Supercritical CO$_2$ with Water Contamination; Mixture Thermodynamic Properties at Compressor Conditions

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Motivation

- Direct-fired cycles are partially closed-loop systems where CO2 is recycled and compressed after water is condensed out of the exhaust

- Compressors in direct-fired cycles will likely be required to operate with CO2 contaminated with some level of water as the working fluid

- Water contamination will lead to droplet generation *at all* operating pressures of relevance and despite the CO2 being at supercritical conditions relative to its pure phase properties

- Generation of water rich droplets at compressor inlet potentially has significant implications for erosion and blade damage for long term operation

- Focus of our paper is on the development of accurate models for phase boundaries, density and enthalpy for supercritical CO_2 contaminated with water that can be integrated into modeling tools
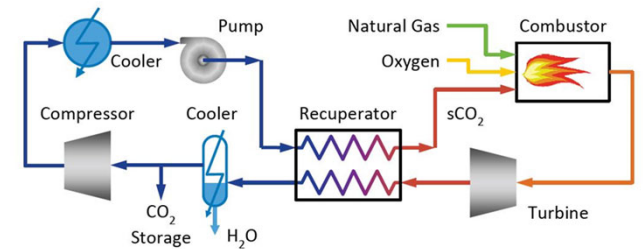

From White and Weiland (2018)
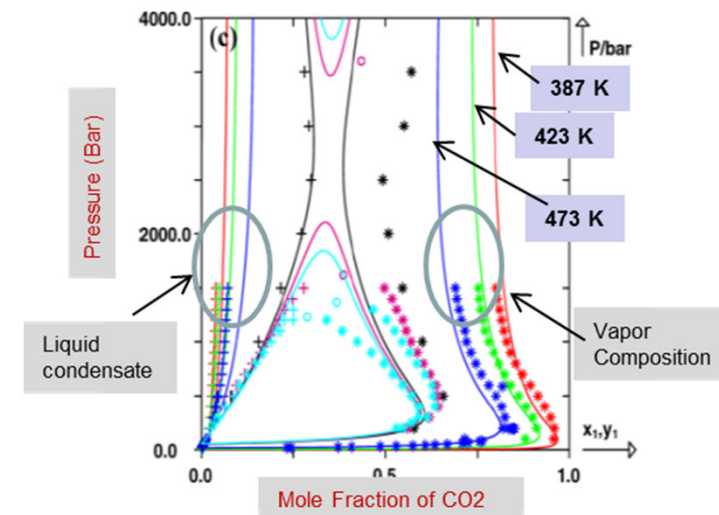
Qian, Privat, and Jaubert (2013)

Objectives for Characterizing Mixtures of CO_2/Water

- Development and Validation of of EoS/Thermodynamic Model for CO_2/Water Binary Mixture in the window of operation **290 < T < 340 K and 70 bar < P < 200 bar**.

  ➢ vapor-liquid equilibrium phase boundary as a function of temperature and pressure

  ➢ mixture density as a function of (T, P, composition)

  ➢ mixture enthalpy as a function of (T, P, composition)

- Develop analytical correlations for VLE Phase Boundaries of CO_2/Water Mixtures

- The developed models were trained and evaluated against experimental data whenever available

VLE Phase Behavior of CO$_2$/Water

- CO2/water binary mixture exhibits Type III VLE phase behavior
- Because of the large disparity in molecular polarity, CO2 and water phase separate into water-rich aqueous phase (L1) and CO2-rich liquid (L2) or vapor (V) phase
- Phase Diagram is not closed and phase separation occurs at all pressures (results shown to 25 MPa)
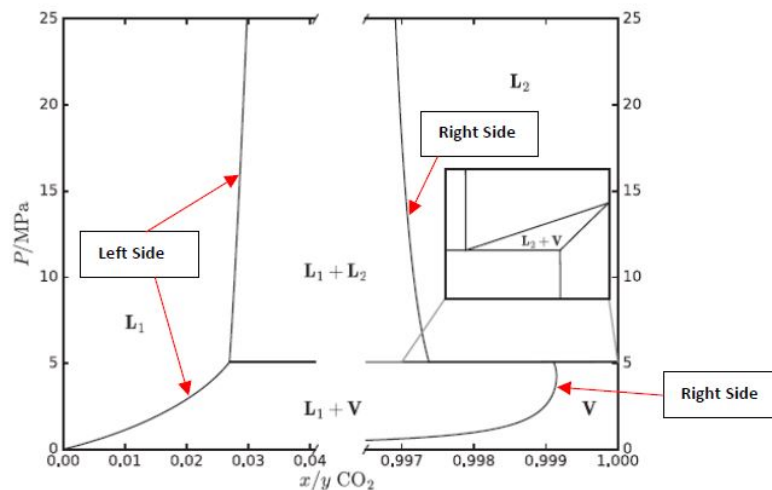
V: CO2-rich vapor phase
(right side of phase diagram)

**L1:** Water-rich (CO2-lean) aqueous liquid phase
(left side of phase diagram)

L2: CO2-rich liquid phase or supercritical compressed CO2 fluid
(right side of phase diagram)

T > UCEP, only L1+L2 phase coexistence
T < UCEP, existence of L1+V, L1+L2, and L2+V phase equilibrium.

- In the window of operation **(290 < T < 340 K and 70 bar < P < 200 bar):**

  ➢ Water rich Droplets with dilute CO2 (water-rich liquid L1) will exist at all conditions through compressor exhaust potentially leading to erosion in diffuser and volute in addition to impeller
  ➢ Vapor phase or supercritical fluid will be CO2 rich mixture (L2 or vapor V phase)
  ➢ Activity Coefficient/Fugacity ($\gamma - \phi$) Model for VLE Prediction developed since existing models in literature are inadequate

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Review of Vapor-Liquid Equilibrium (VLE) Test Data for CO2+Water Mixtures

- Large number of VLE experiments reported in open literature

- Not all studies however have measured the composition of both liquid and vapor phases at fixed temperature and pressure
  - Some studies measured only solubility of CO2 in liquid water while others measured the solubility of water in gas or liquefied CO2 phase

- Test data spans from 1 bar to 1000 bar in pressure and 273 K to 642 K in Tempearture

- Blue rectangle represents window of interest
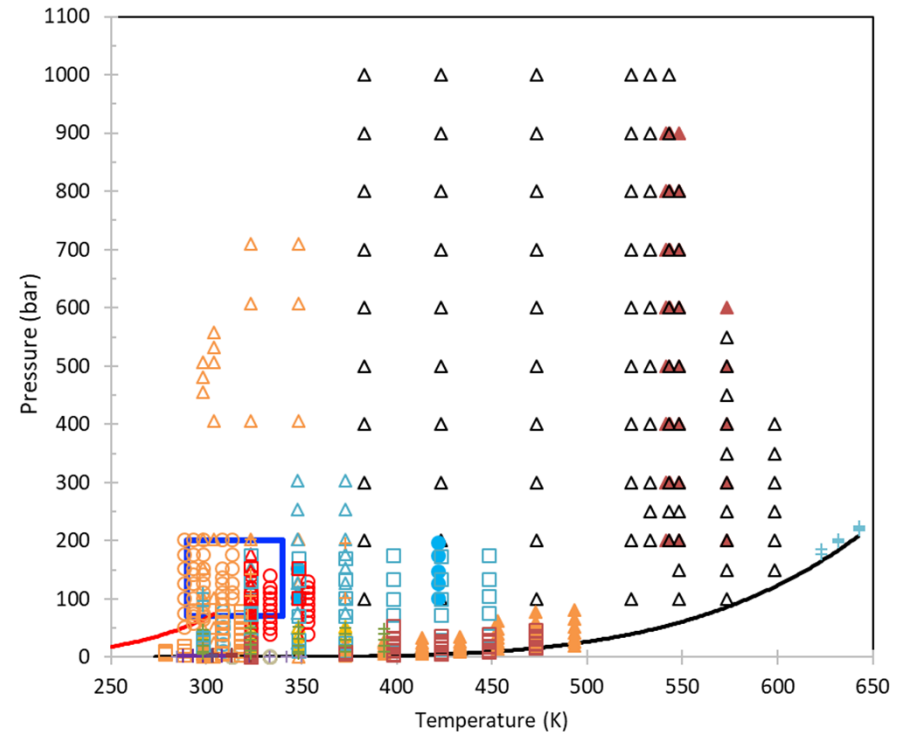
Assessment of Equation of State Models for Phase Equilibrium Prediction

- We have assessed the applicability and accuracy of common equations of state (EoS) for predicting the VLE of CO2/Water mixture
- EoS models evaluated include Peng-Robinson (PR) EoS, Soave-Redlich-Kwong (RKS) EoS, Lee-Kesler-Plocker (LKP) EoS, GERG EoS, REFPROP (v. 10) EoS (NIST), and an Activity Coefficient-Equation of State ($\gamma - \phi$) model (developed at Rutgers).
- No single thermodynamic model is able to predict all the phase boundaries (L1+L2, L1+V, L2+V) accurately in the window of operation.
- REFPROP yields accurate pure component properties and one-phase mixture properties.

Performance and Convergence of Phase Equilibrium Calculations in Windows of Operation				
	L1+L2	L1+V	L2+V	Remarks
PR (Aspen Plus 8.6)	Yes	Yes	No	Inaccurate L1 and L2 composition
RKS (Aspen Plus 8.6)	Yes	Yes	No	Inaccurate L1 and L2 composition
LKP (Aspen Plus 8.6)	Yes	Yes	No	Inaccurate L1 and L2 composition
GERG (Aspen Plus 8.6)	Yes	Yes	---	Inaccurate L1 and L2 composition
REFPROP v10 (NIST)	No	Yes	Yes	The only model that predicts L2+V phase boundary; phase equilibrium calculations did not converge for L1+L2 conditions
$\gamma - \phi$ Model (Rutgers)	Yes	Yes	No	Does not apply to L2+V phase boundary; accurate predictions of the phase compositions of L1+L2 and L1+V

Models used in VLE calculations

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Activity Coefficient/Fugacity $(\gamma - \phi)$ Model for VLE Prediction

- The fugacities of the components in the aqueous liquid phase (L1) are modeled as using activity coefficients. Since the L1 phase is a very dilute solution of CO2-in-water, the fugacities are represented by:

$$\hat{f}_w^{L1} = x_w \cdot f_w(T,P) \quad \text{and} \quad \hat{f}_{co2}^{L1} = x_{co2} \cdot H_{co2,w}(T,P)$$

Here, $f_w(T,P)$ represents the fugacity of pure water and $H_{co2,w}(T,P)$ is the Henry's constant of CO2 in water. Activity coefficients $\gamma_w = 1$ and $\gamma_{co2} = 1$.

- The fugacities of the components in the CO2-rich gas phase (V) or CO2-rich liquid (or, compressed CO2 fluid) (L2) phase are modeled using the Peng-Robinson equation of state.

$$\hat{f}_w^{L2} = y_w \cdot P \cdot \hat{\phi}_w^{L2} \quad \text{and} \quad \hat{f}_{co2}^{L2} = y_{co2} \cdot P \cdot \hat{\phi}_{co2}^{L2}$$
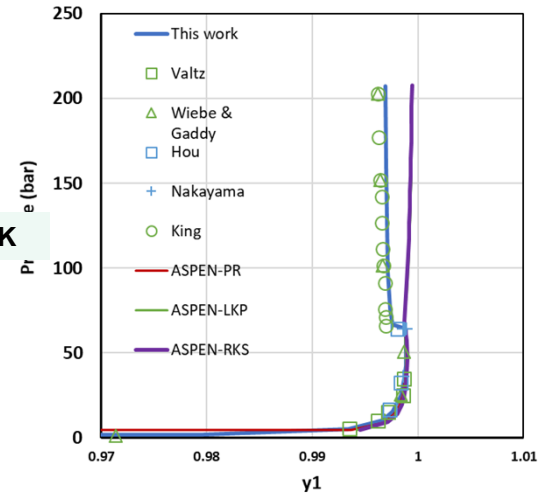
Here, $\hat{\phi}_w^{L2}$ and $\hat{\phi}_{co2}^{L2}$ are the fugacity coefficients of water and CO2, calculated using the **Peng-Robinson EoS**.

- The parameters of the $\boldsymbol{\gamma - \phi}$ model were trained using data and the model was validated against VLE data in the window of operation.

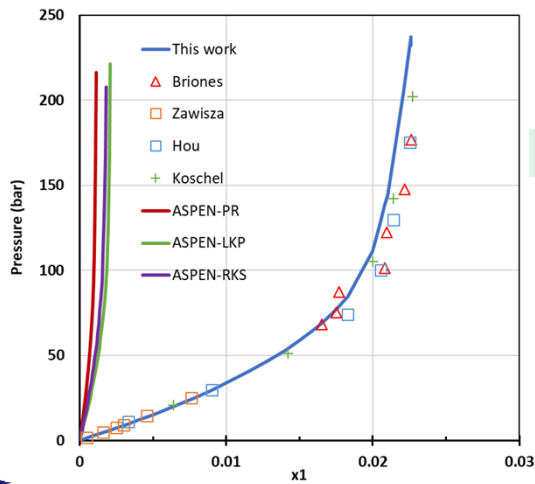# Predictive Performance of the $\gamma-\phi$ model for Phase Composition
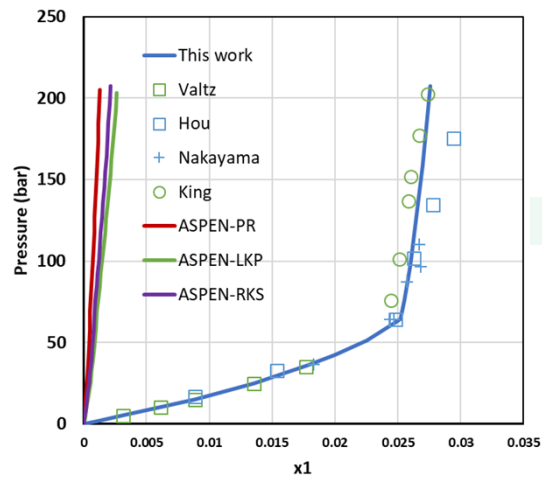
VLE CO2/Water, T=298 K

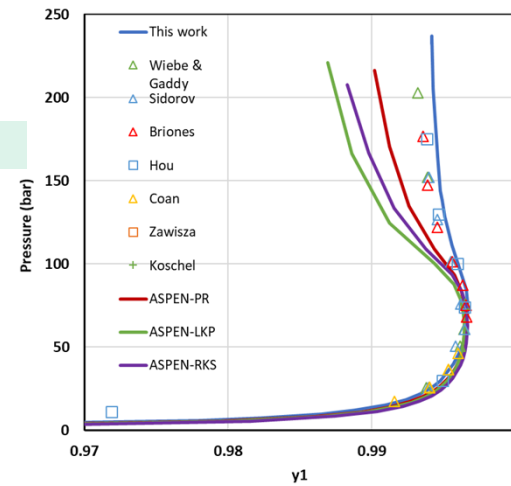VLE CO2/Water, T=323K

x1 = CO2 mole fraction in water-rich L1 liquid phase

y1 = CO2 mole fraction in CO2-rich liquid (L2) or vapor (V) phase

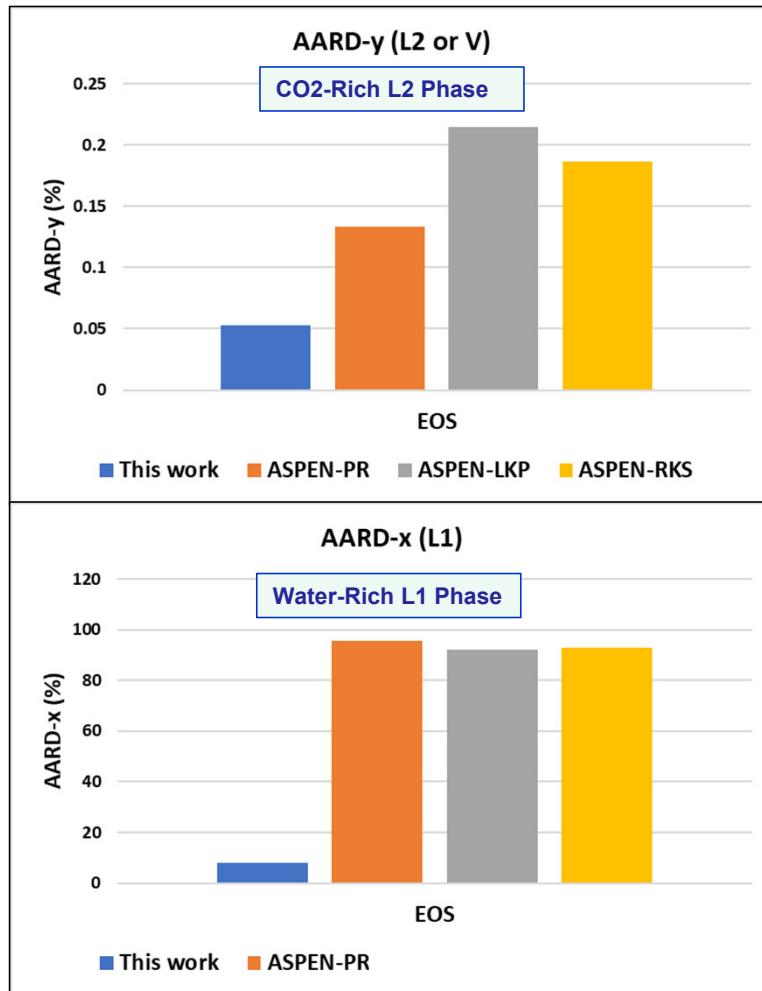# Predictive Performance of the $\gamma-\phi$ model for Phase Composition

Average absolute relative percent deviation (AARD%) of model prediction versus experimental data in window of operation: 70-200 bar

- The $\gamma-\phi$ model gives the most accurate predictions of the mole fraction of CO2 in the CO2-rich liquid (L2) or CO2-rich vapor (V) phase, with the smallest AARD-y < 0.08%, compared with PR, RKS and LKP.

- The $\gamma-\phi$ model is able to capture the 'kink' (at ~ 60 bar for T=298 K) when the system transitions from liquid-vapor (L1-V) to liquid-liquid (L1-L2) phase equilibrium.

- The PR, RKS and LKP EoS greatly underestimate the solubility (mole fraction x1) of CO2 in the water-rich liquid phase (L1) with an AARD-x ~90%. In comparison, the $\gamma-\phi$ model performs much better with an AARD-x < 8%.

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Comparison of Correlation vs Model Predictions

- $x_{L1} = b_1(T) * P^2 + c_1(T) * P + d_1(T)$

$y_{L2/V} = a_2(T) * P^3 + b_2(T) * P^2 + c_2(T) * P + d_2(T)$
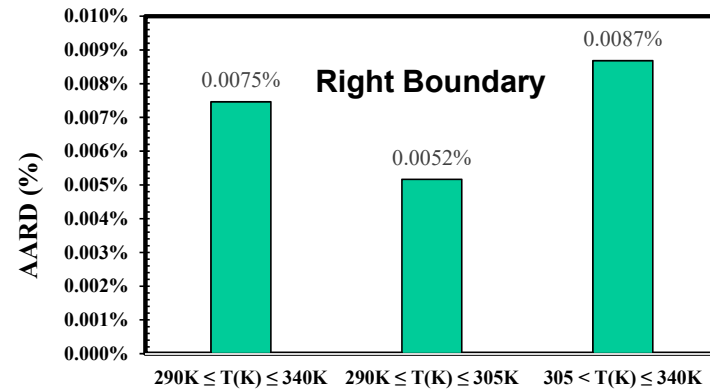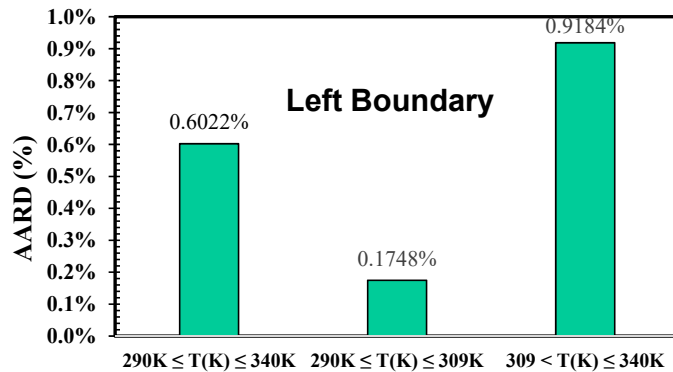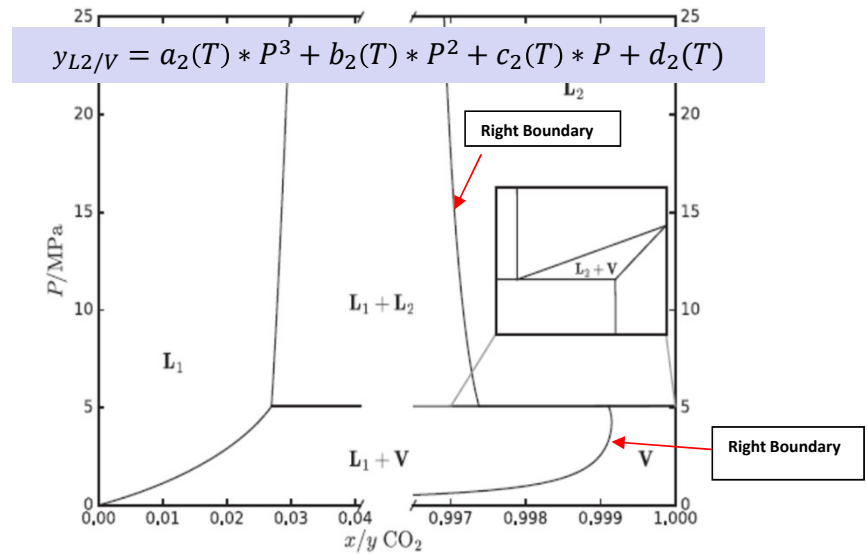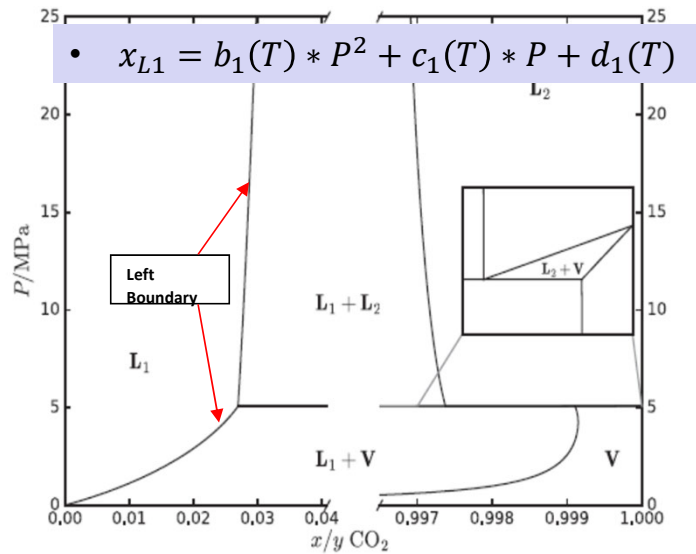
Models for Predicting Mixture Density $\rho(T, P, x_{co2})$

- In the window of operation, the mixture exists as:
    - L1 = very dilute CO2-in-Water liquid phase ($x_{co2} < 0.03$)
    - L2 or V = very dilute water-in-CO2 liquid (L2) or vapor (V) phase ($x_{co2} > 0.996$ or $x_{water} < 0.004$))
- Because the system exists as dilute solutions, CO2/Water mixture density can be estimated as perturbations of the pure water density (for L1) or pure CO2 density (for L2 or V).
    - This is achieved by representing mixture density as expansion in the solute mole fraction.
- Advantages: Numerically stable, computationally inexpensive.
- We have developed two models for density prediction:
    - **Model *d*-LM1:** predicts the density of the dilute CO2-in-Water L1 phase
    - **Model *d*-LM2:** predicts the density of the dilute water-in-CO2 liquid (L2) or vapor (V) phase
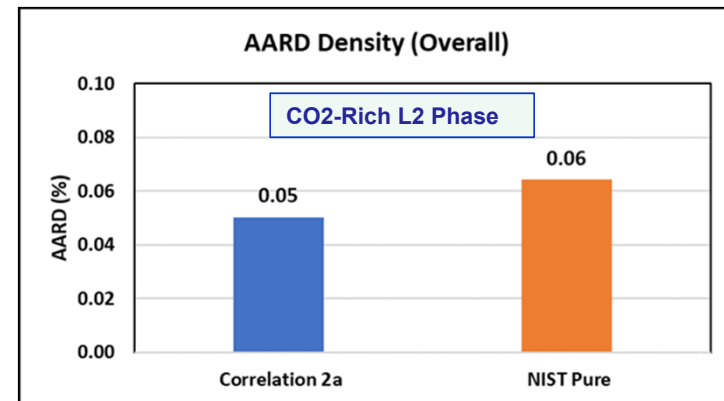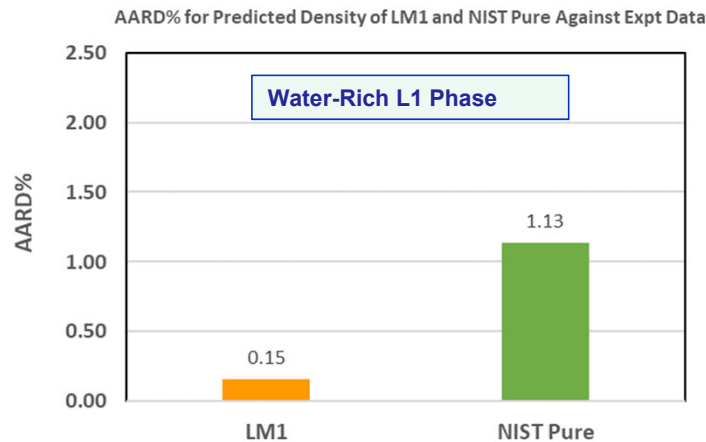
Using mole fraction weighted density from pure fluid NIST values is acceptable
Similar conclusions were reached for enthalpy of the mixture

Model h-LM1 for Estimating Enthalpy $h(T, P, x_{co2})$ of Liquid Phase L1

Molar enthalpy of mixture of phase L1 (x_1= CO2 mole fraction < 0.03):

$$h \cong x_1 \bar{H}_1^\infty + (1 - x_1)h_2$$

Molar enthalpy of pure water $h_2(T, P)$ -   Available from NIST

Infinite dilution partial molar enthalpy of CO2 in water $\bar{H}_1^\infty(\mathbf{T}, \boldsymbol{P})$:

$$\bar{H}_1^\infty(T, P) = \alpha * \frac{h_2^{NIST}(T, P_s)}{h_2^{NIST}(298, P_s)} \quad \text{[J/mol]}$$

$$\alpha = 1638.346 \qquad \text{[J/mol]}$$

$$h_2^{NIST}(298, P_s) = 1877.2 \qquad \text{[J/mol]}$$

- The linear model **h-LM1** for predicting the mixture enthalpy of liquid phase (L1) is represented by the above equations.

- There is no experimental data available for enthalpy for the water-rich L1 phase, therefore REFPROP calculated values for mixture enthalpy are used for comparison.

Model h-LM1 for Estimating Enthalpy $h(T, P, x_{co2})$ of Phase L2 and V

- Nine isotherms within the window at 13 pressures and 4 different compositions (x1=0.006, 0.008, 0.01, 0.015) were evaluated in this comparison.

- **Model h-LM1** is able to represent the REFPROP results very well with AARD% ranging from 0.87% to 1.76% for the four compositions evaluated. For all the four compositions, we observed that the AARD% is larger at T < 300 K than at higher temperatures.

- Our evaluation shows that using pure water enthalpy (NIST) to represent that of the dilute CO2-in-Water liquid mixture (L1) yields a AARD% < 2%.

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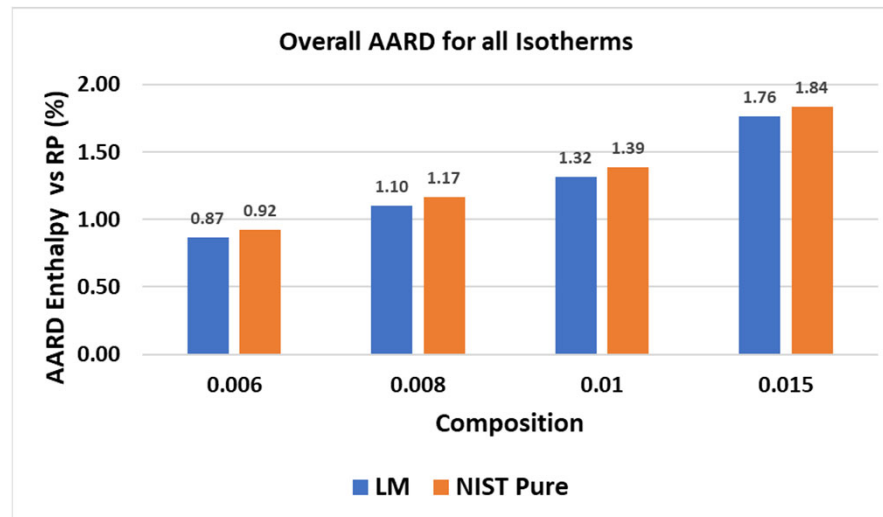
Model h-LM2 for Estimating Enthalpy $h(T, P, x_{co2})$ of Phase L2 and V

Molar enthalpy of mixture of phase L1 (x_1= CO2 mole fraction > 0.996):

$$h \cong x_1 h_1 + (1 - x_1)\bar{H}_2^\infty$$

Molar enthalpy of pure CO2, $h_1(T, P)$ -   Available from NIST

Infinite dilution partial molar enthalpy of water in CO2 $\bar{H}_2^\infty(T, P)$:

$$\bar{H}_2^\infty(T, P) = \alpha * \frac{h_1^{NIST}(T, P_c)}{h_1^{NIST}(298, P_c)}, \quad \text{[J/mol]}$$

$$\alpha = 12652.39748 \quad \text{[J/mol]}$$

$$h_1^{NIST}(298, P_c) = 11694 \quad \text{[J/mol]}$$

Molar enthalpy of pure CO2, $h_1(T, P_c)$ -   Available from NIST

- The linear model **h-LM2** for predicting the mixture enthalpy of liquid phase (L2) or vapor (V) phase is given by the above equations.

- There are no experimental data available for enthalpy for the CO2-rich liquid (L2) and vapor (V) phase, therefore REFPROP calculated values for mixture enthalpy are used for comparison.

Model h-LM2 for Estimating Enthalpy $h(T, P, x_{co2})$ of Phase L2 and V

- Eleven isotherms within the window at four different compositions (x1=0.9978, 0.998, 0.999, 0.9995) and 13 pressures that encompass the L2 and V phase were evaluated in this comparison.

- **Model h-LM2** is able to represent the REFPROP results very well with overall AARD% ranging from 0.23 to 0.04 at the four compositions considered.

- The enthalpy of the dilute water-in-CO2 L2 or V phase can be well represented by its pure CO2 values with AARD% < 0.26%.

Overall AARD for all Isotherms
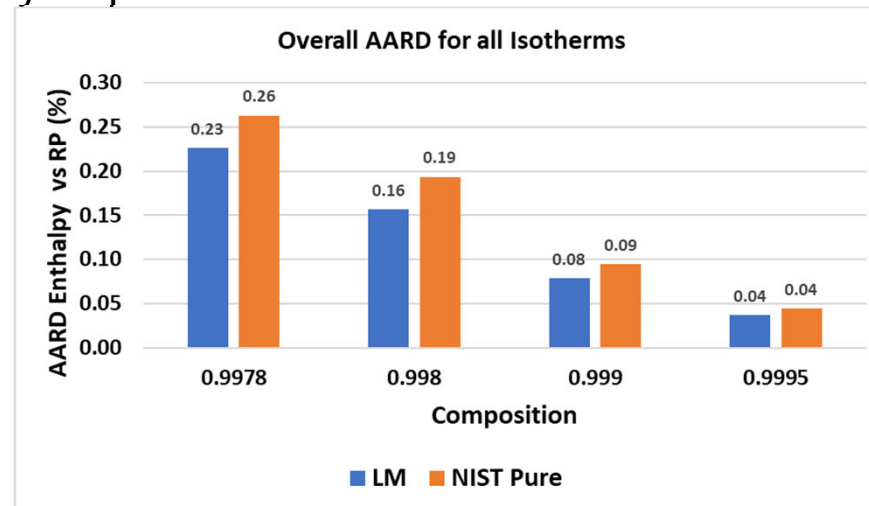
Summary

- Properties of CO2 contaminated with water developed for compressor conditions in a form suitable for integration into modeling tools
- For compressor conditions CO2 and water are practically immiscible; they separate into co-existing dilute CO2-in-water liquid droplets and dilute water-in-CO2 vapor mixtures
- Parameters of the VLE model obtained by regressing model to experimental data
  - ➢ Significant improvement in accuracy of model compared to RKS,PR and LKP EoS predictions
- Analytical thermodynamic models that are linear in CO2 mole fraction have been developed to estimate density and enthalpy of these dilute mixtures
  - ➢ Parameters of these models were obtained by fitting the data against experimental data or NIST REFPROP
  - ➢ Density and enthalpy of these mixtures do not deviate significantly from the pure solvent values
- For CFD and other system level modeling tools within an engineering framework properties of mixture in each phase can potentially be replaced by the pure phase properties of the solvent for computational efficiency

Acknowledgements