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Recovery of Liquid CO_2 from Cleaning Solutions Without Phase Change Using Ultrafiltration and Microfiltration Membranes

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ABSTRACT

Recovery of liquid and supercritical fluid (SCF) CO_2 in the application of CO_2 as processing solvent in extraction, chemical, and biochemical reactions is an important issue. Membrane-based separation may provide an option in recovering CO_2 in liquid and/or SCF phase without expensive, energy intensive recompression. The potential application of microporous inorganic membranes in separating liquid CO_2 without phase change was investigated. A high-pressure membrane filtration unit was designed, built, and tested. Microporous stainless steel (0.2 μm) and ceramic (0.02 μm, and 1000 Dalton) tubular elements were retrofitted into in-house designed, high-pressure housings to test the functionality of the system using Triton X-100 solute in liquid CO_2 as feed. In-house designed fiberoptic cells coupled

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with a UV–VIS spectrophotometer was used for on-line measurement of solute Triton X-100 in the feed and permeate streams. The fiberoptic cell coupled with UV–VIS spectrophotometer was capable of providing on-line concentration measurement of Triton X-100 at operating pressures up to 100 bar. Two different path-length fiberoptic cells, 5.0 mm and 0.5 mm, were designed and built to cover a wide range of solute concentrations. Membrane filtration experiments with ceramic membranes showed that 1000-Dalton membrane offered a solute rejectivity of about 80%. The coarse ceramic membrane (0.02 μm) had a lower rejectivity, which was about 55%. The 0.2-μm stainless steel membrane provided very little solute rejectivity.

Key Words: Liquid and supercritical CO_2; Separation with phase change; Membrane-based separations; Crossflow ultrafiltration and microfiltration; Triton X-100 surfactant.

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INTRODUCTION

Supercritical fluids (SCFs) are gases or liquids above their critical points. Based on their tunable solvent properties, SCF solvent technology has gained interest as a viable separation technique.[1–3] Most of the industrial facilities are accustomed to using chlorofluorocarbons (CFCs) and chlorocarbons for the cleaning of a variety of items. The Montreal Protocol (1987) and amendments to this Act will phase out the use of CFCs because they are toxic, carcinogenic, and implicated in the depletion of the Earth's ozone layer. This has lead to the search of solvent replacements. Supercritical fluids, which have been used in food, fragrance, and petroleum processes for years as solvent, are attractive replacement solvents because of their low environmental impact, high diffusivities, low viscosities, and temperature–pressure dependence of solvent strengths. The most widely used supercritical fluid is carbon dioxide (CO_2), because of its relatively low critical temperature and pressure.[4]

Carbon dioxide in liquid and supercritical (SCF) states is now recognized as an attractive solvent alternative for a variety of chemical and industrial manufacturing processes because it is nontoxic, nonflammable, readily available, inexpensive, and environmentally benign. Because of its unique dissolving power, which is tunable over a broad range of solvent quality, there is a growing interest in using CO_2 in liquid and supercritical fluid (SCF) states as environmentally benign processing solvent in extraction, chemical, and biochemical reactions. Recently, liquid CO_2-based cleaning technologies entered the market place and fine cleaning of electronic circuit boards and

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chips in liquid and SCF CO_2 is also gaining popularity.[5] Use of CO_2 as an environmentally responsible solvent in industrial processes will require recycling of CO_2 to prevent emissions into the atmosphere. In process applications, liquid and SCF CO_2 is decompressed for solute or product recovery. For reuse and recycle of CO_2 at the process condition, recompression of CO_2 then becomes an energy-intensive process. In all these applications, separation and recovery of liquid and SCF CO_2 without phase change is an important issue.

In this context, membrane-based separation may provide an option for separation and recovery of CO_2 without the recompression step. Currently, we are investigating the potential application of microporous ultrafiltration (UF) and microfiltration (MF) membranes in recovery of liquid CO_2 without phase change from process solutions. Polymeric membranes that can meet the high-pressure requirements of the process are not commercially available. The downstream process of the dry cleaning systems is considered, which mainly consists of liquid carbon dioxide and specialty surfactants. A high-pressure membrane filtration unit was designed and built to study crossflow membrane filtration of liquid and SCF CO_2. A commercially available surfactant, Triton X-100 (polyethylene glycol tert-octylphenyl ether), was used as model solute in liquid CO_2-feed to test the rejectivity of the solute. The objective of this article is to report some preliminary test results on the separation and recovery of liquid CO_2 without phase change from process solutions.

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EXPERIMENTAL MATERIALS AND METHODS

A high-pressure membrane filtration unit was designed, built, and tested for filtration of liquid and SCF CO_2. The major consideration in designing the system was the operating conditions. The critical temperature and pressures of carbon dioxide are 31°C and 73.8 bar, respectively. After review of physical properties of liquid carbon dioxide, the operating conditions were set as room temperature and the pressures from 70 to 85 bar and the flow rates in the range of 10 to 250 mL/min, based on the scale of the process. The properties of liquid carbon dioxide, surfactants, and membranes were also taken into consideration in designing of the unit.

The system has to be maintained under high pressure throughout the experimentation to avoid any phase change and must also have the driving force for membrane separation to occur. This could be easily achieved by maintaining a transmembrane pressure drop (ΔP_{TMP}) between 2 to 5 bar. Thar Designs, Inc. built the system based on our design.[6] The schematic diagram of the system is shown in Fig. 1. The major components of the filtration unit include: a liquid CO_2 source tank (1), a feed tank (2) with a quartz view cell (3), a high pressure pump

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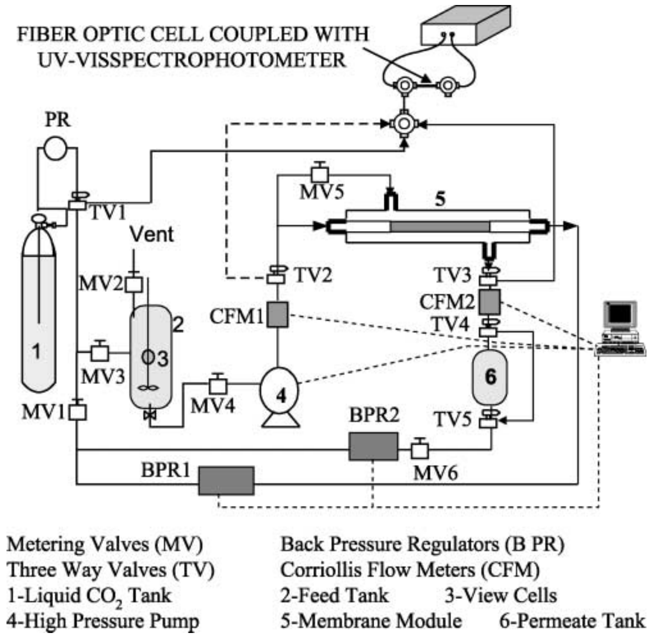

Figure 1. Schematic of high pressure UF and MF membrane filtration system.

(4), a membrane module (5), and a permeate tank (6). The set-up is also equipped with two backpressure regulators (BPR1, BPR2) and two Corriollis mass flow meters (CFM1, CFM2). The high-pressure pump, backpressure regulators and the mass flow meters are computer controlled. The details of the experimental unit are reported elsewhere.[7]

The sampling unit for this high-pressure system was designed using a fiberoptic cell coupled with UV–VIS spectrophotometer, which is shown schematically in Fig. 2. We chose spectrophotometry because we needed only quantitative analysis and it is inexpensive. The fiberoptic cell was used as a sampling cell because of our high-pressure application and it is easily constructed from conventional fittings.

A Cary-50 Conc UV–VIS Spectrophotometer (Varian Analytical Instruments, Walnut Creek, CA) was used for the concentration measurement in this work. The instrument was fitted with the fiberoptics interface, which was placed in the sample compartment to focus the beam from the source into the input fiber and from the output fiber to the detector. Instrument control and data collection were performed using the Cary Win UV Concentration

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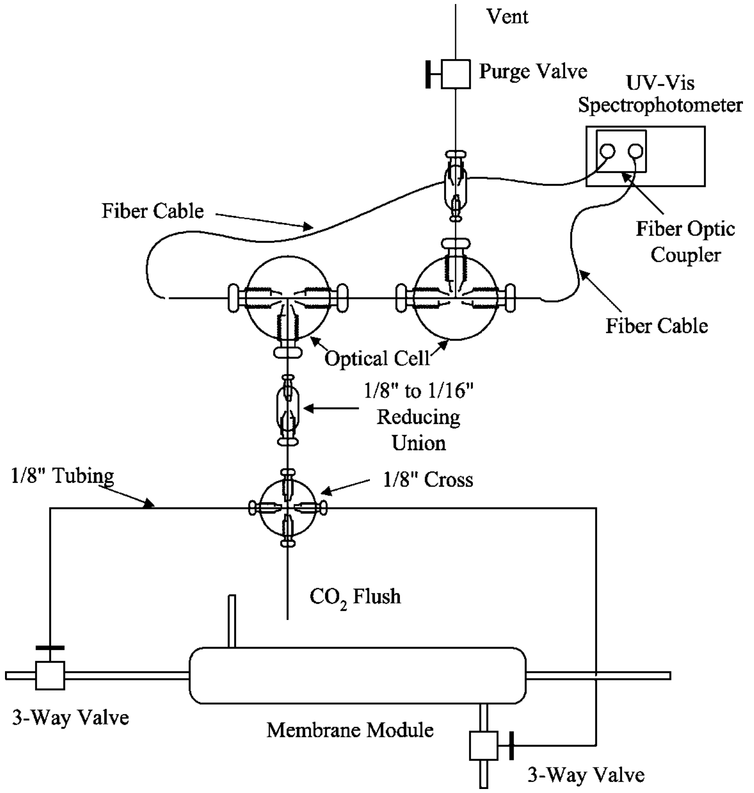

Figure 2. Schematic of fiberoptic based system coupled with UV–VIS spectroscopy.

software installed on a PC. Two fiberoptic cells with different path lengths, 5 mm and 0.5 mm, were constructed, thus facilitating measurement of samples over a wide concentration range. The cells were constructed from commercially available stainless steel unions and fittings. The optical fibers used for this work was comprised of a 600-μm high OH^- silica core surrounded by silica cladding and a polyimide buffer, with a total outer diameter of 710 μm and a numerical aperture of 0.22. The proximal end of each fiber was fitted with an SMA 906 connector for coupling to the Cary-50 UV–VIS fiberoptics interface, and the distal end was sealed into a high-pressure cell. The details of the fiberoptic cell design is given elsewhere.[8]

The entire system was tested for its functionality by using the stainless steel membrane module (in-house design) with liquid carbon dioxide as feed

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solution. Control over pressures in the system was adequate and carbon dioxide in the permeate side could be maintained in liquid state at preset transmembrane pressure. After a test run, the membrane module was taken apart and leak tested. No leaks were detected.

A commercially available surfactant, Triton X-100 (polyethylene glycol tert-octylphenyl ether), dissolved in liquid CO_2 was used as a feed for crossflow filtrations using both porous stainless membrane and microporous ceramic membranes. The concentrations of Triton X-100 in the feed and permeate streams were monitored on-line using fiberoptic cell coupled with UV–VIS spectrophotometry. To obtain a calibration curve for spectrophotometry, a series of standard solutions was prepared. Since the system operating at high pressure, it was considered inconvenient to prepare solution in liquid CO_2 media. To overcome this problem, three substituted solvents (hexane, cyclohexane, and ethyl acetate) were investigated. These solvents were chosen to be candidates since they have a polarity similar to that of liquid CO_2. The solutions of Triton X-100 in the candidate solvents were prepared and their spectra were obtained and compared to the solution in liquid CO_2.

The patterns of the spectra of hexane, cyclohexane, and ethyl acetate in 1.0% Triton X-100 is shown in Fig. 3(a). The spectra of liquid CO_2 solution is shown in Fig. 3(b). As seen in Fig. 3(a), both solutions in hexane and cyclohexane show two peaks at 275 nm and 285.1 nm. On the other hand, solutions in ethyl acetate had a pattern of spectrum different from hexane and cyclohexane. The spectrum of ethyl acetate shows one peak at 275 nm, with the highest molar absorptivity among all the candidates. When the spectra of the Triton X-100 solutions in candidate solvents is compared with that of liquid CO_2, which shows one peak at 275 nm, the spectrum of the solution in ethyl acetate shows the most similar behavior to liquid CO_2. Both spectra have a similar pattern and produce a peak at the same wavelength. Therefore, ethyl acetate was chosen to be the substituted solvent for liquid CO_2 to prepare the calibration curve for the concentration measurement because of its high molar absorptivity and the close resemblance to that of liquid CO_2. The detail of the calibration method is reported elsewhere.[8]

RESULTS AND DISCUSSION

Crossflow membrane filtration experiments were performed in both microporous stainless steel membrane and ceramic membranes. The microporous stainless steel tubular elements were obtained from Mott

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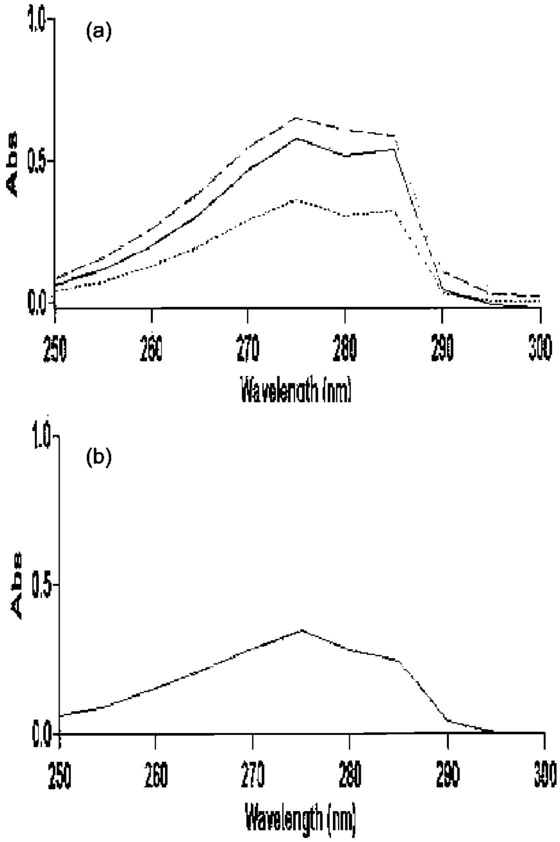

Figure 3. (a) The spectra of Triton X-100 in candidate solvents (dashed line for ethyl acetate, solid line for cyclohexane, and dotted line for hexane). (b) The spectra of Triton X-100 in liquid carbon dioxide.

Corporation. The dimensions and specifications of the stainless steel tubular elements were:

Effective tube length:	31.75 cm
Inside diameter:	0.603 cm
Average pore size:	0.20 μm
Membrane surface area:	60.14 cm^2

The dimensions and specifications of the ceramic membrane elements obtained from U.S. Filter were:

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Effective tube length:	25 cm
Inside diameter:	0.70 cm
Average pore size:	0.020 μm and 1000 Dalton
Membrane surface area:	55 cm^2

The membrane tubes were retrofitted in an in-house-designed membrane housing, as discussed earlier. The permeate flux data for Triton X-100 in liquid CO_2 in the concentration range of 0 to 4 wt% is shown in Fig. 4 as a function of the mass flow rate of the feed. The filtration experiments were conducted at a transmembrane pressure of 2 bar (74 bar feed pressure and 72 bar permeate side pressure), and the operating temperature was in the range of 20°C to 25°C. On-line analysis was performed for Triton X-100 using the fiberoptic cell coupled UV–VIS spectrophotometer for the feed and permeate streams. The rejectivity (%) of Triton X-100 by the membrane was calculated using the following equation:

$$\beta = \left(1 - \frac{C_P}{C_F}\right) \times 100 \qquad (1)$$

where β is solute rejectivity of the membrane, and C_F and C_P are the concentrations of the feed and permeate solutions (wt%), respectively.

The result showed that the 0.2-μm stainless steel membrane provided very little rejectivity of Triton X-100. As seen in Fig. 4, the permeate flux

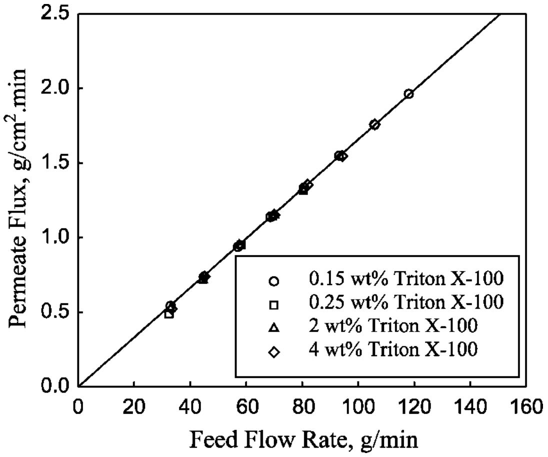

Figure 4. Effect of feed flow rate on permeate flux at various Triton X-100 concentrations in 0.20-μm stainless steel membrane at $\Delta P_{TMP} = 2$ bar.

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increases with increasing feed flow rate but for all concentrations, the flux is almost the same as that of pure CO_2 feed flux. The solid line gives the regressed flux data for pure CO_2 feed. Since the pore size of stainless membrane is significantly larger compared to the molecular size of Triton X-100, the membrane was not expected to provide any rejectivity or selectivity to the solute. This investigative study showed that the membrane the filtration system worked well as designed.

Figure 5 shows the permeate flux of 0.03 wt% of Triton X-100 in liquid CO_2 through the 0.02-μm and the 1000-Dalton ceramic membranes. The 0.02-μm ceramic membranes showed insignificant resistance to the liquid CO_2. Its flux decreased slightly throughout the experiment and ultimately became constant. Due to the difference in the membrane pore size and the molecular size of Triton X-100, it appears that Triton X-100 was barely retained by this membrane. The average pore size of 0.02-μm membrane is equivalent to about 11,500 Dalton. The molecular weight of Triton X-100 is 647 Dalton. The 1000-Dalton ceramic membrane, on the other hand, showed significant resistance to the liquid CO_2 permeate flow. The flux of CO_2 through 1000-Dalton membrane declined dramatically with time and, ultimately, reached a near steady-state value. This decline in liquid CO_2 flux can be

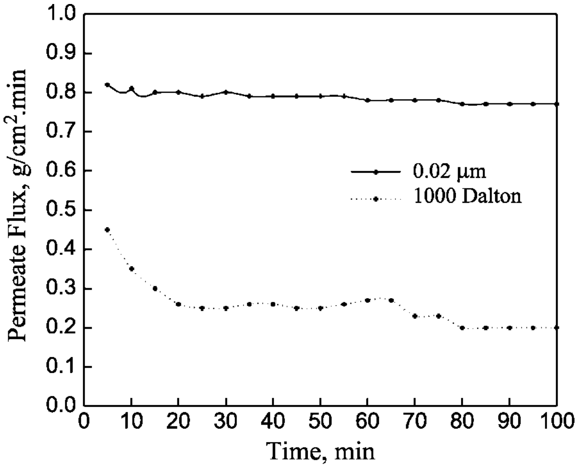

Figure 5. Liquid CO_2 flux variation with time in crossflow filtration of 0.03 wt% Triton X-100 solutions through 0.02-μm and 1000-Dalton ceramic membranes (feed velocity: 40 g/min; $\Delta P_{TMP} = 3.5$ bar).

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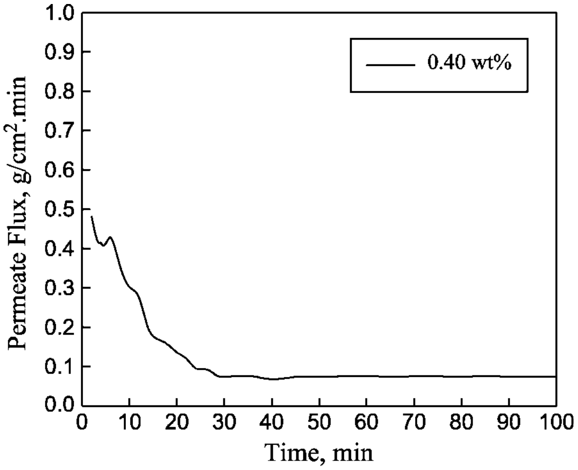

Figure 6. Liquid CO_2 flux variation with time in crossflow filtration of 0.4 wt% Triton X-100 solutions through 0.02-μm and 1000-Dalton ceramic membranes (feed velocity: 70 g/min; $\Delta P_{TMP} = 3.5$ bar).

attributed to development concentration boundary layer and membrane fouling (by pore plugging) by Triton X-100.

The CO_2 flux data for 0.4 wt% Triton X-100 solution in 1000-Dalton ceramic membrane is shown in Fig. 6. With increased Triton X-100 concentration from 0.03 wt% to 0.4 wt%, the rapid decline in CO_2 flux was a clear sign of concentration polarization and membrane fouling. The membrane provided Triton X-100 rejectivity of about 80%.

The performance of 0.02-μm ceramic membrane is shown in Fig. 7 for filtration of Triton X-100 solutions at 0.15, 0.30, and 0.5 wt%. The liquid CO_2 flux data showed that the permeate flux decreased rapidly in the first 30 minutes of operation and then reached to some steady values. The results also showed that with increased solute concentration in the feed, flux decreased as expected. The solute rejectivity of the membrane was found to be as high as 55%.

CONCLUSION

A high-pressure crossflow membrane filtration system was designed, built, and tested for crossflow filtration of liquid CO_2 without phase change. Crossflow filtration experiments with Triton X-100 solutions in liquid CO_2 using 0.02-μm and 1000-Dalton ceramic membranes show that it is possible to separate liquid

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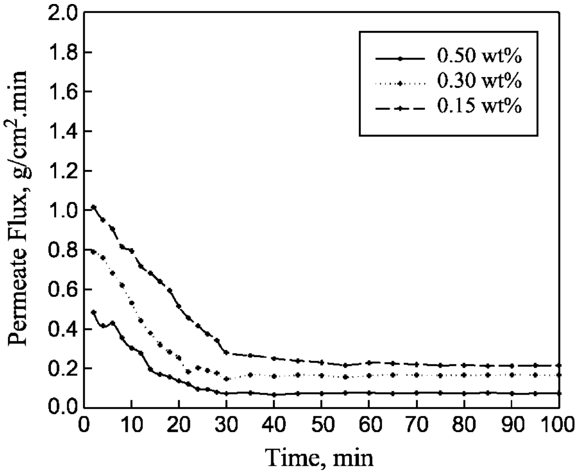

Figure 7. Liquid CO_2 flux variation with time in crossflow filtration of 0.15, 0.30, and 0.50 wt% Triton X-100 solutions, respectively, through 0.02-μm ceramic membranes (feed velocity: 70 g/min; $\Delta P_{TMP} = 3.5$ bar).

CO_2 without phase change. The preliminary test results suggest that it is possible to avoid or eliminate recompression step in the recovery of CO_2 if membrane-based separations is used in handling liquid CO_2-laden process streams.

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