Process Design Optimization Model for Amine Scrubbing

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IEAGHG 8th Post Combustion Capture Conference

16th to 18th September 2025

The University of Texas at Austin
McKetta Department of Chemical Engineering
Cockrell School of Engineering

TxCMP

Modeling and optimization goals

Goal: modeling and optimization of PZAS process design for NGCC and other applications like cogeneration or fired boilers.

- What is the optimal design for a given flue gas and capture rate?
- What is incremental cost of >90% capture?

“Rainier” model:

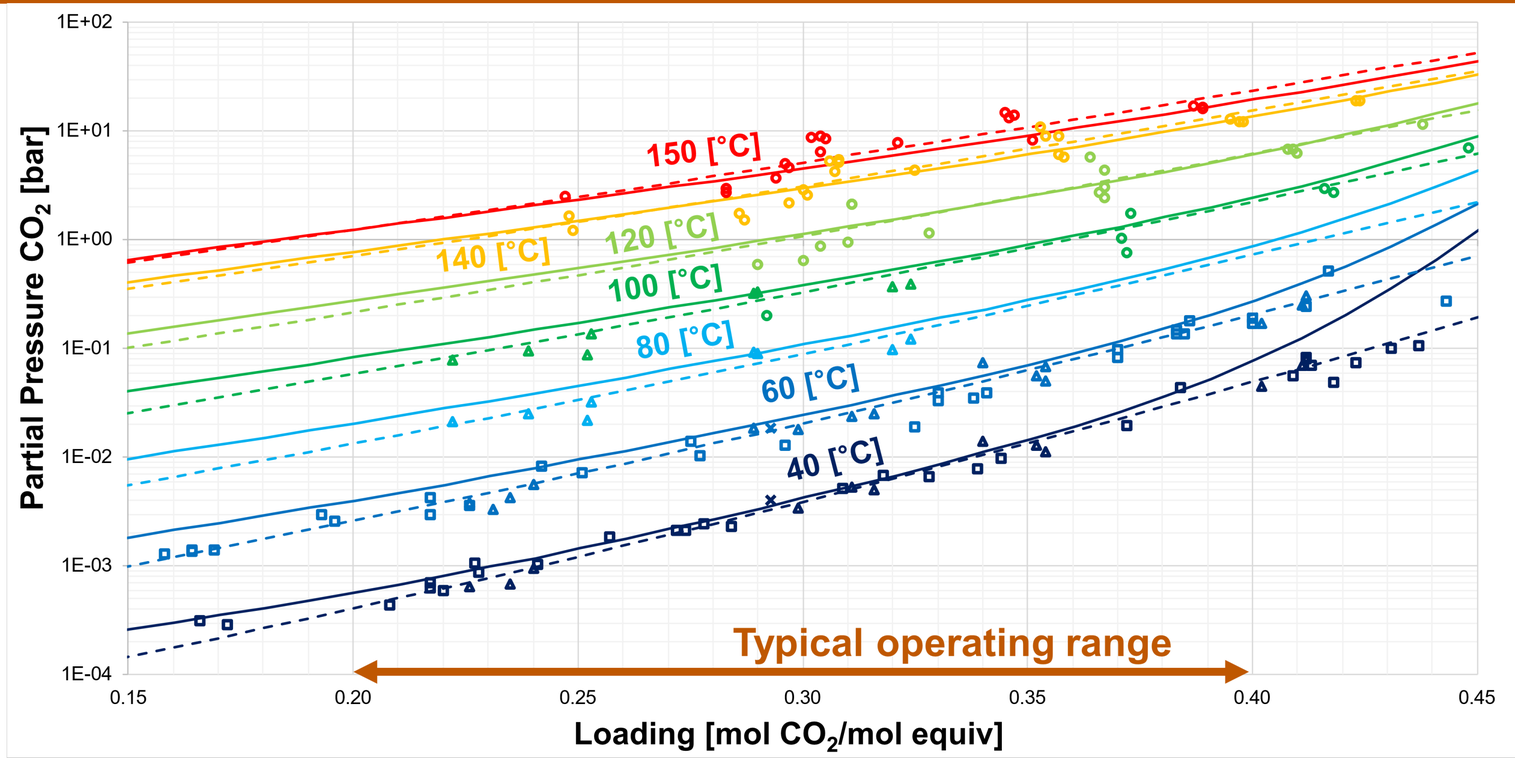
- Equation-oriented model implemented in gPROMS Process®
- Validated using Independence* model + pilot tests (NCCC 2023)
- Capital cost baseline from Mustang Station PZAS FEED

*P T Frailie II. Ph.D. Dissertation. (2014) University of Texas at Austin.

How good is good enough?

Solid curves: Independence (Aspen)

- e-NRTL with many species
- 74 adjustable parameters



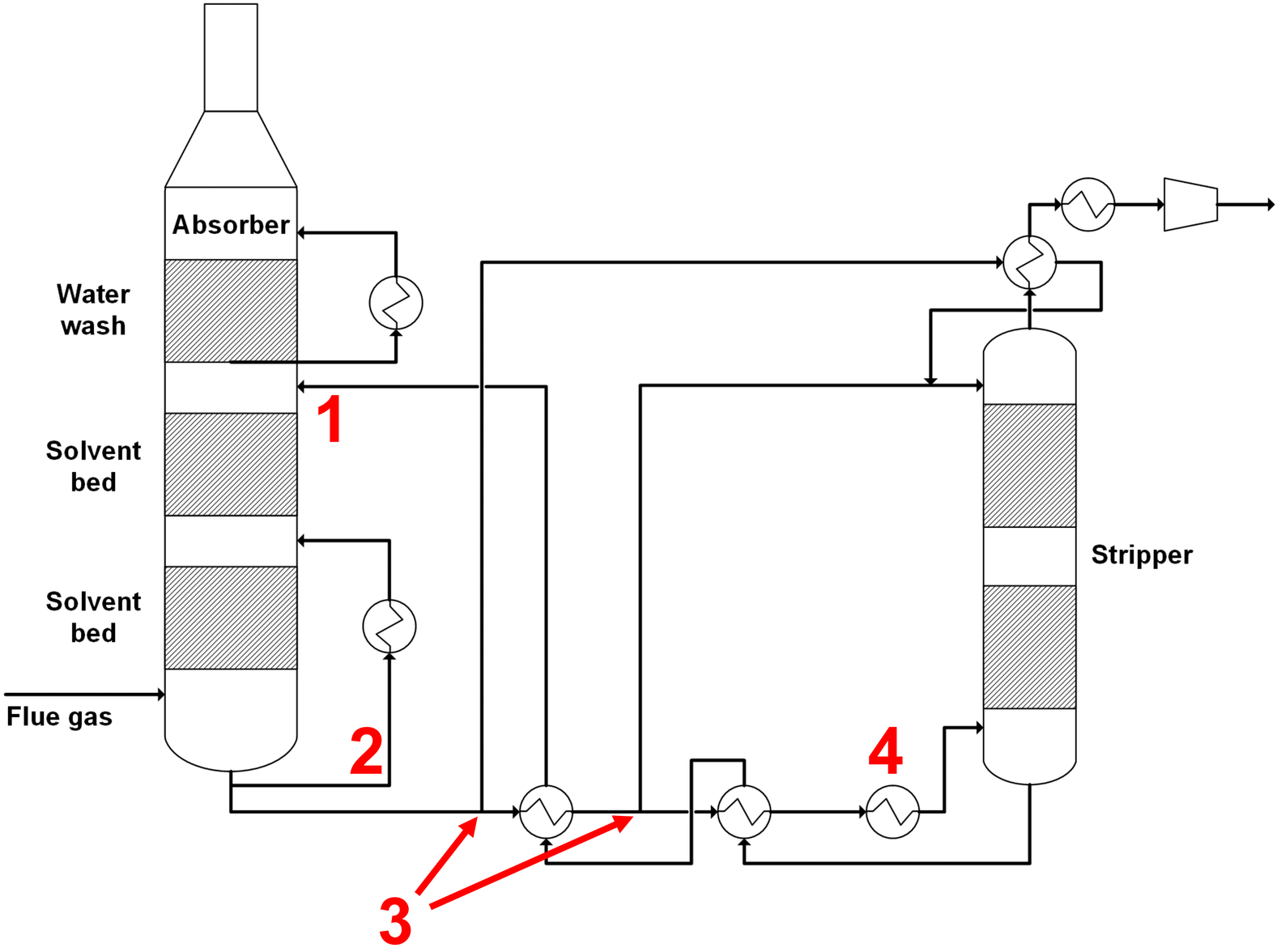
Dashed curves: Rainier (gPROMS)

- Vapor pressure correlations for only 3 apparent species
- $\ln(P_{CO_2}) = 35.5 - 11054\,{}^{1}/_{T} - 18.9\alpha^2 + 4958\,{}^{\alpha}/_{T} + 10163\,{}^{\alpha^2}/_{T}$

Each model needs the right trade-off of model fidelity vs. tractability

Sources are all UT dissertations, Data: Hilliard (2008) [squares], Dugas (2009) [triangles], Xu (2011) [circles], and Nguyen (2013) [crosses]; Independence model: Frailie (2014)

PZAS Flowsheet



Key decision variables:

1. Absorber packing / solvent circulation rate
2. Pumparound configuration
3. Bypass ratios and exchanger sizes
4. SRD and stripper (desorber) operating conditions

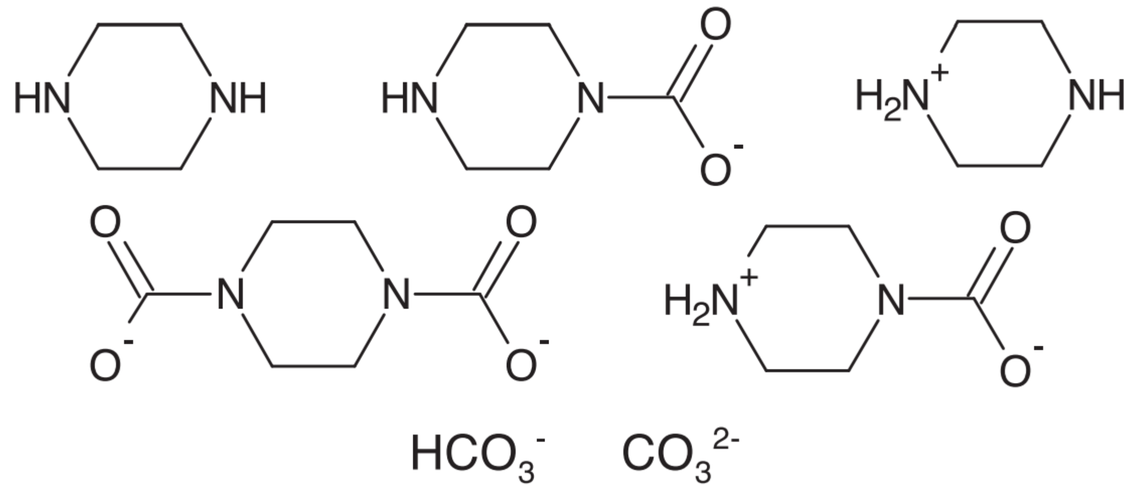
Assumptions in absorber mass transfer model

Absorber and stripper implement medium-order rate-based model

Liquid phase uses apparent species representation
Independence uses true species representation

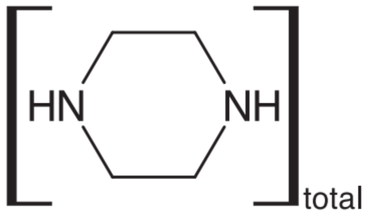
True Species

Defined in Aspen Properties®: CO_2 H_2O



Apparent Species

Defined in gPROMS®:



$[CO_2]_{total}$

$[H_2O]_{total}$

M S Walters et al. *Ind. Eng. Chem. Res.* (2016) https://doi.org/10.1021/acs.iecr.5b04379

Assumptions in absorber mass transfer model

Overall mass transfer resistance is sum of resistances due to diffusion in vapor film, rate-limited reaction in liquid, and diffusion in liquid:

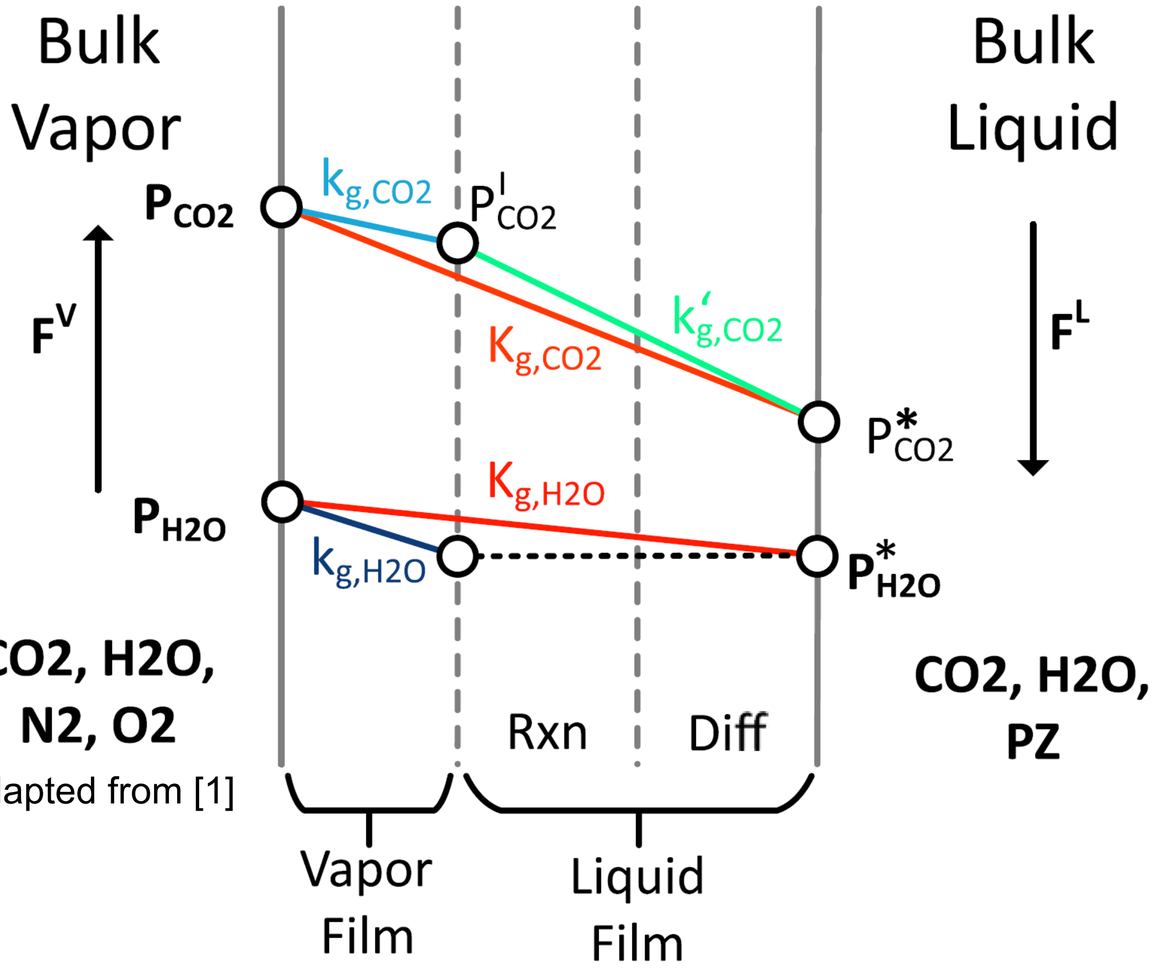


Fig. adapted from [1]

$$\frac{1}{K_{g,co_2} a_e} = \frac{1}{k_{g,co_2} a_e} + \frac{1}{k'_{g,co_2} a_e}$$

Model by Song[2] gives a_e and k_g

What about liquid-side k'_g?

- Rigorous k'_g requires detailed modeling at interface
- Surrogate model needed for Rainier, based on Independence

[1] C Tsay et al. *Appl. Energy* (2019) https://doi.org/10.1016/j.apenergy.2019.113379 [2] D Song. Ph.D. Dissertation (2017) University of Texas at Austin

PZ concentration adjustment

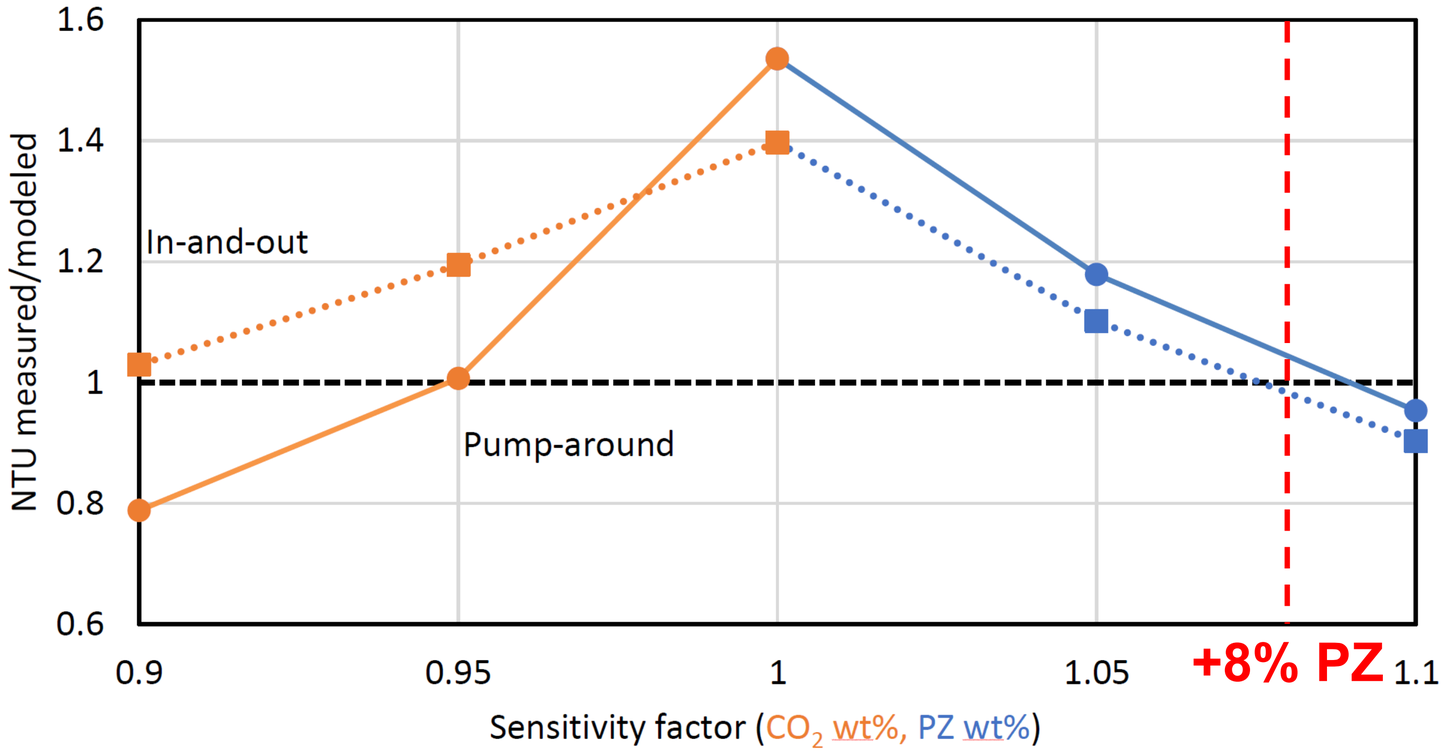
Modeling in Independence of NCCC natural gas campaigns (2019[1], 2023[2]) requires empirical correction of +8% to PZ concentration

Correction applied on absorber side of process results in correct NTU, but creates mass balance error and shifts equilibrium

$$NTU = -\ln(1 - Removal)$$

90% removal → 2.3 NTU

99% removal → 4.6 NTU



[1] T Gao. Ph.D. Dissertation. (2021) University of Texas at Austin [2] M Abreu. Ph.D. Dissertation (2024) University of Texas at Austin

VLE ***DOES NOT*** determine equilibrium within RateSep

In Independence, 3 pairs of forward + reverse kinetic reactions define equilibrium at liquid interface

Rate constants for each are adjustable. The ratio effectively determines equilibrium in a rate-based column stage:

$$\frac{k_f}{k_r} = K_{eq} = \prod_i a_i^{\nu_i} = \exp\left[\frac{-\Delta G^0}{RT}\right] \quad (4\text{-}24)$$

Values chosen so K_{eq} approximates the VLE:

- Wetted wall column data used to fit k_f
- k_r determined by (4-24) **at a specified temperature T_0**
- Different T_0 selected for absorber vs stripper to reduce error

P T Frailie II. Ph.D. Dissertation. (2014) University of Texas at Austin.

k'_g from Independence

Therefore, Rainier should match the **kinetics** of Independence but not necessarily the **equilibrium**.

This brings us back to: $k'_g = ?$

Goals:

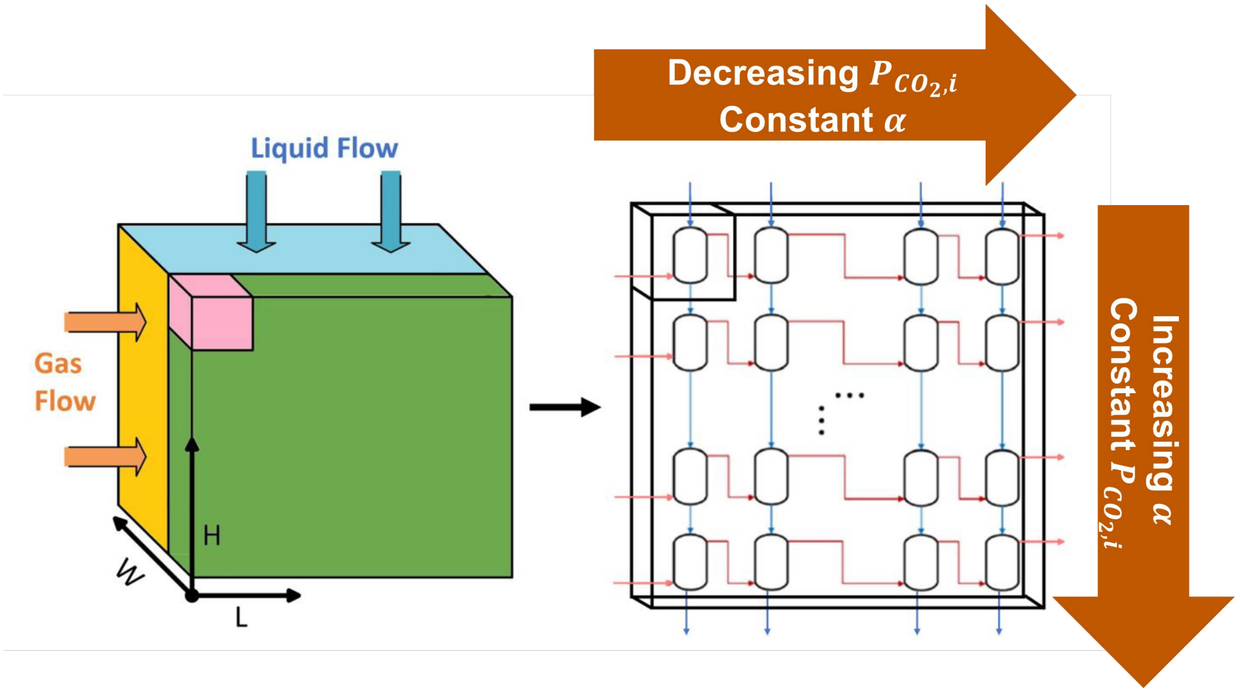
- Select surrogate model $k'_{g,CO_2} = f(X)$ where X is physical properties simulated in Rainier

- Fit model parameters to a suitable training set

- Estimate correct NTUs without affecting mass balance or equilibrium

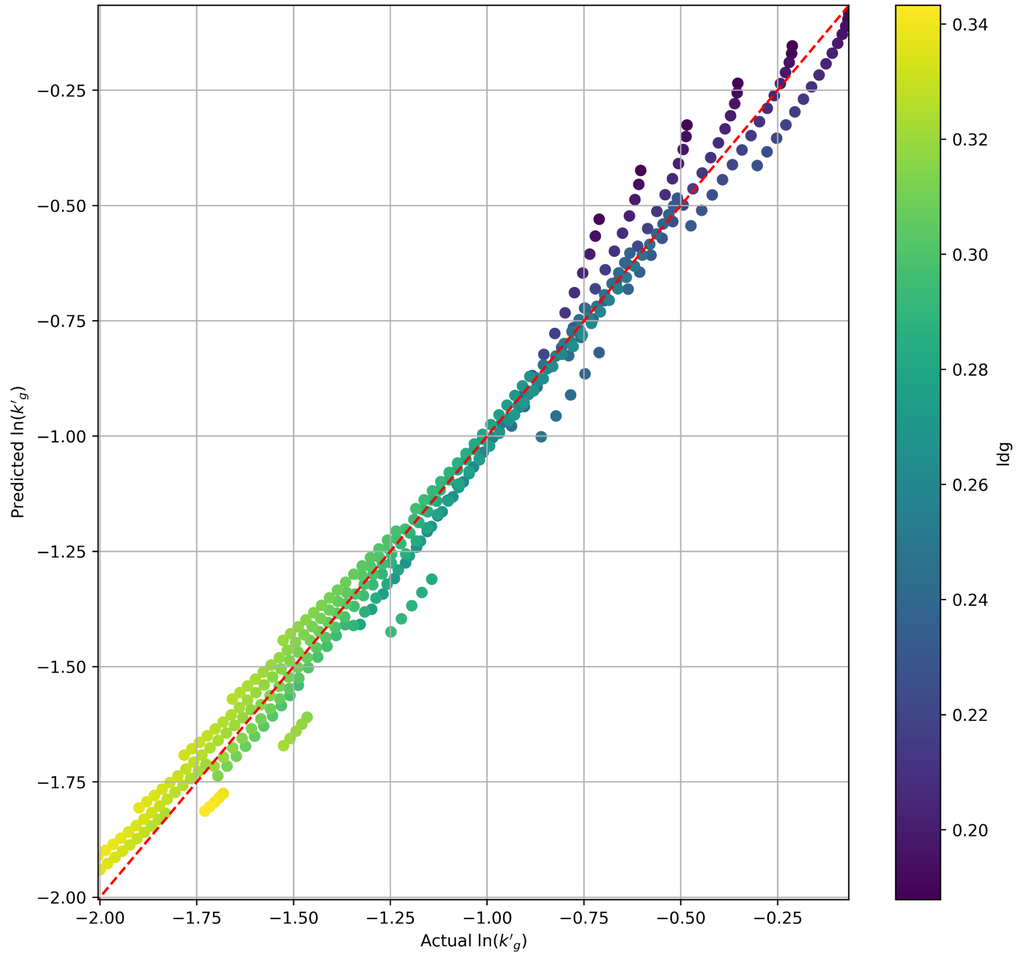
k'_g from Independence: surrogate model

Crossflow model[1] generates dataset of $k'_{g,CO_2} = \frac{N_{CO_2}}{(P_{CO_2,i} - P^*_{CO_2})}$



Surrogate model fitted using bulk properties and adjusted loading:

$$\ln(k'_g) = A + B(\alpha') + C(T_L) + D(P_{CO_2} - P^*_{CO_2})$$



[1] M Abreu. Ph.D. Dissertation (2024) University of Texas at Austin

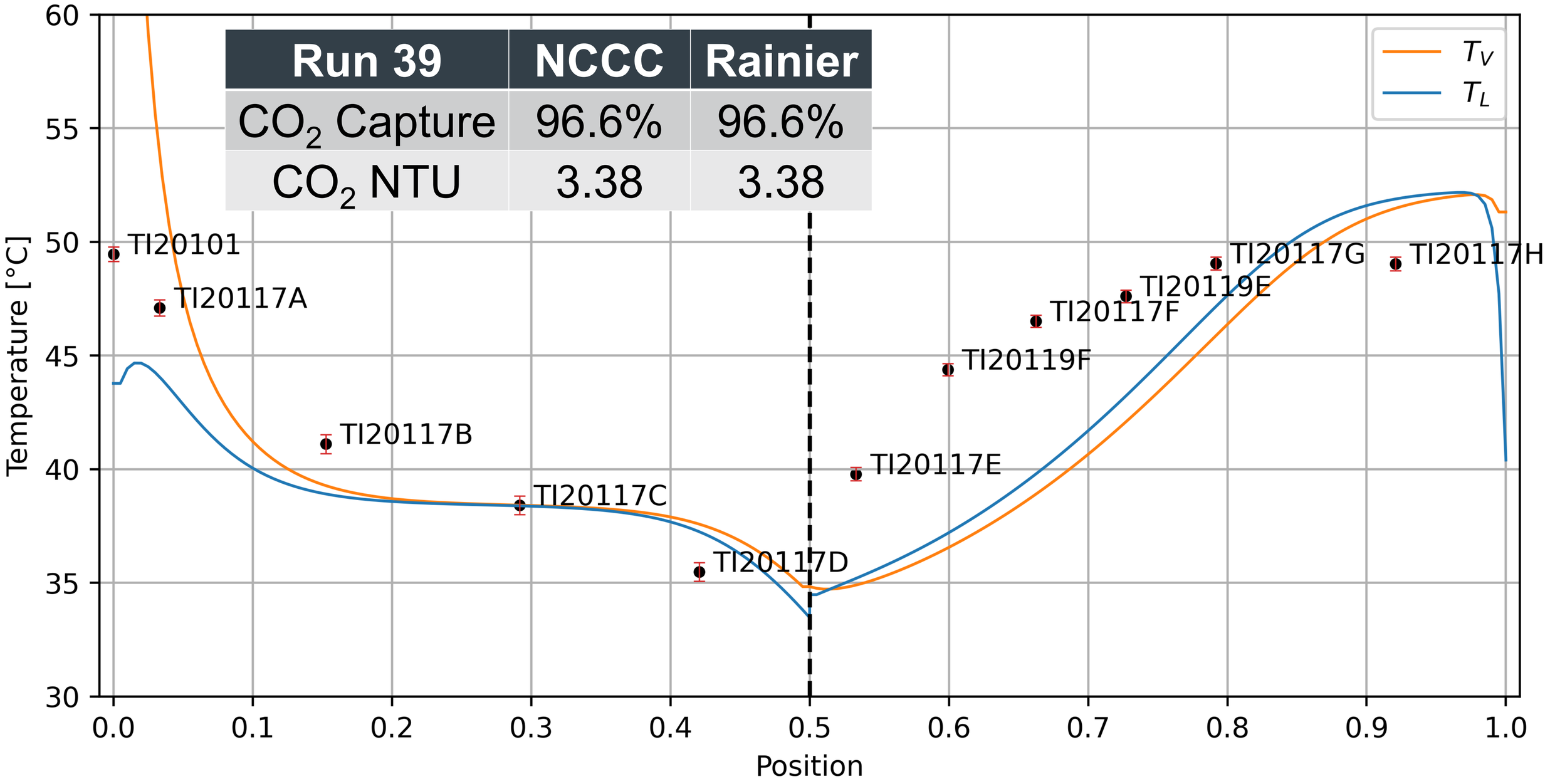
Model validation: NCCC 2023

NCCC steady states simulated to validate model at a different condition:

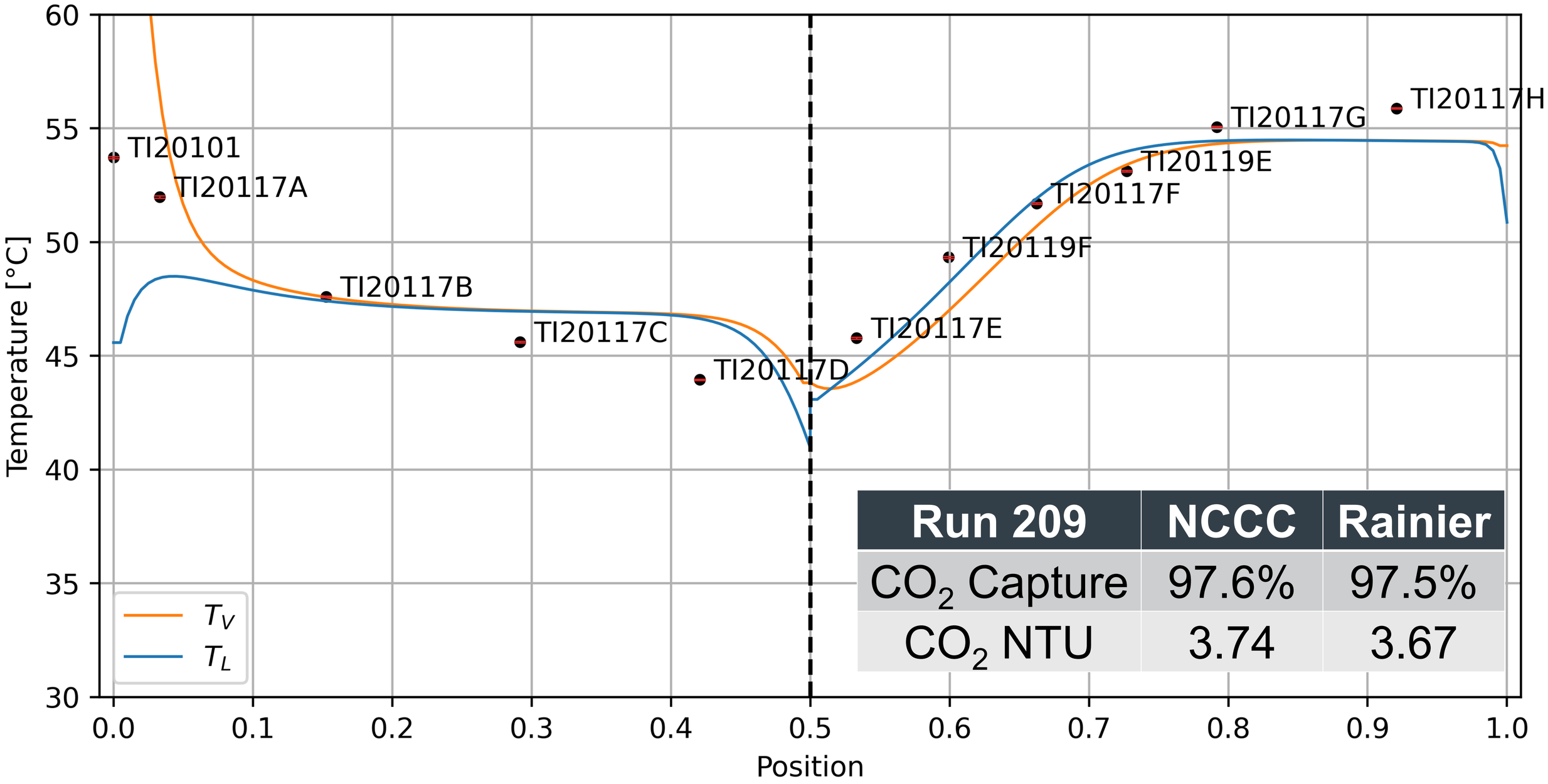
	NCCC	Mustang FEED
Total packing [m]	12 (6+6)	7.6 (2.7 + 4.9)
Flue gas flow [kg/s]	1	430
PA ratio	1.9 – 2.4	3
Flue gas CO_2	4%	4%
Lean loading	0.18 – 0.20	0.20
PZ molality	3.0 – 5.0	5.0
CO_2 removal	82.0 – 97.7%	90.0%

NCCC: baseline run 2023-03-17

Run 39	NCCC	Rainier
CO_2 Capture	96.6%	96.6%
CO_2 NTU	3.38	3.38

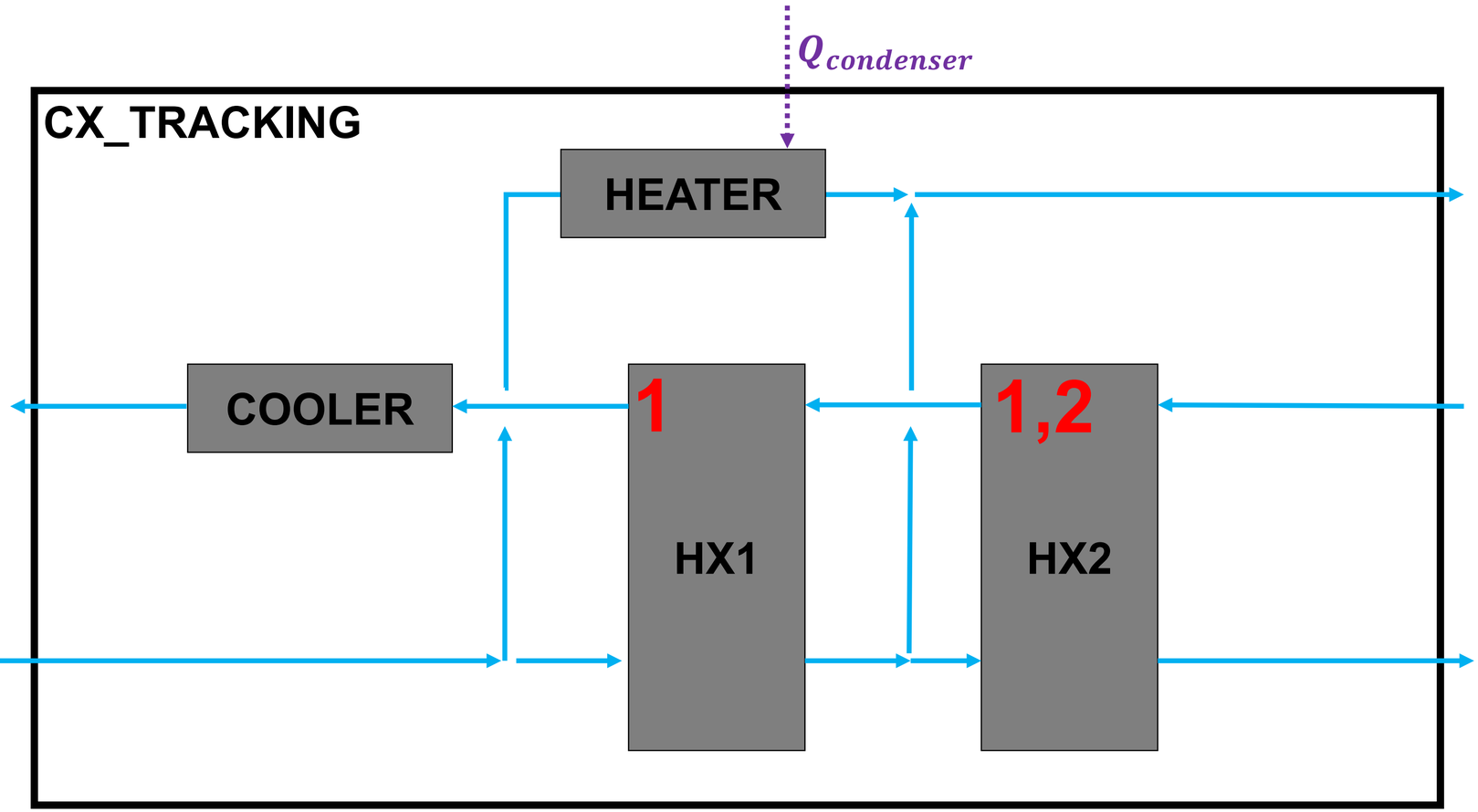


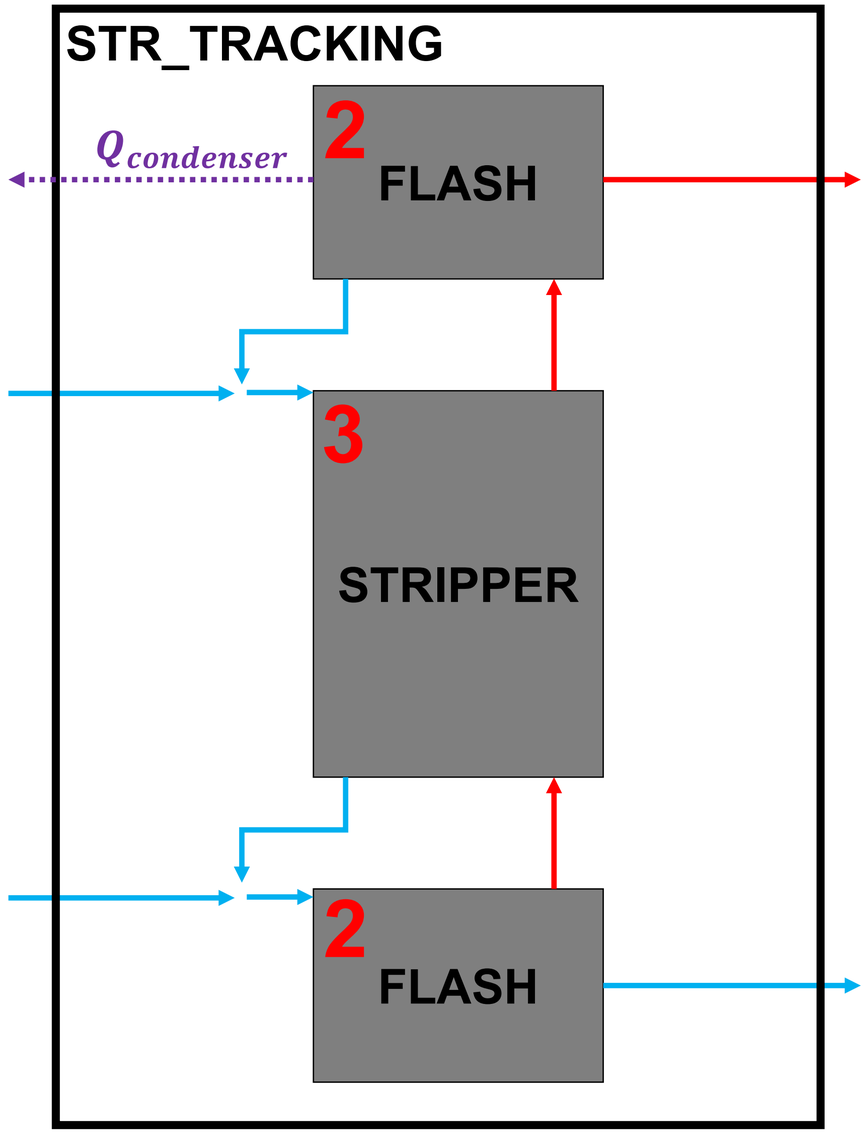
NCCC: hot solvent, high removal 2023-09-01



Run 209	NCCC	Rainier
CO_2 Capture	97.6%	97.5%
CO_2 NTU	3.74	3.67

Heat integration and desorption sections





Key needs:

- C_P dependence on loading
- Robust flash model including HX with flashing
- Rate-based model at stripper conditions

Measured equilibrium pressures* for loaded H_2O-PZ-CO_2 used as basis of thermodynamic model:

- Vapor pressures $P_{vap} = f(T, \alpha)$
- For consistency, $\Delta H^i_{vap} = -R \frac{\partial(lnP_i)}{\partial(1/T)}$

+ Represents experimental data well with a simple set of equations,
− Custom foreign object subroutine needed to solve VLE flash

*Q Xu. Ph.D. Dissertation (2011) University of Texas at Austin

Desorber mass transfer model

Absorber:

$$\frac{1}{K_{g,CO_2} a_e} = \frac{1}{k_{g,CO_2} a_e} + \frac{1}{k'_{g,CO_2} a_e}$$

Stripper:

$$\frac{1}{K_{g,CO_2} a_e} = \frac{1}{k_{g,CO_2} a_e} + \frac{1}{k_{L,CO_2} a_e}$$

In absorber, reactions are rate-limited. k'_{g,CO_2} represents both rate-limited reactions and diffusion.

In stripper, reactions at interface are instantaneous. k_{L,CO_2} represents diffusion only. Therefore, in the stripper all quantities are calculated by Song mass transfer model*

*D Song. Ph.D. Dissertation (2017) University of Texas at Austin

Conclusions

- Equation-oriented model with rate-based mass transfer and appropriate simplifications accurately represents absorber
  - <2% error in NTU prediction for NCCC pilot plant cases
  - Greater error in T profile predictions: <5°C for Rainier vs <2°C for Independence (Abreu, 2024)

- Surrogate model for k'_{g,CO_2} does not require simulating boundary layers and interfacial properties

- VLE flash is challenging in equation-oriented models, and further work is needed to make full-flowsheet model solve reliably for optimization tasks

Acknowledgements

- Texas Carbon Management Program (TxCMP)
- Carbon Capture Simulation for Industry Impact ($CCSI^2$)
- Samsung Fellowship
- Dr. Thomas F. Edgar Endowed Graduate Fellowship in Chemical Engineering

One author of this work consults for a process supplier on the development of amine scrubbing technology. The terms of this arrangement have been reviewed and approved by the University of Texas at Austin in accordance with its policy on objectivity in research. One author also has financial interests in intellectual property owned by the University of Texas that includes ideas reported in this work.

This work was supported by the $CCSI^2$ project of the U.S. Department of Energy through LEIDOS.

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Thank you!

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VLE *DOES NOT* determine equilibrium within RateSep 20

$MDEA + H_2O + CO_2 \rightarrow MDEAH^+ + HCO_3^-$	Equation 4-8	Forward Kinetic
$PZ + H_2O + CO_2 \rightarrow PZH^+ + HCO_3^-$	Equation 4-9	
$MDEA + PZ + CO_2 \rightarrow MDEAH^+ + PZCOO^-$	Equation 4-10	
$2PZ + CO_2 \rightarrow PZH^+ + PZCOO^-$	Equation 4-11	
$MDEA + PZCOO^- + CO_2 \rightarrow MDEAH^+ + PZ(COO)_2^{2-}$	Equation 4-12	
$2PZCOO^- + CO_2 \rightarrow PZ(COO)_2^{2-} + H^+PZCOO^-$	Equation 4-13	
$MDEAH^+ + HCO_3^- \rightarrow MDEA + H_2O + CO_2$	Equation 4-14	Reverse Kinetic
$PZH^+ + HCO_3^- \rightarrow PZ + H_2O + CO_2$	Equation 4-15	
$PZCOO^- + PZH^+ \rightarrow 2PZ + CO_2$	Equation 4-16	
$PZCOO^- + MDEAH^+ \rightarrow MDEA + PZ + CO_2$	Equation 4-17	
$PZ(COO)_2^{2-} + H^+PZCOO^- \rightarrow 2PZCOO^- + CO_2$	Equation 4-18	
$MDEAH^+ + PZ(COO)_2^{2-} \rightarrow MDEA + PZCOO^- + CO_2$	Equation 4-19	
$PZCOO^- + PZH^+ \leftrightarrow H^+PZCOO^- + PZ$	Equation 4-20	Equilibrium
$MDEA + PZH^+ \leftrightarrow MDEAH^+ + PZ$	Equation 4-21	
$MDEA + HCO_3^- \leftrightarrow MDEAH^+ + CO_3^{2-}$	Equation 4-22	

P T Frailie II. Ph.D. Dissertation. (2014) University of Texas at Austin.

VLE ***DOES NOT*** determine equilibrium within RateSep 21

Rate constants for each can be adjusted by setting E_A and k_0:

$$k = k_0 \exp\left[\frac{-E_A}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \qquad (4\text{-}23)$$

Ratio determines K_{eq}:

$$\frac{k_f}{k_r} = K_{eq} = \prod_i a_i^{\nu_i} = \exp\left[\frac{-\Delta G^0}{RT}\right] \qquad (4\text{-}24)$$

Values chosen so K_{eq} approximates the VLE:

- Wetted wall column data used to fit k_f
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VLE *DOES NOT* determine equilibrium within RateSep 22

Equation (4-23) assumes $K_{eq} = A + {}^{B}/_{T}$

For equilibrium calculations, Independence uses (3-2):

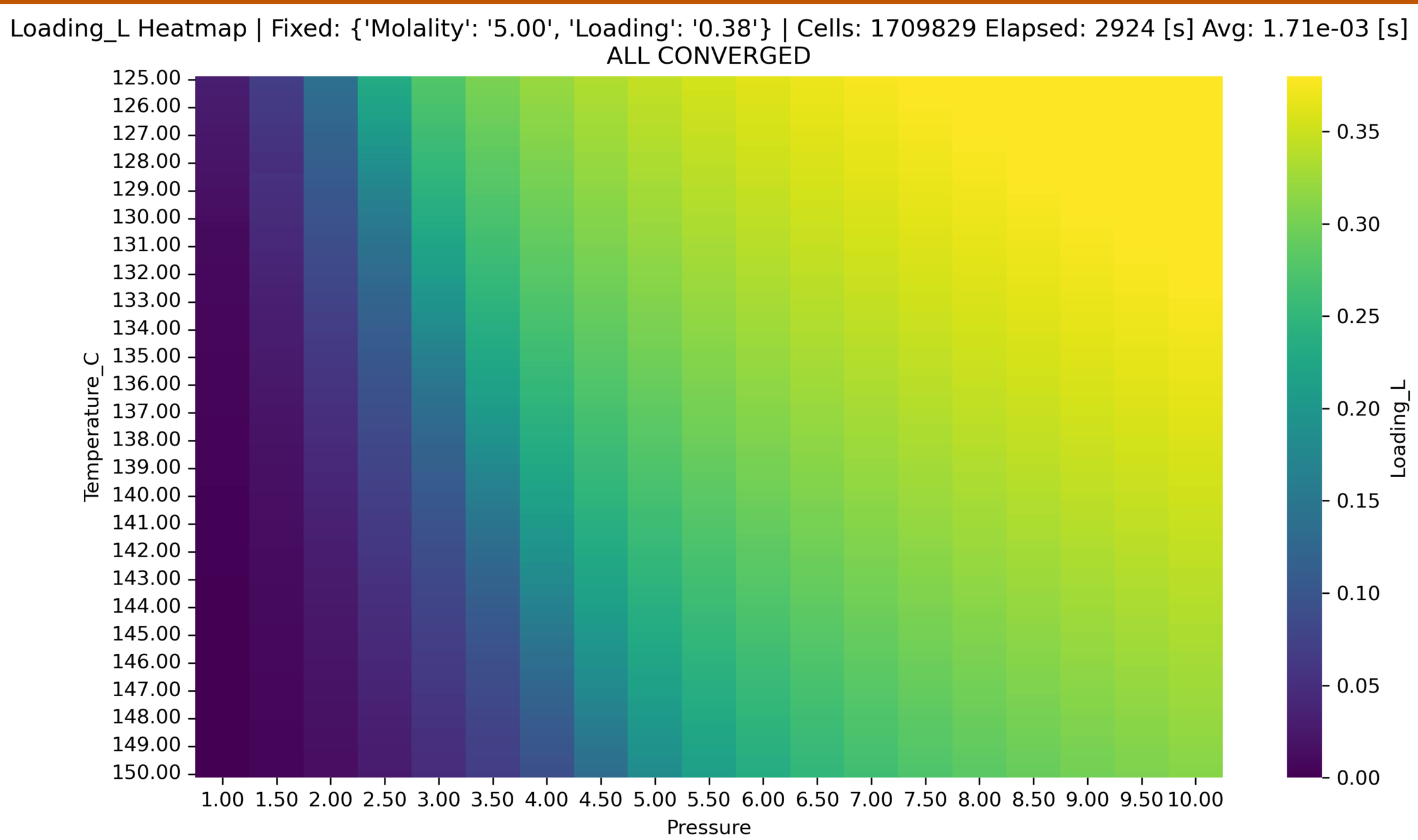
$$\ln K_{eq} = A + \frac{B}{T} + C \ln T + DT \qquad \text{Equation 3-1}$$

$$-\ln K_{eq} = \frac{\Delta G^{o}}{RT} = \frac{\Delta G_0^{o} - \Delta H_0^{o}}{RT_0} + \frac{\Delta H_0^{o}}{RT} + \frac{1}{T}\int_{T_0}^{T} \frac{\Delta C_P^{o}}{R} dT - \int_{T_0}^{T} \frac{\Delta C_P^{o}}{R} dT \qquad \text{Equation 3-2}$$

This creates an inconsistency between K_{eq} in a rate-based column stage vs K_{eq} in an equilibrium flash

The error grows further from T_0

P T Frailie II. Ph.D. Dissertation. (2014) University of Texas at Austin.


Loading_L Heatmap | Fixed: {'Molality': '5.00', 'Loading': '0.38'} | Cells: 1709829 Elapsed: 2924 [s] Avg: 1.71e-03 [s]
ALL CONVERGED
Temperature_C
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Pressure
Loading_L
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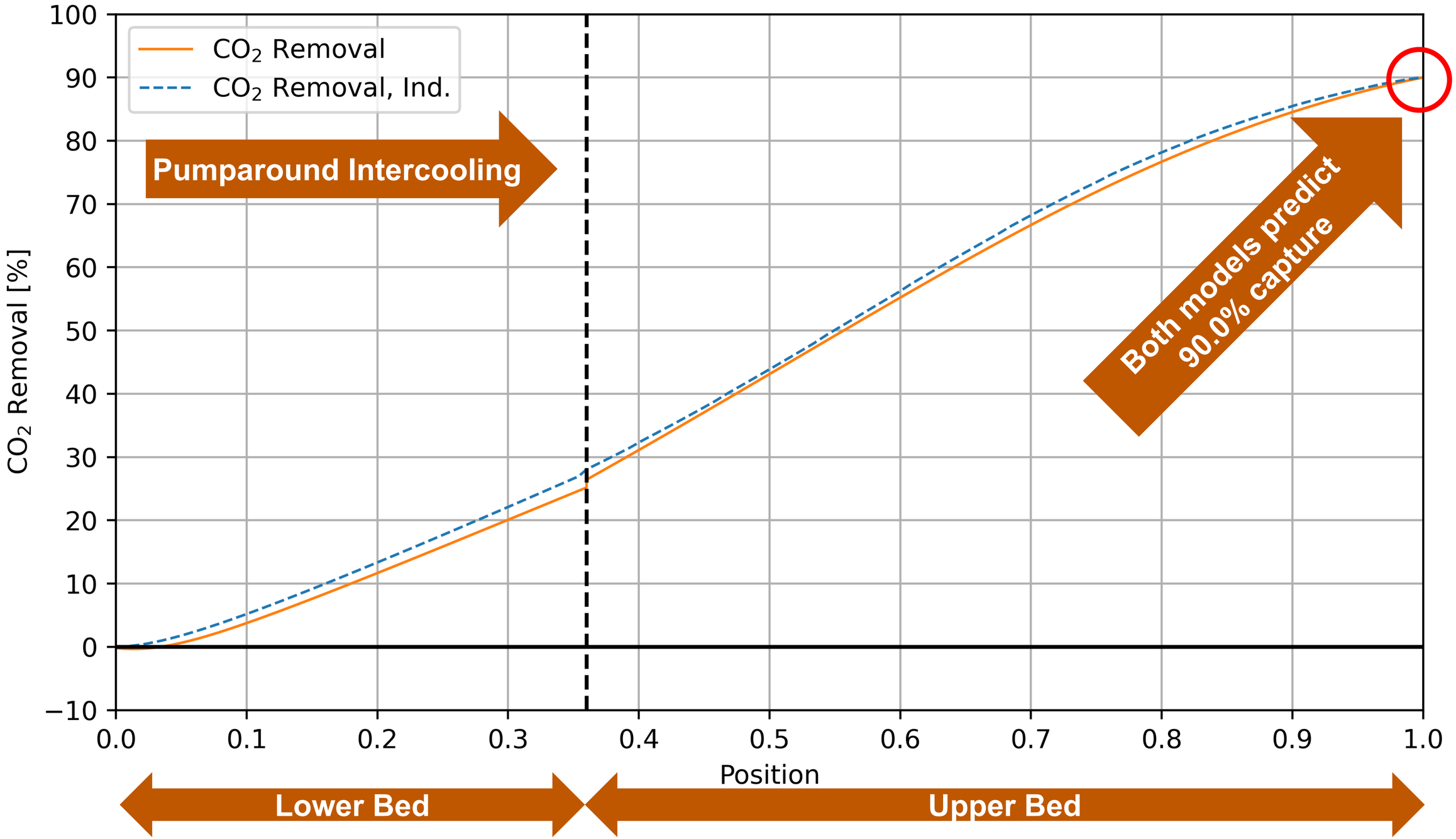
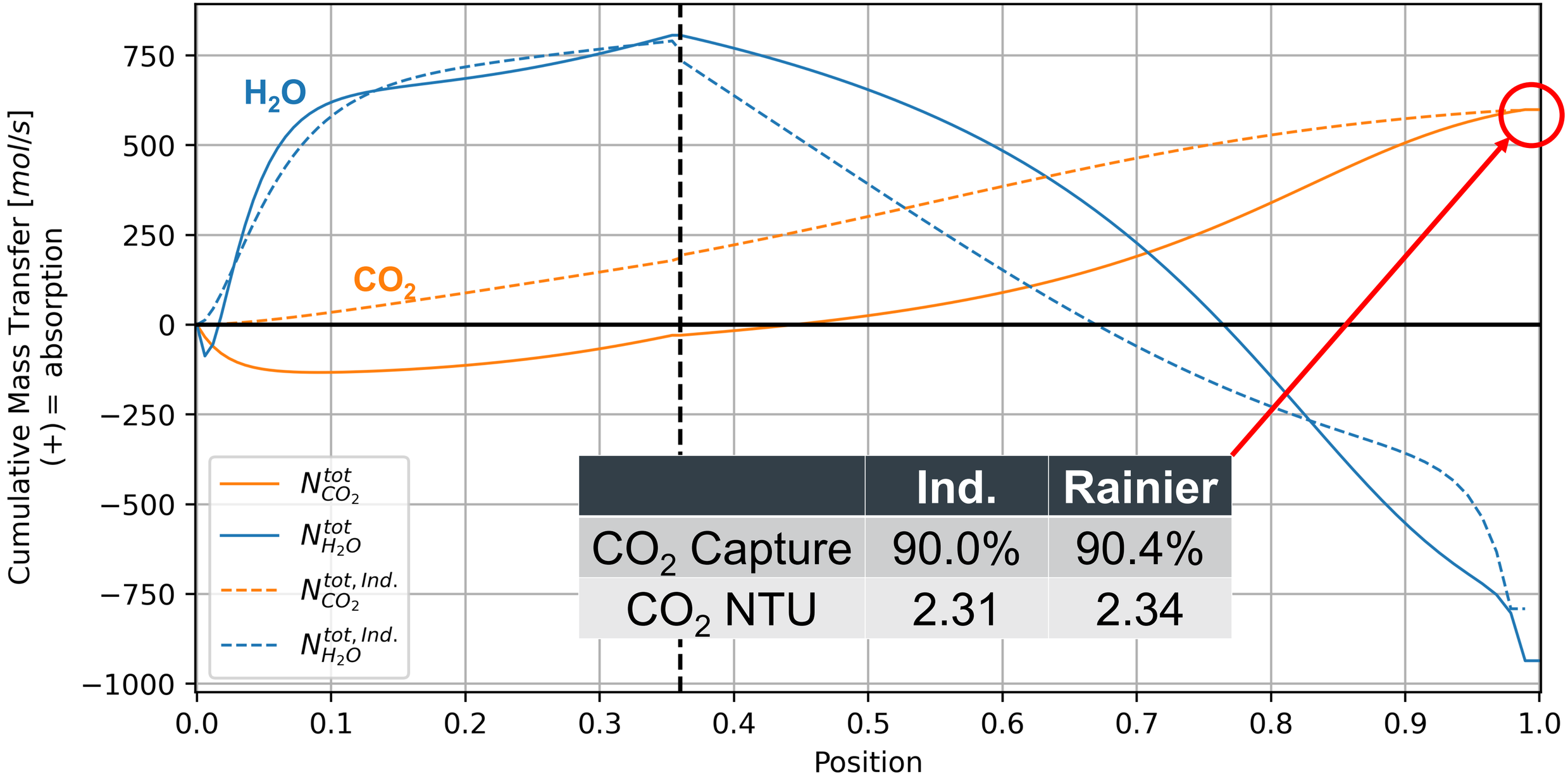
0.05
0.10
0.15
0.20
0.25
0.30
0.35

Results from parameter estimation (old method)

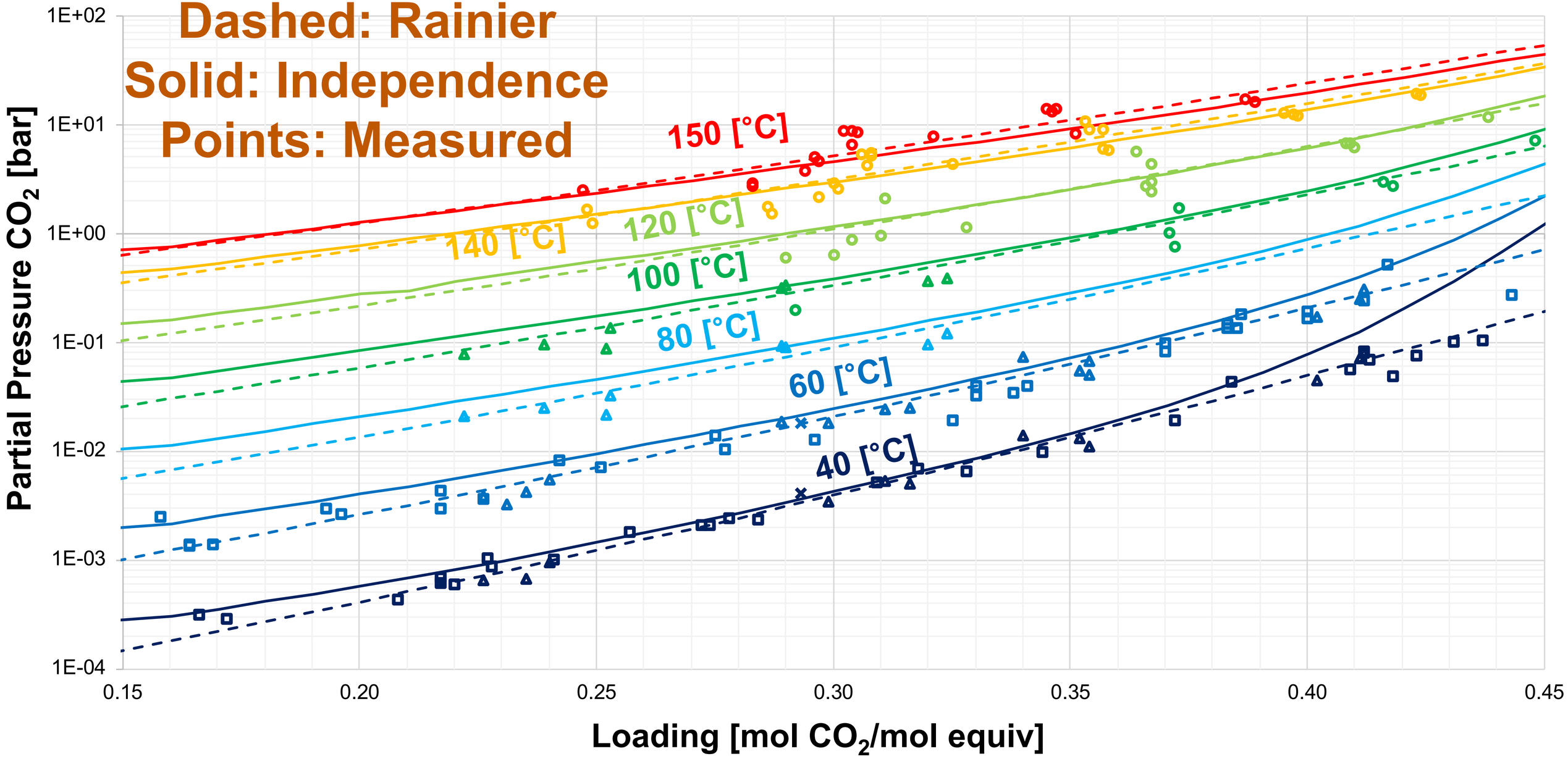


k'_g from Independence: result



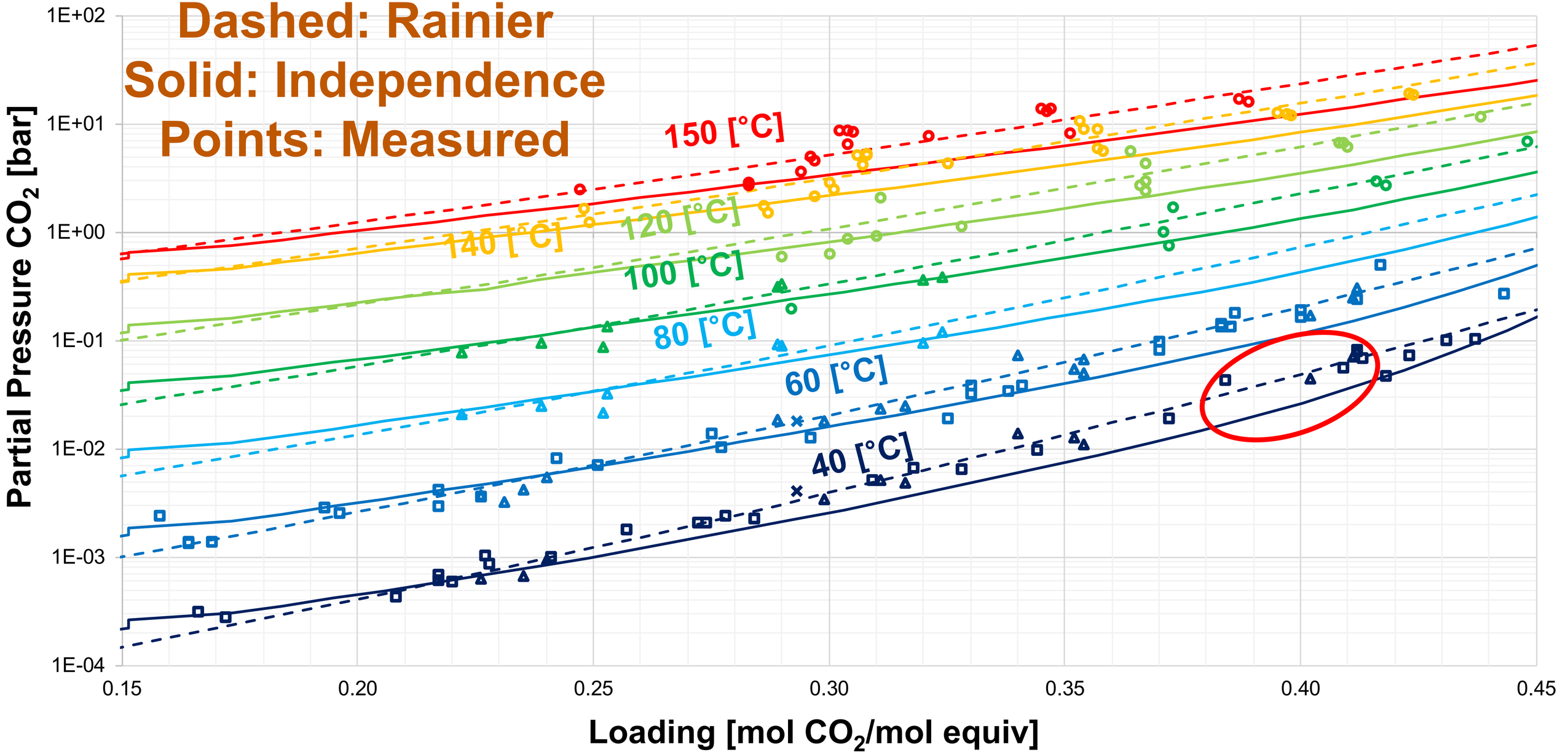
	Ind.	Rainier
CO_2 Capture	90.0%	90.4%
CO_2 NTU	2.31	2.34

CO_2 vapor pressure: how Independence was made



Experimental data from UT dissertations: Hilliard (2008) [squares], Dugas (2009) [triangles], Xu (2011) [circles], and Nguyen (2013) [crosses]

CO_2 vapor pressure: how Independence is used



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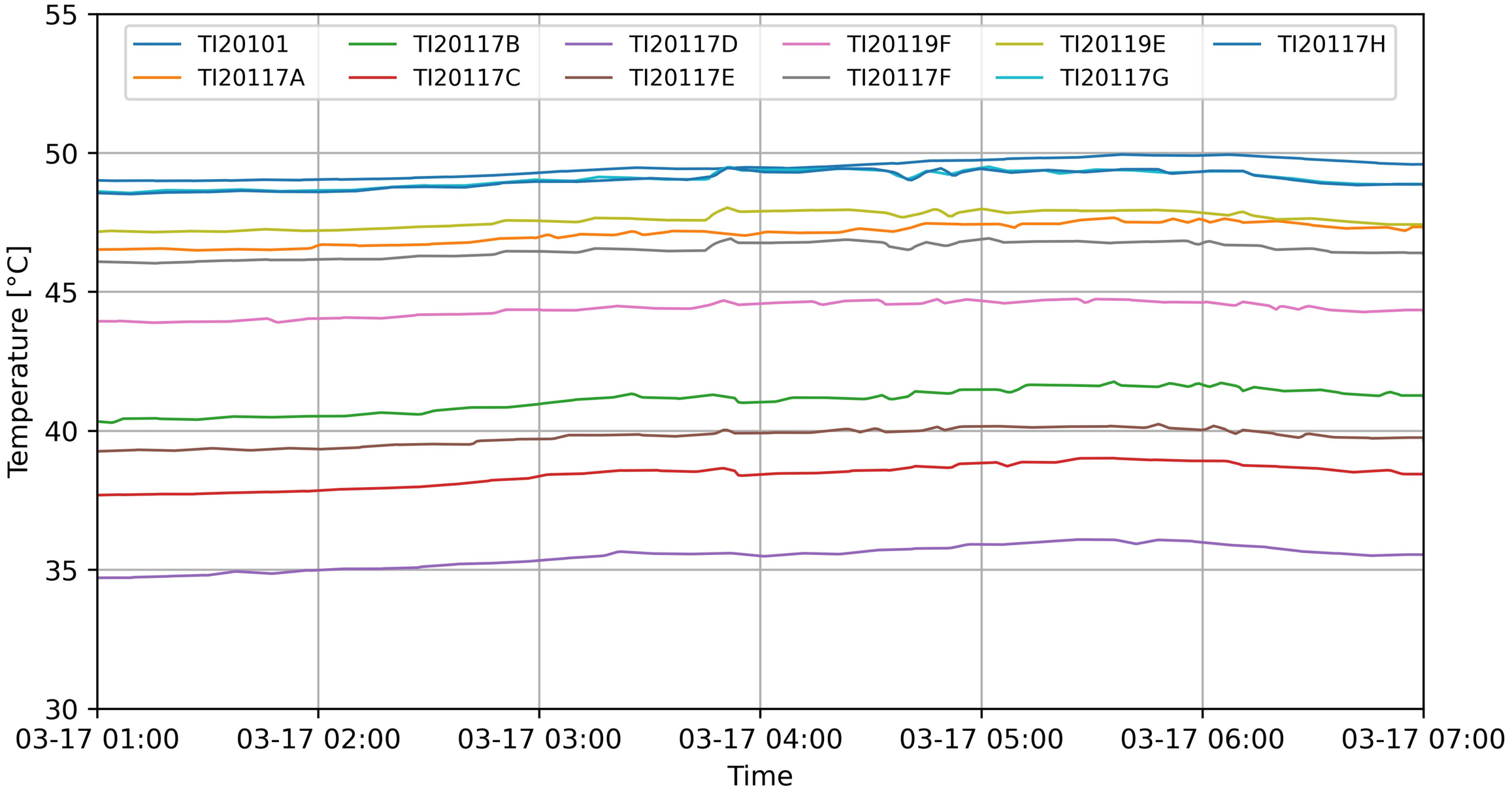
Long-Term Test 1: 2023-03-07 to 2023-03-31



NCCC: baseline run 2023-03-17

Run 39	NCCC	Rainier
CO_2 Capture	96.6%	96.6%
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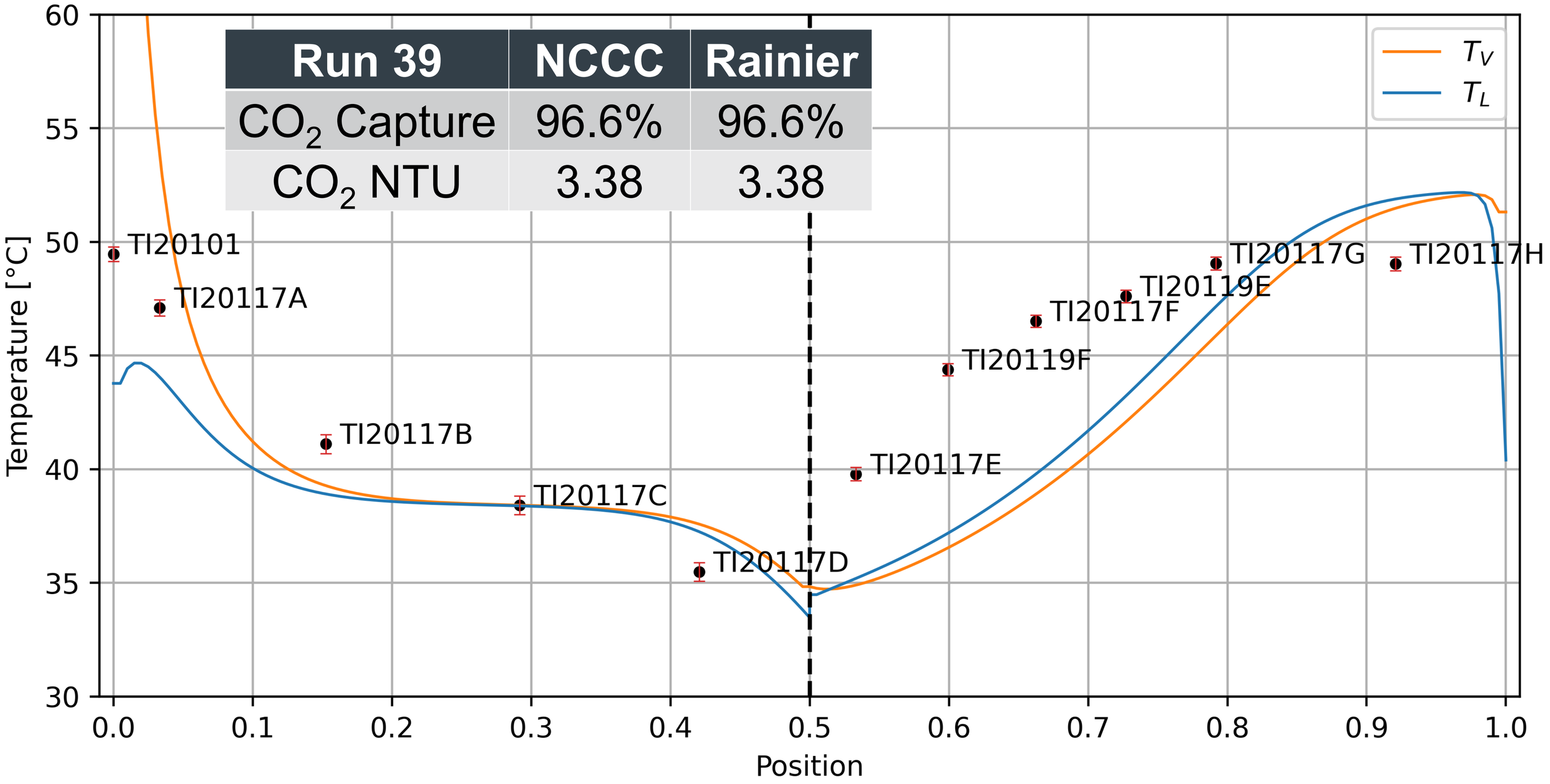
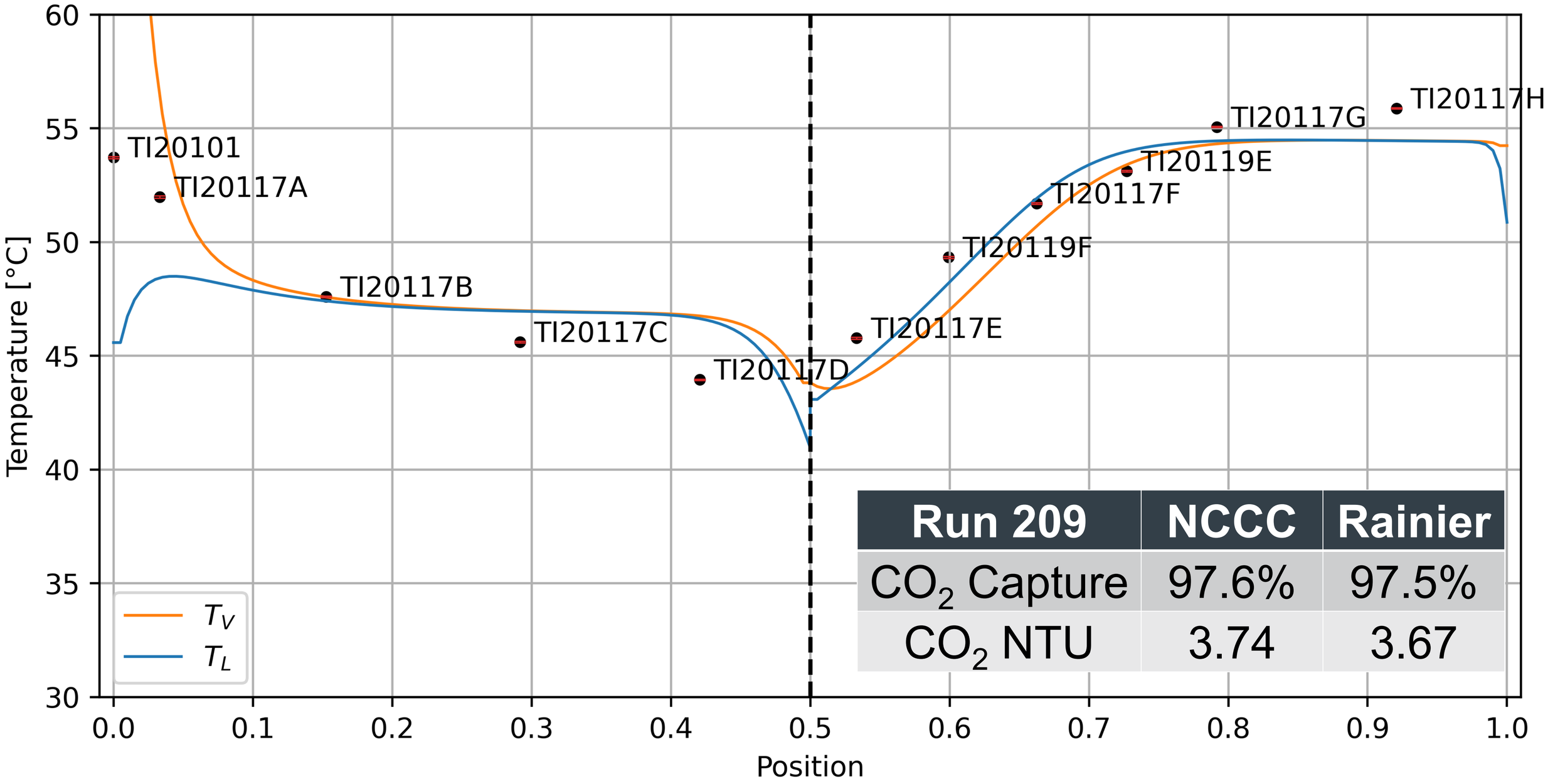
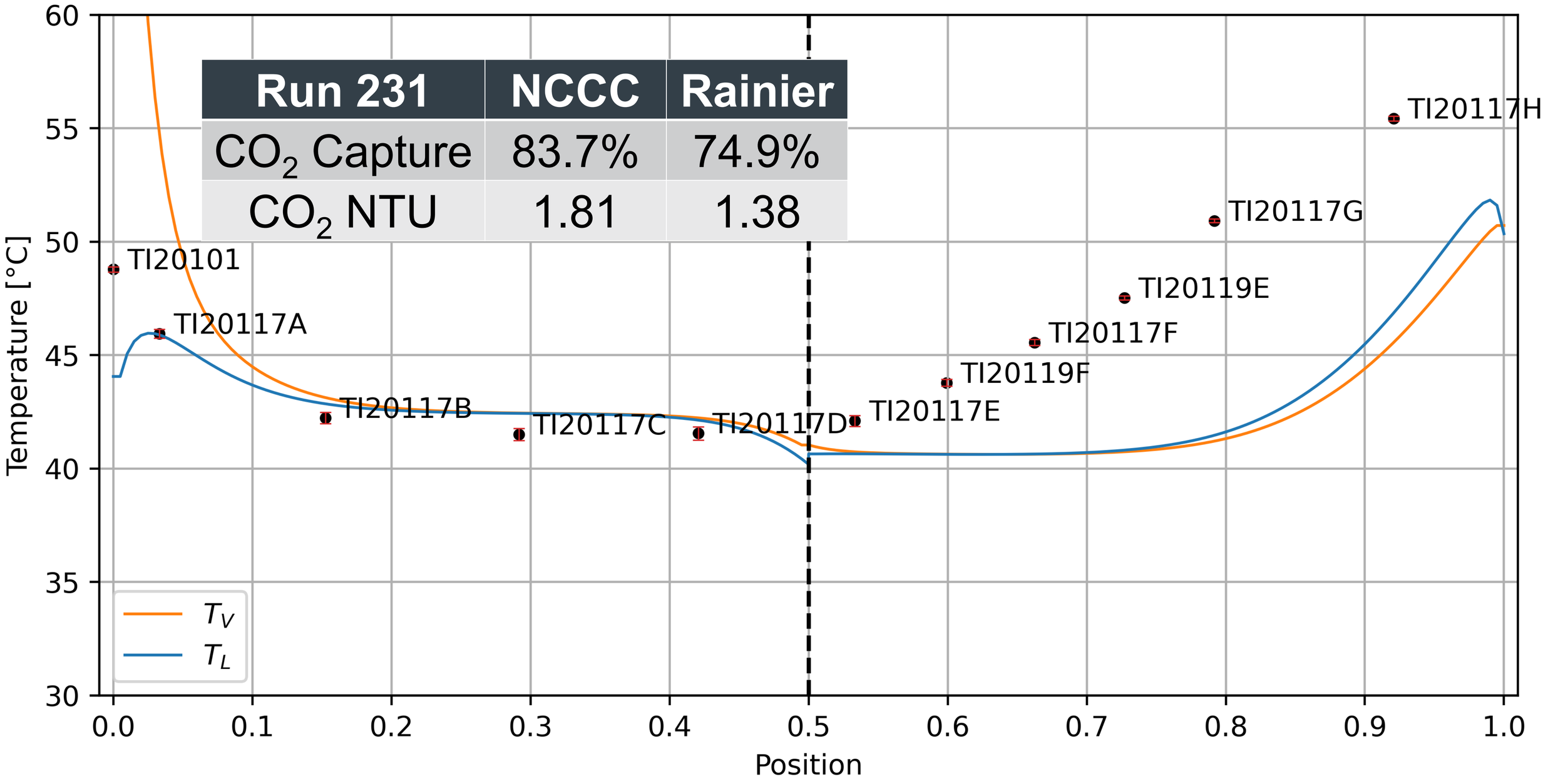


NCCC: hot solvent, high removal 2023-09-01



Run 209	NCCC	Rainier
CO_2 Capture	97.6%	97.5%
CO_2 NTU	3.74	3.67

NCCC: low molality 2023-09-23



New basis: vapor reference state using IGL, with all the nonideality contained in the ΔH_{vap}

This is one approach used by Aspen to calculate liquid H departure:

$$H_i^{*,l} - H_i^{*,ig} = H_i^{*,v} - H_i^{*,ig} - \Delta_{vap} H_i$$

Simplifies to: $H_i^L = H_i^V - \Delta_{vap} H_i$

Note: it is called ΔH of "vaporization" for all the components but it is really "desorption" for CO_2 (and PZ) since reactions are involved

$$H_i^L = H_i^V - \Delta_{vap}H_i$$

Where to get $\Delta_{vap}H_i$?

For thermodynamic consistency, derive from vapor pressure

Thermo is built around correlations for $P_{vap} = f(T, \alpha)$

- H_2O: Antoine equation for pure water, assume ideal behavior
- PZ and CO_2: very different from ideal, use empirical fits

Xu measured equilibrium pressures for loaded H_2O-PZ-CO_2

Q Xu. Ph.D. Dissertation (2011) University of Texas at Austin

Vapor pressure:

$$P_L^{CO_2} = {}^{1}/_{P_{scale}} \exp\left(35.3 - \frac{11054}{T_L} - 18.9\alpha^2 + 4958\,{}^{\alpha}/_{T_L} + 10163\,{}^{\alpha^2}/_{T_L}\right)$$

$$P_L^{PZ} = {}^{x^P}/_{P_{scale}} \exp\left(-123 + 21.6 \ln T_L + 20.2\alpha - 18174\,{}^{\alpha^2}/_{T_L}\right)$$

$$P_L^{H_2O} = {}^{x^W}/_{750}\, 10\text{^}\left(8.07 - \frac{1730}{T_L - 39}\right)$$

x^P and x^W assume that all CO_2 is complexed with PZ:

$x^P = \frac{x^{PZ}}{x^{PZ} + x^{H_2O}}$ and $x^W = \frac{x^{H_2O}}{x^{PZ} + x^{H_2O}}$

Heat of vaporization: $\Delta H_{vap}^{i} = -R\,\frac{\partial(lnP_i)}{\partial(1/T)}$

$$\Delta H_{vap}^{CO_2} = R(11054 - 4958\alpha - 10163\alpha^2)$$

$$\Delta H_{vap}^{PZ} = R(21.6T_L - 18174\alpha^2)$$

$$\Delta H_{vap}^{H_2O} = R\left(1730\,\frac{\ln(10)}{(1 - 39/T_L)^2}\right)$$

$$H_i^L = H_i^V - \Delta_{vap} H_i$$

Sum over components:

$$H_L = H_V^{PP}(T_L, P, x) - \sum_i x_i \, \Delta H_{vap}^i$$

Vapor H from IGL property pkg call:

$$H_V = H_V^{PP}(T_V, P, y)$$

Now the enthalpies for each phase are consistent:

$$N_H^L = N_H^V = h a_e (T^V - T^L)$$

$$N_H^L \times V_{element} = \frac{\partial (F_L H_L)}{\partial z} = \frac{\partial (F_V H_V)}{\partial z}$$

$$\ln\left(k'_{g,CO_2}\right) = c_1 - c_2\alpha$$

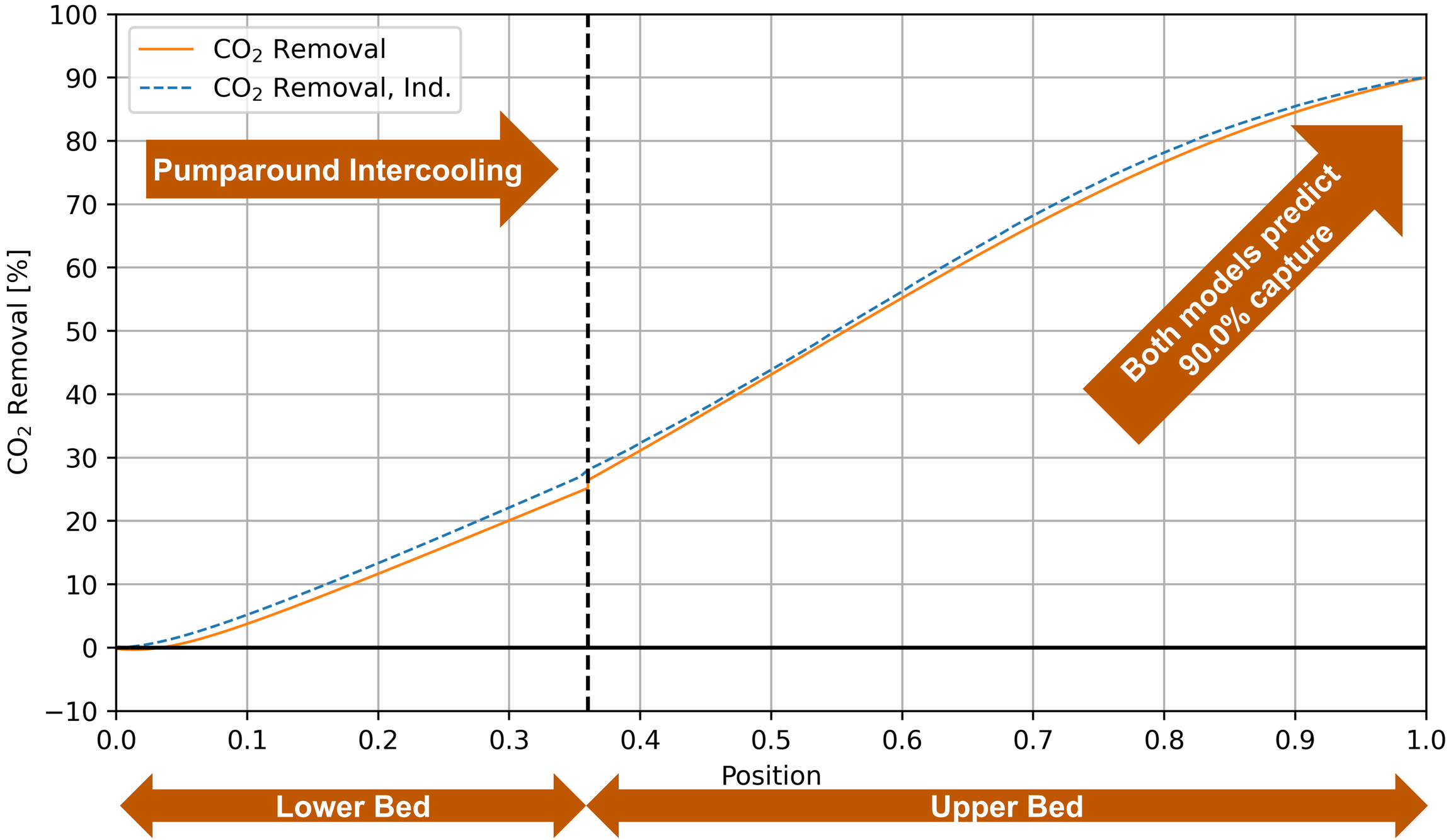
$$\min_{c_1,c_2} Error = w_1 \int_z |\Delta T_L| + w_2 \int_z |\Delta T_V| + \sum_{i=CO_2,H_2O} w_i \int_z \left|\Delta F_{V,i}\right| + w_5 |\Delta\%_{removal}|$$

1. Mustang FEED design case simulated in Independence

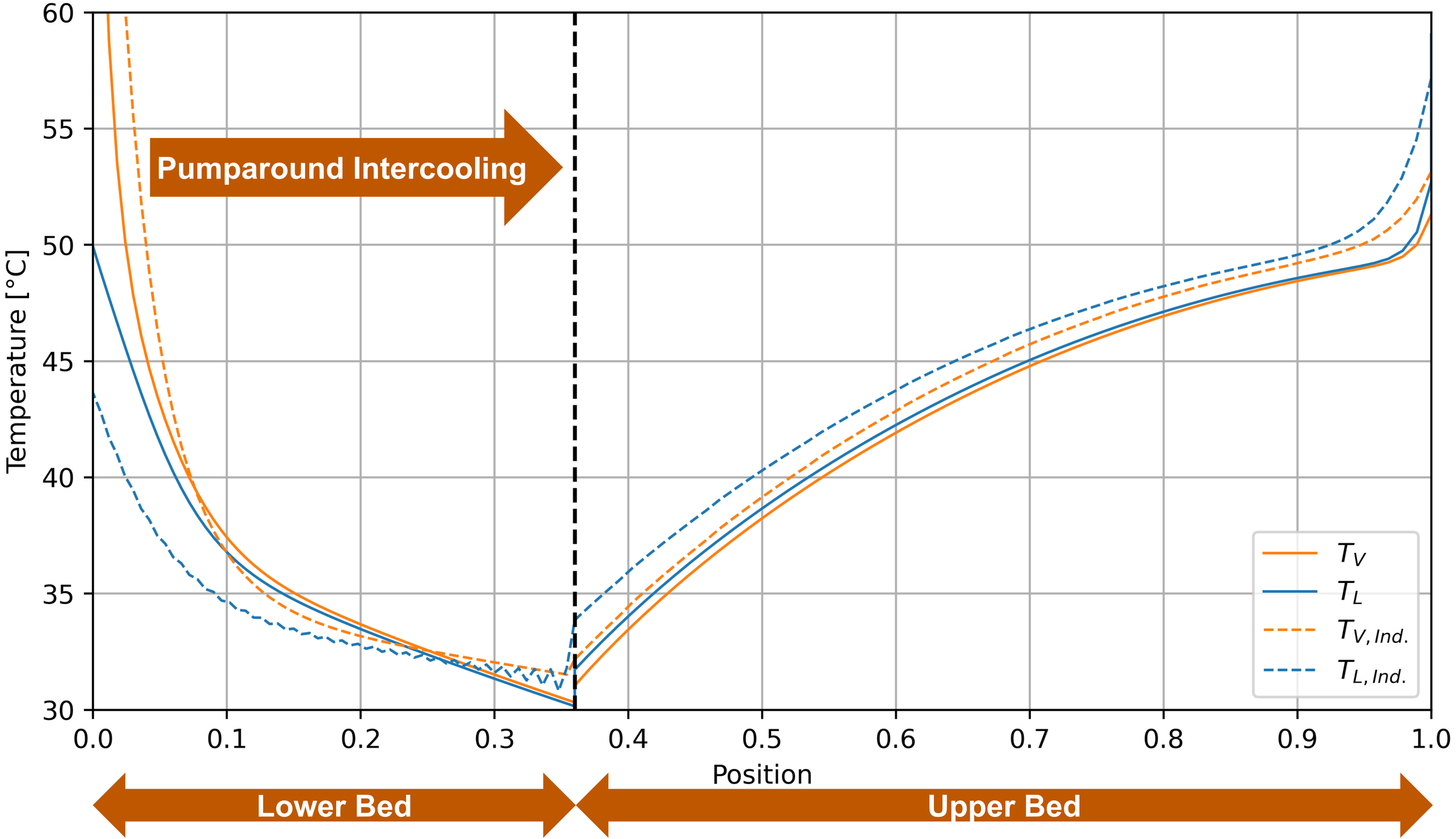
2. Independence profiles loaded into gPROMS model

3. Optimization sets decision variables c_1, c_2 using objective function above (steady-state point optimization using CVP_SS solver)

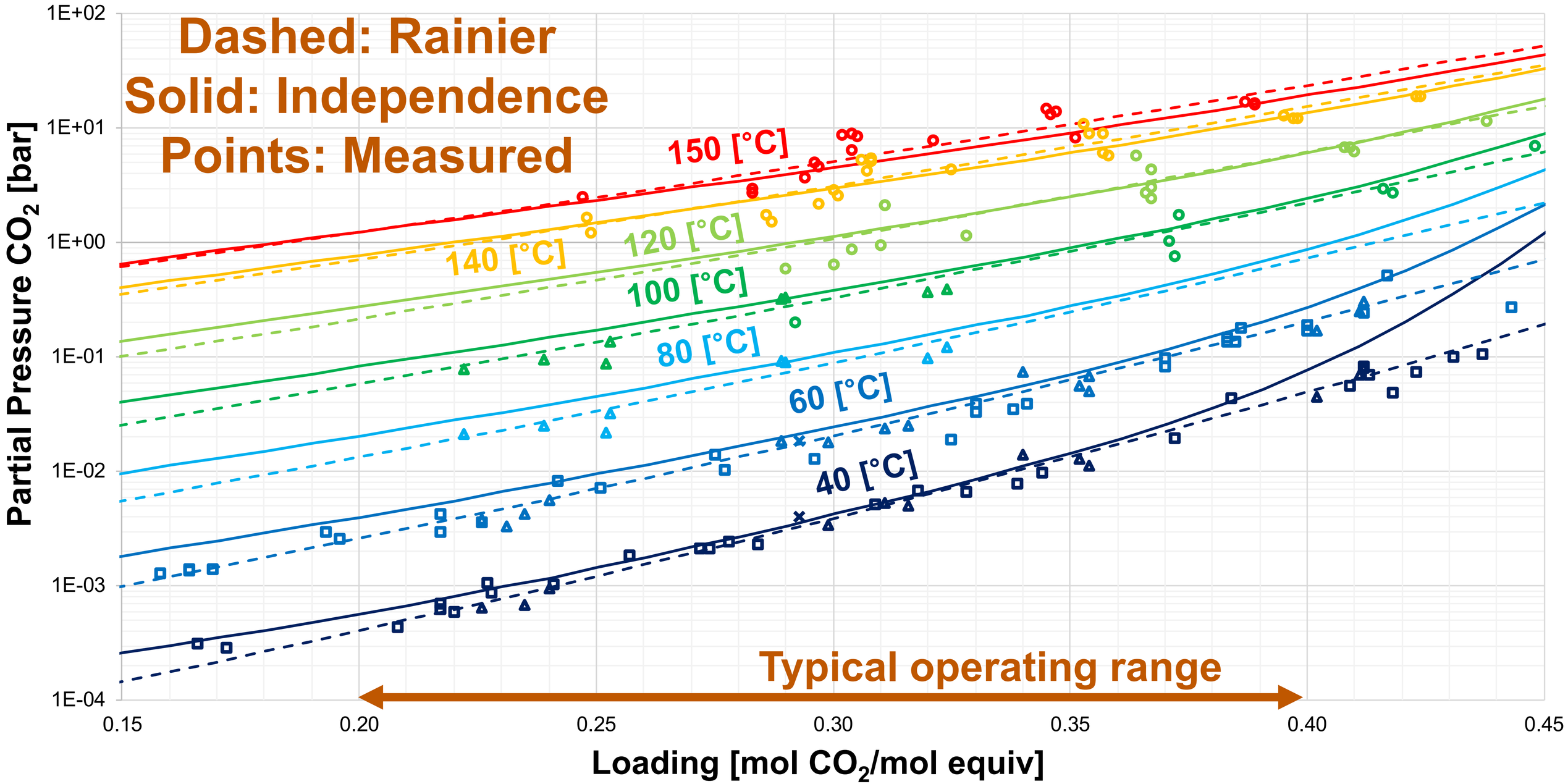
Absorber parameter estimation: CO_2 removal



Absorber parameter estimation: temperature profile



How good is good enough?



Experimental data from UT dissertations: Hilliard (2008) [squares], Dugas (2009) [triangles], Xu (2011) [circles], and Nguyen (2013) [crosses]

How good is good enough?

Solid lines from activity coefficient (e-NRTL) model representing many electrolyte species, with 74 adjustable parameters*.

Dashed lines generated by:

$$\ln(P_{CO_2}) = 35.5 - 11054\,{}^{1}/_{T} - 18.9\alpha^2 + 4958\,{}^{\alpha}/_{T} + 10163\,{}^{\alpha^2}/_{T}$$

Each model needs the right trade-off of model fidelity vs. tractability

*P T Frailie II. Ph.D. Dissertation. (2014) University of Texas at Austin.