Modeling and precipitation mitigation in PZ-based CO_2 capture solvents

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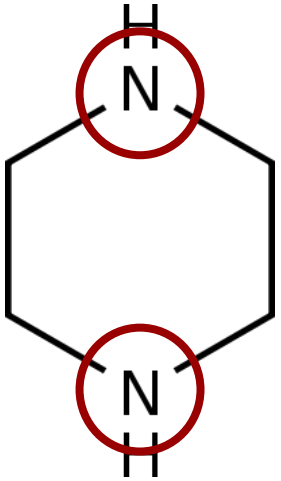
Outline

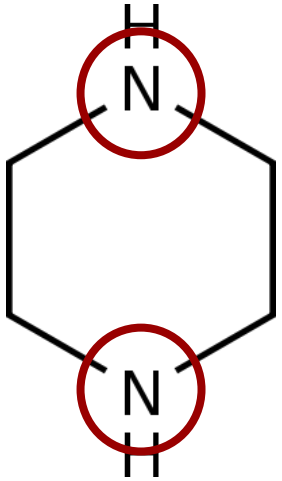
- PZ chemistry
- The extended UNIQUAC model in the context of CO_2 capture using precipitating solvents
- Validation of the extended UNIQUAC model for the PZ-CO_2-H_2O system
  - VLE
  - Speciation
  - SLE
  - CO_2 heat of absorption
- Pilot-scale CO_2 capture with PZ-promoted amines
- Plant operation philosophy with PZ-promoted amines
- Conclusions and future work

Chemistry

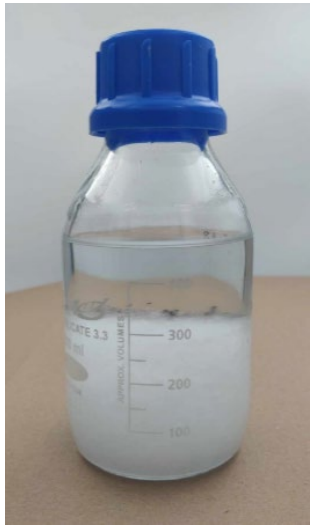
- PZ properties
  - Melting point: 111 °C
  - Boiling point: 146 °C
- Modeling
  - Liquid phase: Extended UNIQUAC
  - Gas phase: SRK EoS
  - VLE: γ–ϕ approach
    - $x_i \gamma_i f_i = y_i \phi_i P$
  - Ion interaction parameters fitted for 6 PZ species
    - H_2PZ, PZH^+COO^-, PZH^+, PZH_2^{2+}, $PZCOO^-$, $PZ(COO^-)_2$
  - 1200 new data points from the PZ literature were used
    - Screened for questionable quality
    - Made available in CERE electrolyte data bank
      - Total 150,000+ data points available to the CERE consortium members



PZ speciation in the liquid phase



- CO_2-water reactions
  - $H_2O \rightarrow H^+ + OH^-$
  - $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$
- PZ speciation is complex
  - $PZ_{(aq)} + H^+ \rightarrow PZH^+$
  - $PZH^+ + H^+ \rightarrow PZH_2^{2+}$
- PZ forms three carbamates
  - A zqitterionic type PZH^+COO^-
    - $PZCOO^- + H^+ \rightarrow PZH^+COO^-$
  - Two active nitrogen groups to bing CO_2, two carbamates: $PZCOO^-$, $PZ(COO^-)_2$
    - $PZ_{(aq)} \rightarrow HCO_3^- \rightarrow PZCOO^- + H_2O$
    - $PZCOO^- + HCO_3^- \rightarrow PZ(COO^-)_2 + H_2O$
- Precipitating solid phases
  - PZ, PZ·½H2O, PZ·6H2O, Ice



Setting up the chemical framework: Concentration scales

- Activity coefficient types
  - $\mu_i = \mu_i^{\theta_s} + RTln\left(\frac{s_i\gamma_i^{\theta_s}}{s_i^{\theta}}\right)$

    $= \mu_i^{o_x} + RTln\left(\frac{x_i\gamma_i^{o_x}}{x_i^{o}}\right)$

    $= \mu_i^{*_x} + RTln\left(\frac{x_i\gamma_i^{*_x}}{x_i^{*}}\right)$

    $= \mu_i^{*_m} + RTln\left(\frac{b_i\gamma_i^{*_m}}{b_i^{*}}\right)$

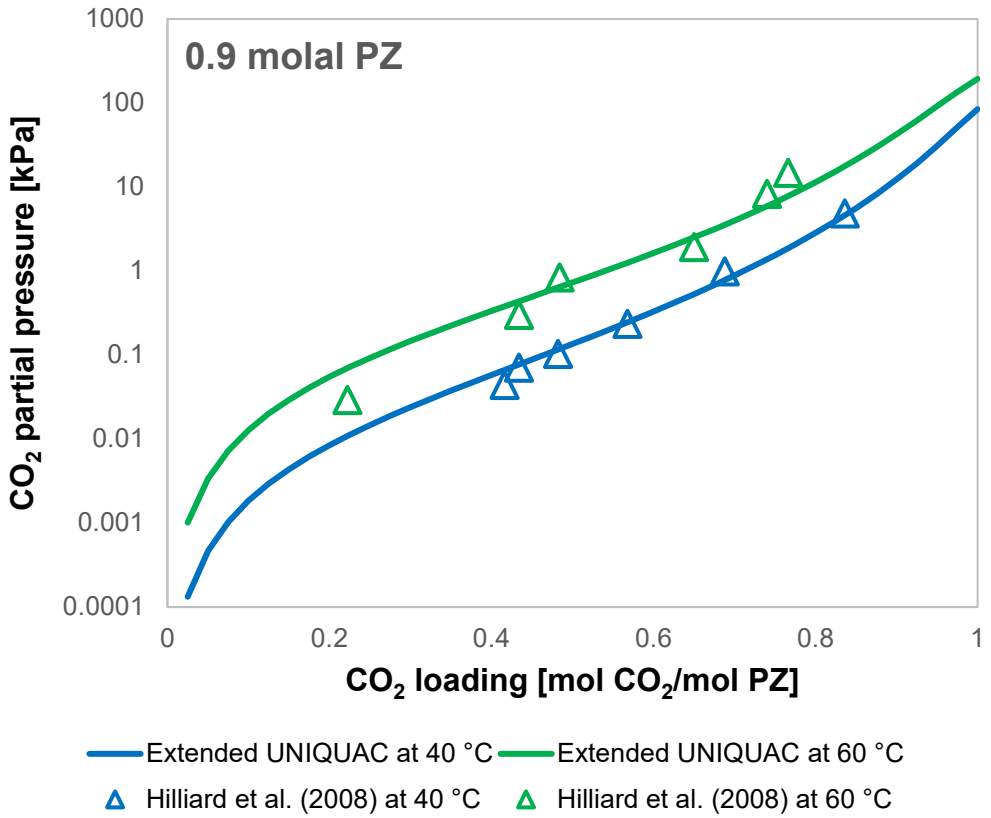
    $= \mu_i^{*_c} + RTln\left(\frac{c_i\gamma_i^{*_c}}{c_i^{*}}\right)$

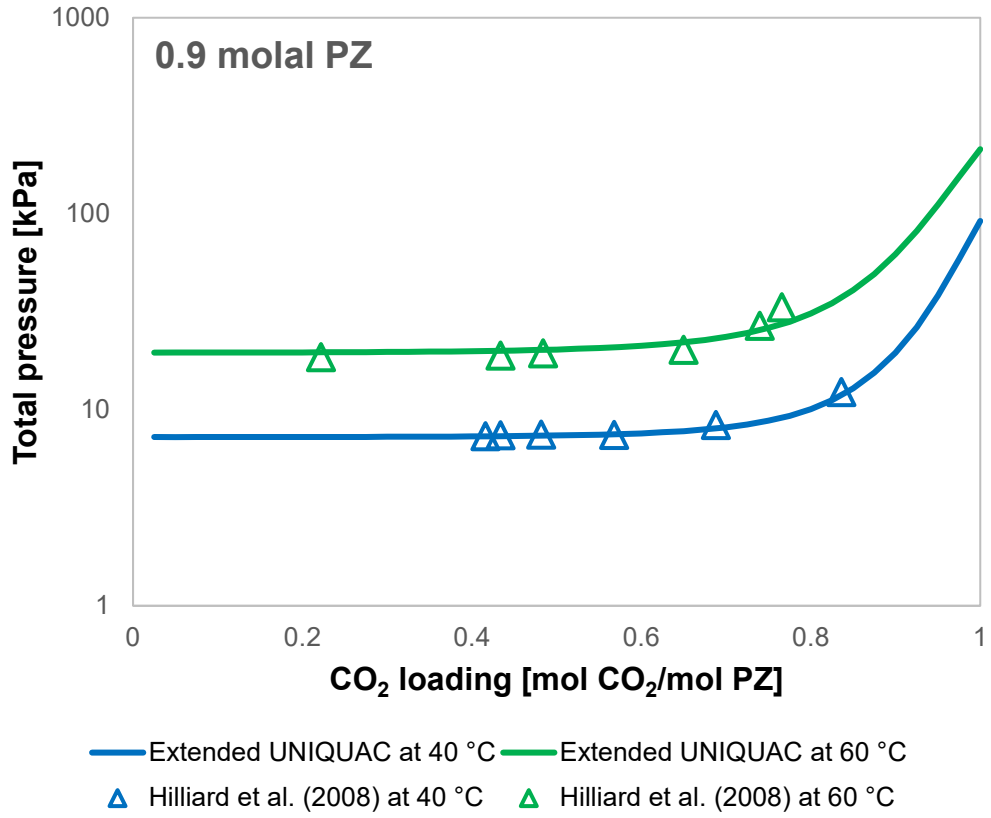
- Concentration scale should be independent of temperature:
  - $\gamma_i^{*_m} = x_s\gamma_i^{*_x} = x_s\frac{\gamma_i^{o_x}}{\gamma_i^{\infty_x}} = \boldsymbol{x_s\gamma_i^{*_c}\frac{\rho_t}{\rho_s}\frac{M_s}{\bar{M}_t} = \gamma_i^{*_c}\frac{\rho_t}{\rho_s}\frac{m_s}{m_t}}$
  - Reporting thermophysical data in molarity scale strictly complicates model parametrization with electrolyte solutions involved such as CO_2 into aqueous amines!

Extended-UNIQUAC model framework

- A local composition model derived by Prof. Emeritus Kaj Thomsen from the original UNIQUAC model (Abrams & Prausnitz, 1975 and Maurer & Prausnitz, 1978)
  - The extra Debye–Hückel term accounts for electrostatic interactions.
    - $G^{ex} = G^{ex}_{combinatorial} + G^{ex}_{residual} + G^{ex}_{Extended\ Debye\text{-}Hückel}$
    - Combinatorial term is independent of temperature but related to the relative size of the species.
    - Residual enthalpic term is temperature dependent with two adjustable parameters to be fitted per pair of species.
    - Debye–Hückel term derives the electrostatic term
      - Accounts for the ion interactions simpler than the original Debye–Hückel law.
      - No adjustable term, function of density and relative permittivity of pure water.
  - Shown to calculate the activity coefficients of electrolyte solutions accurately.
- Currently, the only thermodynamic model able to predict solid phase for complex electrolyte solutions reliably is the extended UNIQUAC. Shown by Darde & Thomsen et al., *Comparison of two electrolyte models for the carbon capture with aqueous ammonia*. Int. J. Greenh. Gas Control, 8, 2012, 61–72, https://doi.org/10.1016/j.ijggc.2012.02.002).

Validation of CO_2-PZ-H_2O system: VLE at low T





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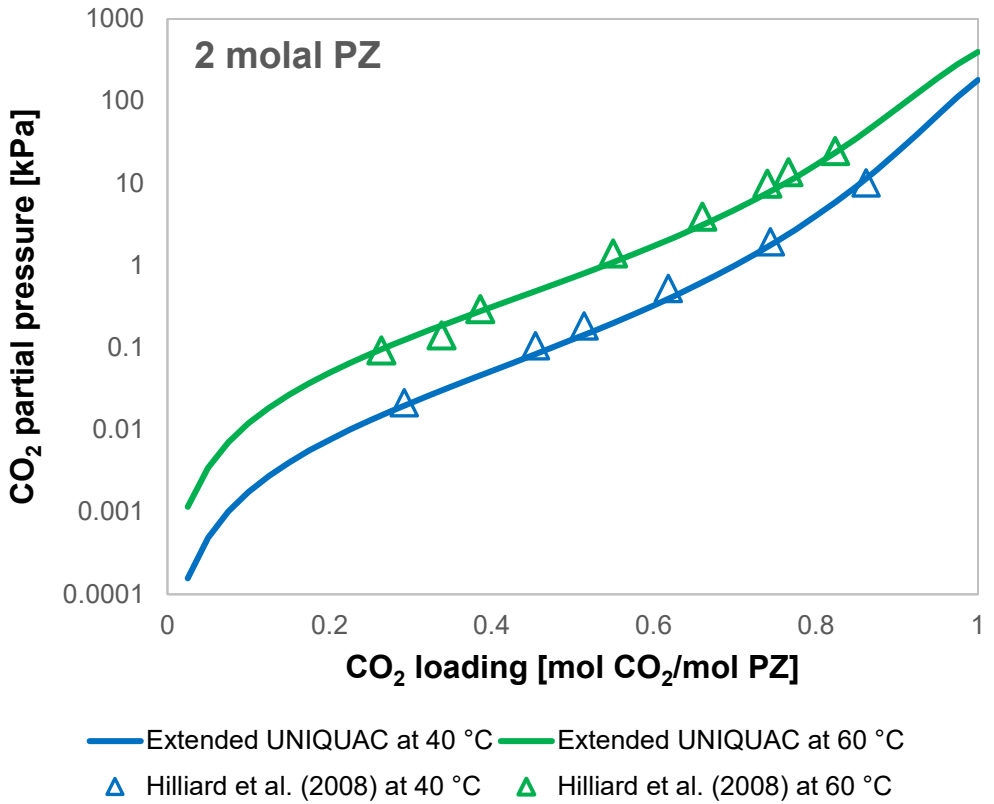

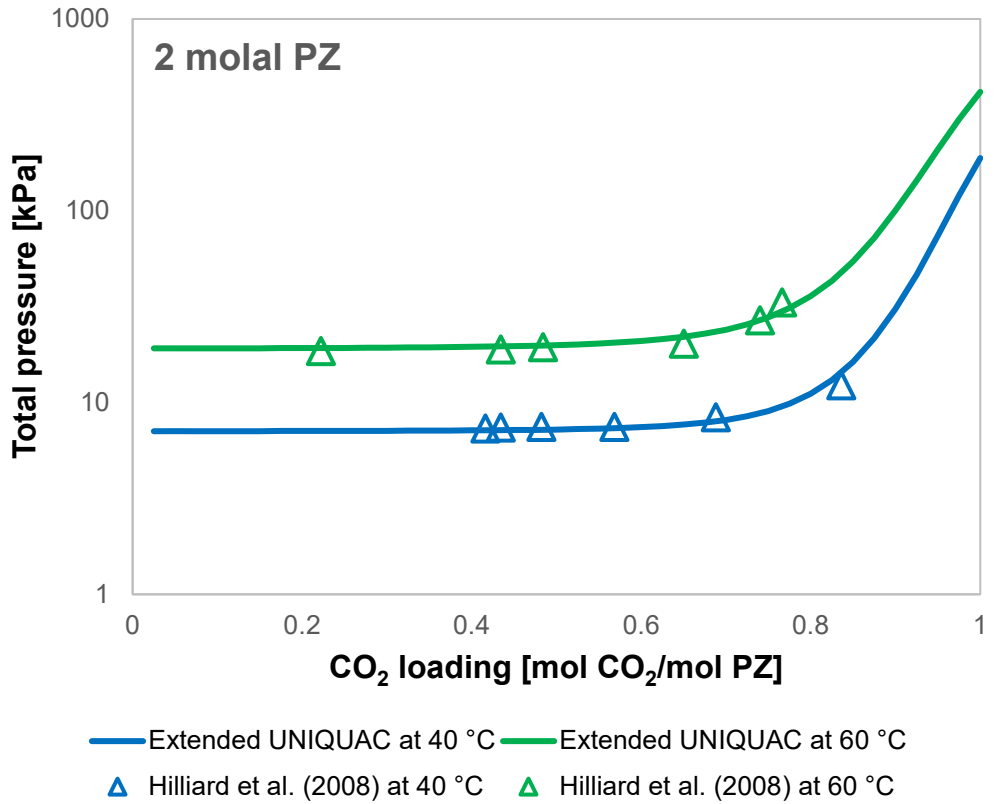

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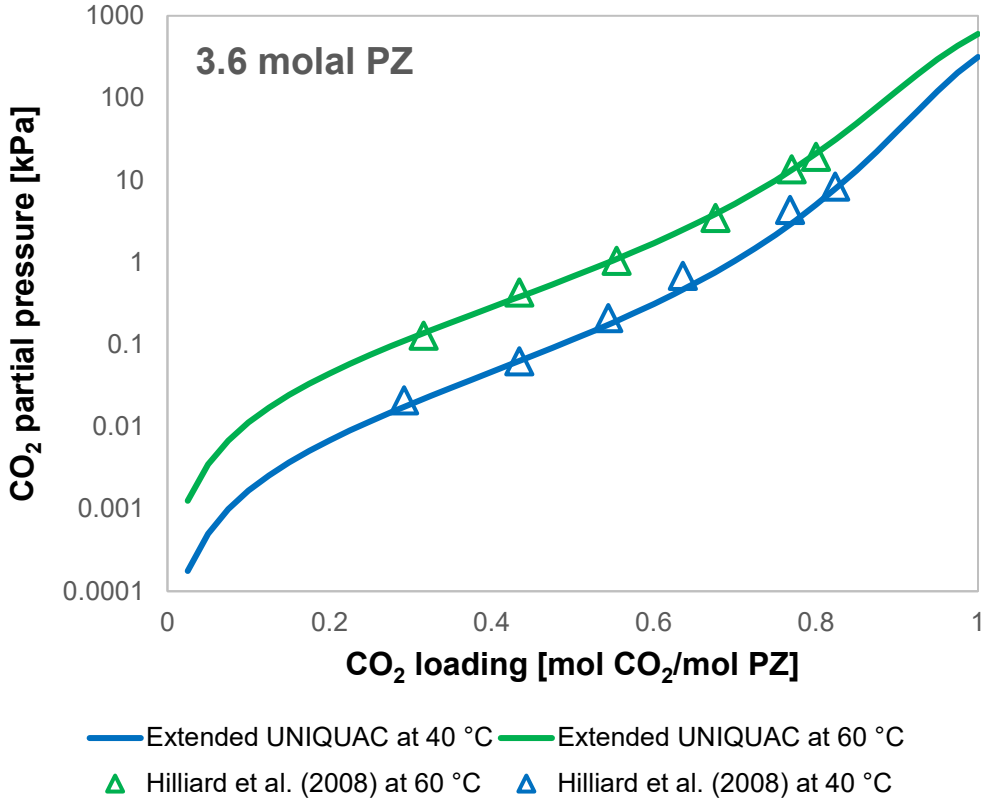
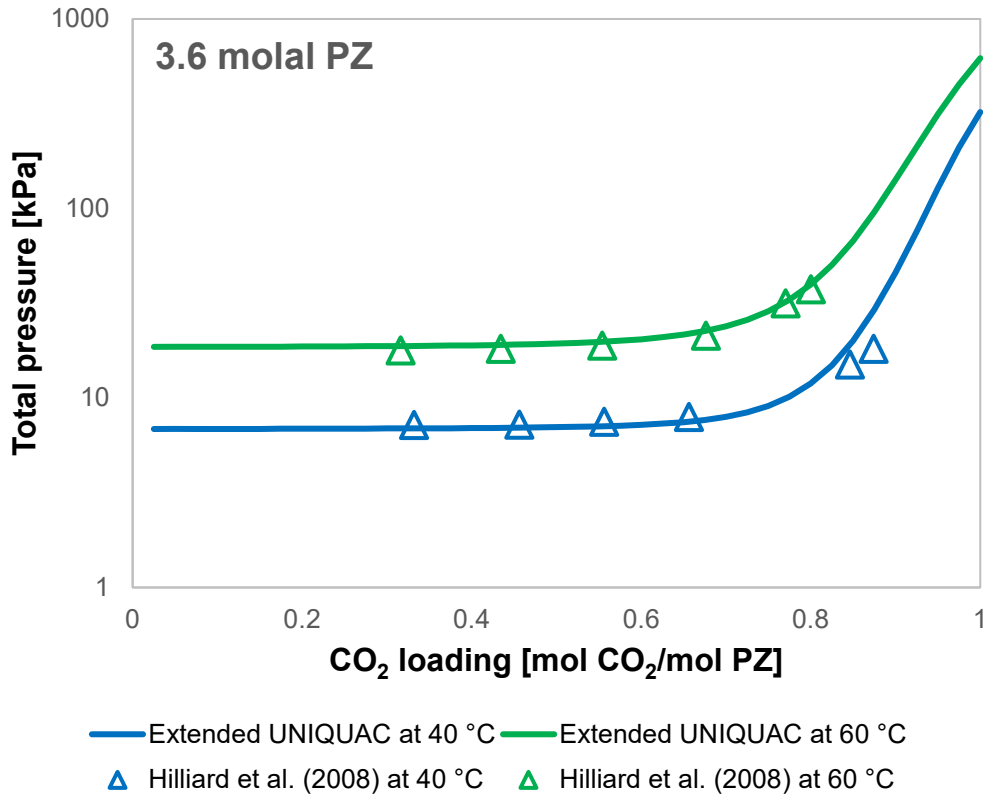
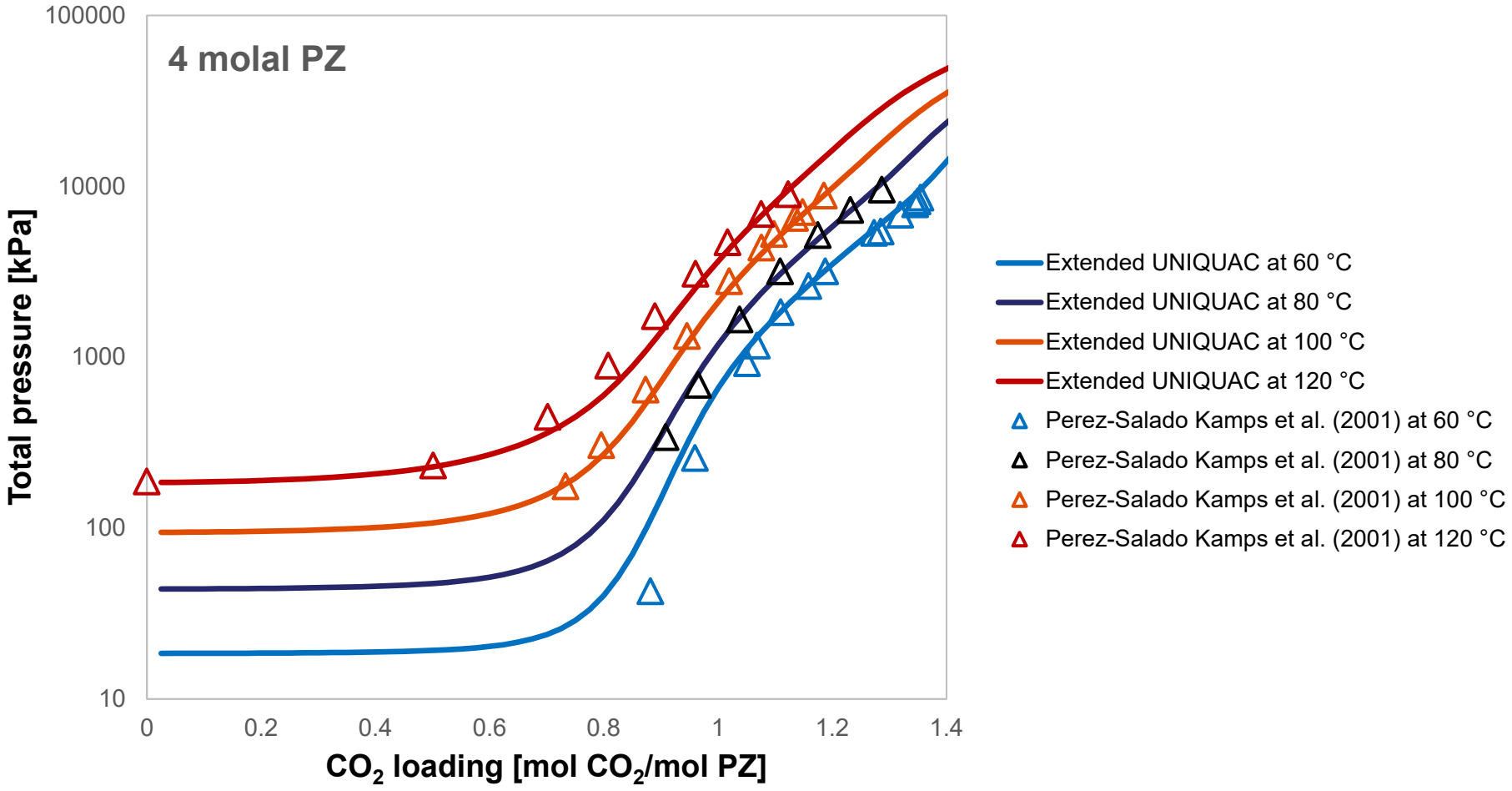
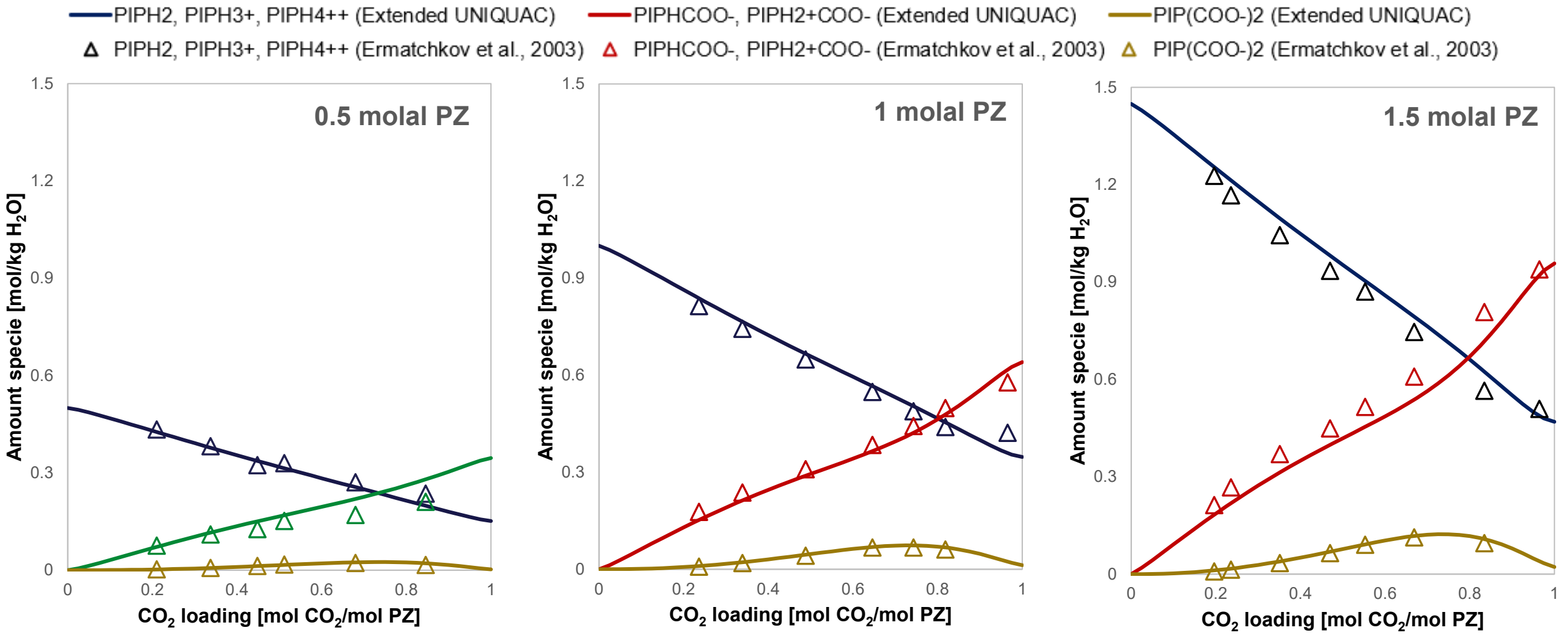




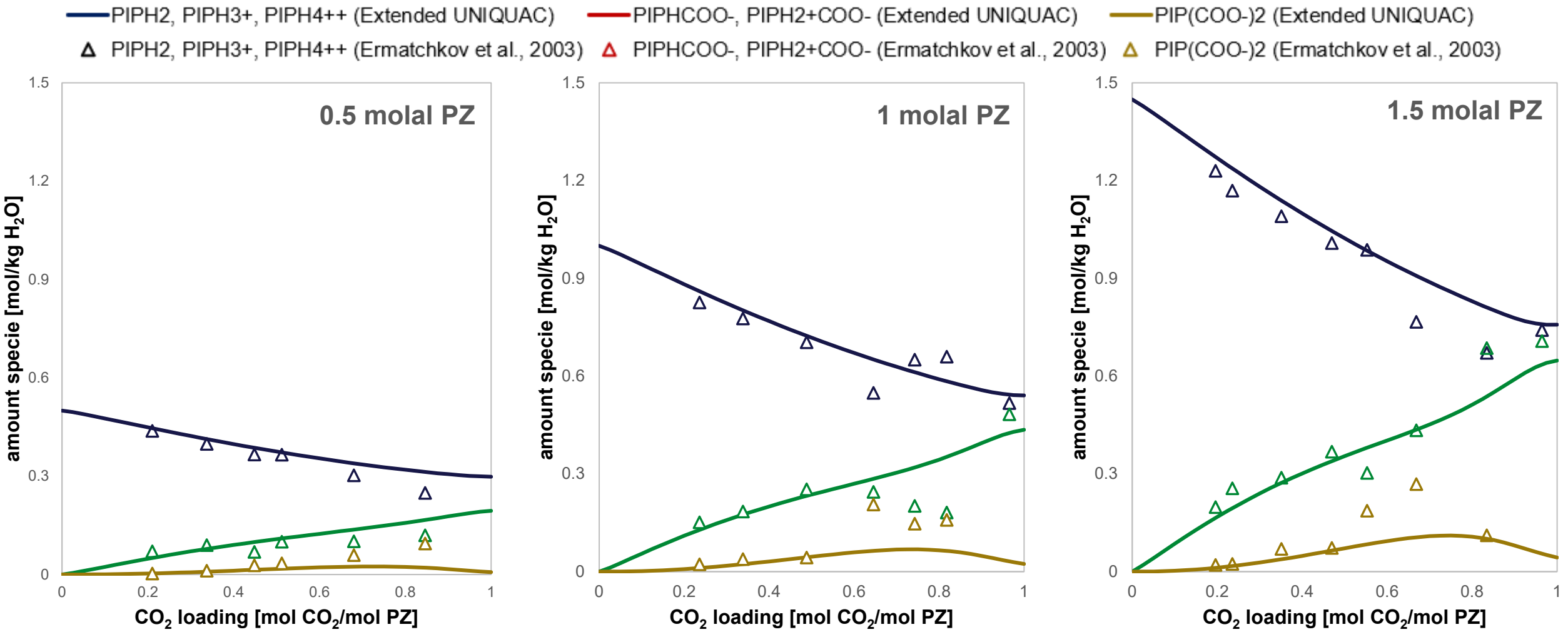
Validation of CO_2-PZ-H_2O system: VLE at higher T



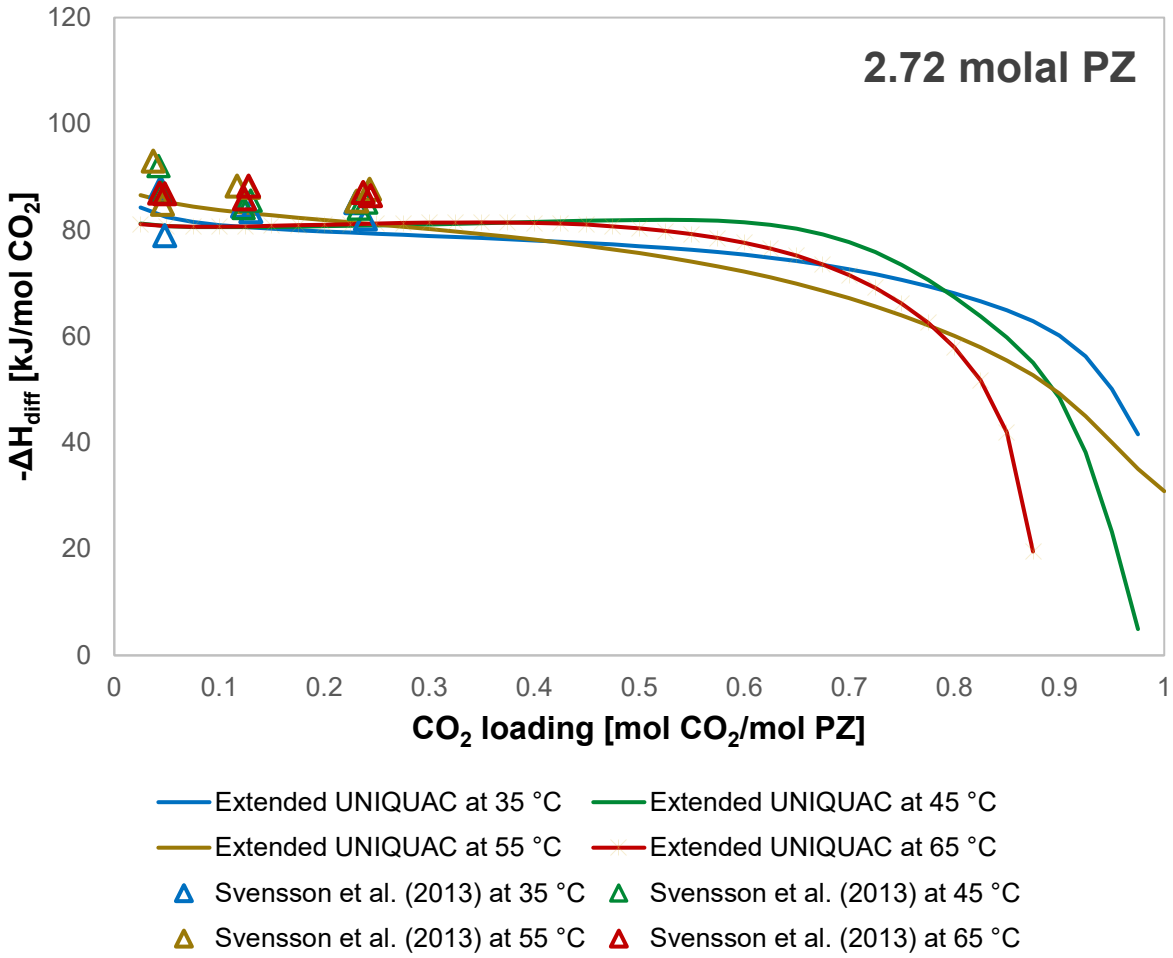
Validation of CO_2-PZ-H_2O system: Speciation at low T (25 °C)

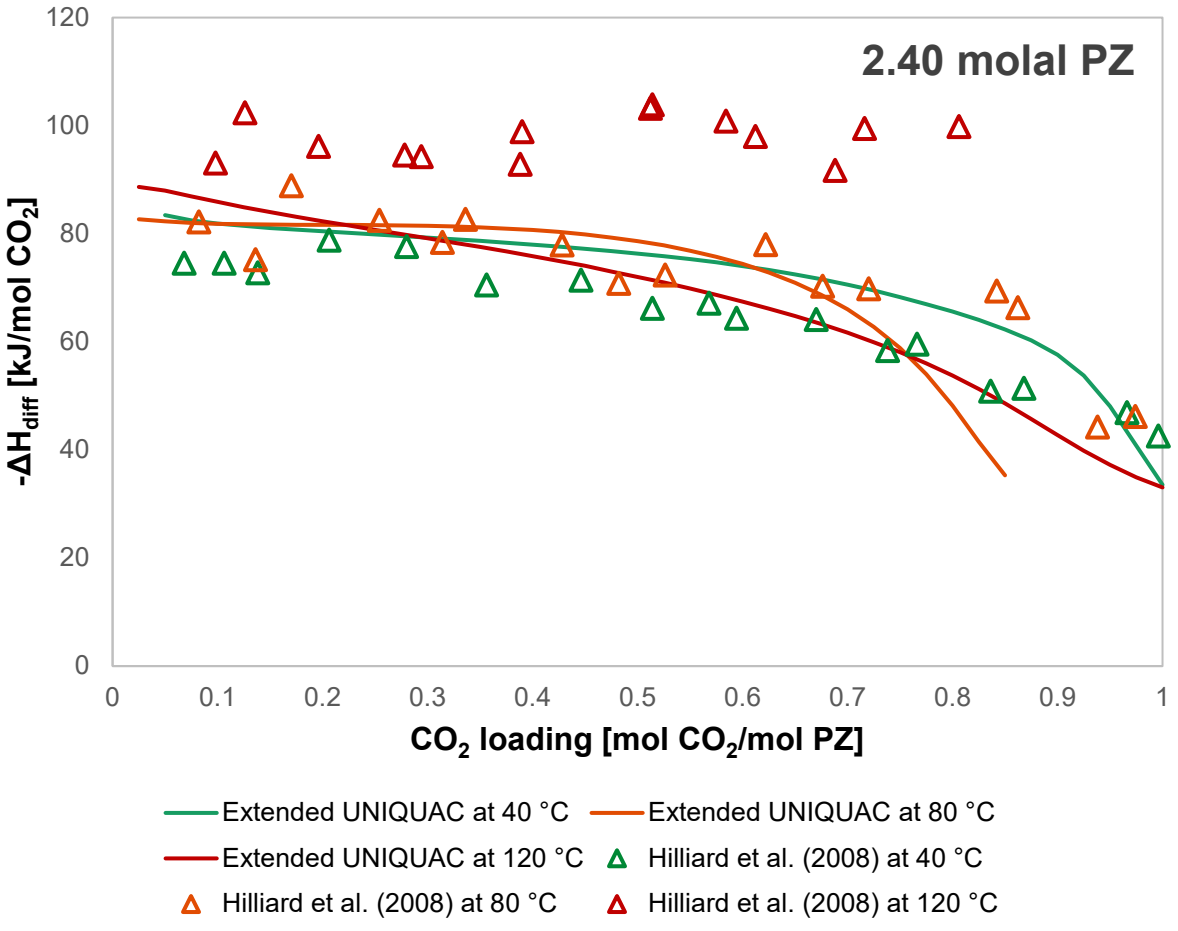


Validation of CO_2-PZ-H_2O system: Speciation at higher T (60 °C)

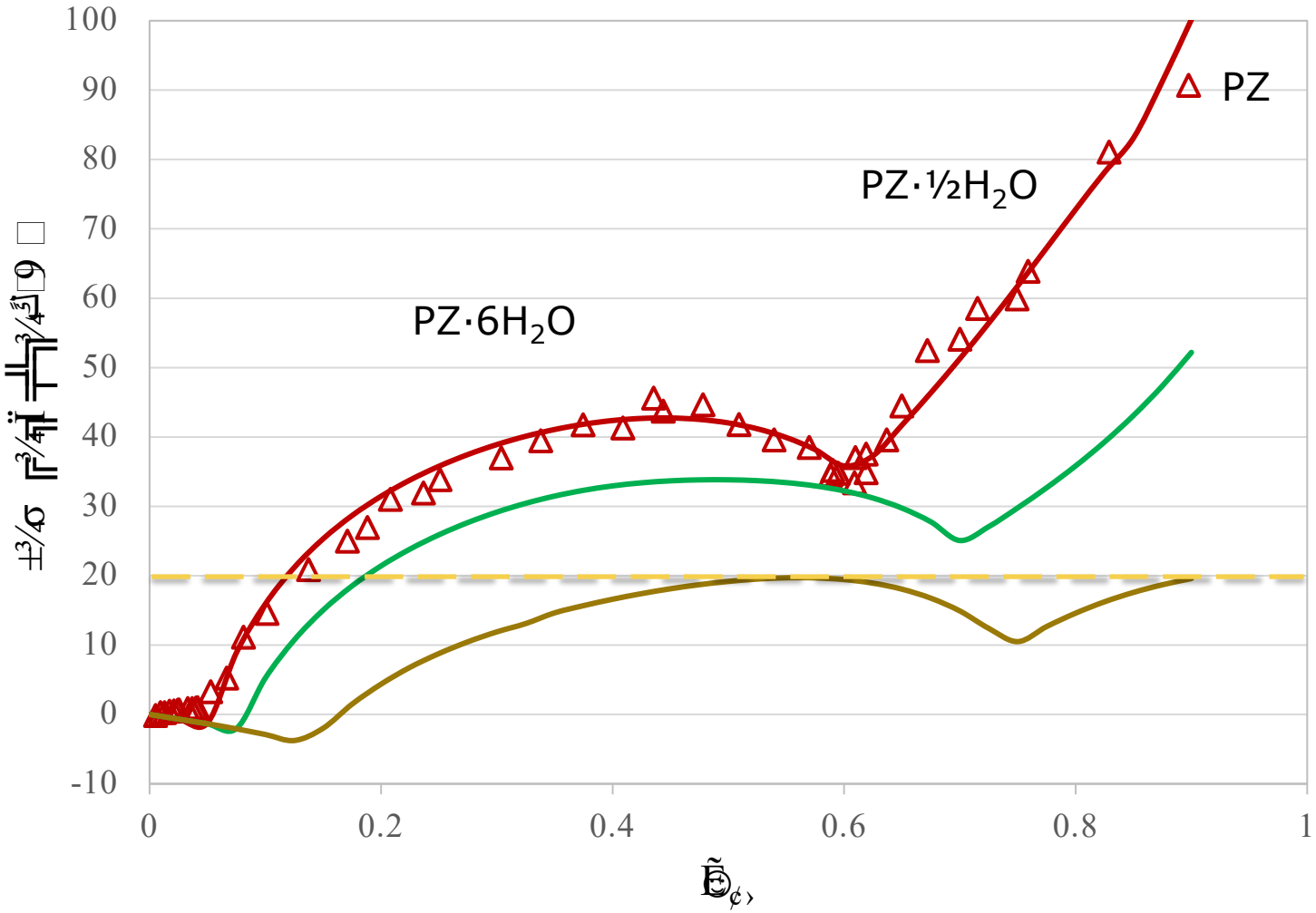


Heat of CO_2 absorption for the CO_2-PZ-H_2O system



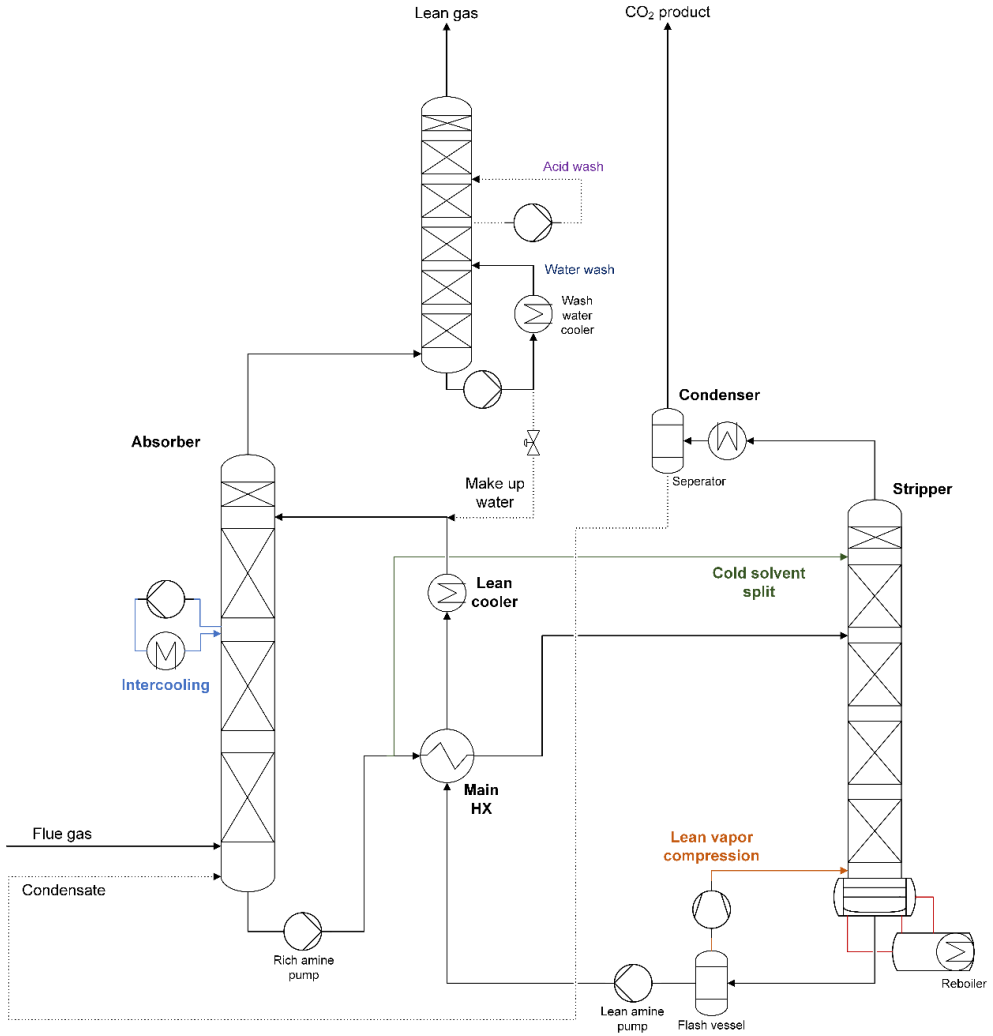


SLE of CO_2-PZ-H_2O system



Lean solutions could easily precipitate even at room temperature!

Pilot-scale CO_2 capture in a cement plant using PZ



Process flow diagram & pilot-scale CO_2 capture plant used in Aalborg Portland cement plant to test advanced process configurations.

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Pilot-scale CO_2 capture in a cement plant with CESAR1: Comparative analysis of specific reboiler duty across advanced process configurations

Isaac Appelquist Løge [a,*], Can Demir [a], Sai Hema Bhavya Vinjarapu [a], Randi Neerup [a], Ebbe Hauge Jensen [b], Jens Kristian Jørsboe [a,b], Maria Dimitriadi [a], Halil Halilov [c], Carsten Fritzner Frøstrup [a], Istvan Gyorbiro [a], Nomiki Kottaki [a], Asams Nelliparambil Jayan [e], Søren Jensen [d], Jakob Lindkvist Karlsson [d], Philip Loldrup Fosbøl [a]

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ARTICLE INFO

Keywords:
CO_2 capture in cement plants
CESAR1 solvent efficiency
Advanced carbon capture configurations
Pilot-scale carbon capture

ABSTRACT

Carbon Capture and Storage (CCS) from hard-to-abate sources is essential to mitigate the impacts of climate change. The CESAR1 solvent is considered the new benchmark solvent; however, its performance is limited in a wide range of advanced process configurations in pilot-scale studies. The scarcity of reliable pilot data from realistic setups retards the rapid advancement of CO_2 capture technology, as it hinders the accurate modeling and design of full-scale plants. In this work, we assess the applicability of the CESAR1 solvent for CO_2 capture in the cement industry at pilot scale, utilizing various advanced process configurations. Here, we present the specific reboiler duty of the CESAR1 solvent utilized in base-case configuration, absorber intercooling, stripper cold feed, variable stripper pressures, and lean vapor compression. All results are presented from verified steady states, including rigorous uncertainty analysis. In the base-case configuration, the plant operates with a specific reboiler duty of 3.39 GJ/t_{CO_2}. The lowest specific reboiler duty for stripper cold feed, absorber intercooling, variable stripper pressures, and lean vapor compression were 3.35 GJ/t_{CO_2}, 3.10 GJ/t_{CO_2}, 2.53 GJ/t_{CO_2}, and 2.03 GJ/t_{CO_2}.

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Pilot-scale CO_2 capture in a cement plant with CESAR1: Higher stripper pressure reduces energy demand and compression work but increases solvent degradation

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ARTICLE INFO

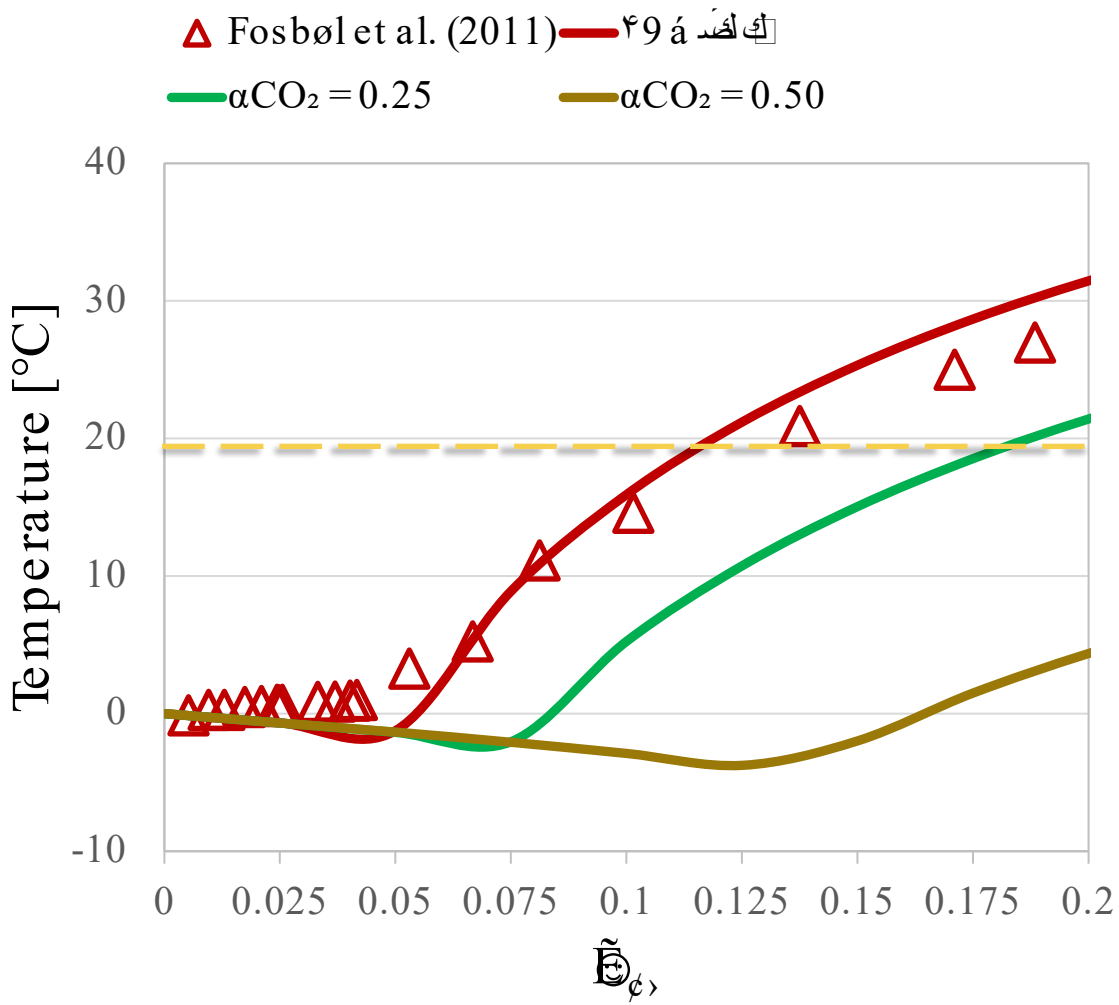
Keywords:
CO_2 capture
CESAR1
Advanced configurations
Pilot-scale

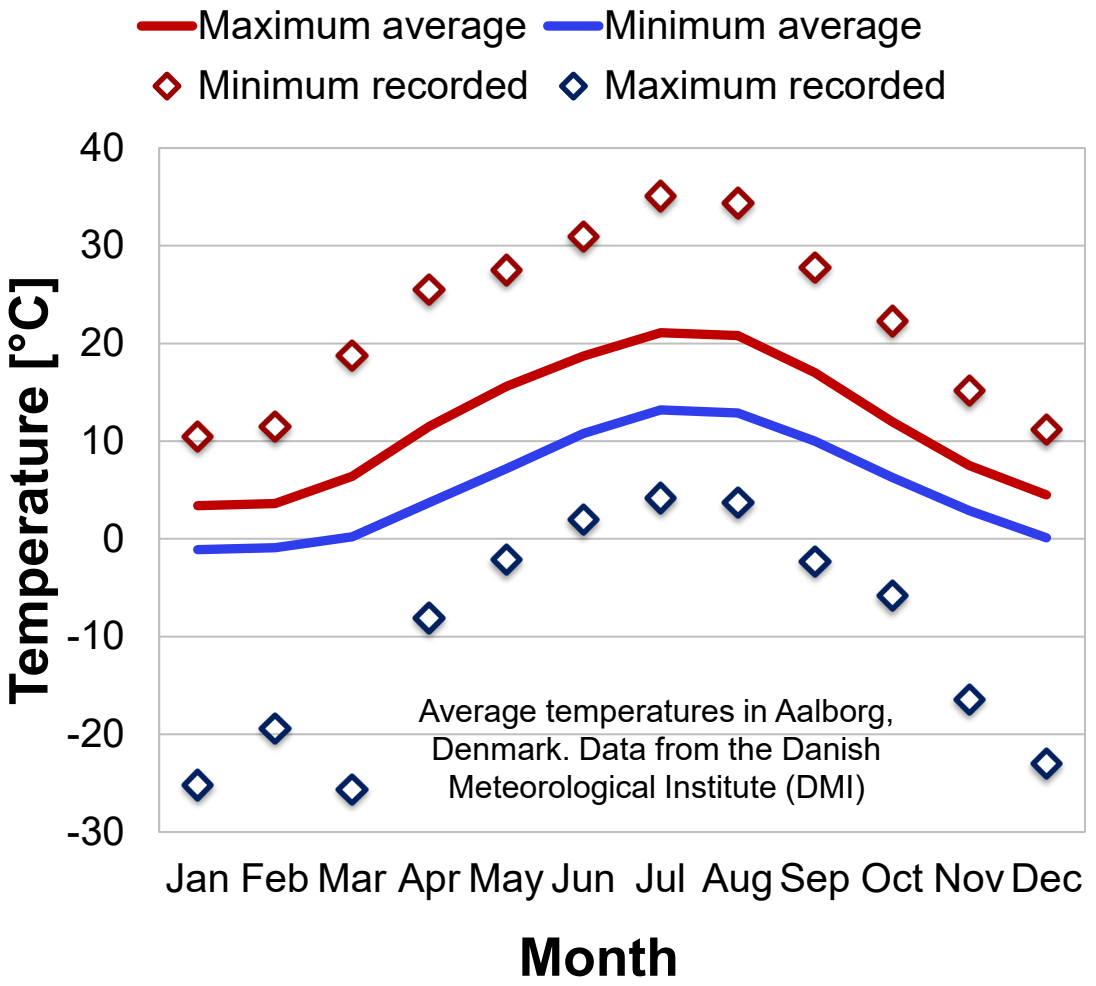
ABSTRACT

Carbon capture from hard-to-abate industries is essential. This study investigates the effect of stripper pressure on the performance of amine-based CO_2 capture from cement flue gas, using the CESAR1 solvent. Through a rigorous data filtering and binning methodology, experimental results were systematically categorized, enabling a precise evaluation of how stripper pressure and stripping intensity affect solvent regeneration, thermal efficiency, and subsequent energy demands. Additionally, a holistic analysis of operating with altered stripper pressure is presented, where downstream compression and solvent degradation are considered. Increasing stripper pressure consistently improves capture efficiency, reduces lean solvent loading, and increases the cyclic capacity, ultimately leading to lower specific reboiler duty.

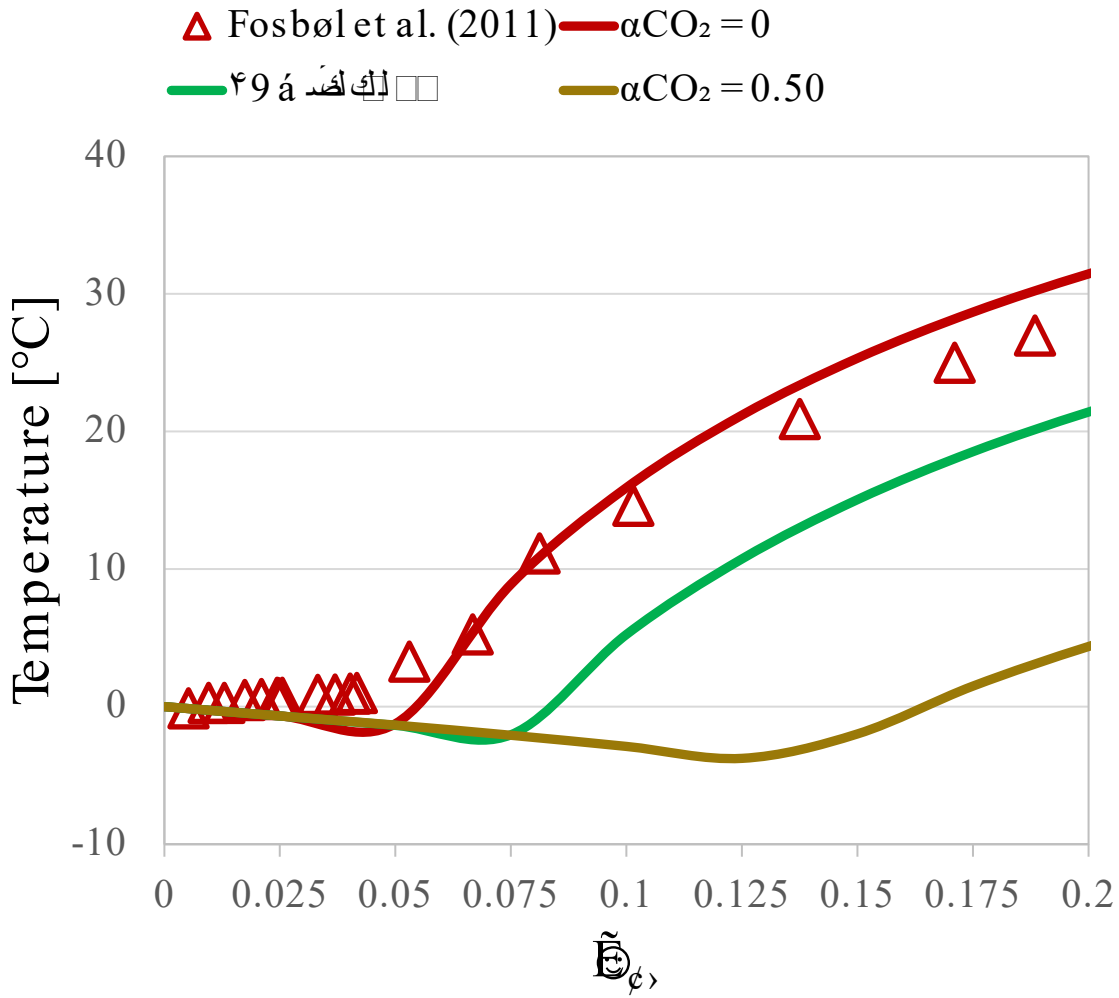
Higher stripper pressure also enhances lean-rich heat exchanger performance by improving temperature differentials. Operating at higher pressure reduces the water load on the overhead condenser, even at elevated temperatures. These conditions, in turn, mitigate overall cooling duties. Elevated stripper pressure decreases both reboiler duty and compression work. From our results, operating at higher pressures does not present downsides. However, degradation rates increase at elevated temperatures. We suggest that the standard operating pressure for capturing CO_2 with the CESAR1 solvent be evaluated, as it provides an opportunity for reduced energy consumption while also monitoring solvent health over extended periods.

Year-round capture at TRL7 with PZ involved



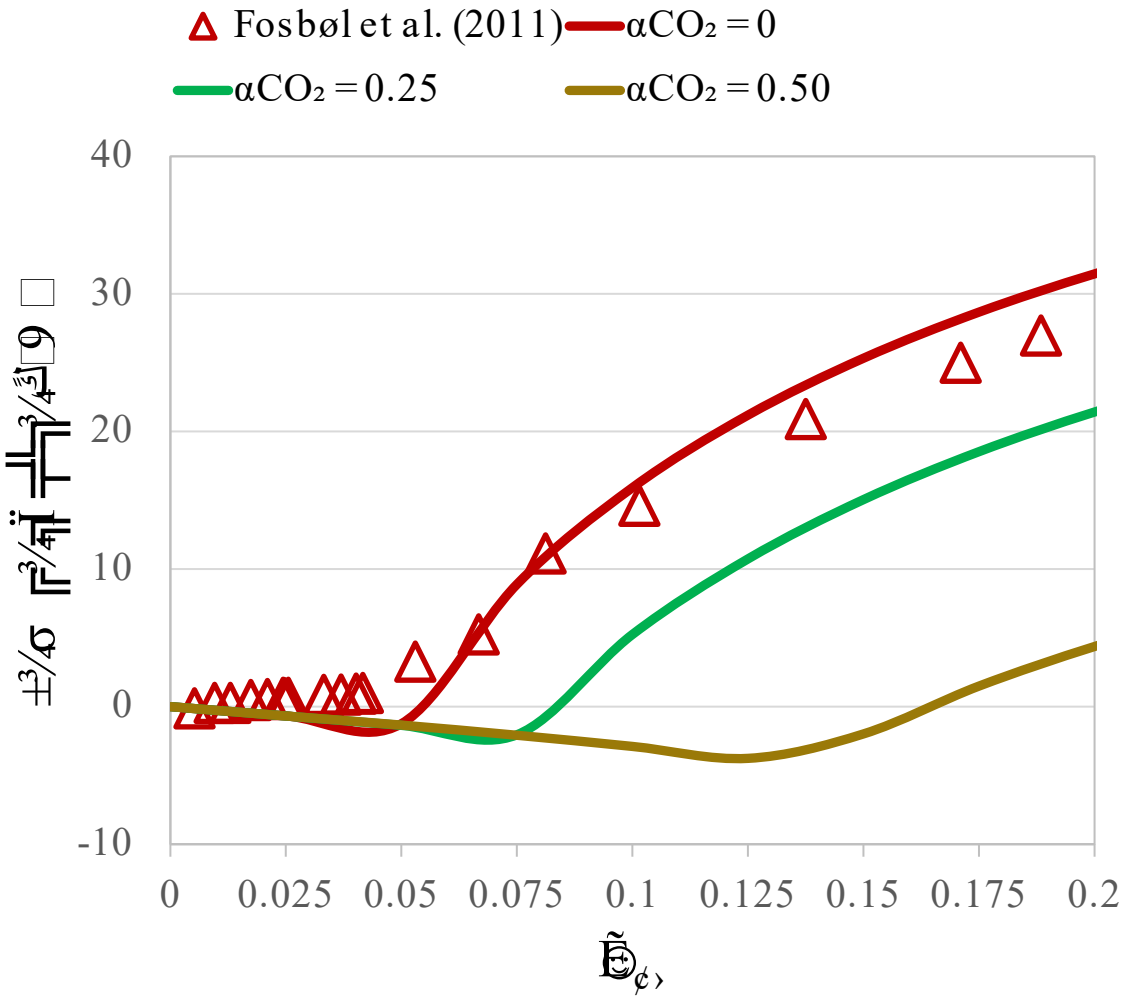


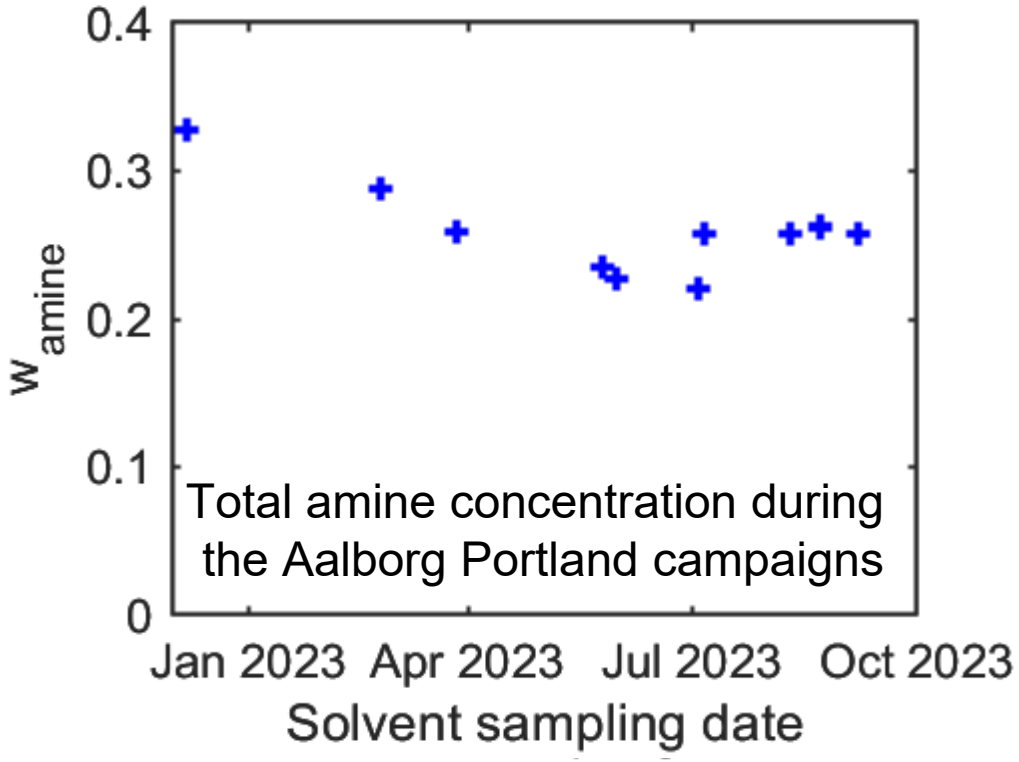
Year-round capture at TRL7 with PZ involved



Heating jacket around the PZ barrel to maintain the liquid phase.

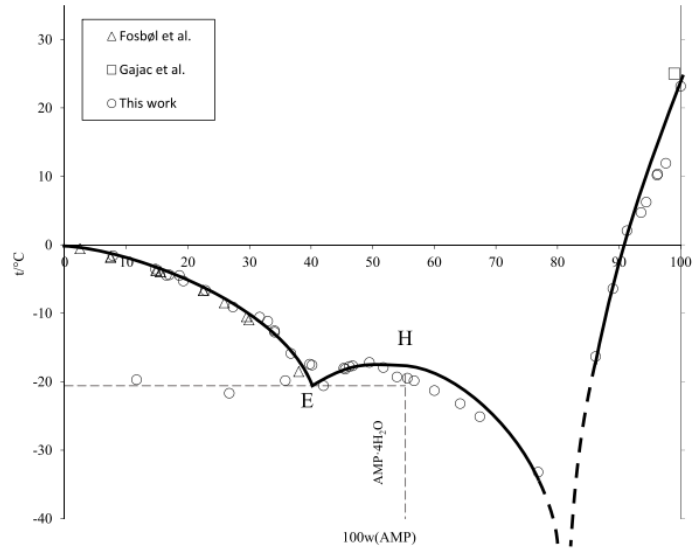
Plant operation is subject to PZ precipitation



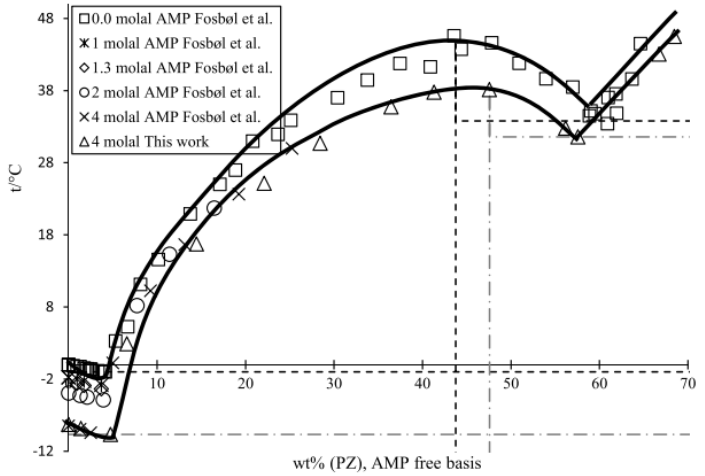


Conclusions

- Modeling philosophy for aqueous amines with CO_2
  - Concentration units should be based without any temperature dependency, fx: molality
  - Solid phase cannot be ignored when PZ is involved
- Model validation
  - Solid-liquid-vapor equilibrium (VLE & SLE)
  - Speciation
- The extended UNIQUAC model for the CO_2-PZ-H_2O system is validated and available in MS Excel macro with possible interpretation to Aspen Plus
  - Accurate thermodynamic property calculations
  - Process simulation, design, optimization, and intensification
- Work in progress: The extended UNIQUAC model for the CESAR blend (CO_2-AMP-PZ-H_2O) system
  - should be available by GHGT-18, see you in Perth, Australia? ☺



Experimental SLE of the AMP-H_2O system. Neerup et al. (2019)



Experimental SLE of the AMP-PZ-H_2O system. Fosbøl et al. (2019)

Acknowledgements

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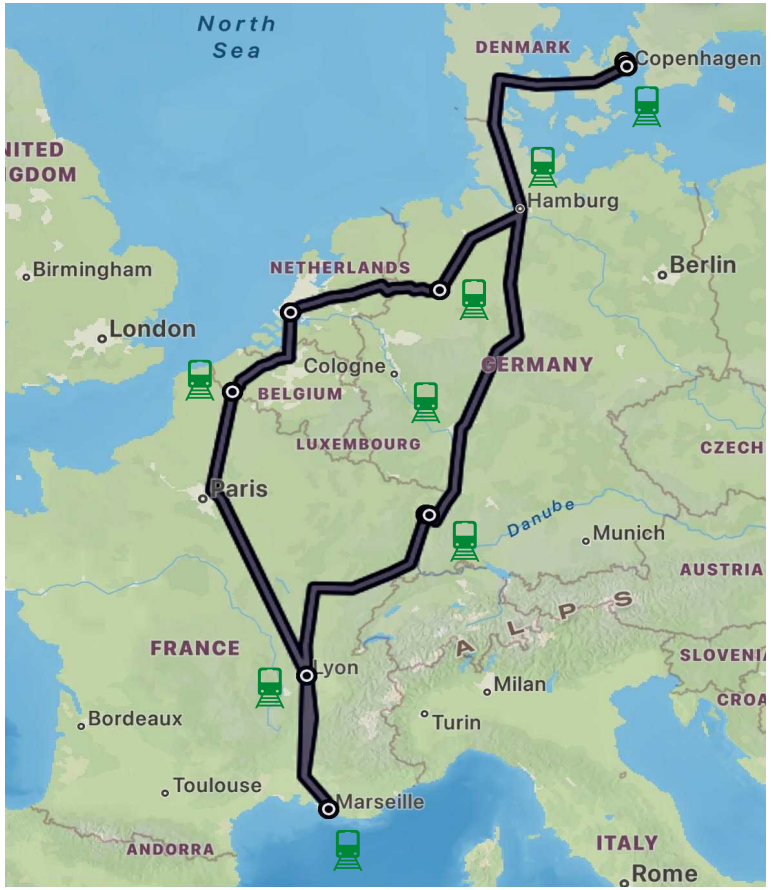
- Financial support from INNO-CCUS (Pool 1, Project 1-P1 CORT — Carbon Capture Open Tests and Review of Technologies).
- Otto Mønsteds Fond for partially funding my attendance at PCCC8.
- My colleagues for encouraging my sustainable travel choices.
  – Especially, Isaac Appelquist Løge!



Thanks for your attention!

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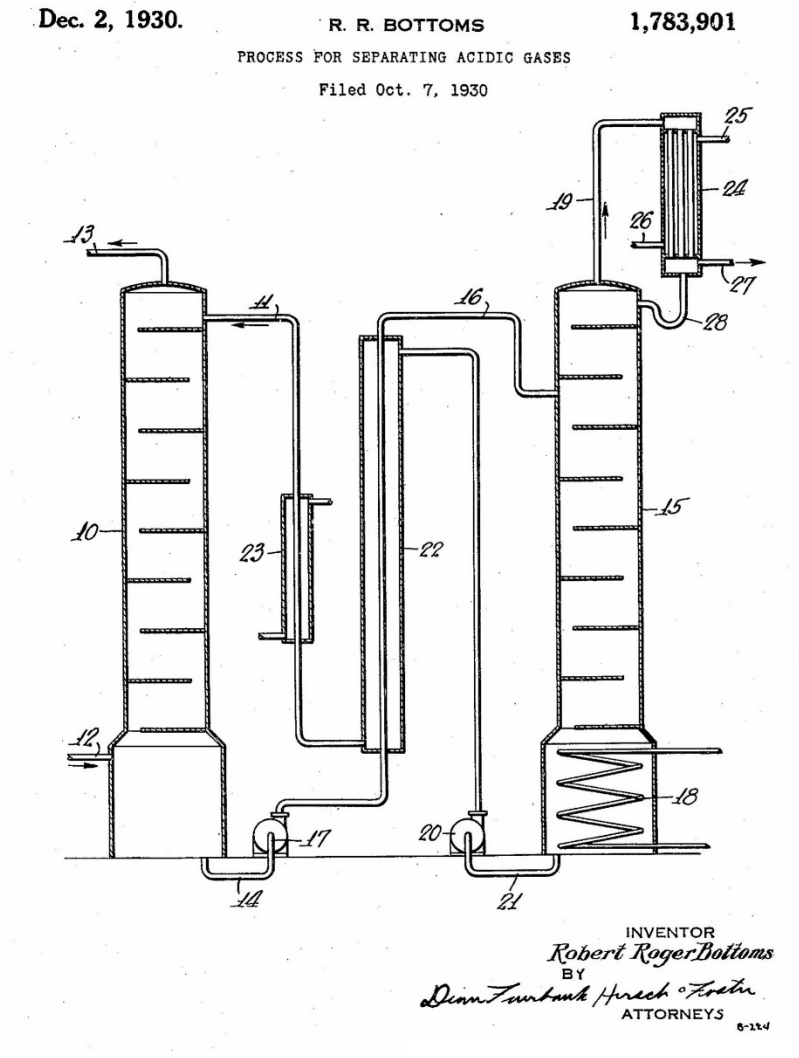
scan to connect


DTU

Acid-gas removal was patented in 1930



eNRTL framework for CESAR compositions

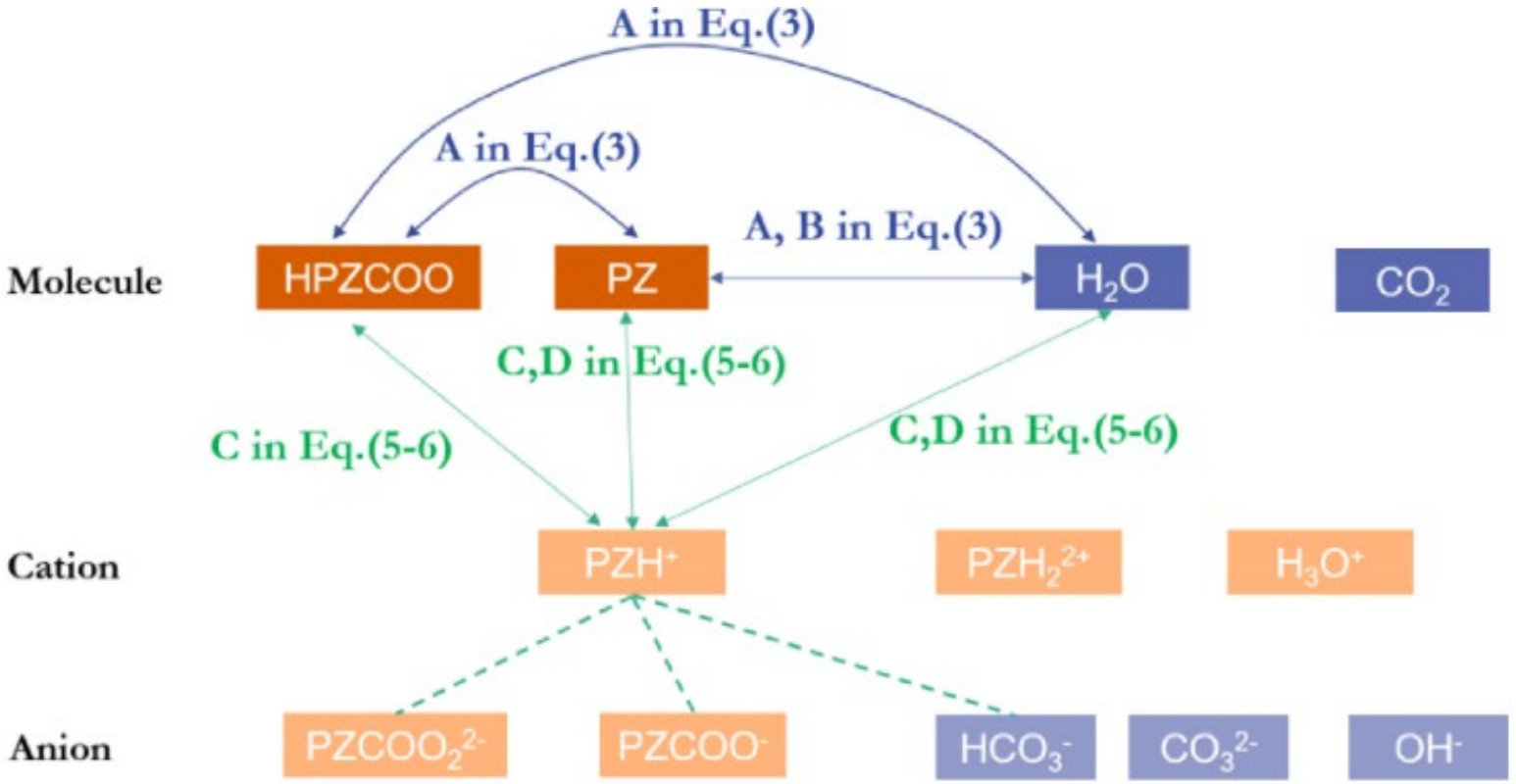
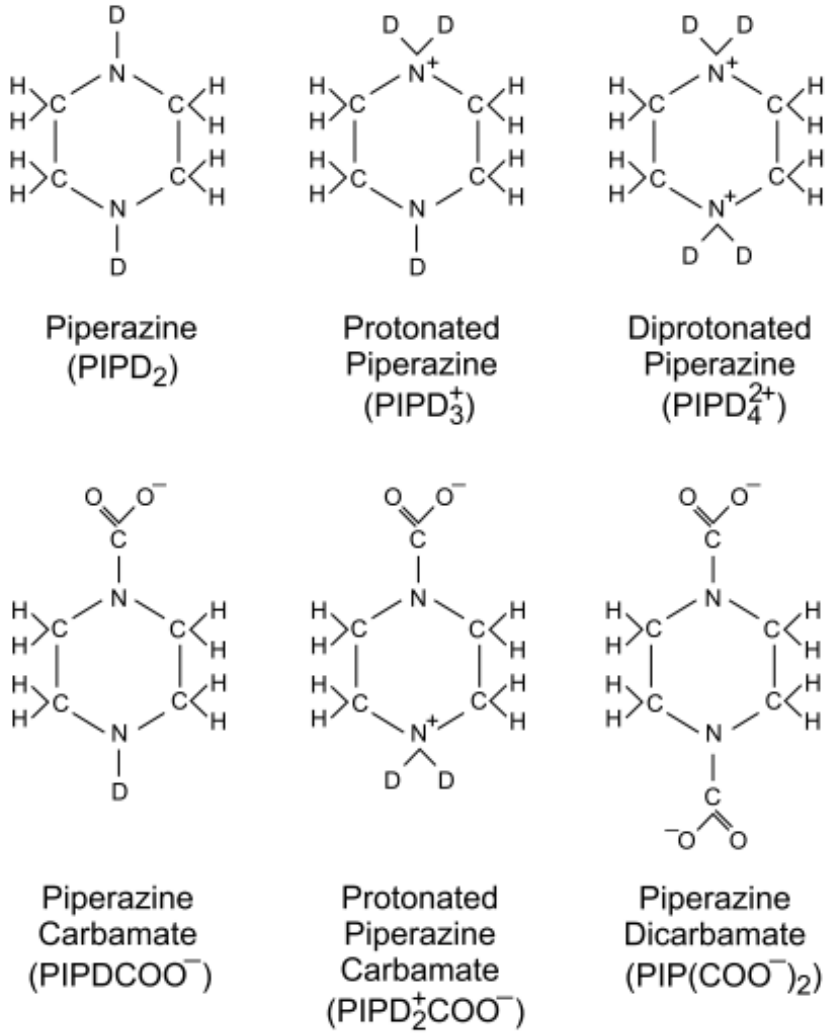


Figure by Spek et al. Separation and Purification Technology

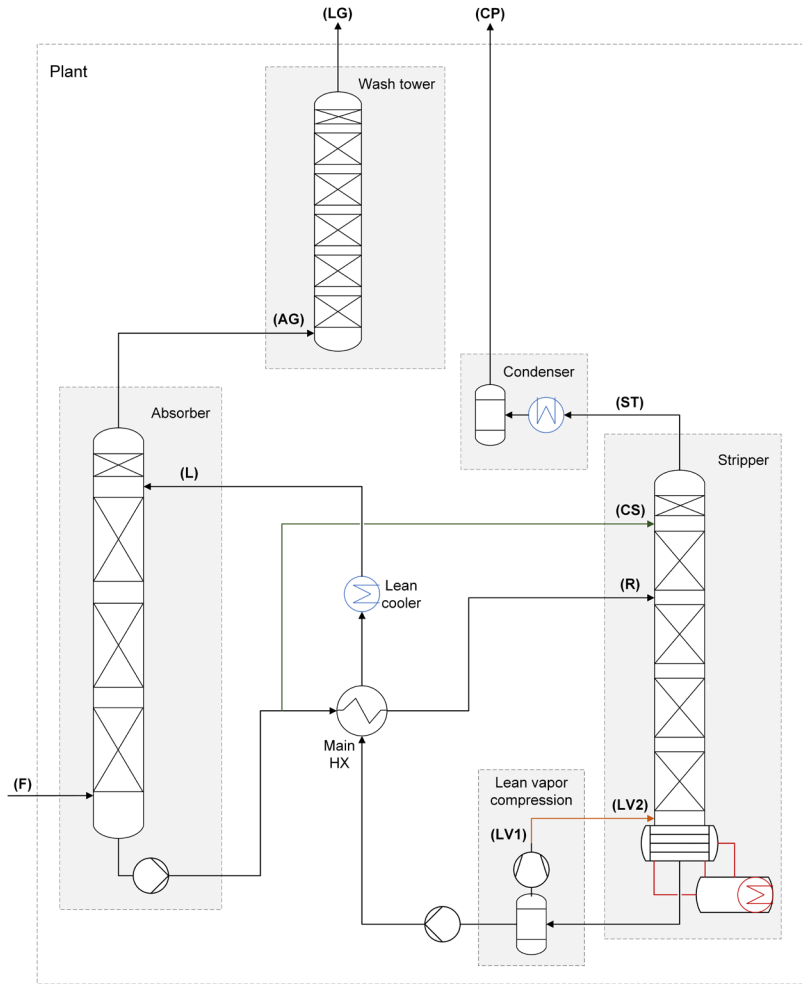
DOI: 10.1016/j.seppur.2024.127924

Speciation in the CO_2-PZ-H_2O system

Figure by Ermatchkov et al.
J. Chem. Thermodynamics
35 (2003) 1277–1289

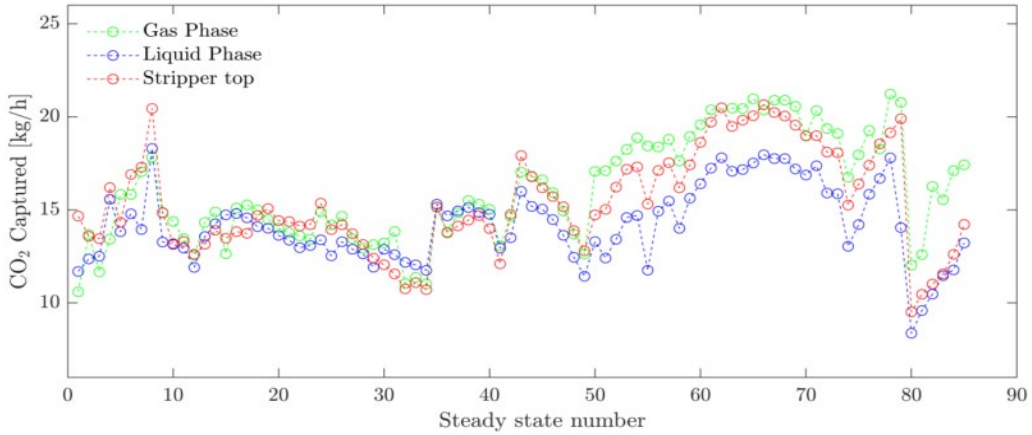


Data reconciliation to ensure accuracy in CO_2 capture and plant performance evaluation

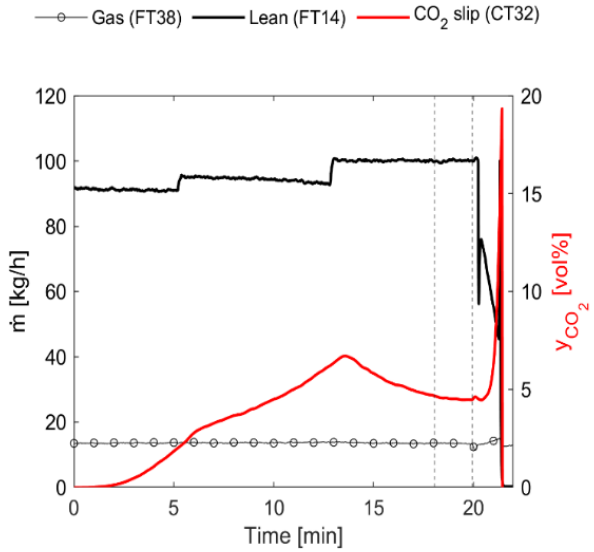


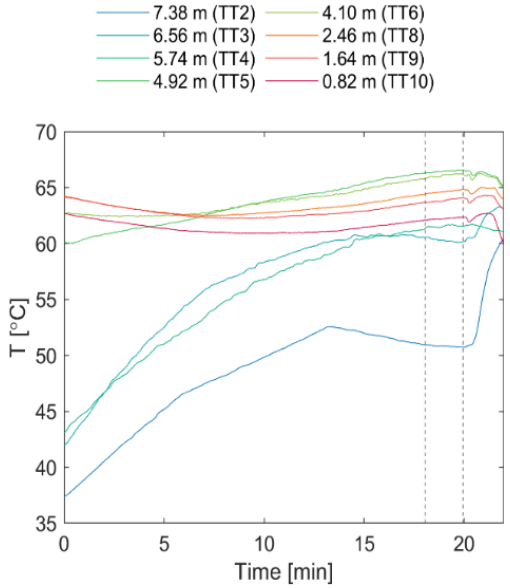
- Gas phase
  - Based on the gas phase CO_2 concentrations and flow rates of the flue gas (F) and cleaned lean gas (LG).
  - $\dot{m}_{CO_2,gas} = \left(y_{CO_2,in} \cdot \dot{n}_{flue\ gas,in} - y_{CO_2,out} \cdot \dot{n}_{flue\ gas,out}\right) \cdot M_{CO_2}$
- Liquid phase
  - Based on the liquid phase CO_2 loadings and flow rates of the lean (L) and rich solvent (R).
  - $\dot{m}_{CO_2,liquid} = \left(\alpha_{rich} \cdot \dot{n}_{rich,amine} - \alpha_{lean} \cdot \dot{n}_{lean,amine}\right) \cdot M_{CO_2}$
- Stripper top
  - Based on the CO_2 flow rate at the condenser (CP).
  - $\dot{m}_{CO_2,stripper} = \dot{m}_{condenser,gas} - \dot{m}_{water,condenser,gas}$

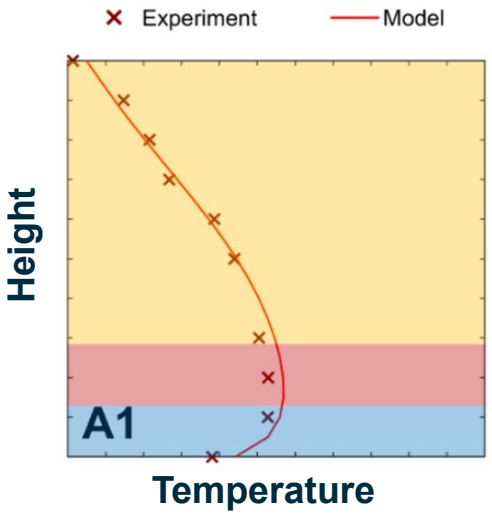
CO_2 captured flow estimated by three methods (adapted from Sai Hema Bhavya Vinjarapu).

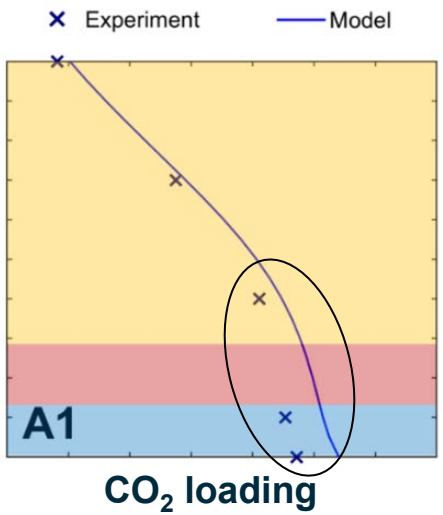


Reconciled plant variables tell more about the steady states









ε/σ values after the data reconciliation problem

SS label	Gas flow ·10³	CO_2 feed ·10³	Lean flow ·10³	CO_2 slip ·10⁵	$w_{CO2,lean}$ ·10²	$w_{CO2,rich}$	$w_{amine,1}$ ·10⁴	$w_{amine,2}$ ·10⁶	$y_{H2O,gasout}$ ·10²	$y_{H2O,recycle}$ ·10²
A1	-2.744	74.86	-10.91	2.157	5.518	-1.256	1.732	15.57	-4.91	15.76
A3	0.160	49.89	-10.68	1.888	4.811	-0.9438	-0.01062	2.067	0.123	-0.2006
A5	0.180	79.13	-13.46	39.12	6.527	-1.380	-0.01133	1.501	0.167	-0.3335
B3	0.177	3.661	-7.319	-92.75	1.550	-0.687	-0.01856	-0.1295	0.514	-0.2560
C1	-4.63	50.87	-22.47	0.0000	2.944	-0.8083	503.56	2011	-10.47	22.76
C2	-17.5	154.4	-120.9	0.2554	8.891	-2.031	1782.7	7118	-22.15	33.02

problem identified