Supercritical CO₂ with Water Contamination : Mixture Thermodynamic Properties at Compressor Conditions

Yee C Chiew
Professor
Rutgers University
New Brunswick, NJ, USA

Warren Jeung
Research Associate
Rutgers University
New Brunswick, NJ, USA

Stephanie Plant
Student
Rutgers University
New Brunswick, NJ USA

Ashvin Hosangadi
Vice President
CRAFT Tech.
Pipersville, PA, USA

Timothy Weathers
Assistant Research Scientist
CRAFT Tech.
Pipersville, PA, USA

ABSTRACT

Compressors in direct-fired sCO₂ cycles may be required to operate with CO₂ contaminated with water as the working fluid. This working fluid is a highly non-ideal mixture that exhibits complex vapor-liquid phase behavior with critical properties that well exceed the critical values of the individual phases comprising it; and multi-phase effects are present even at very high pressures. Hence, reliable and accurate thermodynamic mixture models are required for conditions that are representative of sCO₂ compressors where the temperatures are in the range of 295 K – 340 K and pressures in the range of 70 bar to 200 bar. Analytical correlations for phase compositions (CO₂ and water mole fractions) as a function of temperature and pressure in these mixtures have been developed. Furthermore, new analytical models for estimating the density and enthalpy of dilute CO₂-in-water liquid and dilute water-in-CO₂ vapor mixtures have been formulated. These models were found to quantitatively represent the mixture properties of the liquid and vapor compositions reasonably well when compared with experimental data. These models and correlations will be incorporated within a numerical framework for simulating sCO₂ compressor performance in subsequent efforts.

INTRODUCTION

Direct-fired sCO₂ cycles (e.g. Allam Cycle [1]) are of significant interest to the energy community since they hold the promise of power production with "zero emissions" due to effective carbon capture and storage features [2]. A schematic of a direct fired sCO₂ power cycle loop is shown in Figure 1. The key point to note is that this is a partially closed-loop system where the combustor products directly exhaust into and drive the turbine to generate electricity. The remaining thermal energy in the exhaust is recovered in the recuperator after which the water is condensed out of the exhaust in the cooler. At this stage, a portion of the primarily CO₂ product is drawn from the loop for sequestration or other uses and the remaining CO₂ is recycled, compressed, and injected back into the combustor as a diluent to modulate temperature rise.
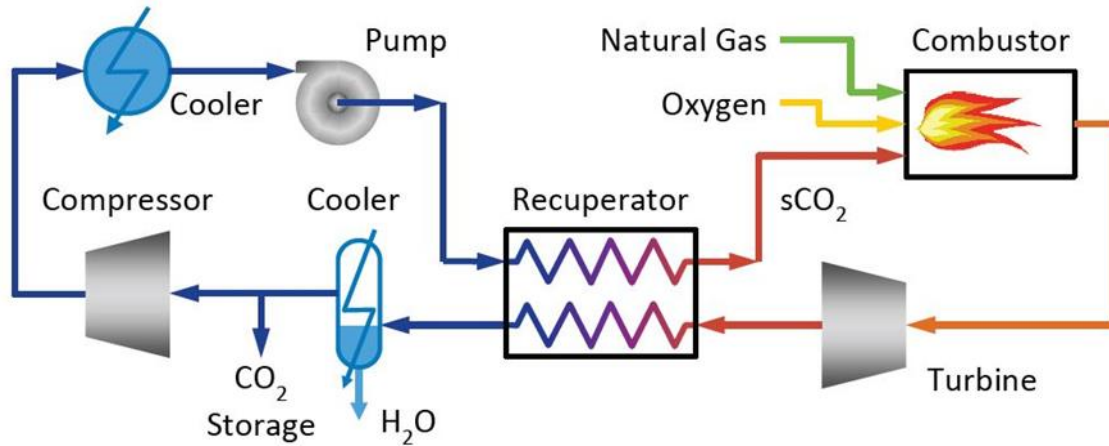
Figure 1. Schematic of a Direct-Fired sCO$_2$ Power Cycle (Taken from[2])

Our interest as part of a DoE funded SBIR effort is in the physics governing compressor operation for sCO$_2$ systems and in particular the development of high-fidelity modeling tools for compressor performance predictions [3],[4]. In indirect sCO$_2$ systems operating with nearly pure CO$_2$ (where the combustor/heat source is in a separate loop from the turbine), the fluid enters the compressor at near critical conditions (304.12 K, 7.37 MPa) and exits the compressor at supercritical pressures and temperatures. At its design point and at other supercritical inlet conditions two phase effects for pure CO$_2$ systems are expected to be minimal although condensation may potentially occur in a small region near the leading edge on the suction side of the blade. However, more substantial two-phase effects are possible when the inlet conditions show larger fluctuations (as is the case for air-cooled cycles) and the compressor operates within the saturation dome. The authors have simulated the Sandia compressor at off-design conditions for subcritical operation with phase change and validated the numerical models with test data [3]. Non-equilibrium droplet condensation models for pure CO$_2$ have also been developed and validated with fundamental nozzle data [4].

For compressors operating in direct-fired cycles (as shown in Figure 1) the physics becomes significantly more complex since it is highly likely that CO$_2$ will be contaminated with some residual water that has not been removed in the cooler. The presence of water even in dilute amounts could significantly affect the thermophysical behavior of the CO$_2$/water mixture; CO$_2$ is a nonpolar fluid while water is a highly polar substance consisting of molecules that can self-associate with each other through hydrogen bonding. The critical points of these two substances are very different (CO$_2$: Tc=304.1 K, Pc=73.8 bar; water: Tc=647 K, Pc=220.6 bar) and they form a highly non-ideal mixture that exhibits complex vapor-liquid phase behavior. Specifically, this mixture may have critical properties that exceed the critical values of the individual phases comprising it. Thus, even at the design conditions, what is a nominally supercritical inlet condition for a compressor operating in pure CO$_2$ may in fact operate at sub-critical inlet conditions when the CO$_2$ is contaminated with water. The effectively sub-critical conditions would lead to generation of water rich droplets which has significant implications for erosion and blade damage for long term operation in addition to any efficiency impact.

The behavior of CO$_2$+water mixture has been studied experimentally and reported in the literature [5]-[8]. Depending on temperature and pressure, phase equilibrium can involve multiple phases including CO$_2$-rich vapor phase (V), CO$_2$-lean aqueous liquid phase (L1), CO$_2$-rich liquid phase (L2) in the regime of interest here. Three phase behavior (V+L1+L2) exists at

temperatures and pressure below the upper critical end point (UCEP) of 7.41 MPa and 304.63 K which is very close to the critical point of pure CO_2; this could potentially affect the compressor depending on how close the design point is to the critical point. At temperatures above UCEP point for a typical compressor operating temperature range, we get a mixture of (V+L1); CO_2-rich vapor phase and CO_2-lean aqueous liquid phase. More importantly, as illustrated in Figure 2 there is no critical point defined (VLE curves not closed) at temperatures representative of compressor conditions and subcritical 2-phase behavior is observed even at very high pressures. Here the liquid phase boundary is on the left half of Figure 2 and is composed primarily of water with dilute amounts of CO_2 while the vapor phase boundary is on the right half of Figure 2 and is primarily a CO_2-rich vapor phase.
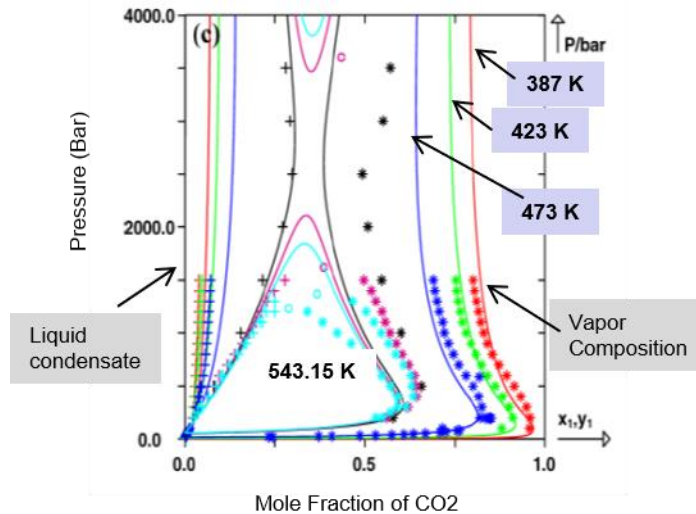

Figure 2. Vapor-liquid equilibrium of CO_2/water at Various Temperatures (from [9])

The focus of this paper is to develop models with quantitative accuracy to identify and predict the phase boundaries, the state of aggregation (vapor or liquid), phase composition, density and enthalpy of CO_2+water mixture for implementation in CFD modeling tools. Attention will be restricted to the following nominal operating window: 290 K < T < 340 K and 70 bar < P < 200 bar. The sections to follow will comprise the following: a) Review of experimental data for CO_2+water mixture properties; b) Evaluate and formulate analytical thermodynamic models for the prediction of mixture properties including VLE boundaries, density, enthalpy in the window of operation, and c) Develop correlations that provide these thermophysical properties as a function of T, P and composition for implementation in CFD tools.

REVIEW OF VAPOR-LIQUID EQUILIBRIUM (VLE) DATA FOR CO_2+WATER MIXTURES

The phase equilibrium of carbon dioxide-water mixtures is complex and it exhibits type III phase behavior based on the classification of Scott and van Konynenburg [10] with a discontinuous vapor-liquid critical curve, a wide region of liquid-liquid coexistence below the critical temperature of CO_2, and very limited mutual solubility in the regions of two- and three-phase equilibria. A large number of vapor-liquid equilibrium (VLE) data have been obtained experimentally and reported in the open literature. Not all of the studies measured the compositions of both the liquid and vapor phases at fixed temperature and pressure. Instead, some of the studies measured only the solubility of carbon dioxide in liquid water while others measured the solubility of water in the gas or liquefied carbon dioxide phase. Figure 3 shows

the thermodynamic states on the P-T plane for which VLE phase properties have been measured. The pressure spans from atmospheric to 1,000 bar and the temperature ranges from room temperature to 642 K. The window of operation (290 K < T < 340 K and 70 bar < P < 120 bar) is represented by the blue rectangle in the figure.
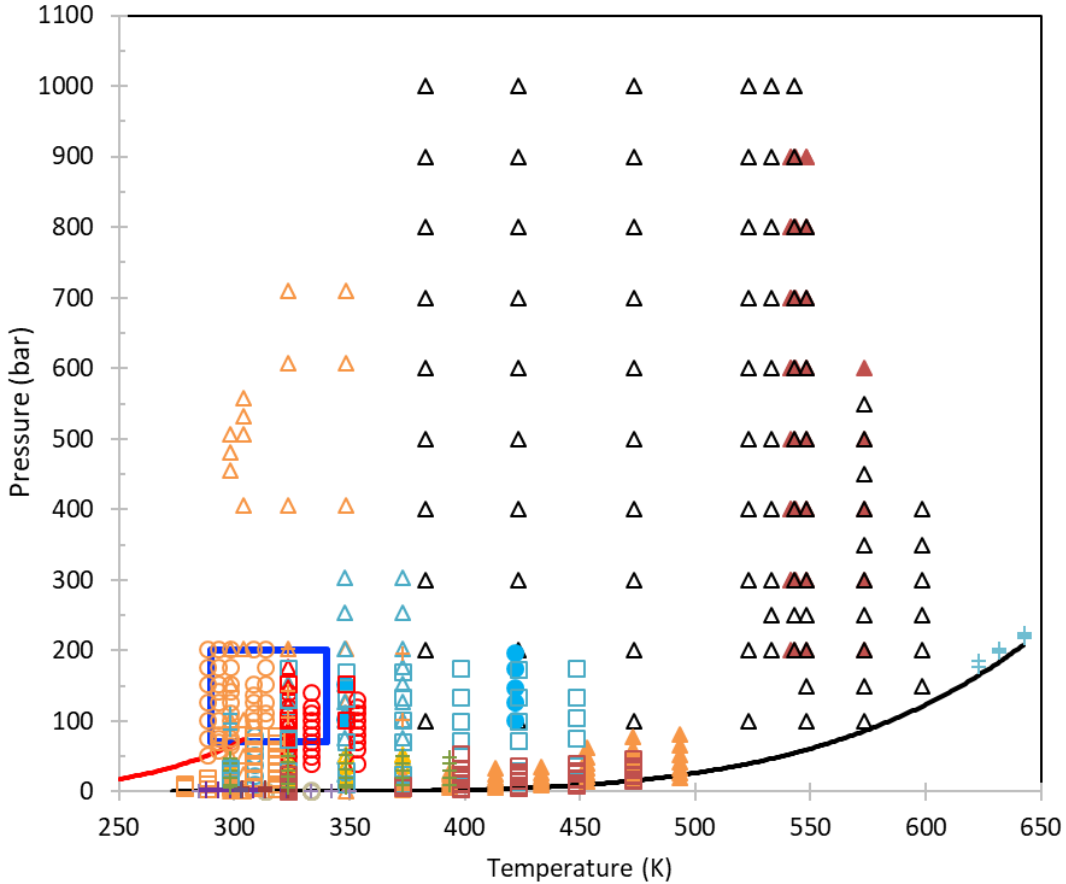

Figure 3. Pressure-temperature thermodynamic states for which vapor-liquid equilibrium data have been measured and reported. The blue rectangle represents the window of operation of interest to this work. The black and red curves represent the saturated vapor pressure of pure water and pure carbon dioxide respectively.

We evaluated the Soave-Redlich-Kwong (RKS), Peng-Robinson (PR) and Lee–Kesler–Plöcker (LKP) equations of state (EoS) to assess their accuracy for predicting the VLE phase diagram in the window of operatiton. These analytical equations of state were selected because of their mathematical simplicity and low computational costs in CFD calculations. We found notable discrepancy between the EoS predictions and experimental data suggesting the need for a more accurate thermodynamic model for VLE estimation. A representative comparison of EoS calculations and experimental data is shown in Figure 4.
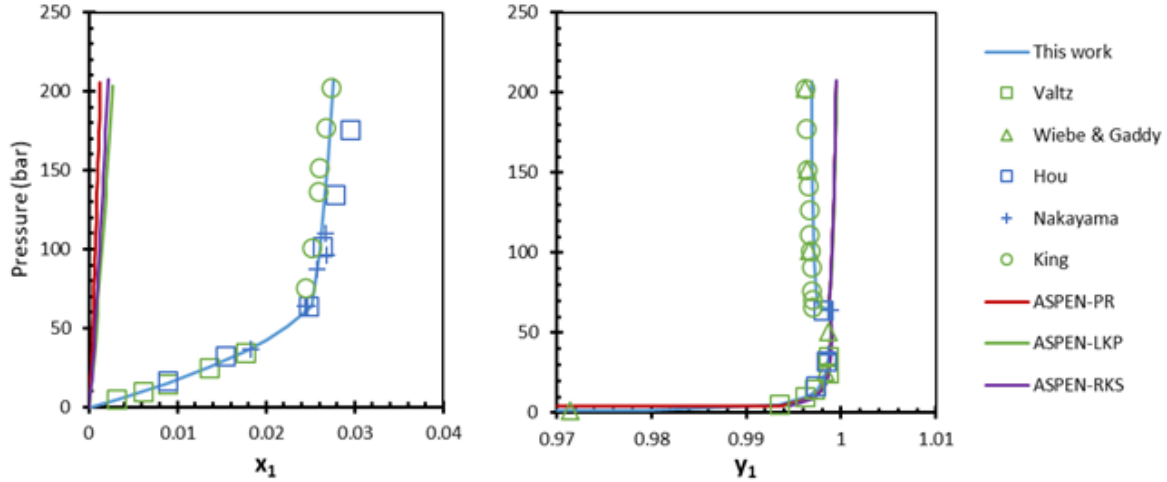
Figure 4. Vapor-liquid equilibrium of CO_2/water at T=298 K. VLE phase boundaries computed using PR, RKS, and LKP equations (Aspen software) are shown. The symbols represent experimental data reported in the literature [11]-[15]. Included in the figure is the predictions based on the thermodynamic γ–ϕ model developed in this work.

The left panel of Figure 4 indicates all three EoS models (calculated using the Aspen Plus software) underestimate the solubility of carbon dioxide in the aqueous liquid phase, with ~90% deviation error between the experimental data and model predictions. This large error stems from the fact that the EoS is unable to represent the properties of the aqueous phase at these conditions. The right panel shows that all three EoS models yield very similar results for the carbon dioxide composition. All of them overestimate the carbon dioxide mole fraction in the CO_2-rich phase and are unable to model the trend of the phase boundary for pressure exceeding ~60 bar. These deficiencies persist at other temperatures within the operating window 290 K < T < 340 K and 70 bar < P <120 bar (not shown here), therefore it is necessary to develop an alternative modeling approach that can model the aqueous phase accurately.

NEW THERMODYNAMIC MODEL FOR CO_2+WATER VLE PREDICTION

Instead of modeling both the water-rich phase and CO_2-rich phase using the same EoS, we have formulated a thermodynamic approach that models the CO_2-rich phase unsing the Peng-Robinson EoS and treat the water-rich phase using dilution solution thermodynamics. VLE phase equilibrium are given by the equal fugacity conditions:

$$y_1 P \hat{\phi}_1^G(T, P, y_1) = x_1 H_{1,2}(T, P) \tag{1}$$

$$y_2 P \hat{\phi}_2^G(T, P, y_2) = x_2 f_2^L(T, P) \tag{2}$$

In the above equations, species 1 and 2 represent CO_2 and water, respectively. The fugacity coefficient of CO_2 and water in the CO_2-rich phase are modeled by the PR EoS while the fugacity of CO_2 (species 1) and water (species 2) for the aqueous phase (right hand side of the above equations) are obtained from the Henry's constant $H_{1,2}(T, P)$ and pure water fugacity $f_2^L(T, P)$, respectively. In the aqueous phase, Henry's law reference state is used for CO_2 and Lewis Randall reference state is used for water. With these reference states, the activity coefficients for CO_2 and water are set to unity for dilute solutions. Using NIST data we obtained

an accurate correlation for the fugacity of pure water in the operating window. We represent the Henry's constant using the Krichevsky-Kasarnovsky thermodynamic relation [15]:

$$lnH_{1,2}(T,P) = lnH_{1,2}^o(T) + \frac{\bar{V}_1^\infty(P-P^o)}{RT} \qquad (3)$$

Here, $\bar{V}_1^\infty$ is the partial molar volume of solute CO_2 in solvent 2 (water) at infinite dilution and P^o denotes a reference pressure. Eq. (3) assumes $\bar{V}_1^\infty$ is independent of pressure. This assumption is valid if the solution temperature is well below the critical temperature of water and is applicable to the situation considered in this work.

Using the correlation for the low pressure Henry's constant $H_{1,2}^o(T)$ [17] and regressing Eq. (3) against VLE data, we obtained a new correlation for the Henry's constant which is used to solve for CO_2-water VLE via in Eq. (1) and (2). The thermodynamic model formulated in this effort (referred to as the $\gamma-\phi$ model) is able to predict the VLE phase boundary of CO_2+water mixture favorably well, and significantly better than the RKS, PR and LKP equations of state as illustrated in Figure 4. Figure 5 compares the predictive performance of the ($\gamma-\phi$) model against the PR, RKS, and LKP EoS. Shown in the figure are the average absolute relative deviation of calculated CO_2 vapor phase (AARD-y) and CO_2 liquid phase (AARD-x) mole fraction relative to the measured mole fraction averaged over all the temperatures and in the pressure range 70 bar < P <200 bar. Figure 5 shows that the thermodynamic $\gamma-\phi$ model is more accurate than the RKS, PR and LKP EoS models.
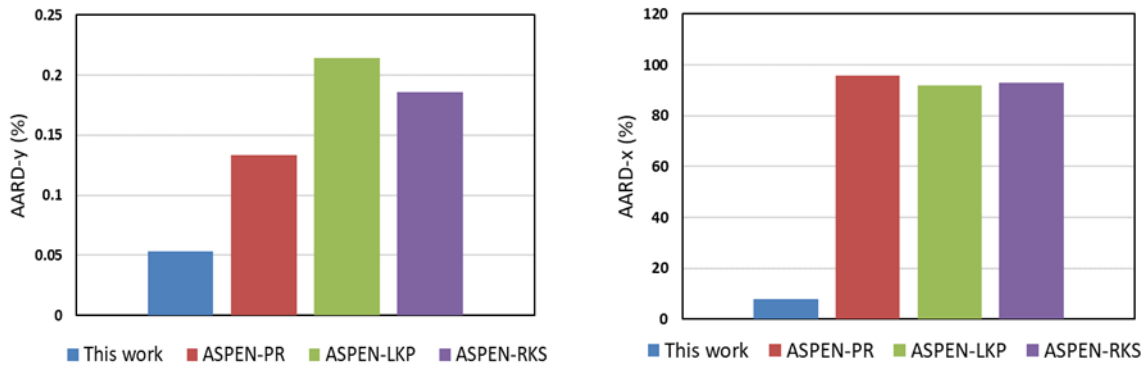

Figure 5. Comparison of the average absolute relative deviation of predicted CO₂ vapor (left panel) and liquid (right panel) phase mole fraction relative to the measured mole fraction averaged over all the temperatures considered and in the pressure range of 70 bar < P <200 bar

NEW ANALYTICAL MODELS FOR MIXTURE DENSITY AND ENTHALPY

For conditions within the nominal operating window 290 K < T < 340 K and 70 bar < P <120 bar, CO_2+water are practically immiscible and phase separtes into very dilute CO_2-in-water and water-in-CO_2 mixtures. It is of interest to develop models for estimating the density and enthalpy of these dilute solutions.

Density of Dilute CO₂-in-Water Mixture

To develop a model for density of dilute CO_2-in-water mixtures, we applied principles of dilute solution thermodynamics to estimate the density and enthalpy. For a dilute CO_2-in-water solution, the molar volume of a CO_2-in-water mixture can be approximated by

$$v = v_2 + x_1(\overline{V}_1^\infty - v_2) \tag{4}$$

Here, $\overline{V}_1^\infty$ is the partial molar volume of CO_2 in water at infinite dilution, v_2 represents the molar volume of pure water (solvent), x_1 is CO_2 mole fraction, and v is molar volume of the mixture. By comparing Eq. (4) with experimental data, we obtained an accurate correlation for $\overline{V}_1^\infty$ [18]:

$$\overline{V}_1^\infty(T, P) = \overline{V}_1^\infty(298, P_s) * [v_2(T, P_s) / v_2(298K, P_s)] \tag{5}$$

where

$$\overline{V}_1^\infty(298, P) = \frac{0.095 RT_{c1}}{P_{c1}} + 2.35 RT / c_2 \tag{6}$$

$$c_2 = (\Delta H_2^{vap} - RT) / v_2(T, P_s) \tag{7}$$

The quantity P_s is the saturation pressure of pure water. The density of a dilute CO_2-in-water mixture can be estimated using Eqs. (4) - (7) and

$$\rho(T, P, x_1) = 1 / v(T, P, x_1) \tag{8}$$

We found that the proposed analytical model is able to predict the density of dilute CO_2-in-water mixture very well with an average absolute relative deviation (AARD%) of 0.15% compared against experimental data in the window of operation. Here, AARD% is defined by:

$$AARD(\%) = \frac{1}{N} \Sigma_i^N \; | \; \frac{\rho_{Model} - \rho_{exp}}{\rho_{exp}} \; | * 100 \tag{9}$$

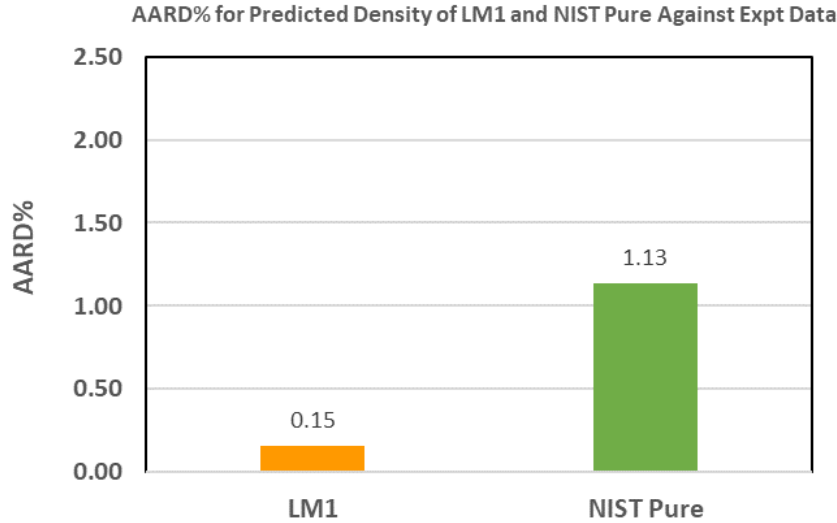AARD% for Predicted Density of LM1 and NIST Pure Against Expt Data

Figure 6 . Overall AARD for density of dilute CO_2-in-Water against experimental from 293-332 K at 76-199 bar at CO_2 mole fractions ranging from 0.009 to 0.029.

Density of Dilute Water-in-CO_2 Mixture

We extend this approach to formulate a analytical linear model (LM) for the density of dilute water-in-CO_2 mixture. In this case, the molar volume of the mixture is

$$v(T, P, y_1) = y_1 v_1 + (1 - y_1)\overline{V}_2^\infty \tag{10}$$

$$\overline{V}_2^\infty(T, P) = -2.00 * 10^{(-5)} * [v_1(T, P_c) / v_1(298K, P_c)] \ [\text{m}^3/\text{mol}] \tag{11}$$

In Eq. (11), the quantity $v_1(T, P_C) = a + bT + cT^2$ where the parameters a, b and c are parameters obtained by regressing the model against NIST REFPROP density results. We calculated the density of a dilute water+CO_2 mixture using the LM model (Eq. (9), (10), and (11)) and compared them with NIST REFPROP data from 290-340 K at 65-200 bar at a CO_2 mole fraction of 0.9995. We found that Eq. (9), (10), and (11) are able to represent the NIST REFPROP data very well with an overall AARD% of 0.05% (see Figure 7 below). We also note from Figure 7 that the density of these dilute water-in-CO_2 mixtures can be well represented by pure CO_2 density.
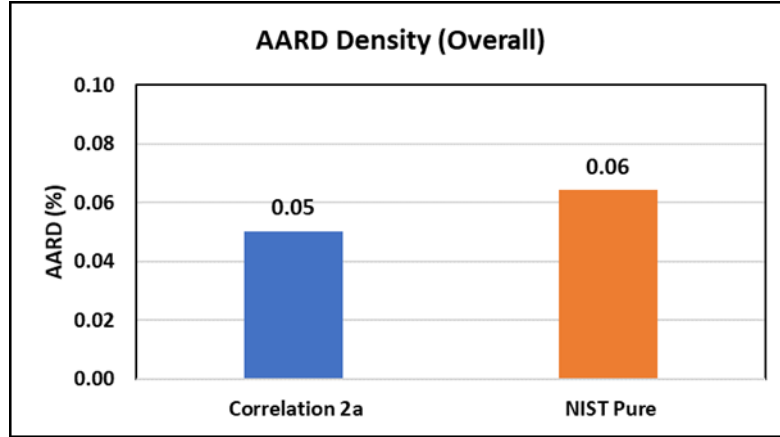
Figure 7. Overall AARD for density against REFPROP for CO_2 Mole Fraction of 0.9995 from 290-340 K at 65-200 bar.

Enthalpy of Dilute CO_2-in-Water Mixture

In addition, we developed the following analytical linear model for the enthalpy of dilute CO_2-in-water mixtures:

$$h = x_1 \overline{H}_1^{\infty} + (1 - x_1)h_2 \tag{12}$$

$$\overline{H}_1^{\infty}(T, P) = \alpha * \frac{h_2(T, P_s)}{h_2(298, P_s)} \quad \text{and} \quad \alpha = 1638.346 \quad [\text{in J/mol}] \tag{13}$$

Here, $h_2(T, P)$ represents the molar enthalpy of pure water. The quantity $\overline{H}_1^{\infty}(T, P)$ is the infinite dilution partial molar volume of CO_2-in-water, given by Eq. (13). In the above equation, $h_2(T, P_s)$ represents the molar enthalpy of pure liquid water at saturation at temperature T. We applied the linear model (LM), Eq. (12) and (13), to calculate the mixture enthalpy over nine temperataures from 290 K to 335 K, 13 different pressures from 75 bar - 195 bar and 4 different compositions (x_{CO2} = 0.006, 0.008, 0.01, 0.015) inside the window of operation and compared them to NIST REFPROP calculations. Figure 8 shows that the AARD% for the linear model (Eq. (12) and (13)) against REFPROP calculations vary from 0.87% to 1.76% as the carbon dioxide mole fraction increases from 0.006 to 0.015. We also considered the case of pure water versus REFPROP and found that the AARD% is small (< 2%) suggesting that the mixture enthalpy of the dilute CO_2-in-water mixture can be reasonably represented by the enthalpy of pure water.
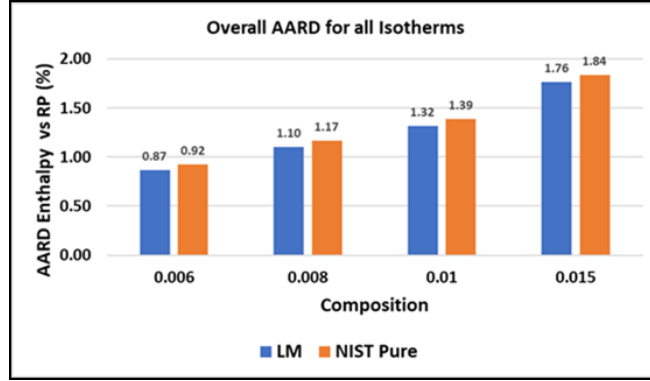
Figure 8. AARD% for the linear model (LM) versus REFPROP results for dilute CO₂-in-water mixtures. AARD% for pure water is also included.

Enthalpy of Dilute Water-in-CO₂ Mixture

The enthalpy of dilute water-in-CO_2 mixture can be represented by the following analytical linear model:

$$h = x_1 h_1 + (1 - x_1)\overline{H}_2^{\infty} \tag{14}$$

$$\overline{H}_2^{\infty}(T,P) = \alpha * \frac{h_1(T,P_c)}{h_1(298,P_c)} \;,\; [\text{J/mol}] \tag{15}$$

$$\alpha = 12652.397 \;\; \text{and} \;\; h_1(298,P_c) = 11,694 \;\; [\text{J/mol}] \tag{16}$$

We applied the linear model (LM), Eqs. (14)-(16) to estimate the mixture enthalpy of dilute water-in-CO_2 mixture at 11 temperatures from 290 K to 335 K, 13 pressures from 75 bar to 195 bar within the window of operation at four different compositions (x_1= 0.9978, 0.998, 0.999, 0.9995) and found that the proposed linear model (Eq. (14)-(16)) is able to represent the REFPROP results very well with overall AARD% ranging from 0.23% to 0.04% (refer to Figure 9 below).
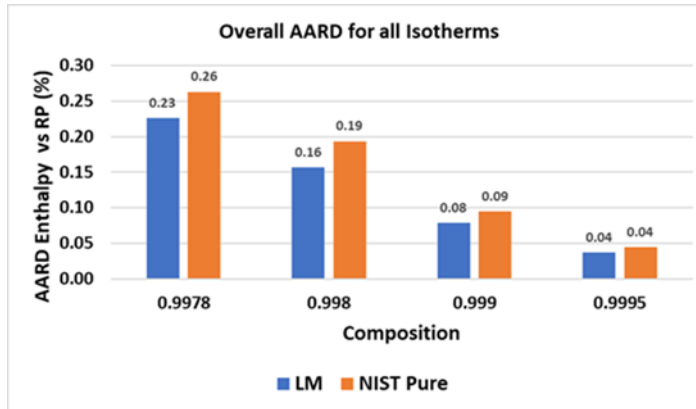

Figure 9. AARD% for the linear model (LM) versus REFPROP results for dilute water-in-CO₂ mixtures. AARD% for pure water is also included.

CORRELATIONS FOR CO₂+WATER VLE PHASE BOUNDARIES

As discussed earlier, we have successfully developed a thermodynamic model that accurately predicts the VLE of CO_2+water at any temperature and pressure within the operating window: 290 K < T < 340 K and 70 bar < P < 200 bar (see Figure 5). Although the VLE $\gamma-\phi$ model can be implemented in a CFD simulation when the phase compositions (CO_2 mole fractions) at given temperature and pressure are needed, these expressions are computationally expensive to compute on the fly. To ensure computational efficiency and speed, we have computed the CO_2+water vapor-liquid phase compositions in 290 K < T < 340 K and 70 bar < P < 200 bar, and correlated them against temperature and pressure. For the case of the dilute CO_2-in-water phase, the CO_2 mole fraction x_1 is represented by

$$x_1 = b_1(T)*P^2 + c_1(T)*P + d_1(T) \tag{17}$$

where b_1, c_1 and d_1 are temperature dependent coefficients. Similarly for the dilute water-in-CO_2 phase, the CO_2 mole fraction y_1

$$y_1 = a_2(T)*P^3 + b_2(T)*P^2 + c_2(T)*P + d_2(T) \tag{18}$$

Here, a_2, b_2, c_2 and d_2 are temperature dependent coefficients. These coefficients are represented as polynomials and are obtained by comparing them to $\gamma-\phi$ model calculations. We found that the correlations Eq. (17) and (18) are able to accurately reproduce the phase compositions predicted by the VLE thermodynamic model.

Comparison of these two calculations for temperature and pressure inside the operating window shows AARD% of 0.92% and 0.009% for the dilute CO_2-in-water and water-in-CO_2 phase boundaries, respectively. Figure 10 shows representative comparison of the phase boundary calculated from using the correlations and the VLE thermodynamic model along with experimental data. It is clearly seen that the correlations are able to represent the compositions of the VLE phase boundaries accurately and they can be implemented in CFD computational tools for turbomachinery simulations without large cost overheads.
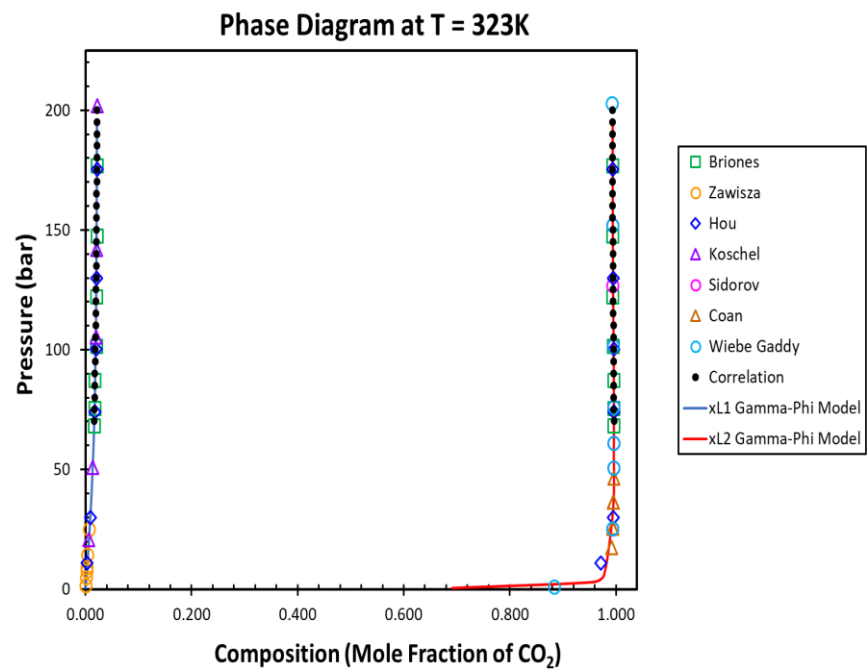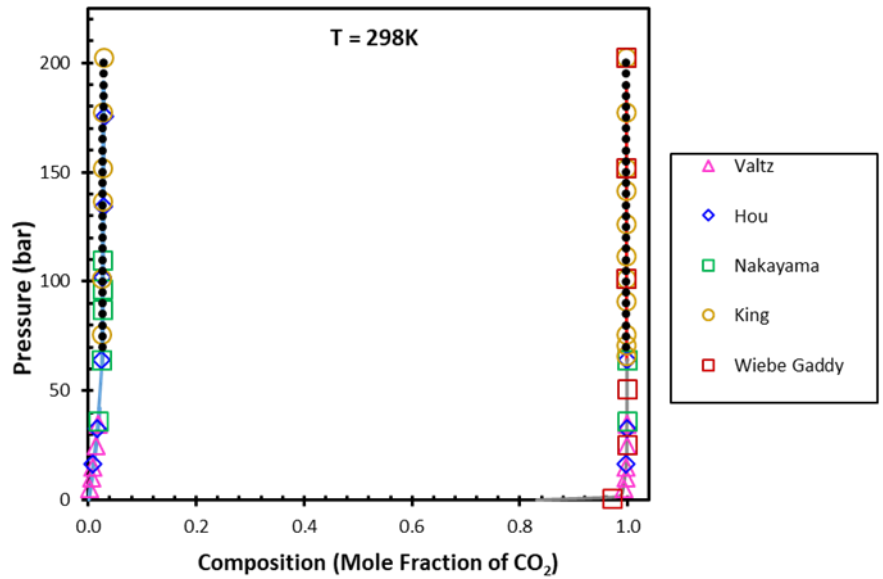
Figure 10. P-x-y phase diagram for CO_2+water mixture at 298 K and 323 K. Black circles represent prediction of the phase boundaries using the correlations. Solid curves represent predictions from the thermodynamic VLE γ–ϕ model. Open symbols represent experimental data [11-15,19-23].

CONCLUDING REMARKS

Thermodynamic models with quantitative accuracy to identify and predict the vapor-liquid phase boundary of CO_2+water mixtures for the nominal operating window: 290 K < T < 340 K and 70 bar < P < 200 bar, have been developed for implementation in CFD modeling tools. Parameters for the VLE model were obtained by regressing the model to experimental data in this operating window. The VLE model is able to represent experimental VLE data favorably well, and notably better than the predictive accuracy of RKS, PR and LKP equations of state. We computed the compositions of the co-existing CO_2-in-water and water-in-CO_2 phases as a function of temperature and pressure and developed analytical expressions for the phase compositions as a function of temperature and pressure. These correlations ensures computational efficiency and ease of phase equilibrium property retrieval in CFD turbomachinery simulations.

For the temperature and pressure range considered here, CO_2 and water are practically immiscible; the system phase separates into coexisting dilute CO_2-in-water liquid mixture and dilute water-in-CO_2 vapor mixtures. Analytical thermodynamic models that are linear in CO_2 mole fraction have been developed to estimate the density and enthalpy of these dilute mixtures. The parameters for these models were obtained by fitting the model against experimental data or NIST REFPROP data. The linear analytical models were found to represent the density and enthalpy of these dilute solutions very well. Our analysis further indicates that the density and enthalpy of these mixtures do not deviate significantly from their pure solvent values, hence for CFD simulations for engineering applications, it might be advantageous to represent the properties of dilute mixtures by the properties of the pure solvent for computation efficiency and speed.

REFERENCES

[1] Allam, R., et al., "The Oxy-Fuel, Supercritical CO_2 Allam Cycle: New Cycle Developments to Produce Even Lower-Cost Electricity from Fossil Fuels Without Atmospheric Emissions," ASME Turbo Expo 2014.
[2] White, C., and Weiland, N., "Preliminary Cost and Performance Results for a natural Gas-Fired Direct SCO_2 Power Plant, "The 6th International Supercritical CO_2 Power Cycles Symp, 2018.
[3] Hosangadi, A., Liu, Z., Weathers, T., Ahuja, V., and Busby, J., "Modeling Multi-Phase Effects in CO_2 Compressors at Subcritical Conditions," *J. Engg. Gas Turbines and Power*, Vol.141., August 2019.
[4] Brinckman, K. Hosangadi, A., Liu, Z., and Weathers, T., "Numerical Simulation of Non-Equilibrium Condensation in Supercritical CO_2 Compressors", ASME Turbo Expo 2019.
[5] Wiebe, R. "The Binary System Carbon Dioxide-Water under Pressure." *Chem. Rev.* (1941) 20, 475-481.
[6] Bamberger, A., Sieder, G., Maurer, G., "High-pressure (vapor_liquid) equilibrium in binary mixtures of (carbon dioxide-water or acetic acid) at temperatures from 313 to 353 K." Journal of Supercritical Fluids 17 (2000) 97–110.
[7] Chapoy, A., Mohammadi, A.H., Chareton, A., Tohidi, B., and Richon, D., "Measurement and Modeling of Gas Solubility and Literature Review of the Properties for the Carbon Dioxide-Water System." Ind. Eng. Chem. Res. (2004) 43, 1794-1802.
[8] Alain Valtz, Antonin Chapoy, Christophe Coquelet, Patrice Paricaud, Dominique Richon, "Vapour–liquid equilibria in the carbon dioxide–water system, measurement and modelling from 278.2 to 318.2K." *Fluid Phase Equilibria,* 226 (2004) 333–344.

[9] JW Qian, R Privat, JN Jaubert, "Predicting the phase equilibria, critical phenomena, and mixing enthalpies of binary aqueous systems containing alkanes, cycloalkanes, aromatics, alkenes, and gases (N2, CO_2, H2S, H2) with the PPR78 equation of state," Industrial & Engineering Chemistry Research 52 (46) (2013) 16457-16490

[10] Scott, R.L., van Konynenburg, P.H., Critical lines and phase equilibria in binary van der Waals mixtures, Philosophical Transactions of the Royal Society of London, Series A, 1980 298, 495-540.

[11] Valtz, A., Chapoy, A., Coquelet, C., Paricaud, P., Richon, D., Vapor-liquid equilibria in the carbon dioxide-water system, measurement and modelling from 278.2 to 318.2K, Fluid Phase Equilib., 2004, 226, 333-344.

[12] Wiebe, R., Gaddy, V.L., Vapor Phase Composition of Carbon Dioxide-Water Mixtures at Various Temperatures and at Pressures to 700 Atmospheres, J. Amer. Chem. Soc. 1941, 63, 475-477.

[13] Hou, S.-X.; Maitland, G.C.; Trusler, J.P.M., Measurement and modeling of the phase behavior of the (carbon dioxide + water) mixture at temperatures from 298.15 K to 448.15 K. J. Supercrit. Fluids, 2013, 73, 87-96.

[14] Nakayama, T., Sagara, H., Arai, K., Saito, S., High pressure liquid-liquid equilibria for the system of water, ethanol and 1,1-difluoroethane at 323.2 K, Fluid Phase Equilib., 1987, 38, 109-127.

[15] King, M.B., Mubarak, A., Kim, J.-D., Bott, T.R., The mutual solubilities of water with supercritical and liquid carbon dioxide, J. Supercrit. Fluids, 1992, 5, 296-302.

[16] Krichevsky, I.R., Kasarnovsky, J.S., Thermodynamical calculations of solubilities of nitrogen and hydrogen in water at high pressures, J. Amer. Chem. Soc, 1935, 57, 2168-2171.

[17] Posey, M.L. and Rochelle, G.T., A thermodynamic model of methyldiethanolamine-CO_2-H2S-water, Ind. Eng. Chem. Res., 1997, 36, 3944-3953.

[18] Chialvo, A.A., On the Solubility of Gases in Dilute Solutions: Organic Food for Thoughts from a Molecular Thermodynamic Perspective, Fluid Phase Equilib., 2018, 472, 94–106.

[19] Briones, J. A.; Mullins, J. C.; Thies, M. C.; Kim, B. U. Ternary phase equilibria for acetic acid-water mixtures with supercritical carbon dioxide. Fluid Phase Equilib., 1987, 36, 235-246.

[20] Zawisza, A.; Malesinska, B. Solubility of carbon dioxide in liquid water and of water in gaseous carbon dioxide in the range 0.2-5 MPa and at temperatures up to 473 K. J. Chem. Eng. Data, 1981, 26, 388-391.

[21] Coan, C. R.; King, A. D. Solubility of water in compressed carbon dioxide, nitrous oxide, and ethane. Evidence for hydration of carbon dioxide and nitrous oxide in the gas phase. J. Am. Chem. Soc., 1971, 93, 1857-1862.

[22] Koschel, D.; Coxam, J. -Y.; Rodier, L.; Majer, V. Enthalpy and solubility data of CO_2 in water and NaCl(aq) at conditions of interest for geological sequestration. Fluid Phase Equilib. 2006, 247, 107-120.

[23] Sidorov, I. P.; Kazarnovskii, Y. S.; Goldman, A. M. Solubility of water in compressed gases. Tr Gosudarst Nauch Issled I Proekt Inst Azot Prom. (Trudy GIAP) 1952; (1):48–67.

ACKNOWLEDGEMENTS

Disclaimer: "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views of and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."