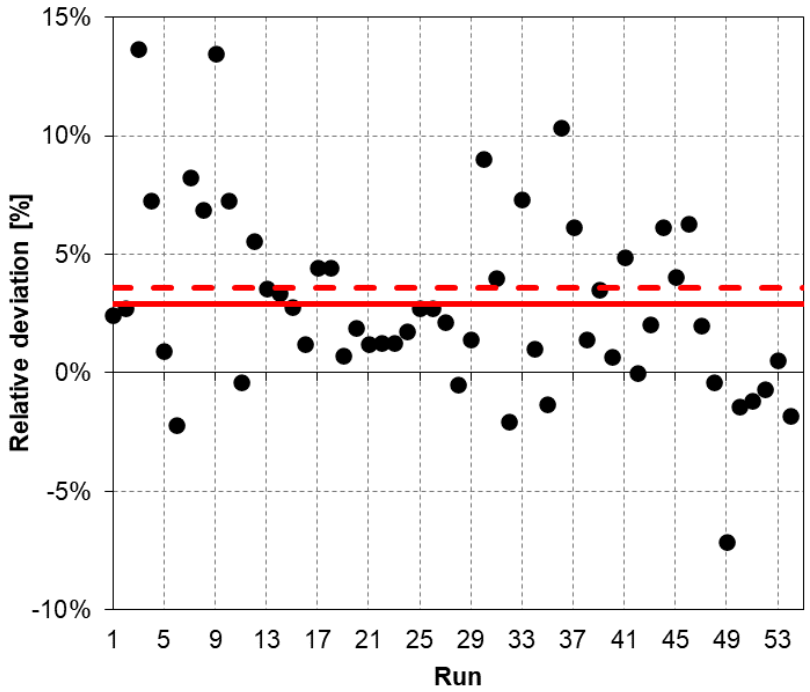
Results: residual charts - absorber

Captured CO_2 mass flow



	All runs	5.5% vol	12% vol
ARD%	-1.41	3.35	-4.42
AARD%	4.49	3.35	5.63
Stand Dev [kg/h]	1.47	0.81	1.81

Rich loading



	All runs	5.5% vol	12% vol
ARD%	2.88	1.63	3.81
AARD%	3.59	2.10	4.69
Stand Dev	0.0080	0.0081	0.0025

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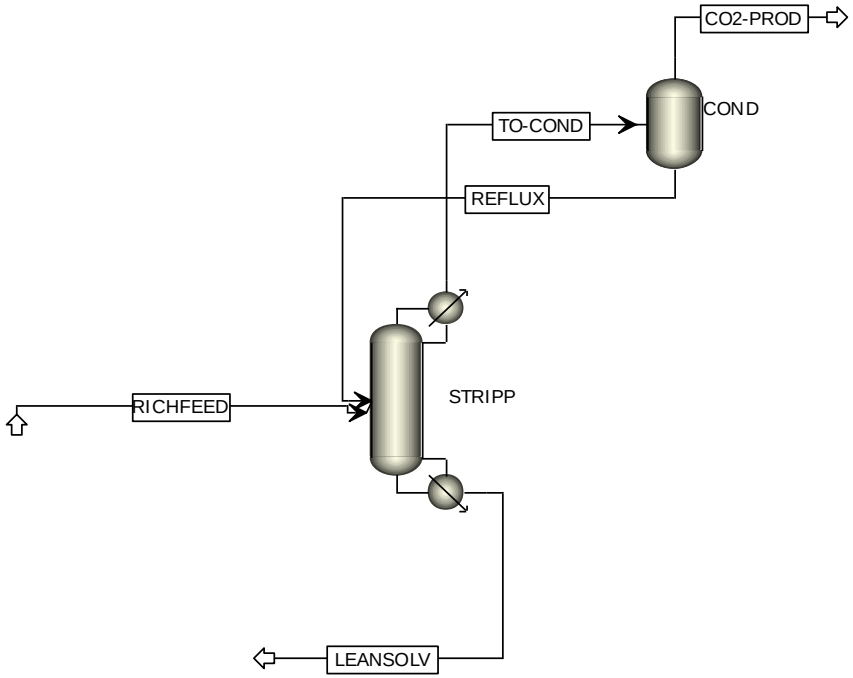
Model validation on Tiller data: open loop - stripper



- INPUT DATA (equal to exp data)

  - Solvent loading after absorption
  - Feed temperature
  - Column pressure and pressure drops
  - **Duty**
  - Column design (packing height, diameter)

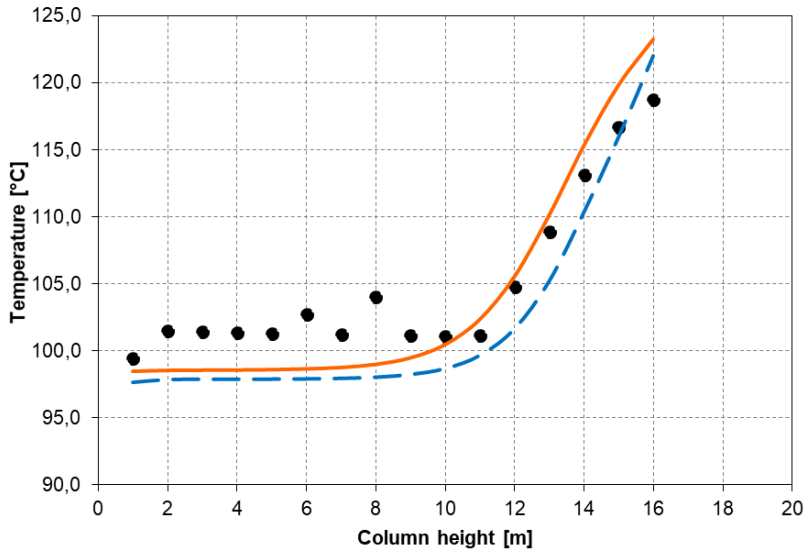
- OUTPUT (to compare)

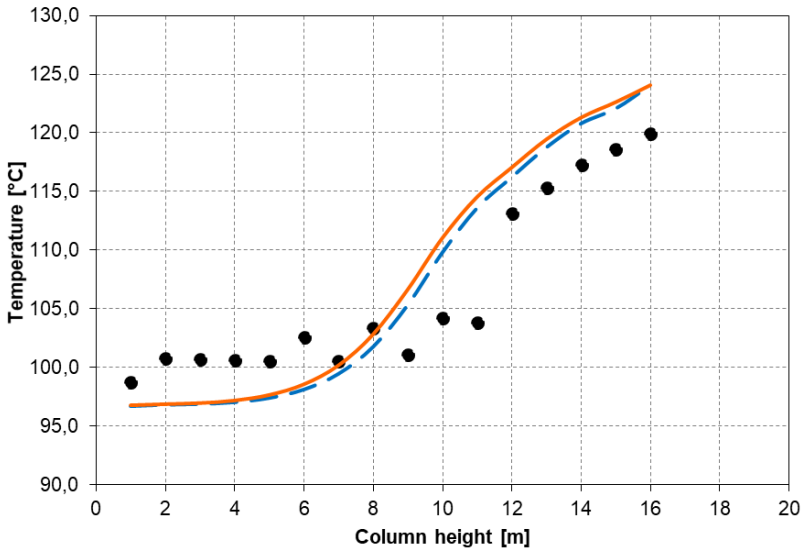
  - **Released CO_2 flow**
  - **Specific reboiler duty (SRD)**
  - **Temperature profile**
  - lean loading of the regenerated solvent

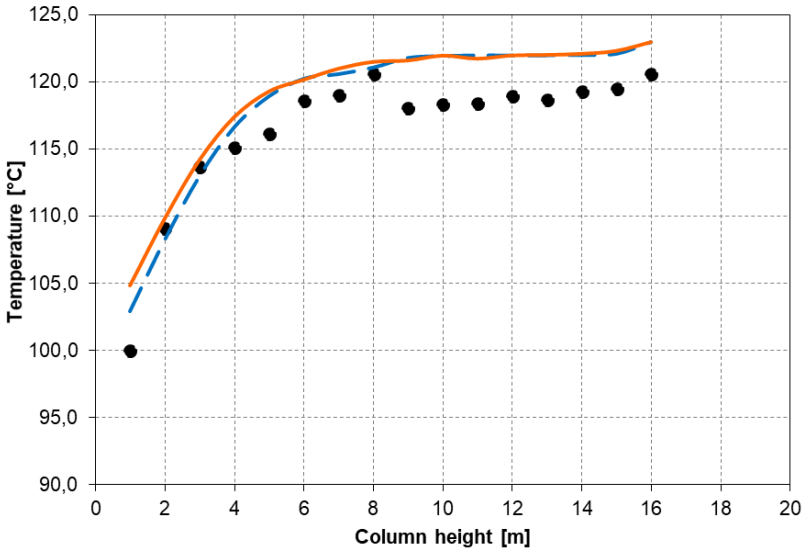
Kinetics is disregarded (only mass transfer)

All 53 Tiller runs have been tested.

Results: absorber temperature profiles (5.5 mol%) - stripper



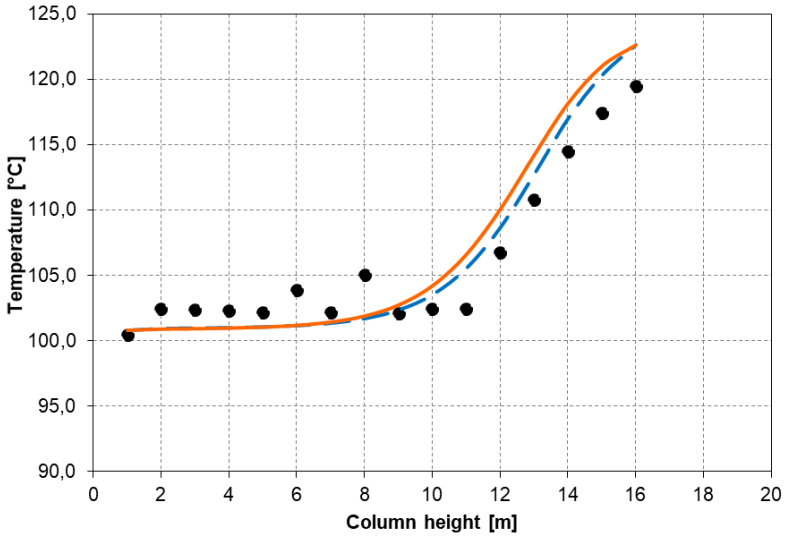


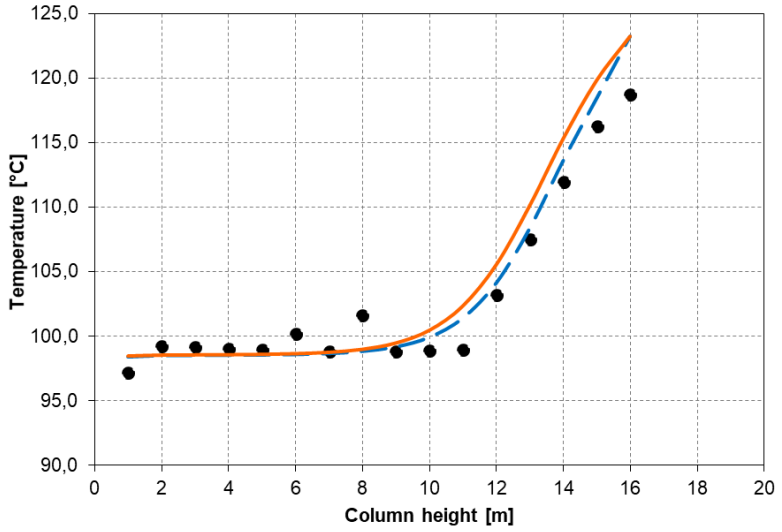


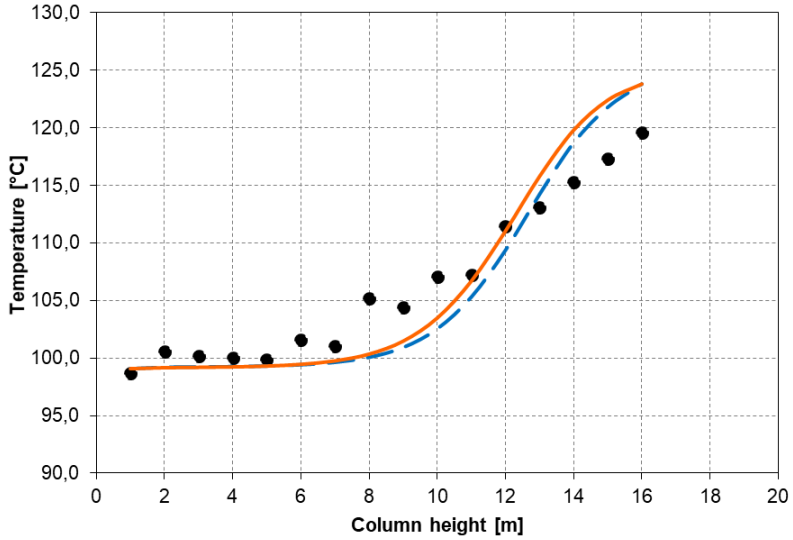
Vapour (orange solid)
Liquid (blue dashed)

	All runs	5.5% vol CO_2	12% vol CO_2
ARD%	2.21	2.19	2.23
AARD%	2.84	2.81	2.87
Stand Dev [°C]	1.58	4.31	4.59

Results: absorber temperature profiles (12 mol%) - stripper





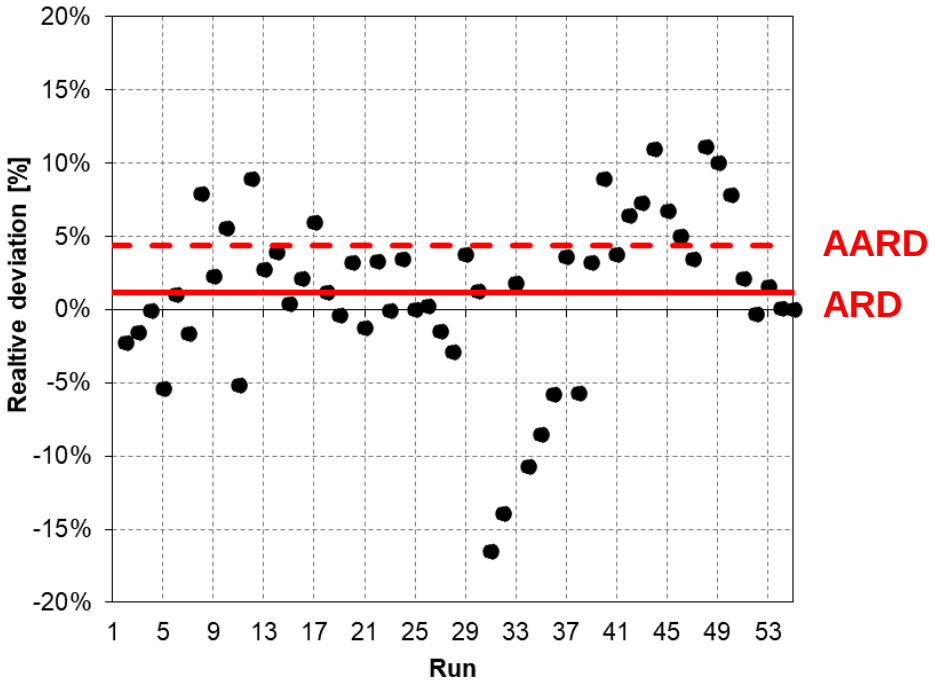


Vapour (orange solid)
Liquid (blue dashed)

	All runs	5.5% vol CO_2	12% vol CO_2
ARD%	2.21	2.19	2.23
AARD%	2.84	2.81	2.87
Stand Dev [°C]	1.58	4.31	4.59

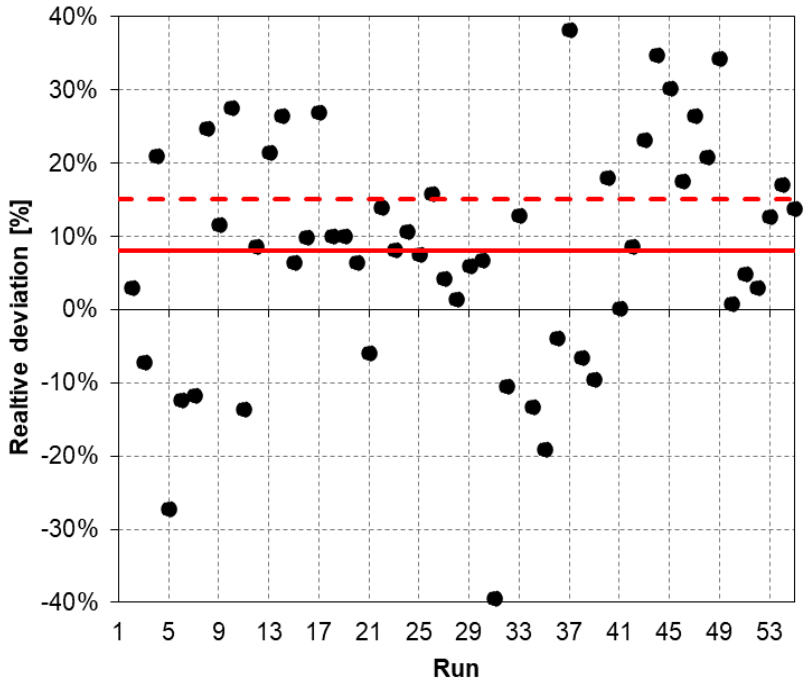
Results: residual charts - stripper

Released CO_2 mass flow



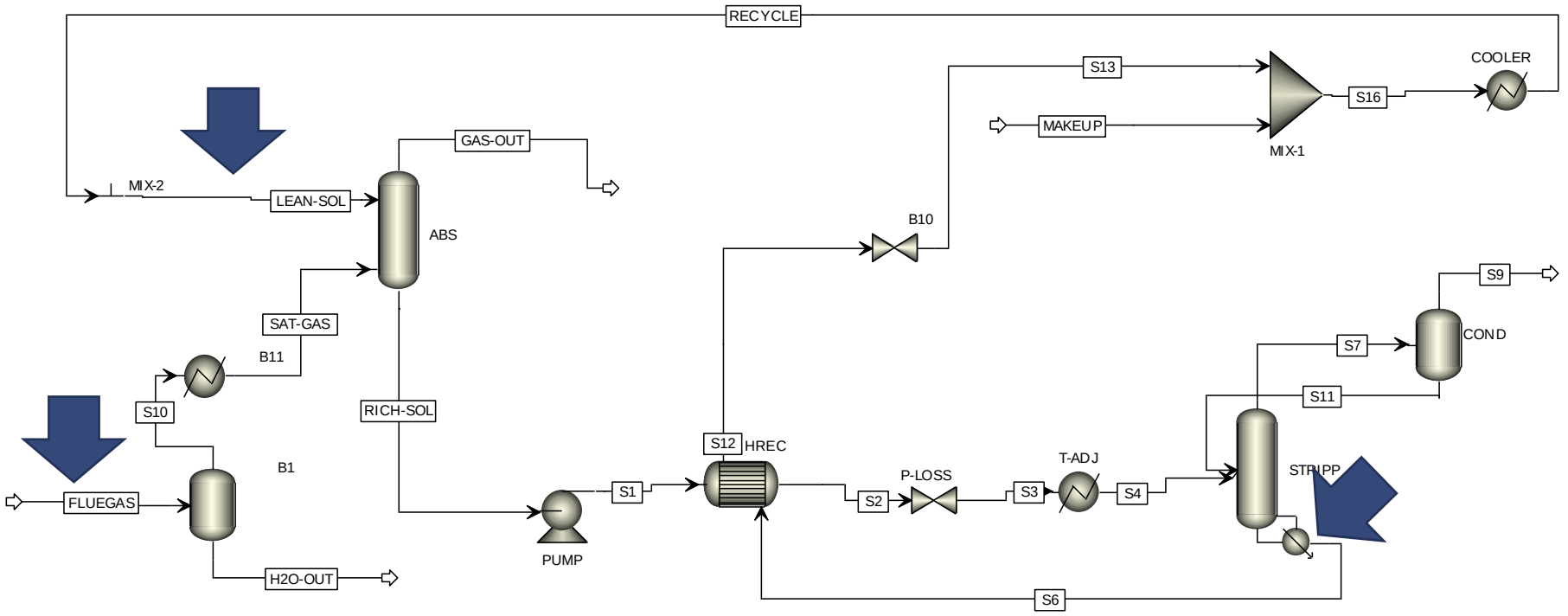
	All runs	5.5% vol	12% vol
ARD%	1.18	1.61	0.88
AARD%	4.38	2.13	5.87
Stand Dev [kg/h]	1.58	0.60	2.01

Lean loading



	All runs	5.5% vol	12% vol
ARD%	7.99	10.4	5.57
AARD%	15.0	12.2	17.0
Stand Dev	0.012	0.009	0.013

Model validation on Tiller data: close loop



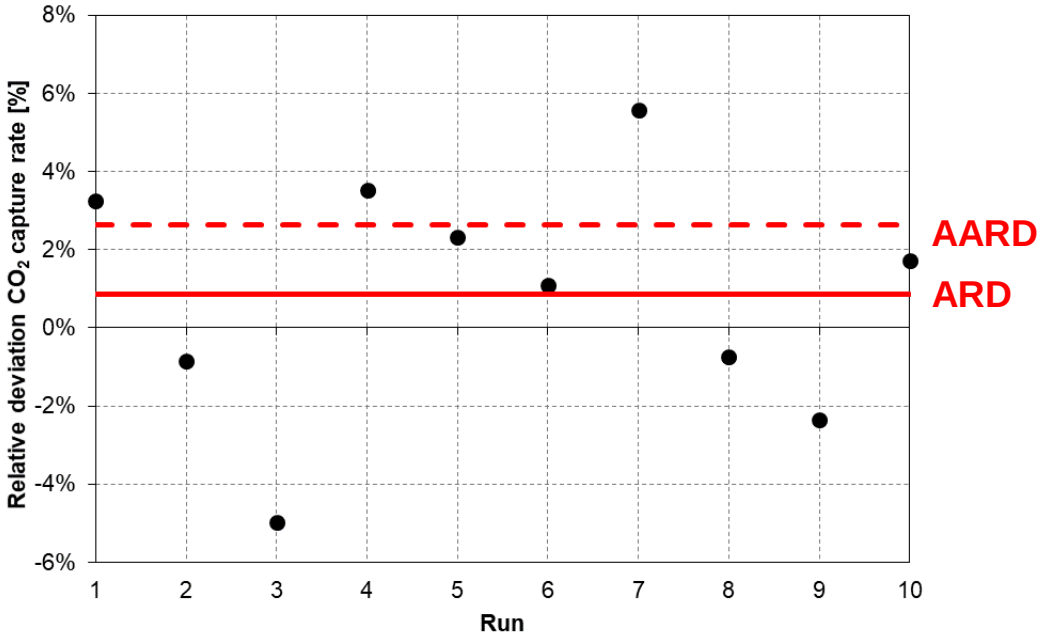
Assigned:

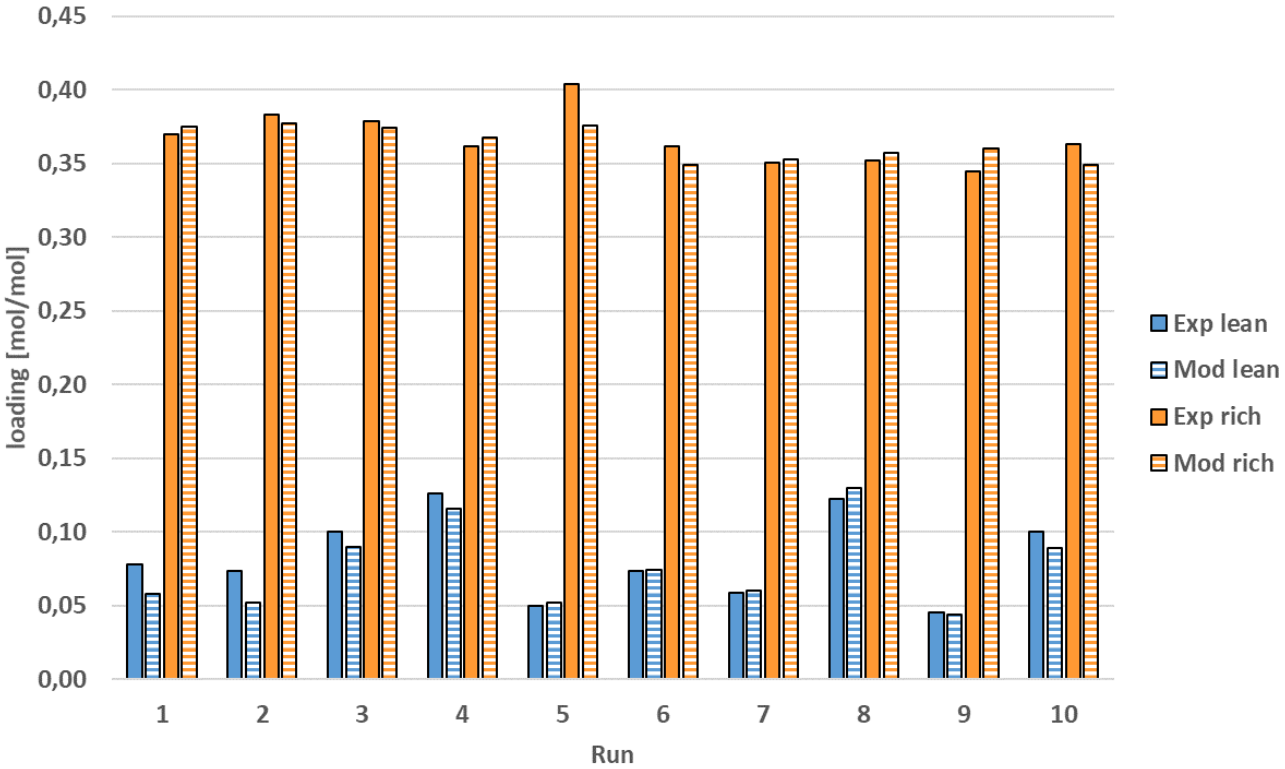
- Stripper duty
- Solvent and gas T, P, flow and composition

To compare:

- CO_2 capture ratio
- Cycling capacity
- T profiles

Model validation on Tiller data: close loop - results





	Capt. ratio	Cycling capacity
ARD%	0.86	1.30
AARD%	2.64	4.34

Conclusions

- Comprehensive model: thermodynamics – kinetics – mass transfer
- The new HS3 model in Aspen Plus V11.0 has been validated on Tiller data
- Both open and close-loop validations have been successfully accomplished
- **Validation** provides average errors below 5% for the main KPI (capture rate, energy consumption, cycling capacity)

Why HS3?

- **Energy savings: -11 to -15%**
- **Lower liquid amount**

	5% vol flue gas				11% vol flue gas			
	HS3 (model)		MEA 30% w (model)		HS3 (model)		MEA 30% w (model)	
Cap. Ratio	SDR	Lean – L/G	SDR	Lean – L/G	SDR	Lean – L/G	SDR	Lean – L/G
90%	3.45	0.077 - 15.3	3.86	0.268 - 35.6	3.07	0.073 - 12.8	3.49	0.34 - 32.0
95%	3.50	0.058 - 15.5	-	-	3.11	0.056 - 12.9	3.54	0.32 - 32.1

Specific Reboiler Duty [MJ/kg_{CO2}]

L/G ratio [$kg_{solvent}$/kg_{CO2}]

data for optimized MEA solvent plant by Abu-Zahra, 2007 and Jaeuk Choi, 2019

M.R.M. Abu-Zahra, L. H.J. Schneiders, J. Niederer, P.H.M. Feron, G. Versteeg, *CO2 capture from power plants: Part I. A parametric study of the technical performance based on monoethanolamine*, International Journal of Greenhouse Gas Control, 1(1), April 2007, 37-46, https://doi.org/10.1016/S1750-5836(06)00007-7

J. Choi, H. Cho, S. Yun, M-Gi Jang, Se-Young Oh, M. Binns, Jin-Kuk Kim, *Process design and optimization of MEA-based CO2 capture processes for non-power industries*, Energy, 185, 2019, 971-980, https://doi.org/10.1016/j.energy.2019.07.092

Publications

[1] M. Gilardi, F. Bisotti, A. Tobiesen, H. K. Knuutila, D. Bonalumi, *An approach for VLE model development, validation, and implementation in Aspen Plus for amine blends in CO2 capture: the HS3 solvent case study*, International Journal of Greenhouse Gas Control, June 2023, https://doi.org/10.1016/j.ijggc.2023.103911

[2] M. Gilardi, F. Bisotti, H. K. Knuutila, D. Bonalumi, *HS3 as a novel solvent for carbon capture: ELECNRTL model validation and application to an industrial case study with a comparative assessment against benchmark MEA,* paper under submission

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An approach for VLE model development, validation, and implementation in Aspen Plus for amine blends in CO_2 capture: the HS3 solvent case study

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Thank you for listening

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Q&A

Thank you for your kind attention