FLOW VELOCITIES OF SUPERCRITICAL CARBON DIOXIDE UNDER CONDITIONS OF NATURAL CONVECTION

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A system for circulating supercritical CO_2 under conditions of natural convection was developed for applications in analytical chemistry. The system uses a closed-loop, which is loaded with a given quantity of CO_2. Heating and cooling applied along different parts of the loop induces fluid flow by natural convection. Key variables in the system are the amount of CO_2 loaded, r_{ini}, that determines the overall system density, and the heater and cooler temperatures. A chemical tracer (acetone) was used to measure the flow velocities by observing its UV absorbance. Densities examined ranged from 300 to 800 kg/m^3 at pressures up to 15 MPa. With an external heater arrangement, flow velocities as high as 5 m/min could be obtained. With an internal heater design, flow velocities as high as 6.5 m/min could be obtained. On the other hand, flow velocities showed the greatest change with pressure around the critical density. Simulation and correlation of the data were examined. A one-dimensional simulation could reproduce some of the results to within 35%. The flow rates achieved in the system were correlated in terms of Grashof and Prandtl numbers and a dimensionless effective density difference between heating and cooling sources. The data were also correlated with an empirical equation in terms of system variables. Internal heating allowed control of heat input. Velocities obtained from internal heating were higher than those obtained from external heating. The loading of the circulation loop with densities less than the critical density of CO_2 gave the highest flow velocities. The circulation system should find use in extended-time extractions, sample preparation and enrichment for analytical applications, catalytic reactions, slurry suspensions, dyeing and other applications.

INTRODUCTION

Supercritical fluid chromatography (SFC) and supercritical extraction (SFE) are well-established analytical methods that depend on the transport of analytes via a mobile supercritical phase that is usually chosen to be carbon dioxide. SFC has been used for the separation of enantiomeric amino alcohols [1] and a wide range of chiral separations [2]. SFE is routinely used in EPA methods 3560 and 3561 for hydrocarbon analyses [3]. In both SFC and SFE, it is frequently necessary to deal with complex substrates such as soils or natural matrices, for which sample preparation can be very important. Smith [4] notes that SFE can give variable results for real sand and soil matrices due to differing interactions, moisture content, and organic components. In other words, SFE lacks methods for the pretreatment of solid matrices or sample enrichment.

In this work, we would like to introduce a system for sample preparation or enrichment that uses thermal convection to circulate a supercritical fluid within a closed loop. In the system development, the fluid velocities that are attainable for various conditions are important for practical use. We therefore report results in terms of fluid and mass velocities for a range of fluid conditions and two possible heater arrangements. Simulation and correlation of the flow velocities as a function of operating conditions were examined.

MATERIALS AND METHODS

Carbon dioxide (99.9%, Nippon Sanso, Tokyo) and acetone (99%, Wako Chemical Co., Osaka) were used as received. A schematic of the experimental prototype device used in our studies is shown in **Figure 1**. The device consisted of a closed circulation loop section, a CO_2 loading section, a velocity measurement section, and a tracer injection section. The circulation loop (12.7 mm O.D.) was made up of a heater, an extraction cell and a coiled double-pipe heat exchanger that was cooled with a chiller. The CO_2 loading section consisted of a gas cylinder and load cell.

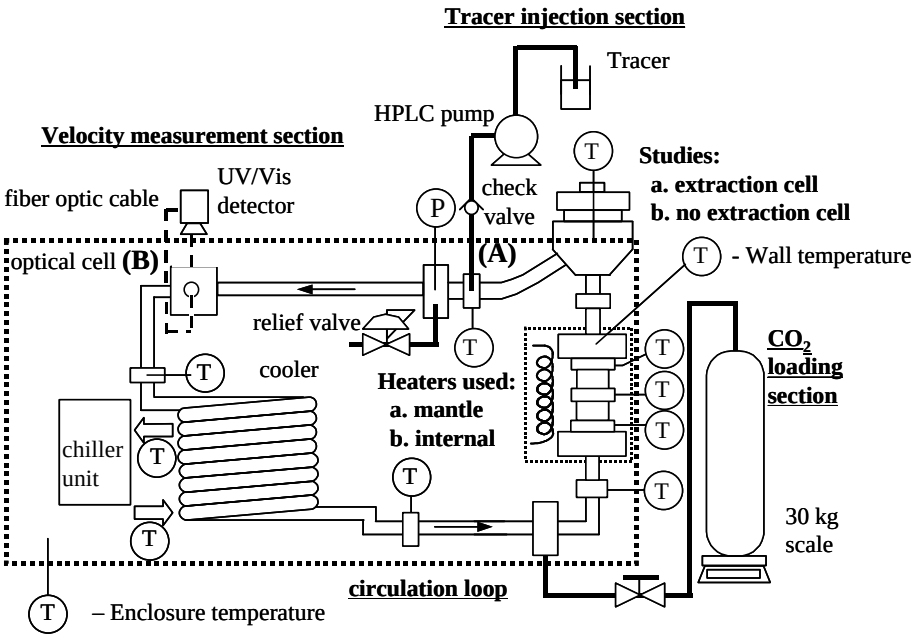

Figure 1. Prototype circulation device for analytical applications.

Two different methods of heating the CO2 were examined as shown in **Figure 1**: (a) external (mantle) heating and (b) internal heating. The velocity measurement section used an optical cell and UV/vis spectrophotometer and a tracer injection section that used a HPLC pump and check valve. Temperature was measured with K-type thermocouples and pressure was measured with an electronic gauge.

Average CO_2 flow velocity in the circulation loop was measured by introducing acetone tracer into the system and observing its UV absorbance with the optical cell over a given time period. After attainment of steady-state, about 0.15 g acetone was injected into the apparatus at point A (**Figure 1**) over a 2 s interval. As the acetone circulated, it passed through the optical cell at point B, and its UV absorbance at 270 nm was measured over a period of about 20 minutes. Temperature, pressure, and absorbance traces were recorded with computer. Further details on the system and flow measurement method may be found in ref. [5].

RESULTS

External heater

Initial experiments made with the system used an external heater and the range of conditions shown in **Table 1**. In those experiments, an effective density difference was determined between the heater and cooler from:

$$\Delta r_{eff} = r_{cooler} - \frac{\sum (r_{heater} \cdot \Delta z_{heater})}{z_{heater}} \quad (1)$$

where z_{heater} is the length of the heated portion of the system and Δz_{heater} represent lengths of 1 mm segments that were used to fit the temperature profile of the heated section. As shown in Table 1, velocities as high as 4 m/min could be obtained for fairly modest (5 to 10 ^oC) temperature differences between the heater and cooler.

Simulations were made with a one-dimensional finite difference method according to methods proposed in the literature [6]. The steady-state solution of

Table 1. Velocities obtained for various loading densities, pressures, and cooler/heater temperatures. Effective density difference is described in the text.

Initial Loading Density	Pressure	Effective Density Difference	Temperature cooler	heater	Average Flow Velocity	Average Mass Velocity
[kg/m^3]	[MPa]	[kg/m^3]	[^{o}C]	[^{o}C]	[m/min]	[g/min]
550	10	101	41.2	44.7	3.6	156
	12	98	48.9	55.2	4.0	172
628	7.8	78	29.4	33.1	3.7	170
	9	116	33.1	38.0	3.7	182
	10	106	37.3	42.2	3.6	178
	12	105	43.5	50.8	4.0	195
800	9	121	15.0	25.2	3.1	197
	10	108	19.5	27.1	2.5	159
	12	107	24.1	32.4	2.7	168

* values based on largest heat fluxes with mantle heater

the continuity, momentum, and energy equations is the main interest in this work:

$$(ru)_{i+1} = (ru)_i \tag{2}$$

$$p_{i+1}A_{i+1} + r_{i+1}A_{i+1}\left(g\frac{\Delta x}{2} + u_{i+1}^{\ 2}\right) = p_iA_i + r_iA_i\left(g\frac{\Delta x}{2} + u_i^{\ 2}\right) - r_iF \tag{3}$$

$$\left(H_{i+1} + \frac{u_{i+1}^{\ 2}}{2}\right) = \left(H_i + \frac{u_i^{\ 2}}{2}\right) - g\frac{\Delta x}{2} + \frac{Q_w\Delta x}{(ruA)_i} \tag{4}$$

Properties used in the calculations were those given in refs [7]-[10]. First, the initial T_{in}, P_{in} and r_{in} were set at a point in the loop and at the system pressure. A velocity was assumed and Δx was incremented. Then, eqs. (2)-(4) were used to determine u_1, P_1, and H_1. Knowledge of P_1 and H_1 allowed determination of a new density, r_{new}. This iteration was repeated until the densities converged. Once the density for a single grid, Δx, was converged, the process was repeated around the loop to provide T_{out} and P_{out}. For a correct solution, T_{out} and P_{out} were determined to match T_{in} and P_{in} within a given tolerance. Over the range of densities and pressures shown in **Table 1**, one-dimensional finite-difference simulation could predict the velocities to within about 35%.

A correlation in terms of dimensionless groups was determined to be as follows:

$$u = 2.2\cdot\log\left[Gr\cdot Pr^{-1}\cdot\Delta r_{eff}\cdot r_{ini}^{\ -1}\right] - 11.2 \tag{5}$$

where r_{ini} is the initial density, and Gr and Pr are the Grashof and Prandtl numbers averaged according to the heated and cooled lengths of the apparatus, and Δr_{eff} is the effective density difference determined from eq. (1). Correlation of the data with Eqn (2) gave an R^2 value of about 0.90.

Empirical correlation of the data gave the following equation:

$$u_{av,cal} = 0.0265\Delta r + 13.8\ln P - 1.06\cdot10^{-6}P - 0.45r_{load} - 17.3 \tag{6}$$

where u is in m/min, P is in MPa and Δr is in kg/m^3. Eq. (6) could represent the

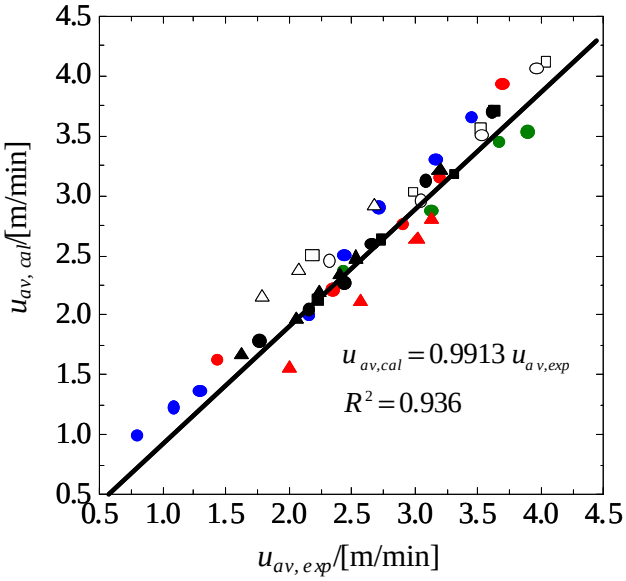

Figure 2. Correlation of velocities with eq. (6) for conditions given in

data to within about 10% as shown in **Figure 2**.

Internal heater

One common feature noted about the velocities measured as a function of pressure at given loading densities was the tendency of the velocity to reach a constant value after a certain given heat input. This can be regarded as the deterioration of the heat transfer according to fluid flow and proximity to the critical point.

With the introduction of an internal heater instead of the external heater as noted in **Figure 1**, effect of actual heat input could be studied. For this study, the extractor was replaced with a section of tubing.

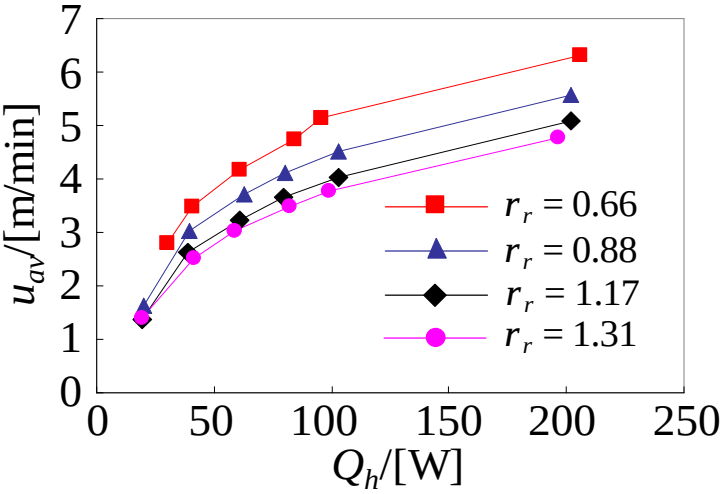

Figure 3. Dependence of velocity on heat input, Q_h, for various reduced densities, $r_r = r_{load}/r_c$. T_{cooler} = 50? .

Figure 3 shows some of the results for a range of reduced densities and for a fixed cooler temperature of 50 ^oC. Fluid temperatures in the heater were generally 5 ^oC to 10 ^oC above the cooler temperature. Reynold's numbers for the experiments shown in **Figure 3** ranged from about 3000 to more than 12000. Heat losses were minimized with insulation on all lines and so the higher cooler temperature means that the state of the entire circulation loop was supercritical. As shown in **Figure 3**, the general trend for all velocities with respect to heat input and reduced density were similar. Increasing heat input caused the velocities to monotonically increase. Larger velocities could be obtained as the reduced density became gas-like. In fact, velocities were very close for the case of r_r greater than 1 as shown in **Figure 3**.

Olson and Allen [7], in their studies on convective heat transfer, found that heat transfer coefficients depend greatly on the level of heat flux in addition to the flow rate and proximity of the system to the pseudocritical point. The data in Figure 3 does show that the velocities attained are not directly proportional to the heat input and that the velocities tend to plateau as heat input increases. Reduced densities removed from the pseudocritical point tended to give higher velocities. These effects and their correlation are presently under investigation and more detailed CFD simulations are in progress [12].

CONCLUSIONS

High flow velocities of almost 7 m/min are attainable with supercritical carbon dioxide in a prototype closed-loop circulation system. Flow velocities depended on system loading density and the temperature difference between heating and cooling sources. Simulation could predict velocities generally to within 35%. Velocities could be correlated to within about 10%. Internal heating gave higher velocities than external heating probably since a larger percentage of the energy input could be imparted to the fluid. Loading densities that were somewhat lower than the critical density allowed higher velocities to be obtained.

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