

# A New Phase Behavior Apparatus for Supercritical Fluid Extraction Study

Huey-Ing Chen,<sup>\*,†</sup> Hong-Yi Chang,<sup>†</sup> Edward T. S. Huang,<sup>‡</sup> and Ting-Chia Huang<sup>†</sup>

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 70101, and  
CIRES, University of Colorado, Boulder, CO 80309

A high-pressure phase behavior apparatus is presented in this paper. One new feature of the apparatus is a “rodded cylinder”, which greatly simplifies the equipment design. This experimental apparatus is capable of performing vapor–liquid equilibrium tests at pressures up to 40 MPa and temperatures up to 150 °C. Test runs of the apparatus have been made to study the phase behavior of CO<sub>2</sub>-containing binary and ternary fluid mixtures. The measured compositions of equilibrium vapor and liquid phases are in good agreement with those reported in the literature. This apparatus is useful for generating data required for process designs of supercritical fluid extraction.

## Introduction

For many chemical process designs, high-pressure vapor–liquid equilibrium (VLE) data for the fluid mixtures of interest are required. These data are also useful in tuning the equation of states for calculations of thermodynamic behavior of specific fluid mixtures. In recent years, because of the increased interests in supercritical fluid extraction processes, there has been a great demand for high-pressure experimental VLE data. Several recent papers reviewed the experimental apparatus for generation of these data.<sup>1–4</sup>

The measurement of phase equilibria involves the determinations of pressure, temperature, phase compositions and phase amounts. To perform such an experiment, a high-pressure chamber that can contain a fluid mixture existing as equilibrium vapor and liquid is needed. The chamber needs a stirring device to mix the two-phase fluid in order to achieve thermodynamic equilibrium. A glass window attached to the chamber is necessary for visual determination of the height of the liquid level. To withdraw high-pressure fluid samples for compositional analyses, the chamber requires a liquid sampling port at the bottom and a vapor sampling port at the top. Furthermore, a device is required to maintain the pressure of the chamber constant while fluid sample is withdrawn from the chamber.

In this paper, we present a new phase behavior apparatus that is simple and compact with the following features: (a) a “rodded cylinder” with a view window, which eliminates the complex stirring device; (b) one single sampling port from which both the liquid- and vapor-phase samples can be taken; and (c) a requirement of less than 100 cm<sup>3</sup> of total fluid sample for each experiment and the small mass of the compact stainless steel apparatus, which make it possible for the apparatus to achieve thermodynamic equilibrium in a short time.

To test the reliability of the apparatus, we measured isothermal VLE data for the binary carbon dioxide–

ethanol system and the ternary carbon dioxide–ethanol–water system. Numerous experimental data for these two systems are available in the literature.<sup>5–20</sup>

## Experimental Equipment

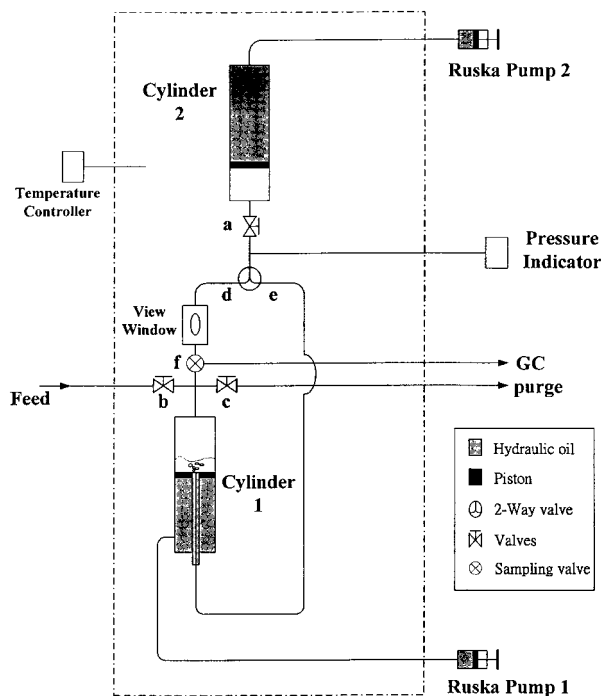
A schematic diagram of the apparatus is shown in Figure 1. The apparatus, housed in a constant-temperature oven, consists of five units: two high-pressure cylinders (cylinder 1 and cylinder 2), a view window, a fluid sampling valve, and a two-way valve. Cylinder 1 (a cylinder with a rodded piston) is positioned at the bottom, cylinder 2 at the top, and the two-way valve, the view window, and the sampling valve in the middle. To minimize the dead volumes in the system, all of these units are interconnected using 1/16-in. o.d. stainless steel tubing. The internal volume of each of the two cylinders is about 100 cm<sup>3</sup>. The internal volume is varied with a piston, which is in turn driven by a Ruska pump filled with hydraulic oil. The piston of cylinder 1 is attached to a 0.25-in. o.d. stainless steel tubing (or rod), which is connected to the two-way valve. During the phase behavior experiment, vapor is in cylinder 2, liquid is in cylinder 1, and the vapor–liquid interface can be seen in the view window. Mixing of vapor and liquid is accomplished by circulating vapor between the two cylinders. This requires that the piston of one cylinder be advanced and the piston of the other cylinder be retracted, while the system pressure is kept constant at the test pressure.

The temperature of the oven was controlled and measured to within  $\pm 0.1$  °C. The pressure was measured to within  $\pm 0.1$  bar with a Validyne pressure transducer. The transducer was calibrated with a dead-weight tester. The Ruska pumps read volumes to 0.01 cm<sup>3</sup>. The two high-pressure cylinders, CFR-100–10 (cylinder 2) and CBR-100 (cylinder 1), were purchased from Temco Inc., Tulsa, OK. The view window (Ruska part no. 2328–702) and the two Ruska pumps were purchased from Ruska Instrument Corporation, Houston, TX. The high-pressure sampling valve and two-way valve were acquired from Valco Instruments Inc., Houston, TX. The experimental apparatus was designed to operate at pressures up to 40 MPa and temperatures up to 150 °C. A gas chromatograph (GC-14A, Shimadzu

\* Author to whom correspondence should be addressed.  
Fax: +886-6-2344496. E-mail: hueying@mail.ncku.edu.tw.

<sup>†</sup> National Cheng Kung University.

<sup>‡</sup> University of Colorado.



### Constant Temperature Oven

**Figure 1.** Schematic diagram of high-pressure apparatus.

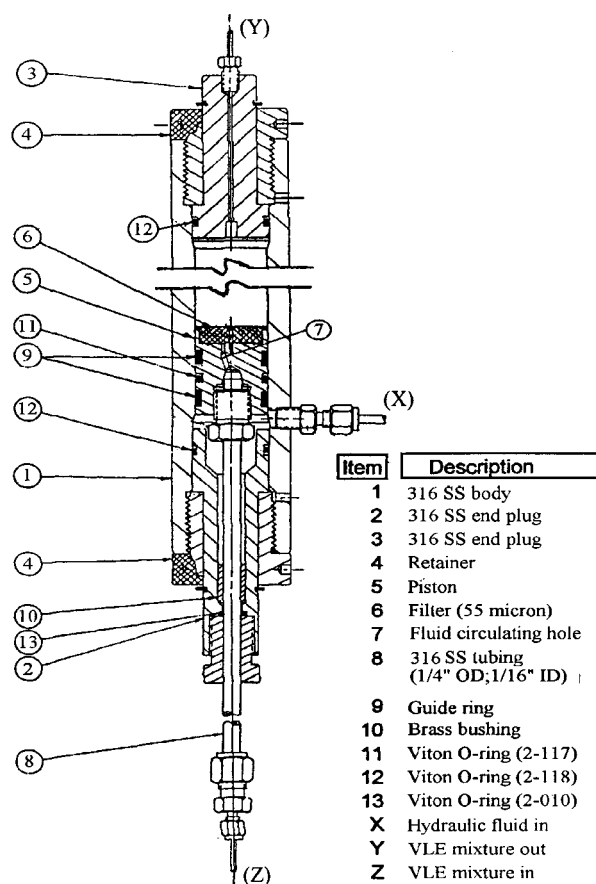
Co., Japan) was installed online to the system to analyze compositions of equilibrium vapor and liquid samples via the Valco sampling valve.

Carbon dioxide (purity 99.99%) was supplied by Yun Shan Co., Taiwan, and ethanol (purity 99.8%) was purchased from Riedel da Haen AG, Germany. These were used without further purification. The deionized water used in the experiments was further purified by distillation.

### Detailed Design of Rodded Cylinder

A new design of the rodded cylinder (cylinder 1 or CBR-100) is shown in Figure 2. The body (#1 of Figure 2) of CBR-100 had an i.d. of 1 in., an o.d. of 1.6 in., and a total length of 14 in. CBR-100 was modified from a standard Temco cylinder to meet the design specified for this apparatus. This was accomplished by (a) drilling a small hole through a standard Temco piston and attaching a 0.25-in. o.d. stainless steel tubing (or rod) to the piston and (b) modifying a standard Temco end plug such that the 0.25-in. o.d. tubing could slide through the end plug (#2 of Figure 2). The two modifications resulted in a unique rodded piston, which consisted of a modified piston (#5), a filter (#6), stainless steel tubing (#8), an O-ring (#11), and two guide rings (#9). The stainless steel tubing had an i.d. of  $1/16$  in., which allowed incoming vapor from cylinder 2 to enter cylinder 1. The vapor entered cylinder 1 from point Z via the stainless steel tubing, the piston small pinhole, and the filter. The purpose of the filter (a 55- $\mu$ m porous disk) was to disperse the vapor in order to enhance mixing efficiency of vapor and liquid in cylinder 1.

The piston was mobilized in the cylinder by hydraulic oil, which entered or exited the cylinder via point X. Parker O-rings were used to seal the fluids in the cylinder. The nominal size of the O-rings for the two end plugs was 2-118 (#12), that for the piston was 2-117 (#11), and that for the 0.25 in. o.d. tubing was 2-010



**Figure 2.** Design of a rodded cylinder (Temco CBR-100).

(#13). The choice of the material for the O-rings depended on the nature of fluids to be used in the experiments. For  $\text{CO}_2$  as a solvent, Viton O-ring with a durometer of 90 is recommended.

### Compositional Analysis

The compositions of high-pressure vapor and liquid samples were analyzed using an online gas chromatograph equipped with a thermal conductivity detector (TCD). Helium flowing at a rate of 30 mL/min was employed as the carrier gas. The GC column used was a 2-m-long stainless steel column, which was packed with Porapak Q and heated to a temperature of 150  $^{\circ}\text{C}$ . The Valco sampling valve had a volume of 1  $\mu\text{L}$ . Each sample was analyzed at least five times, and the reproducibility of the analyses was within 3%.

### Experimental Procedure

The following experimental procedure is described for  $\text{CO}_2$ -containing fluid mixtures. (a) Heat the oven to the desired temperature  $T_1$ . Calculate the required amounts of each component in order to prepare a mixture of a desired composition. (b) Use a vacuum pump to evacuate the system to vacuum from valve b. Meter the precalculated amount of  $\text{CO}_2$  into cylinder 2, and then close valve a. (c) Close valve c, and evacuate the rest of the system through valve b. Meter precalculated amounts of the other liquid components into the system, and then close valve b. (d) Open valve a, and adjust the system pressure to the test pressure  $P_1$ . (e) Switch the two-way valve to e, start pushing  $\text{CO}_2$  from cylinder 2 to cylinder 1, and retrieve the rodded piston in cylinder 1 while

**Table 1. Measured Compositions of Equilibrium Vapor and Liquid Samples for the CO<sub>2</sub>–Ethanol System**

run	<i>T</i> (°C)	<i>P</i> (MPa)	liquid phase				vapor phase			
			exptl <i>X</i> <sub>CO<sub>2</sub></sub>	avg <i>X</i> <sub>CO<sub>2</sub></sub>	lit. Lim et al. <i>X</i> <sub>CO<sub>2</sub></sub>	deviation %	exptl <i>Y</i> <sub>CO<sub>2</sub></sub>	avg <i>Y</i> <sub>CO<sub>2</sub></sub>	lit. Lim et al. <i>Y</i> <sub>CO<sub>2</sub></sub>	deviation %
1	50	8.20	0.506	0.507	0.537	5.6	0.973	0.972	0.973	0.1
			0.509				0.967			
			0.506				0.975			
2	50	7.40	0.422	0.421	0.433	2.8	0.956	0.954	0.986	3.2
			0.420				0.952			
			0.420				0.954			
3	50	6.47	0.342	0.343	0.342	−0.3	0.962	0.970	0.973	0.3
			0.343				0.977			
			0.344				0.970			
4	50	5.03	0.248	0.248	0.266	6.8	0.980	0.980	0.985	0.5
			0.249				0.981			
			0.248				0.980			
			0.248				0.980			

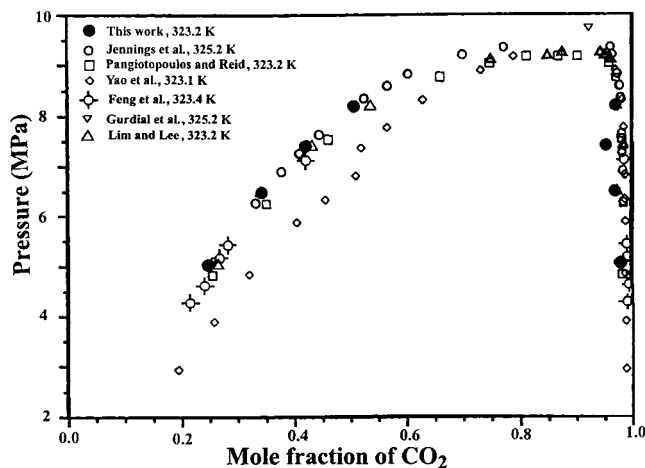
**Table 2. Measured Compositions of Equilibrium Vapor and Liquid Samples for the CO<sub>2</sub>–Ethanol–Water System**

run	<i>T</i> (°C)	<i>P</i> (MPa)	liquid phase				vapor phase			
			experimental		average		experimental		average	
			<i>X</i> <sub>CO<sub>2</sub></sub>	<i>X</i> <sub>EtOH</sub>	<i>X</i> <sub>CO<sub>2</sub></sub>	<i>X</i> <sub>EtOH</sub>	<i>Y</i> <sub>CO<sub>2</sub></sub>	<i>Y</i> <sub>EtOH</sub>	<i>Y</i> <sub>CO<sub>2</sub></sub>	<i>Y</i> <sub>EtOH</sub>
1	50	9.05	0.117	0.295	0.117	0.300	0.952	0.016	0.952	0.015
			0.119	0.302			0.951	0.016		
			0.114	0.303			0.953	0.014		
2	50	9.05	0.225	0.431	0.225	0.427	0.934	0.031	0.920	0.044
			0.223	0.427			0.911	0.051		
			0.228	0.422			0.915	0.049		
3	50	9.05	0.358	0.457	0.357	0.457	0.943	0.025	0.944	0.024
			0.359	0.456			0.945	0.023		
			0.355	0.459			0.943	0.025		

maintaining the pressure at  $P_1$ . The porous disk (or filter) in cylinder 1 allows the gas to be bubbled through the liquid phase to enhance the mixing efficiency. (f) When the piston reaches the end of cylinder 2, switch the two-way valve to d, and start pushing the rodged piston upward to move the gas from cylinder 1 to cylinder 2. Stop pumping the gas when the gas–liquid interface is observed in the view window. During this displacement process, the system pressure is maintained at  $P_1$ . (g) While the system pressure remains constant at  $P_1$ , repeat steps e and f until there is no change in the total volume of the fluid in the system. This is an indication that the vapor–liquid equilibrium has been reached at  $T_1$  and  $P_1$ . (h) When ready to perform a liquid-phase compositional analysis, adjust the system so that the liquid level can be seen in the view window. Because the Valco sampling valve f is located beneath the view window, the sampling loop in the valve f will be filled with the liquid sample to be analyzed. If a gas-phase sample is to be taken, the liquid level is lowered into cylinder 1. The sampling loop will then be filled with the gas sample. To perform the analysis of the high-pressure fluid sample, turn the Valco sampling valve f, and the fluid sample in the loop will be swept by a carrier gas into the GC unit for compositional analysis.

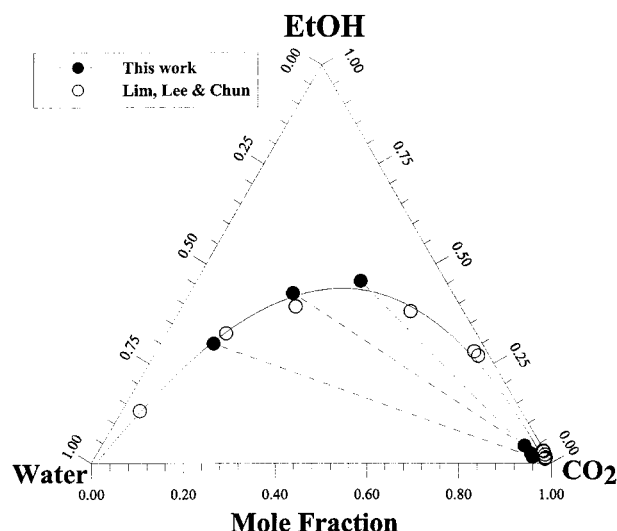
## Experimental Results

The vapor–liquid equilibrium data for the CO<sub>2</sub>–ethanol and the CO<sub>2</sub>–ethanol–water systems were measured at 50 °C, and the results are summarized in Tables 1 and 2. For the binary CO<sub>2</sub>–ethanol system, the VLE experiments were performed at pressures between 5.03 and 8.20 MPa. The data in Table 1 show that reproducibility for compositions of the vapor and

**Figure 3.** Phase diagram for the carbon dioxide–ethanol system at 50 °C.

liquid phases is quite good. There are a number of reports on the VLE data for the CO<sub>2</sub>–ethanol system in the literature.<sup>5–11</sup> Figure 3 compares the data of this study and those of others. Except for the data of Yao et al.,<sup>12</sup> the results of this study are in good agreement with those of five different reports. In Table 1, the data of this study are compared with those of Lim et al.<sup>11</sup> The vapor compositions are in agreement to within 3.2%, and the liquid compositions are in agreement to within 6.8%.

For the CO<sub>2</sub>–ethanol–water system, the VLE experiments for three mixtures were conducted at 50 °C and 9.05 MPa. Table 2 shows good reproducibility of the measured compositions, and Figure 4 shows good agreement between the data of this work and those of Lim et al.<sup>11</sup>



**Figure 4.** Phase diagram for the carbon dioxide-ethanol-water system at 50 °C and 9.05 MPa.

## Conclusions

(1) This paper describes a new phase behavior apparatus, which can be assembled from off-the-shelf equipment. (2) The apparatus is compact and easy to operate. Upon change of the experimental conditions (e.g., pressure, temperature, or composition), the phase equilibrium of the fluid mixtures usually can be attained within 1 h, and the VLE data can be obtained rapidly. (3) VLE experiments have been conducted for CO<sub>2</sub>-containing fluid mixtures. The measured compositions of the equilibrium vapor and liquid samples at 50 °C and pressures up to 9.05 MPa are in good agreement with the literature values.

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