Environmental Science & Technology

Determination of Dew Point Conditions for CO₂ with Impurities Using Microfluidics

Wen Song, Hossein Fadaei, and David Sinton*

Mechanical and Industrial Engineering and Institute for Sustainable Energy, University of Toronto, 5 King's College Road, Toronto, Ontario M5S 3G8, Canada

S Supporting Information



ABSTRACT: Impurities can greatly modify the phase behavior of carbon dioxide (CO_2) , with significant implications on the safety and cost of transport in pipelines. In this paper we demonstrate a microfluidic approach to measure the dew point of such mixtures, specifically the point at which water in supercritical CO_2 mixtures condenses to a liquid state. The method enables direct visualization of dew formation (~ 1–2 μ m diameter droplets) at industrially relevant concentrations, pressures, and temperatures. Dew point measurements for the well-studied case of pure CO_2 -water agreed well with previous theoretical and experimental data over the range of pressure (up to 13.17 MPa), temperature (up to 50 °C), and water content (down to 0.00229 mol fraction) studied. The microfluidic approach showed a nearly 3-fold reduction in error as compared to previous methods. When applied to a mixture with nitrogen (2.5%) and oxygen (5.8%) impurities—typical of flue gas from natural gas oxy-fuel combustion processes—the measured dew point pressure increased on average 17.55 \pm 5.4%, indicating a more stringent minimum pressure for pipeline transport. In addition to increased precision, the microfluidic method offers a direct measurement of dew formation, requires very small volumes (~10 μ L), and is applicable to ultralow water contents (<0.005 mol fractions), circumventing the limits of previous methods.

INTRODUCTION

Carbon dioxide (CO_2) injection underground is emerging as an important technology for anthropogenic climate change mitigation as well as enhanced energy resources extraction.^{1–3} Economic usage and storage of CO_2 mandates a network of pipelines to safely and reliably transport the fluid from large point sources to their respective injection sites.^{4,5} The most cost-effective method of transport minimizes pumping through CO_2 pressurization to its supercritical state so as to take advantage of its liquid-like density and gaseous mobility.^{6,7}

Centralized emission sources such as coal-fired power plants and other industrial sites are ideal candidates due to the scale and cost at which CO₂ can be captured.⁵ Economic feasibility necessitates that impurities, including water as well as nitrogen, oxygen, and sulfur compounds remain present in the final CO₂ product, with output impurity levels as high as 15%.^{7,8} The presence of such impurities, however, influences the phase dynamics of the CO₂ stream and directly impacts the safety and cost of transport in pipelines.⁹

Impurities in industrially generated CO_2 mixtures generate a phase envelope in which more than one phase can exist.¹⁰ Two phase flow in a pipeline designed for single phase flow is both dangerous and costly, and the prospect of the two-phase region imposes more stringent requirements on the allowable region for safe operation.¹¹ Specifically, water vapor condensation on pipe walls and subsequent liquid-phase acidification leads to corrosion and ultimately failure.¹² Impurities in CO₂ induce water condensation at pressures and temperatures higher than that of pure CO₂, thereby reducing the operating range available for transport.⁷ Pipeline pumping requirements significantly influence the cost feasibility of sequestration projects.⁵ It is thus critical to determine the dew point of the mixture, the lowest temperature and pressure conditions such that the mixture remains single phase supercritical without water dropout. While extensive experimental and theoretical data is available for the binary water-CO₂ system, $^{13-26}$ there is insufficient data available for pipeline design with industrially relevant CO₂

| Received: | October 15, 2013 |
|------------|-------------------|
| Revised: | December 22, 2013 |
| Accepted: | February 6, 2014 |
| Published: | February 6, 2014 |

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Environmental Science & Technology

mixtures. This deficiency of data is due, in part, to a lack of rapid methods to determine the dew point of CO_2 mixtures under relevant temperatures and pressures.

Empirical relationships such as the Peng-Robinson equation of state have been used to determine dew points of binary CO₂rich mixtures.¹³ King et al. $(1992)^{14}$ and Spycher et al. $(2003)^{13}$ were able to accurately predict the dew point of binary CO₂-water dew points from 15 to 110 °C and for pressures up to 60 MPa. However, complex phase dynamics of multicomponent mixtures are governed by properties such as intermolecular attraction, species, and composition, which are not amenable to direct prediction. Various detection methods have been used to study the solubility of water in binary and some ternary hydrocarbon mixtures, including the chilled mirror hygrometer, a NIST-referenced benchmark method.²⁷ However, operating ranges available to chilled mirror hygrometers are not relevant to CO₂ transport in industrial-scale projects. Specifically, most hygrometers are limited to water concentrations above 0.05 mol fractions with a maximum pressure of 2 MPa, whereas typical operating conditions for CO2 transport are 35-50 °C, 8.6-17.2 MPa, and less than 0.005 mol fraction in water content.⁷ In addition to limited operating ranges, conventional dew point measurements require extensive infrastructure, resulting in a high cost to provide dew point pressures over a range of temperatures for a given mixture.

Microfluidics presents an opportunity for fast and inexpensive quantification of phase change for ultralow water concentrations. Microfluidic devices have the unique advantage of high surface area to volume ratios; this attribute lends well to the detection of phase behavior for low concentrations with much more ease than those of conventional methods.²⁸ Recently, microfluidic approaches have been developed to inform thermal oil recovery,^{29,30} carbon sequestration,^{31,32} diffusion of CO₂ in brine,³¹ and diffusion of solvents in oil.³³ Notably, in fluid property measurements, microfluidics has offered orders of magnitude improvements over classical pressure-volume-temperature (PVT) cells.^{33,34} Microfluidic methods benefit from small sample volumes, relatively rapid transport, facile control of temperature and pressure, capacity for high pressure operation, and potential for multiplexing.

In this paper, a microfluidic approach is presented to determine the dew point in multispecies mixtures at pressures, temperatures, and compositions relevant to CO_2 transport. The dew point condition is observed directly in a temperatureand pressure-controlled glass microchannel. A stainless steel chip holder system with thermal control was developed for chip operation at high pressures and temperatures. To validate the approach, pure CO_2 and water was tested with results compared to previous experimental data and empirical relations. The same method was then applied to measure dew point conditions of water in a CO_2 stream with impurities typical of CO_2 captured from natural gas oxy-fuel combustion processes. This method enables direct visualization and quantification of phase change on-chip and provides a fast and economic method to delineate the limits for the safe transport of industrial CO_2 .

EXPERIMENTAL METHOD

Microfluidic Chip. A microfluidic chip was fabricated by etching a straight channel onto a piece of chrome-plated $3'' \times 1''$ Scott D263T borosilicate float glass (S.I. Howard Glass, Worcester, MA) using photolithography and wet etching. These techniques were previously demonstrated in-house.²⁹ A glass substrate was chosen due to its water-wettability,

pressure and temperature tolerance, and imperviousness to supercritical CO₂. The 6 cm × 100 μ m channel was etched to the center of the chip and square hatches were created around the channel to enhance bonding quality, resulting in improved pressure resistance. Inlet and outlet ports with a diameter of 1 mm were created by drilling into the glass prior to bonding. The etched surface was then bonded to a glass cover slide at 625 °C for 4 h to create the microfluidic chip.

A stainless steel chip holder, as shown in Figure 1, was fabricated to enable the microfluidic chip for operation at



Figure 1. Schematic of microfluidic approach with high pressure, high temperature stainless steel chip holder and a $1'' \times 3''$ glass chip. The viewing window enabled direct microscopy visual access to the sample. Heat cartridges maintained the temperature of the unit and a thermocouple was attached on the top surface of the chip for thermal control (1 mm beside the microchannel).

pressures beyond the critical pressure of CO₂. Two 50W miniature high temperature cartridge heaters (McMaster Carr #8376T22) were used to heat the holder and the chip such that on-chip visualization could be realized at the desired temperatures. The cartridges were inserted into two grooves on the top surface of the chip holder which were symmetrically placed about the microchannel. The heaters were regulated using an Omega CNi 1643-DC temperature controller (Omega Engineering Inc., Laval, QC, Canada). A thermocouple connected to the controller was adhered on the top surface of the chip 1 mm away from the center of the microchannel. Silicone heat-sink compound (McMaster Carr # 10405K79) was applied between the heaters and the steel block to aid in heat transfer. Super insulating thin aerogel (McMaster Carr #9590K8) supported by a thin aluminum sheet was used to cover the top surface of the manifold to reduce heat loss to the environment. Chip temperature was measured over an hour and showed fast initial response and stable thermal control (refer to Supporting Information (SI) Figure SI 1). An inlet and an outlet port were created on the steel holder to load the chip with high pressure fluids. O-rings (Double seal BUNA-N 004, McMaster Carr #90025K119) were used to create a leakfree interface between the steel manifold and the glass chip.

Mixture Preparation. Figure 2 shows the experimental setup. Water was first added to pure CO_2 (research grade CO_2 with 99.99% purity and less than $10 \times 10^{-6} \text{ mol}_w/\text{mol}_t$ initial water content, Praxair) and a simulated flue gas mixture (Praxair) to create the wet mixture. Deionized water was injected using a 50 μ L glass syringe (Hamilton syringe, luer tip 80501) into a sealed steel cylinder initially filled with CO_2 (150 mL, Swagelok 316L-50DF4–150) at atmospheric conditions to create the specific water content. The amount of water required to create



Figure 2. Experimental setup for sample preparation and high pressure, high temperature dew point testing. Wet mixtures were pressurized and heated in the pump and the microfluidic chip was filled at low flow rates of 1 μ L/min. Backpressure was maintained by a microvalve during filling. Dew point was determined (with no flow) through direct visualization using bright field imaging with an inverted microscope (OLYMPUS CKX41) and camera system.

the desired water concentration was calculated based on the known volume of the sample preparation system and the preparation temperature and pressure. The volume of the sample preparation system was approximated as that of the preparation cylinder (150 mL). Measurements and analysis of any additional dead volume in connecting tubes and valves indicated this value was accurate to within 0.4%. The volume of water addition, $V_{\rm H_2O}$, required to generate $V_{\rm sample} = 150$ mL of wet mixture at the preparation conditions with the desired water concentration, $y_{\rm H_2O}$, in the initial pure CO₂ or CO₂-mixture was determined according to the following:

$$V_{\rm H_2O}(P, T) = \frac{\psi(P, T)}{1 + \psi(P, T)} V_{\rm sample}$$
(1)

Where ψ is defined as

$$\psi(P, T) = \frac{y_{H_2O}}{1 - y_{H_2O}} \frac{M_{H_2O}}{M_{CO_2}} \frac{\rho_{CO_2}(P, T)}{\rho_{H_2O}}$$
(2)

$$y_{\rm H_2O} = \frac{w_{\rm H_2O}/M_{\rm H_2O}}{\sum_{i=1}^n w_i/M_i}$$
(3)

$$M_{\rm CO_2} = \sum_{i=1}^n y_i M_i \tag{4}$$

The mole and mass fractions of water in the prepared sample are given by $y_{\rm H_2O}$ and $w_{\rm H_2O}$, respectively; M_i and y_i are the species' molar masses and mole fractions, and $M_{\rm CO_2}$ is the molar mass of pure and impure CO₂; $\rho_{\rm H_2O}$ is the density of water at injection conditions; and $\rho_{\rm CO_2}(P,T)$ is the density of pure and impure CO₂ at single-phase preparation conditions, as predicted by Peng–Robinson Equation of State (PR EOS).³⁵ For each test, the water volume to be injected into the cylinder was first calculated based on planned experimental conditions, and then the precise concentration was determined from the known water volume injected and the final mixture pressure and temperature. The range of conditions was achieved by injecting water volumes between 40 and 140 μ L, depending on the desired final mixture properties. Specifically, once the water was injected, the pump fully pressurized the preparation cylinder. The pump was run until fully empty to minimize trapped volume. Thus the final mixture pressure (and thus concentration) was a function of the initial fluid pressure in the pump. Although with this procedure it was not possible to generate a particular water content a priori, this procedure reliably generated mixtures with known water concentration. SI Figure SI 2 plots the mixture density, $\rho_{CO_2}(P,T)$, and shows the effect of the nitrogen and oxygen impurities on density as a function of pressure and temperature. With these impurities, the total density decreases for a given temperature and pressure, and the pressure required to transition to dense-phase increases for a fixed temperature.

The cylinder with water and CO_2 (at initial low pressure), connected with flow lines and valves to the rest of the setup, was submerged in a 75 °C water bath (Thermo SCIENTIFIC HAAKE SC150) and pressurized in a stepwise fashion using a syringe pump (TELEDYNE ISCO model D-260) to about 20 MPa. The pump was thermally controlled by circulating heated water from the water bath through its built-in heating jacket. The cylinder was filled to such a point that the syringe pump piston was in its uppermost position (empty configuration), after which the pressurized system was left to equilibrate. The preparation conditions, given in Table 1, were well above (more than 6 MPa) the expected dew points for all water contents used in the present study and were thus chosen to generate a well-mixed, single-phase fluid sample with the

| Table 1. Dew Point Conditions for the Synthetic | CO_2 |
|---|--------|
| Mixture at the 31, 35, 40, and 50°C Isotherms | |

| | P _{prep} | Vinj | | y_{H_2O} [mol _w /mol _t | P _{pure} | $P_{2.5\% N_2, 5.8\% O_2}$ | % | | |
|--|-------------------|------|------|---|-------------------|----------------------------|--------|--|--|
| ['C] | [MPa] | [µL] | ['C] | X 1000] | [MPa] | [MPa] | change | | |
| 75 | 22.19 | 40 | 31 | 1.11 | N/A* | 6.93 | | | |
| 75 | 22.75 | 75 | 31 | 2.04 | 6.89 | 7.69 | 11.61 | | |
| 75 | 21.63 | 100 | 31 | 2.83 | 6.94 | 7.79 | 12.18 | | |
| 75 | 21.65 | 140 | 31 | 3.96 | 12.75 | 14.35 | 12.57 | | |
| 75 | 22.19 | 40 | 35 | 1.11 | N/A | 7.24 | | | |
| 75 | 22.75 | 75 | 35 | 2.04 | 7.51 | 8.87 | 18.09 | | |
| 75 | 21.63 | 100 | 35 | 2.83 | 7.74 | 8.65 | 11.77 | | |
| 75 | 21.68 | 120 | 35 | 3.39 | 7.97 | 9.48 | 18.96 | | |
| 75 | 21.68 | 120 | 35 | 3.39 | 7.97 | 9.72 | 21.98 | | |
| 75 | 21.68 | 120 | 35 | 3.39 | 7.97 | 9.72 | 21.98 | | |
| 75 | 21.65 | 140 | 35 | 3.96 | 9.62 | 12.51 | 30.08 | | |
| 75 | 22.19 | 40 | 40 | 1.11 | N/A | 7.58 | | | |
| 75 | 22.75 | 75 | 40 | 2.04 | N/A | 9.45 | | | |
| 75 | 21.63 | 100 | 40 | 2.83 | 8.22 | 9.38 | 14.06 | | |
| 75 | 21.68 | 120 | 40 | 3.39 | 8.45 | 9.51 | 12.61 | | |
| 75 | 21.65 | 140 | 40 | 3.96 | 9.13 | 10.86 | 18.89 | | |
| 75 | 22.19 | 40 | 50 | 1.11 | N/A | N/A | | | |
| 75 | 21.63 | 100 | 50 | 2.83 | N/A | 8.10 | | | |
| 75 | 21.68 | 120 | 50 | 3.39 | 8.34 | 10.14 | 21.53 | | |
| 75 | 21.65 | 140 | 50 | 3.96 | 9.56 | 11.41 | 19.41 | | |
| $\ensuremath{^*\!A}$ dew point does not exist at this temperature, pressure, and w | | | | | | | | | |
| content in the pure CO ₂ -water binary system. | | | | | | | | | |

desired concentrations. The hydrated sample was then loaded into the syringe pump, which was maintained at equilibrium with the sample cylinder, by lowering the piston from its uppermost position. After filling a sufficient amount of sample $(\sim 50 \text{ mL})$ into the pump, the moisture-addition cylinder was isolated from the experiment. The pump temperature (75 °C) was sufficiently high to ensure a single phase condition. All connections between the pump, moisture-addition cylinder, and the visualization platform were made with stainless steel tubing which was encased in heating water jackets to prevent premature condensation. All valves and tubing connections were submerged in the heated water bath to maintain a single-phase fluid. A small circulation pump (Hydor Pico II Mini Pump) was used to flow water from the 75 °C water bath through each water jacket as well as deliver heated water to the built-in jacket on the syringe pump head. The minimum measured temperature at the flow outlet was 72.2 °C, well above the required temperature to prevent such untimely condensation.

Single phase, moist CO₂ was initially introduced to the microfluidic visualization platform by incrementally releasing the upstream needle valve (McMaster Carr #4800K62) while keeping the downstream microvalve (UpChurch Micro-Splitter Valve 10-32 Grad - P-470) fully closed to maintain backpressure. Chip pressure was monitored with a downstream pressure transducer (Swagelok PTI-S-NG5000-15AO). Sudden transitions during pressurization were avoided to prevent rapid gas expansion and possible channel rupturing.

Fresh sample was introduced to the microchannel by allowing ultralow flow ($\sim 1 \ \mu L/min$), sufficient to fill the chip with fresh uniform test sample while maintaining the pressure safely above the dew point pressure. Specifically, the pressure drop at this flow rate was estimated to be ~ 0.04 MPa, whereas the injection pressure exceeded the dew point pressure by more than 4 MPa. The backpressure valve was then closed, isolating

the test sample within the confines of the microchannel. The chip temperature was held constant while system pressure was incrementally decreased (via the pump) until the droplets were observed. System pressure was reduced gradually, with maximum expansion rates of 5 mL/min to minimize transient effects. The phase condition was monitored for 15 min at each pressure to allow sufficient time for potential droplet formation. Once the first droplets formed (indicating system pressure had dropped below the dew point pressure), the pressure was tuned at small increments in the vicinity to delineate the particular dew point pressure. Specifically, the following criterion was used to determine the dew point:

- (i) If no droplets are observed, or if the observed droplets shrink, then P > P_{dew}(T,w_{H,O});
- (ii) If droplets are observed to grow, then $P < P_{dew}(T, w_{H_2O})$; and
- (iii) If droplets remain unchanged, then $P = P_{dew}(T, w_{H,O})$.

The dew point was determined as the point at which droplet sizes stayed constant, that is, the rates of condensation and evaporation were equal. For each dew point collected, the pressure was increased again to reach single phase and the dew detection procedure was repeated to ensure consistent data. The microchannel was imaged by a digital camera (COOL-SNAP MYO), and the images were automatically transferred to a computer for analysis.

RESULTS AND DISCUSSION

Pure CO₂ and a synthetic CO₂ mixture typical of oxyfuel combustion with 2.5% N₂ and 5.8% O₂ were tested in this work.⁷ Experiments were conducted for pressures between 6.55 and 14.35 MPa and temperatures between 31 and 50 °C. Droplet formation and growth was observed within seconds of pressure reduction below the dew point pressure. Images were taken at a fixed location over time to track droplet formation and droplet size evolution. Droplet growth due to both condensation and coalescence were observed. For validation, the method was first applied to the well-studied CO₂-water system.

The images in Figure 3 show the observed field of view for the CO₂-water system prior to dew formation ($P > P_{dew}$, Figure 3a) and after initially dropping below the dew point pressure ($P > P_{dew}$, Figure 3b). As shown, droplets on the order of $D = 1-2 \mu m$ are sharply visible using brightfield microscopy,



Figure 3. Microfluidic detection of the dew point. The system is depressurized from a single phase mixture for $P > P_{dew}$ (a), until water droplets are visualized for $P < P_{dew}$ (b). The pressure is then finely tuned until such a point when the droplets are neither growing nor shrinking, the dew point. The scale bar represents 10 μ m.



Figure 4. Dew point data obtained using the proposed microfluidic method plotted against theoretical values and experimental results as given by Spycher et al.¹³ Water solubility in mole fractions is shown as a function of pressure along the 31, 35, 40, and 50 $^{\circ}$ C isotherms.



Figure 5. The two-phase envelope delineating the effect of water content, temperature, and pressure on water solubility in three dimensions. Results from the present method are plotted with previous theoretical and experimental data as indicated.¹³

in part due to the strong contrast in refractive index ($n_{\rm CO2} = 1.00$, $n_{\rm H2O} = 1.33$) and associated lensing at the high-curvature (small radius) droplets. With visible dew formation, the pressure was increased to reduce droplet size and subsequently finely tuned to determine the pressure at which the droplet size remained constant with time ($P = P_{\rm dew}$).

Figure 4 shows measured dew point data for pure CO_2 and water mixtures plotted with both experimental results and theoretical predictions from literature data.^{13,17–26} Dew point pressures were obtained using the microfluidic approach for different water contents on the 31, 35, 40, and 50 °C isotherms. The data are given in Table SI 1 in the SI. The two-phase envelope resulting from the combined effect of water content, temperature, and pressure on the water solubility is shown in three dimensions in Figure 5. As shown, the microfluidic results correspond closely to both previous experimental and theoretical results. The slope of the water solubility diagram near the critical pressure (P ~ 7 MPa) is very high for the 31 °C isotherm case (Figure 4), due to the proximity of the critical point. Notably, the predicted sharp slope in this case is reproduced well by the microfluidic approach, an area for which there is insufficient previous data. The more gradual transitions for higher temperature cases are also well reproduced and in good agreement with previous measurements where available. With the exception of the low temperature case, there was very sparse previous experimental data available for cases below 0.0035 water content. This low-water content range is accessible with the microfluidic approach, with results corresponding closely to theory.

To assess the accuracy of the microfluidic approach, the percent deviation between the theoretical values of water solubility in pure CO_2 and the experimental results from this



Figure 6. Deviation of microfluidic results from theoretical values in blue, compared to deviation of literature experimental data from theoretical values in yellow for dew point pressure of water in pure CO_2 . Dew point pressure data collected using the microfluidic method had a standard deviation of 4.84% error from the theoretical, whereas the data in the literature as taken from Spycher et al.¹³ presented a standard deviation of 12.69% error from the theoretical values,¹³ indicating a nearly 3-fold improvement in precision.

work and the literature are presented in Figure 6. As shown, the data obtained using the microfluidic approach had, in general, smaller deviations from the theoretical dew points, and were centered closely to the 0% deviation. The standard deviations of the dew point pressure error using the microfluidic method and the experimental data from the literature data are 4.84% and 12.69%, respectively, indicating a nearly 3-fold improvement in precision.

With respect to sources of error in the dew point measurements, the expected sources are those associated with maintaining and measuring the temperature and pressure within the system. In addition, as with all dew point measurement methods, it is important to consider the effect of the detected water droplets on the mixture properties. Specifically, droplet formation reduces the local mole fraction of the vapor phase water within the mixture, thereby altering the mixture properties for the remaining vapor. To mitigate this effect, the pressure was fine-tuned in the vicinity of the dew point to achieve zero droplet growth for very small droplets (i.e., smaller than initially formed on first pass of the P_{dew}). To quantify the potential influence of lost (condensed) water, droplet volumes were calculated directly from the droplet sizes imaged at P_{dew} and relevant contact angles. For the case of water content $y_{\rm H_2O}$ = 0.004 at 40 °C, for instance, the mole fraction of condensed water was on the order of 2.3%, or $\Delta y_{\rm H,O}$ = 0.000092. In principle, the maximum potential impact of this condensed volume on P_{dew} measurement should depend on the local slope of the water solubility curve, ranging from a 0.86 MPa underestimate at 0.00489 water mole fraction and 13.2 MPa, to no detectable change at 0.00305 water mole fraction at 40 °C (calculation details in SI). These levels are both conservative and low. It is also noteworthy that the worst case error estimated at higher water contents and pressures is higher than that determined by direct method validation (i.e., the comparison of these measurements with previous theory

and experiments). Collectively, these results demonstrate (a) the validation of the approach as an improvement over existing dew point measurement methods, as well as (b) the applicability of the microfluidic approach to dew point measurements in low-water content mixtures typical of pipeline systems.

Dew point data were collected for the impure CO₂ mixture in a similar fashion as that for the binary water-CO₂ mixture. The results for this 2.5% N_2 , 5.8% O_2 mixture are as shown in Figure 7, and tabulated in Table 1. For reference, the results collected for the impure CO2 mixture were compared with theoretical data for pure CO2 due to a lack of theoretical or experimental results in the literature for this, albeit typical, mixture. The general trend of the dew point curve for the impure mixture is similar to that of the pure CO₂ case, with water solubility increasing with temperature. In terms of deviation from the pure case dew point pressures for the impure CO₂ case, several aspects are noteworthy: (1) dew formation is observed at higher pressures (i.e., earlier) in the mixture case as compared to that of pure CO₂-water, as indicated by the shift to the right in all cases plotted in Figure 7; (2) deviations are highest near the critical point for the pure CO₂ case (most notably in the lowest water contents, which present no dew point in the pure CO_2 case); (3) away from the critical point, the dew point pressures were on average 17.55% higher with a relatively small $(\pm 5.4\%)$ standard deviation. While the literature offers no direct quantitative comparison, the general trends observed are in agreement with reduced solubility of water in this mixture as expected from theory, and particularly with nitrogen exhibiting a lower water solubility than CO2.36-38 Collectively, these results quantify dew point pressures relevant to oxy-fuel generated CO₂ streams, indicate an 17.55% increase in pumping pressure required for natural gas oxy-fuel combustion streams, and demonstrate the applicability of the microfluidic approach to the analysis of dew points under conditions relevant to CO₂ transport in pipelines.



Figure 7. Measured dew points of water in the synthetic CO_2 mixture with 2.5% N_2 and 5.8% O_2 (typical of oxy-fuel combustion⁷) compared to the theoretical water solubility of *pure* CO_2 -water case on the 31, 35, 40, and 50 °C isotherms (dashed lines).¹³ Conditions for which no condensation was observed are indicated by the red semidashed lined. The dew points for the impurity case are shifted to the right and down, indicating a reduction in water solubility and an, on average, 17.55% increase in pumping requirements to maintain single-phase flow.

Implications. Microfluidics enables rapid and accurate measurement of dew point conditions for CO₂ mixtures with impurities relevant to CO2 transport in pipelines. The most significant implication of this work is the demonstration of efficacy and precision at which dew point pressures can be determined, and the associated potential to enable safe transport of industrially relevant CO2 streams. Dew droplets (~1-2 μ m diameter) were visualized directly within the microfluidic system at point of measurement. Well-studied binary mixtures of pure CO₂ and water provided validation of the approach. The microfluidic approach exhibited a nearly 3-fold improvement in precision compared to data found in the literature. A synthetic CO₂ mixture common to oxy-fuel combustion flue gas $(2.5\% N_2, 5.8\% O_2)$ was then tested. The results indicate a more stringent pumping requirement for single-phase transport, with dew point pressures 17.55% higher than those for the corresponding binary CO₂-water case. This study clearly demonstrates the need to characterize water phase dynamics in CO₂ mixtures for safe and effective transport, and validates the use of a microfluidic approach for CO2-stream specific dew point measurement.

ASSOCIATED CONTENT

Supporting Information

A document with Supporting Information including on-chip temperature control, pure and synthetic CO_2 mixture density calculations, measured dew point data for the binary system of water and pure CO_2 , and the change in vapor phase water content due to condensed droplets is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sinton@mie.utoronto.ca.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge funding from Carbon Management Canada, Theme B: Emerging Technologies, Project B-04, and ongoing funding from the Natural Science and Engineering Research Council of Canada (NSERC). The authors also gratefully acknowledge infrastructure funding from the Canada Foundation for Innovation (CFI) as well as DuPont Canada for partially funding the Queen Elizabeth II Scholarship in Science and Technology.

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