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Detection of bubble and dew point using optical thin-film interference

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ABSTRACT

Bubble and dew point data are essential for many practical applications, and particularly the safe pipeline transport of post-capture CO_2 which contain impurities. These mixtures show highly composition-specific phase properties, necessitating much more experimental data and motivating more rapid and inexpensive measurement methods. Here we demonstrate a responsive small-scale pressure–volume–temperature (PVT) cell system enabled by thin-film interference, and its application to an industrially-relevant post-capture CO_2 mixture stream. The small (5 mL) volume is one-to-two orders of magnitude faster to equilibrate than conventional PVT cells with viewing windows. Inside the cell, top and bottom optical fiber sensors detect bubble and dew points, respectively. At vapor–liquid transition points, the reflection spectrum from the optical fiber tips report clear interference patterns caused by a thin film on the sensor. In addition to sharply delineating the phase change condition, the sensor also reports the real time thickness of the film (accuracy on the order of 1 μm). The method is validated with the well characterized pure CO_2 test case (average error of 2.8 bar as compared to NIST data), and applied to an industrially-relevant CO_2 stream, characteristic of post-capture oxyfuel combustion – an important source for downstream CO_2 utilization and storage.

1. Introduction

Fluid phase behavior at high pressures is central to a wide range of processes including petroleum reservoir engineering, high-pressure chemical reactors, and transport and storage of natural gas and CO_2 [1]. Phase behavior of CO_2 is of much interest due to concerns over global CO_2 emissions and related industrial applications in enhanced oil recovery and carbon sequestration. Pipeline transport of CO_2 is central to all current and eventual large-scale CO_2 applications [2]. Effective transport requires that CO_2 remains in a dense phase (either liquid or supercritical), and thus measurement and knowledge of the phase behavior of industrially-relevant CO_2 is essential.

In contrast to laboratory grade CO_2, industrially-relevant CO_2 streams contain a variety of impurities, often including N_2, O_2, Ar, CO, H_2O, SO_x, NO_x, H_2S and other components depending on the source process [3]. Typical sources include power plants, refineries, upgraders, cement plants and steel plants. The presence of impurities in the CO_2 stream significantly impacts the phase behavior, as indicated by current models [4–7]. For instance, phase diagrams of CO_2 and N_2 binary mixtures studied equation of state models show significant deviation from pure CO_2 phase behavior (e.g. a 40% increase in saturation pressure at 0 °C of CO_2 with 5 mol% N_2) [4]. In another approach, a ternary mixture of N_2, O_2 and CO_2 at low temperature was modeled by combining experimental data from the three binary subsystems [5]. In general models indicate that even relatively low concentrations of air-derived impurities (N_2, O_2 and Ar) can considerably increase the saturation pressure and decrease the critical temperature of CO_2 streams [4,6]. The implications for transport are particularly significant. Maintaining a dense phase will require either lower temperatures (generally not feasible), or increased pressures leading to increased capital and operating costs.

Current methods of measuring fluid phase transition include analytical (~40%) and synthetic (~60%) approaches [1]. In analytical methods, fluid is sampled from both phases of an equilibrium mixture and the composition of each phase is measured using chromatography or spectroscopy [8,9]. Challenges include sampling an equilibrium mixture without significantly disrupting the equilibrium, and relatively high capital and labor costs. Synthetic approaches can determine phase behavior of prepared mixtures with known compositions without sampling [1]. Synthetic-visual techniques are the most common methods, involving a pressure–volume–temperature (PVT) cell with a visualization window which allows direct observation of phase transition as a function of cell pressure and temperature [10,11]. Synthetic-nonvisual experimental methods have also been developed, using acoustics [12,13], quartz sensors [14–16] and infrared spectroscopy [17].

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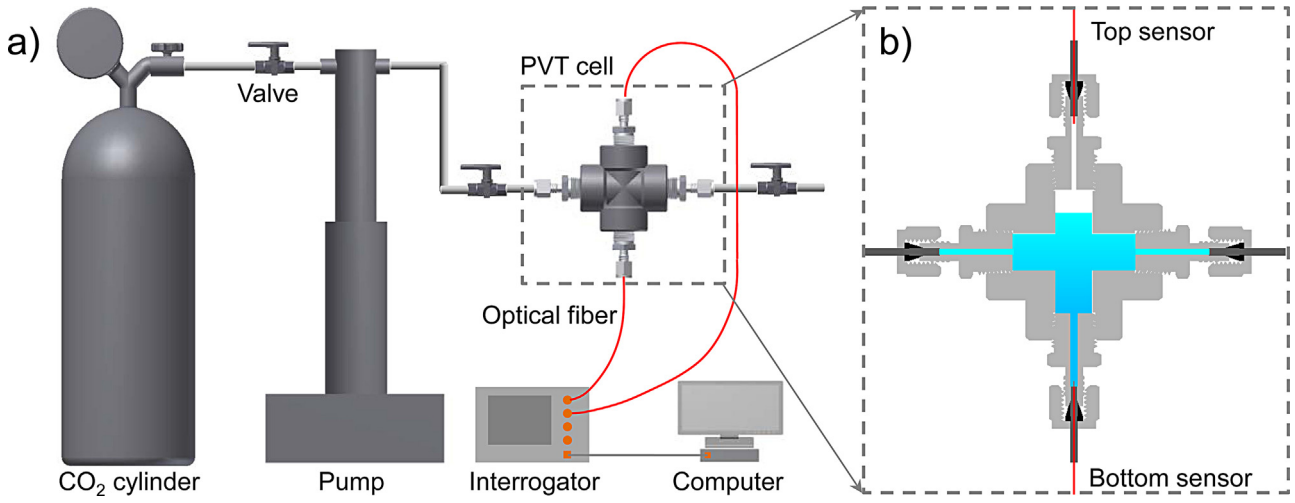

Fig. 1. (a) Schematic of experimental apparatus integrating gas cylinder, pump, PVT cell, optical interrogator, and computer; (b) internal features of the PVT cell with optical fiber sensors.

Microfluidic-based PVT devices were developed to measure physical properties such as diffusivity of immiscible fluid mixtures, showing orders of magnitude improvement in speed and sample volume [18,19]. Another microfluidic PVT approach was developed to analyze phase diagrams of vapor–liquid systems [20]. The depressurization of the sample as it flowed through the microfluidic chip mimicked the fluids transition from reservoir to surface. Recently we developed a microfluidic approach to detecting liquid water condensation at very low concentrations in supercritical CO_2 using direct observation [21]. A localized surface plasmon resonance based sensor was demonstrated to detect dew condensation on gold/ceramic nanocomposite [22]. To enable more accurate and automated optical detection, optical fibers are a preferred approach. We have previously developed ultra-sensitive optical fiber sensors to detect dissolved CO_2 in brine at reservoir temperatures and pressures [23]. Optical fiber sensor has been used to determine relative humidity in air [24]. Reflection-based optical fiber sensors have also been applied to directly detect phase transition [25,26]. In general, optical fiber sensors offer many benefits for PVT related studies, including high accuracy, robustness, fast response, compact size and low cost.

The method presented in this paper is a new synthetic-nonvisual approach which exploits the principle of thin-film interference on reflection-based optical fiber sensors. During vapor–liquid phase transitions, the reflection spectra of the optical fiber sensors show transient interference patterns caused by accumulation of thin films of vapor or liquid phase on the sensor. This new PVT system was first applied to determine the vapor–liquid phase transition of pure CO_2 – enabling validation of the technique. Then, the phase transition envelope for an industrially-relevant CO_2 stream from oxyfuel combustion was measured. The experimental result – a first – was compared with predictions from two common models.

2. Experimental

2.1. Experimental setup

The schematic of experimental apparatus is shown in Fig. 1a. A cross-shaped PVT cell was connected to a high-pressure syringe pump (Teledyne ISCO Model 260D) and a cylinder containing CO_2 samples. Optical fibers sensors were inserted both at the top and bottom of the PVT cell. The temperature of the PVT cell was controlled by emersion in a water bath (Polystat cooling/heating circulating bath, 6.5 L), while the pressure was controlled by the pump. The two optical fiber sensors were connected with an optical interrogator (Micron Optics SM 125). The optical interrogator delivered a broadband incident light (1510–1590 nm) to each of the optical fiber sensors and detected the spectra of reflected light from the sensors in real time.

The internal features of the PVT cell are shown in Fig. 1b. The stainless steel PVT cell had an internal volume of about 5 mL and four 1/8″ NPT ports. The left and right ports allowed loading and purging the fluid samples, respectively. The top and bottom ports immobilized the top and bottom optical fiber sensors, respectively. The optical fiber sensor was single mode (core/cladding/coating: 9/125/245 μm). One distal end of the fiber was cleaved to generate a flat fiber tip to serve as the reflection sensor surface. The other distal end was connected to the interrogator. The top and bottom fiber tips were positioned axially to be just inside the fluid cavity of the PVT cell. The optical fiber was sealed with a PEEK sleeve and compression fittings, as detailed elsewhere [23].

2.2. Sensing mechanism: thin-film interference

Fig. 2 shows the principle of detection of vapor–liquid phase transition with a fluid sample. If the fluid sample surrounding the fiber tip exists as a single phase (Fig. 2a), such as single vapor or liquid phase, the incident light traveling inside the fiber core will be partially reflected at the fiber/fluid interface. The reflection light intensity is a function of refractive index of the fluid sample near the end of the fiber. This single-phase reflection mode is the previous approach to phase detection with reflection-based optical fiber sensors [25,26].

Fig. 2b shows the thin-film approach developed in this work. Specifically, in dew-point detection, any liquid forming (from an otherwise gaseous mixture) forms preferentially at the bottom of the PVT cell, and is subsequently detected by the bottom optical fiber sensor. Both types of phase transitions (dew-point and bubble-point) can exhibit temporary thin films on the sensor surface. In the case of dew formation, a thin layer of liquid film would be condensed on the fiber tip while the surrounding medium is still in vapor phase (Fig. 2b). In the case of bubble formation, either a thin vapor film or a thin liquid film is possible during transition, depending on the wettability of the sensor (typical silica fibers are highly hydrophilic and thus liquid films are expected during transition). Thin films on the end of the fiber optic generate interference as shown at right in Fig. 2b. Constructive interference, as shown, is an additive effect of a wave reflected at the first