Supporting Information for:

Determination of dew point conditions for CO_2 with trace impurities using

microfluidics

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In the following sections, we provide information to supplement the article content. This material was not included in the article itself because it is not an original finding. This document describes the on-chip temperature control, density calculations for pure and impure CO_2 used to determine the amount of water addition required to prepare hydrated samples, the dew point conditions measured for the pure CO_2-water case in the validation study, and the error associated with localized condensation.

On-chip temperature control

The microfluidic chip was thermally controlled using a PID controller and thermocouple feedback system. Typical temperature measurements are shown in Figure SI 1, where the system is maintained at an initial temperature, and system response upon temperature change is stabilized within 10 minutes. The chip temperature fluctuations are largely contained within $\Delta T = \pm 1°C$.
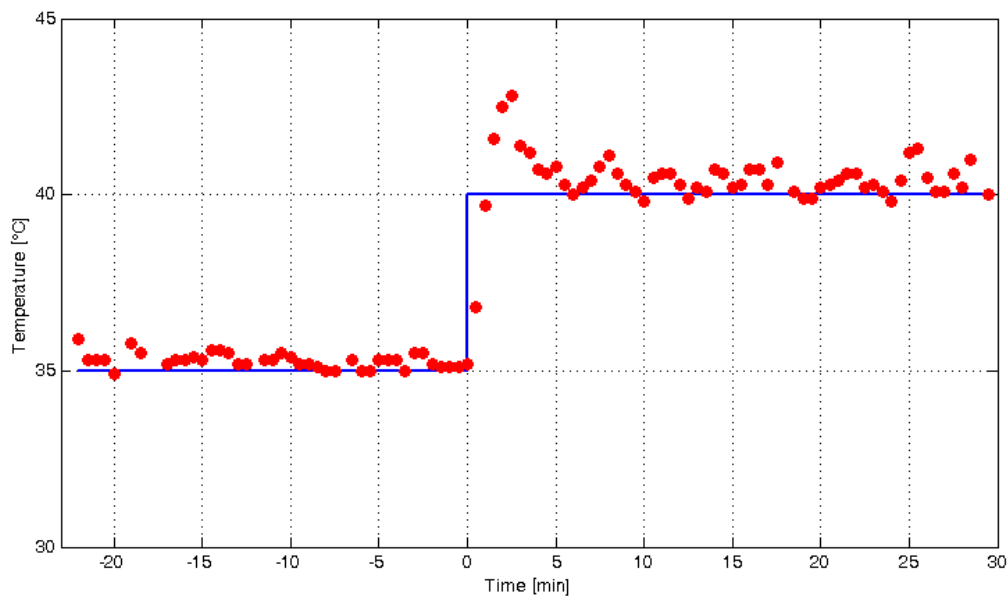

Figure SI 1. Temperature measurements on chip as controlled by a PID controller and thermocouple feedback. Temperature is initially set to 35°C and increased to 40°C at time t = 0 in a step-wise fashion. The chip reaches thermal equilibrium within 10 minutes and fluctuations are largely contained within $\Delta T = \pm 1°C$.

Pure and impure CO_2 density calculation

Pure CO_2 and impure CO_2 mixture densities were calculated using the Peng-Robins Equation of State[1] and shown in Figure SI 2.
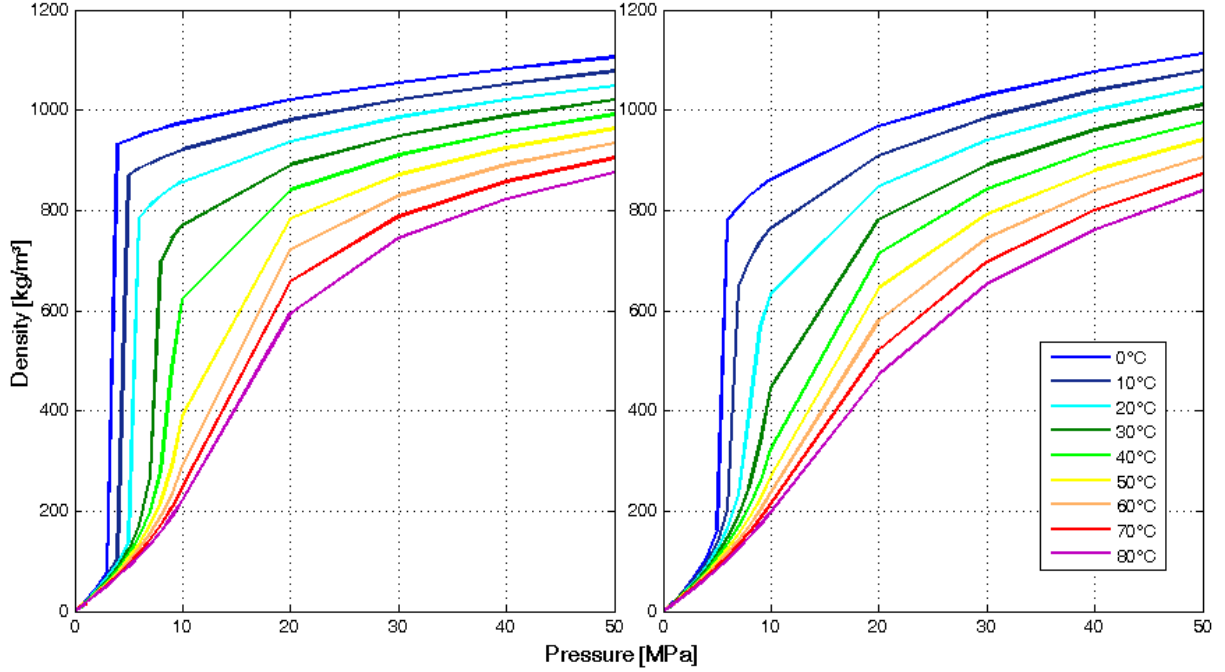
Figure SI 2. Comparison of pure (left) and anthropogenic (right) CO_2 densities with pressure along common isotherms as predicted by the Peng-Robinson equation of state.[1] The synthetic CO_2 mixture was composed of 2.5% N_2, 5.8% O_2, and 91.7% CO_2, representative of oxyfuel combustion flue streams. The impure CO_2 density is lower than that of pure CO_2 for any given temperature and pressure condition.

The densities were calculated as follows, using the mixing rules outlined by Peng and Robinson[1] to calculate the mixture molar masses, M_{CO_2}, in which y_i and M_i are the mole fractions and molar masses of each species, a_{mix} and b_{mix} are the molecular attraction and repulsion factors of the mixture, and v_m is the specific volume of the mixture:

$$\rho_{impure\ CO_2} = \frac{M_{CO_2}}{v_m}, \qquad M_{CO_2} = \sum_{i=1}^{n} y_i M_i \tag{SI 1}$$

$$P = \frac{RT}{v_m - b_{mix}} - \frac{a_{mix}}{v_m(v_m + b_{mix}) + b_{mix}(v_m - b_{mix})} \tag{SI 2}$$

Where for each species i, the molecular attraction and repulsion factors, and reduced temperatures are found using the acentric factor, ω_i, and critical temperature and pressures, T_{ci} and P_{ci}, of each species:

$$a_i = \frac{0.45724 R^2 T_{c,i}^2}{P_{c,i}} \left[1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2)(1 - T_{r,i}^{0.5})\right]^2 \tag{SI 3}$$

$$b_i = \frac{0.07780 R T_{c,i}}{P_{c,i}} \tag{SI 4}$$

$$T_{r,i} = \frac{T_i}{T_{c,i}} \tag{SI 5}$$

And applying the following mixing rules,[2]

$$a_{mix} = \sum_{i=1}^{n}\sum_{j=1}^{n} y_i y_j a_{ij} \tag{SI 6}$$

$$b_{mix} = \sum_{i=1}^{n} y_i b_i \tag{SI 7}$$

Where a_{ij} is taken as the geometric mean of a_i and a_j for $i \neq j$.

Dew point data for water in pure CO_2

Table SI 1. Dew point data for water in pure CO_2 using the microfluidic approach (P_m), verified with theoretical values (P_t).

T [°C]	y_{H_2O} [mol_w/mol_t x 1000]	P_t [MPa]	P_m [MPa]
31	2.37	6.94	6.55
31	2.37	6.94	6.76
31	2.37	6.94	6.91
31	2.37	6.94	6.96
31	3.08	7.00	7.17
31	3.47	8.43	7.62
35	2.29	7.57	8.47
35	2.37	7.63	7.45
35	2.37	7.63	8.14
35	2.37	7.63	8.27
35	3.08	7.86	8.00
35	3.47	8.03	7.72
35	3.47	8.03	7.76
40	2.37	7.94	7.93
40	2.37	7.94	8.07
40	3.08	8.33	8.34
40	3.47	8.51	8.48
40	3.47	8.51	8.55
40	4.50	10.90	10.82
40	4.69	11.87	13.17
50	3.47	8.69	8.52
50	4.50	10.15	10.07

50	4.50	10.15	10.07
50	4.50	10.15	10.34
50	4.69	10.37	10.07

*: A dew point does not exist for this temperature, pressure, and water content in the pure CO_2-water binary system.

Vapor phase water content change due to condensed droplets

Assuming the droplets are in the shape of spherical caps, total condensed volume per visualization volume, V_{vis}, was calculated as the sum of all visualized volumes in a given area, based on the visualized droplet radii, a, and contact angle, θ.

$$V_{H_2O} = \sum_{i=1}^{N} V_{cap,i} \, , N = number\ of\ droplets\ in\ V_{vis} \tag{SI 8}$$

$$V_{cap} = \frac{\pi a^3}{3 \sin \theta} (1 - \cos \theta) \left(1 + \frac{1 - \cos \theta}{\sin^2 \theta} \right) \tag{SI 9}$$

And the change in vapor-phase water content is calculated as:

$$\frac{\Delta y_{H_2O}}{y_{H_2O}} = \frac{y_{cond}}{y_{H_2O}} = \frac{1}{y_{H_2O}} \frac{V_{H_2O}/\left(V_{vis} - V_{H_2O}\right)}{\frac{V_{H_2O}}{V_{vis} - V_{H_2O}} + \frac{M_{H_2O}}{M_{CO_2}} \frac{\rho_{CO_2}}{\rho_{H_2O}}} \tag{SI 10}$$

For a typical case in which the test mixture with 0.00489 mole fraction of water was tested at 40°C and 13.18MPa, a conservative contact angle of 10° between the liquid phase and glass finds a 2.3% change in the vapor-phase water content, $\Delta y_{H_2O}/y_{H_2O}$. For this particular data point, the point coinciding with the shallowest slope on the water solubility diagram (i.e. worst case) for all the data points taken in this study, 2.3% change in vapor-phase water content results in a 0.85MPa reduction in the detected dew point pressure. This represents an error of 6.5%, and is the upper bound in the microfluidic dew point pressure error. It was thus found that the visualized condensed volume did not drastically reduce the overall water mole fraction of the mixture, and therefore does not significantly affect the accuracy of our measurements.
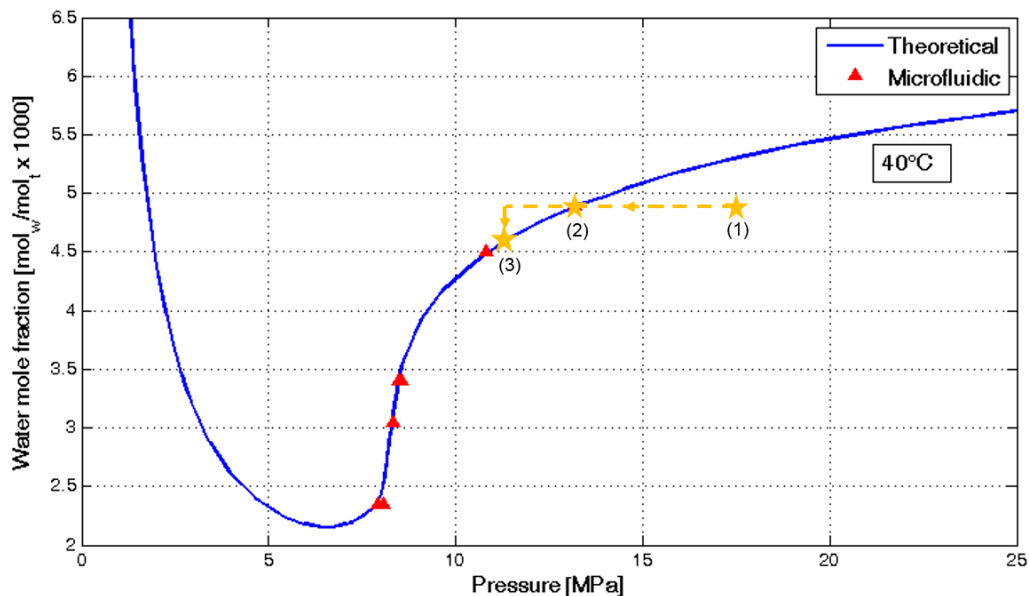
Figure SI 3. Visual detection of dew formation for y_{H_2O}=4.89‰ on the 40°C isotherm. Dew is visualized 1 minute after the pressure is reduced to 13.18MPa, while the system remains single-phase for all higher pressure. The theoretical dew point pressure is 13.31MPa. Isothermally decreasing the pressure from point (1) in the single phase region, to point (2) at the dew point and then to (3) causes a change in the local water content and can affect the dew point pressure measurement. However, the typical case presented here shows a small change in the local water content.

References

1. Peng, D.-Y. & Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **15,** 59–64 (1976).

2. Prausnitz, J. M., Lichtenthaler, R. N. & Azevedo, E. G. de. *Molecular Thermodynamics of Fluid-Phase Equilibria*. (Prentice Hall PTR, 1999).