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Compressed solvents for the extraction of fermentation products within a hollow fiber membrane contactor

Geoffrey D. Bothun [a], Barbara L. Knutson [a,*], Herbert J. Strobel [b], Sue E. Nokes [c], Esteban A. Brignole [d], Soledad Díaz [d]

[a] *Department of Chemical and Materials Engineering, University of Kentucky, 177 Anderson Hall, Lexington, KY 40506-0046, USA*
[b] *Department of Animal Sciences, University of Kentucky, Lexington, KY 40546-0215, USA*
[c] *Department of Biosystems and Agricultural Engineering, University of Kentucky, Lexington, KY 40546-0276, USA*
[d] *PLAPIQUI-UNS-CONICET-CC 717, 8000 Bahía Blanca, Argentina*

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Abstract

The feasibility of extracting aqueous ethanol and acetone within a hollow fiber membrane contactor (HFC) has been examined using compressed CO_2 (69 bar), ethane (69 bar), and propane (34.5 bar) at ambient temperature. Ethanol and acetone were chosen as 'model' fermentation products to further examine the potential for extractive fermentation with compressed fluids. Aqueous and compressed solvent streams were contacted within a single hydrophobic isotactic polypropylene membrane fiber (0.6 mm ID; 106.7 cm in length; 75% porosity), providing a porous barrier between the two immiscible phases. The amount of solute extracted was determined as a function of the aqueous flowrate (tubeside) and molar solvent to feed ratio. The amount of aqueous ethanol (10 wt.%) and acetone (10 wt.%) extracted from binary feed solutions with compressed propane ranged from 6.4 to 14.3% and 21.8 to 90.6%, respectively, as a function of the aqueous flowrate (0.1 to 2 ml/min) and molar solvent to feed ratio ($S/F = 1$ to 10). Comparatively, ethanol extraction with compressed CO_2 ranged from 4.7 to 31.9% with similar variations in the aqueous flowrate (0.1 to 1 ml/min) and molar solvent to feed ratio (3 and 10). Acetone extracted with CO_2 ranged from 67.9 to 96.1% when varying the aqueous flowrate (0.1 to 1 ml/min) at a molar solvent to feed ratio of 3. Ternary ethanol/acetone/water mixtures were also examined to determine the effect of multi-solute aqueous solutions. The effect of aqueous and compressed fluid flows on extraction are interpreted based on the equilibrium distributions of the solutes between water and the compressed fluid (estimated using a group contribution association equation of state (GCA–EOS)) and the mass transfer characteristics of the compressed fluid.

Keywords: Compressed fluid; CO_2; Propane; Extractive fermentation; Hollow fiber contactor (HFC)

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1. Introduction

Supercritical and compressed fluid technologies have recently been extended to bioprocessing as an alternative to conventional separation techniques

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* Corresponding author. Tel.: +1-859-257-5715; fax: +1-859-323-1929
E-mail address: bknutson@engr.uky.edu (B.L. Knutson).

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such as extraction with organic solvents and distillation [1–3]. Unlike traditional organic solvents, the solvent strength and selectivity of compressed fluids are easily tuned with temperature and pressure. Depressurization leads to a solvent-free solute and aqueous phase, which is very important for biologically based separations where solvent toxicity and contamination are serious concerns. In addition, high mass transfer rates are inherent to these processes due to low kinematic viscosities associated with supercritical and compressed fluids [1,4]. For some solute/solvent systems, supercritical fluid-based extraction processes may be more energy efficient than distillation due to the ability to separate both volatile and nonvolatile components at low temperatures and mild pressures [1,2].

The productivity of many fermentation processes is limited by product inhibition, requiring the development of in situ extractive fermentation techniques that are biocompatible and provide adequate separation. There have been numerous studies on the extraction of various organic solutes from aqueous solutions with compressed or supercritical CO_2 (SC-CO_2). In particular, the extraction of alcohol has been investigated in an effort to reduce energy consumption associated with dehydration and to take advantage of enhanced mass transfer associated with SC-CO_2 [3,5–11]. Although numerous studies have demonstrated the ability of CO_2 to extract fermentation products from aqueous solutions, compressed CO_2 is not biocompatible with most microorganisms, making it a poor solvent for the in situ extraction of fermentation broths [2]. The toxicity of SC-CO_2 to microorganisms has been partially attributed to the acidic pH that results from the increased CO_2 solubility at high partial pressures [12–14] and a potential anesthetic effect observed on yeast [15].

The investigations of phase behavior of compressed light hydrocarbon/aqueous ethanol systems show that comparable distribution coefficients and loading of ethanol in the extractant phase may be achieved at lower pressures relative to compressed CO_2 [16–27]. In addition, Brignole and coworkers [20,23,26] have demonstrated that compressed propane, also acts as an entrainer to break the ethanol–water azeotrope. Light-hydrocarbon solvents, such as ethane and propane, may also be more appropriate for bioprocessing applications due to potentially improved biocompatibility [28] and their reduced solubility in water relative to compressed CO_2. Recent investigations of the biocompatibility of compressed solvents were performed to determine the feasibility of in situ extractive fermentation for the conversion of cellobiose to ethanol with anaerobic, non-growing *Clostridium thermocellum* [28–30]. Fermentation in the presence of compressed CO_2 (70 bar, 333 K) reduced the activity of *C. thermocellum*, resulting in decreased cellobiose utilization and an 80% reduction in ethanol production [28]. In the presence of compressed ethane and propane (70 bar, 333 K), ethanol production decreased by approximately 60%. Although significant, the inhibition by compressed hydrocarbons was much less than that observed for incubations in the presence of excess pentane, heptane, and hexane at atmospheric pressure, which rendered the cells completely inactive [29]. In addition, the presence of compressed propane increased the selectivity of the fermentation to the product ethanol relative to the acid products, lactate and acetate. The observed solvent toxicity was attributed to the direct contact of the cells with the aqueous–hydrocarbon interface, or phase toxicity [30]. In contrast, molecular toxicity, which describes the effect of dissolved solvent molecules within a single (aqueous) phase, had a negligible effect on the activity of non-growing *C. thermocellum* [29].

One approach to minimizing the cell contact with the solvent interface is to implement a membrane partition in the form of a hollow fiber membrane contactor (HFC) [31]. There are many processing advantages to HFC-aided solvent extraction relative to conventional extraction, including high throughput, increased sterility, high mass transfer efficiency, and the elimination of emulsions [32]. HFCs have traditionally been used to remove volatile organics from contaminated aqueous streams using a gas sweep or conventional organic solvents [32–37]. The extraction performance and wide-range applicability of HFCs has led investigators to explore HFC-aided extractive fermentation for ethanol production by *Sacchar-*

omyces cerevisiae (yeast). These studies have shown increased ethanol productivity using long-chain alcohols as extracting solvents [38–41]. The toxic effect of organic solvents on microorganisms generally decreases with increasing chain length, requiring the use of long-chain compounds for in situ extraction [42]. Such solvents have high viscosities relative to water, requiring a diluent (typically kerosene) for processing. In addition, ethanol partitioning into the solvent phase decreases with increasing chain length, illustrating the tradeoff between biocompatibility and ethanol extraction [43].

Compressed CO_2 has recently been introduced as an alternative to organic solvents for the recovery of aqueous solutes using HFCs [44], Robinson and Sims [44,45] have shown that a wide range of aqueous organic solutes can be extracted at relatively low pressures (69–100 bar) and ambient temperatures. Specifically, greater than 95% extraction has been achieved for aqueous streams containing volatile organic compounds such as acetone, tetrahydrafuran, dichloroethane, toluene, and chloroform [45]. Recovery and recycling of the compressed solvent is achieved through depressurization, eliminating the need for further aqueous-phase purification steps.

The objective of this work is to extend HFC extraction to compressed hydrocarbons by determining the feasibility of ethanol and acetone recovery from aqueous solutions with compressed ethane and propane, and comparing this recovery to extractions performed with compressed CO_2. Extraction within a single fiber-isotactic polypropylene HFC was investigated as a function of solute, compressed solvent, aqueous phase (tubeside) flowrate, and molar solvent to feed ratio. Ethanol and acetone, which have largely varying compressed solvent–water equilibrium distributions as predicted by the group contribution association equation of state (GCA–EOS) [16,21,22,24], were chosen as ‘model’ fermentation products, and fed countercurrent to the solvent phase as 10 wt.% aqueous solutions. Compressed ethane (69 bar) and propane (34.5 bar) at ambient temperature were employed as potential hydrocarbon extracting solvents. Compressed CO_2 (69 bar) at ambient temperatures was also used as an extractive solvent to provide a comparison to previous studies.

2. Experimental design

2.1. Materials

Propane (99.0%) and ethane (99.0%) purchased from Scott Specialty Gas and CO_2 (99.99%) purchased from AGA Specialty Gas were used without further purification. Absolute ethanol and HPLC grade acetone (99.7%) were purchased from Aaper Alcohol and Chemical Co. and Mallinckrodt Baker, Inc., respectively. Aqueous solutions were prepared with deionized water.

2.2. Apparatus

A single fiber membrane contactor was purchased from Porocrit^{TM} (Berkeley, CA). The HFC is constructed with a single hollow fiber lumen (106.7 cm in length; 1.02 mm OD; 0.6 mm ID) housed in stainless steel tubing (3.18 mm OD, 1.52 mm ID). The membrane fiber (0.2 μm pore radius) is made of microporous hydrophobic isotactic (semicrystalline) polypropylene (75% porosity). Scanning electron microscope images of the fiber are provided in Fig. 1. The lumen tubeside is connected at both ends with epoxy to medical-grade syringe tips. The shellside inlet and outlet ports are located at each end of housing and are isolated from the tubeside.

A schematic of the experimental apparatus, containing the HFC and the custom designed flow system, is given in Fig. 2. A countercurrent mode of contacting was used, with the aqueous phase fed tubeside and the compressed solvent phase passing shellside. The aqueous–solvent interface was maintained within the fiber wall by controlling the transmembrane pressure ($\Delta P_{tr} = P_{aqueous} - P_{solvent}$), or axial pressure drop. ΔP_{tr} was maintained between 0.2 and 0.7 bar during the HFC experiments. Aqueous feed was introduced using an HPLC pump (Valco^{TM} Series III Digital Pump, 0–10 ml/min) and compressed solvent was supplied with an ISCO syringe pump (model

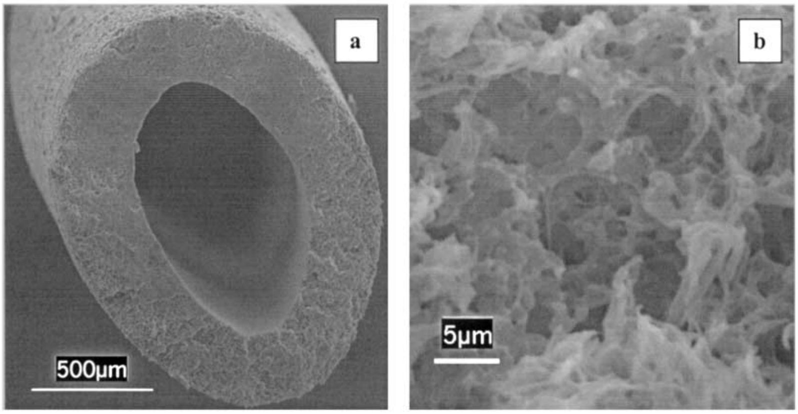

Fig. 1. Scanning electron microscope micrographs of the polypropylene membrane fiber cross-section at magnifications of (a) 60 × (500 μm) and (b) 4000 × magnification (5 μm).

500D). A pressurized view cell (70 ml Jerguson view cell, rated to 345 bar) was used to equalize the pressure between the aqueous raffinate and compressed solvent feed by maintaining a constant level of the interface. Pressure was monitored at the HPLC pump, ISCO syringe pump, and by a digital pressure gauge (Druck® model DPI 280, ± 0.1 bar) located at the top of the equalizing vessel. The position of the interface was visually monitored and adjusted by removing raffinate using an outlet micrometering valve (Autoclave®, model 10VRMM2812). The transmembrane pressure was

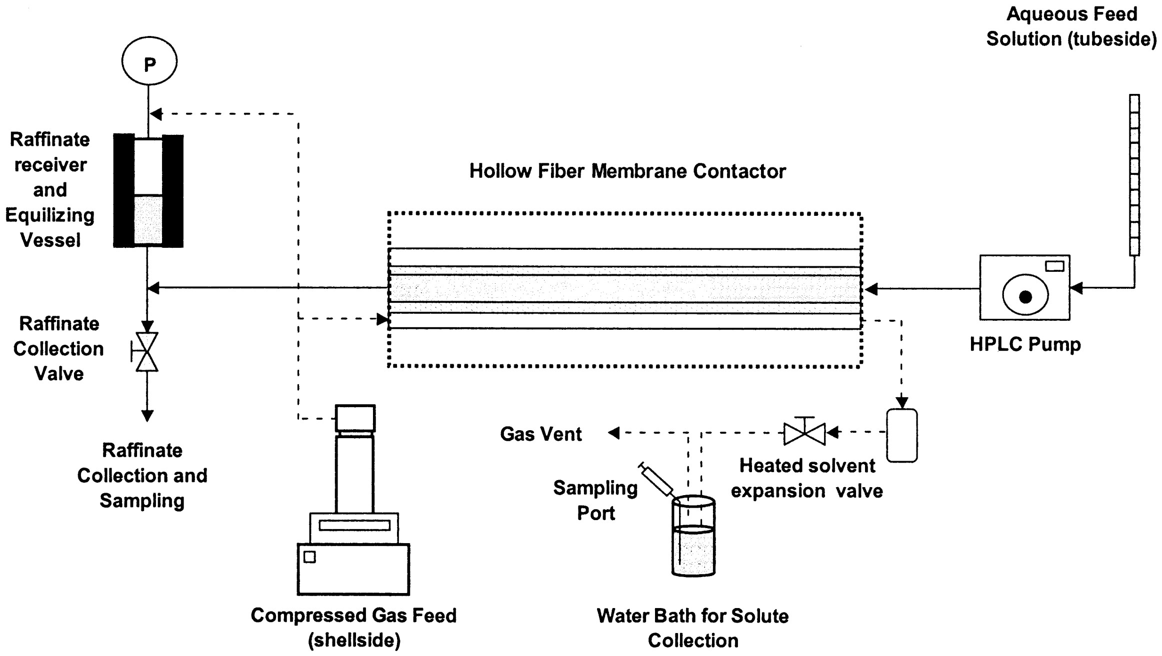

Fig. 2. Schematic of the HFC extraction apparatus. Shaded regions and solid lines identify the presence and flow of the aqueous phase, respectively. Dashed lines represent the flow of compressed solvent. The perforated boundary around the contactor indicates a plexiglass outer shell.

approximated as the difference between pressure at the aqueous feed and the solvent feed. The gas phase was expanded through a heated solvent expansion micrometering valve (model 10VRMM2812) into a cooled water bath (~0 °C) containing small glass beads to remove extracted solute.

2.3. Operation

The entire HFC system was first filled with the compressed solvent using an ISCO syringe pump operated in constant pressure mode (propane, 34.5 bar; ethane, 69 bar; CO_2, 69 bar). All experiments were performed at ambient temperature (298 K). An aqueous feed solution (10 wt.% ethanol; 10 wt.% acetone; or a mixture of 5 wt.% ethanol and 5 wt.% acetone) was then introduced tubeside at the desired flowrate. The aqueous (tubeside) flowrates ranged from 0.1 to 2.0 ml/min, corresponding to linear velocities of 0.6 to 11.8 cm/s or residence times within the fiber between 180 and 15 s. As the aqueous phase entered the fiber lumen, the compressed solvent phase was displaced into the membrane and shellside, establishing an interface at the lumen inner diameter. Aqueous raffinate was collected in the equalizing vessel until a compressed solvent/aqueous phase interface was visually established.

The position of this interface was maintained by removing raffinate through the raffinate collection micrometering valve. After the interface was established in the equalizing vessel, countercurrent compressed solvent flow was achieved by operating the syringe pump in constant flow mode at the desired molar solvent to feed ratio (S/F, 1 to 10). The S/F ratios studied correspond to flowrates of 0.15–6.0 ml/min, linear velocities of 0.1–5.8 cm/s, and residence times between 1067–18 s, respectively. The heated solvent expansion valve was then adjusted to release the compressed gas phase and maintain the desired operating pressure. Raffinate samples were collected after an aqueous solution of 10–20 times the tubeside volume had passed through the system. Samples were placed into sealed vials and stored under refrigeration until analysis. As suggested by the manufacturer, periodic maintenance included regenerating the hydrophobicity of the fiber by washing with isopropyl alcohol and drying with nitrogen gas.

2.4. Analysis

The concentrations of ethanol and acetone in samples of the feed and raffinate were analyzed by a gas chromatograph (GC; Hewlett–Packard 6890) equipped with a capillary column (cross-linked FFAP) and a thermal conductivity detector (TCD). Sample injections of 0.5 μl were vaporized at the septum port at 175 °C and carried by helium through the column at 25 cm/s. The temperature was held at 70 °C for 3 min within the column and then raised to 120 °C at a rate of 20 °C/min. Each sample was analyzed in triplicate. The percentage of solute extracted (or experimental extraction efficiency, ϕ_{exp}) is reported, and is based on the difference between the feed and raffinate concentration divided by the feed concentration.

3. Results and discussion

Compressed ethane (69 bar), propane (34.5 bar), and CO_2 (69 bar) were examined as potential solvents for the extraction of dilute aqueous ethanol and/or acetone (10 wt.%) within the HFC at ambient temperatures. Physical properties associated with these solvents at the experimental conditions and their critical properties are given in Table 1. Experiments were performed at pressures corresponding to liquid conditions of the pure compressed solvent at ambient temperature. The equilibrium distribution coefficients of the solutes between the compressed solvent and water phase ($m_i = y_i/x_i$) were predicted using the GCA–EOS, which was developed to predict phase behavior of aqueous oxychemicals and compressed gas solvents [16,21,22,24]. Predictions of the ethanol distribution coefficient between water and propane at 298 K were made in the present work with revised parameters, including a temperature dependent parameter, for extrapolation of literature data [19] to ambient temperatures. The GCA–EOS parameters required for the predictions of all the systems studied are given in Table 2.

Table 1
Physical properties of ethane, propane, and CO_2 at experimental conditions

Compressed solvents at 298 K						Critical properties[a]	
Fluid	Pressure (bar)	Density (g/ml)[b]	Kinematic viscosity (cm^2/s)[c,d]	Diffusivity (10^4 cm^2/s)[e]		Temperature (T_c, K)	Pressure (P_c, bar)
				Ethanol	Acetone		
Ethane	69	0.34	1.2×10^{-3}	2.2	2.6	305.42	48.8
Propane	34.5	0.48	2.2×10^{-3}	1.2	1.1	369.82	42.5
CO_2	69	0.71	2.4×10^{-4}	7.3	6.7	304.19	73.8

[a] Based on DIPPR data [46].
[b] Modified Benedict Webb Reubin EOS [47].
[c] Orbey and Sandler, 1993 [48].
[d] Generalized correlation for gas viscosity [49].
[e] Estimated via Wilke–Chang.

The equilibrium distribution coefficients (m_i) of ethanol and acetone between the compressed solvent (ethane, 69 bar; propane, 34.5 bar; and CO_2, 69 bar) and the aqueous phase are presented as a function of pressure at 298 K (Fig. 3). At these operating conditions, the ethanol distribution coefficients (m_{ethanol}) were calculated as 0.04, 0.065, and 0.1 for ethane, propane, and CO_2,

Table 2
Revised lists of (a) pure group and (b) binary interaction parameters used in the GCA–EOS

Group	Qi	Ti	gi*	gi′	gi″
(a) Pure group parameters					
WS CH_3[a]	0.848	600.0	316910	0.9274	0
CH_2OH[c]	1.124	512.6	787954	0.3635	0
CH_3CO[a]	1.488	600.0	888410	0.7018	0
H_2O[c]	0.866	647.3	1383954	0.2493	0
CO_2[a]	1.261	304.2	531890	0.578	0
Propane[a]	2.236	369.8	436890	−0.463	0
(b) Binary interaction parameters					
Group I	Group j	Kij*	kij′	αij	αji
WS CH_3	CH_2OH[c]	0.85	0	1.62	11.9
	CH_3CO[a]	0.834	0.084	0.854	5.146
	H_2O[c]	0.6	0	1.2	1.2
	Propane[a]	1	0	0	0
	CO_2[a]	0.892	0	3.369	3.369
CH_2OH	H_2O[c]	0.92	0	0.7024	6.35074
	Propane[b]	0.8686	0.1	11.9	1.89
	CO_2[a]	1.1	0	−7.5	−6.5
CH_3CO	H_2O[b]	0.954	0	11.0146	19.0813
	Propane[a]	0.784	0	5.146	0.691
	CO_2[a]	1.025	0.108	0.17	0.17
H_2O	Propane[a]	0.6	0	22.2426	0.4898
	CO_2[a]	1.1	0	−1.98	−0.5

[a] Jørgensen, 1988 [52].
[b] Present work.
[c] Gros et al., 1996 [21].

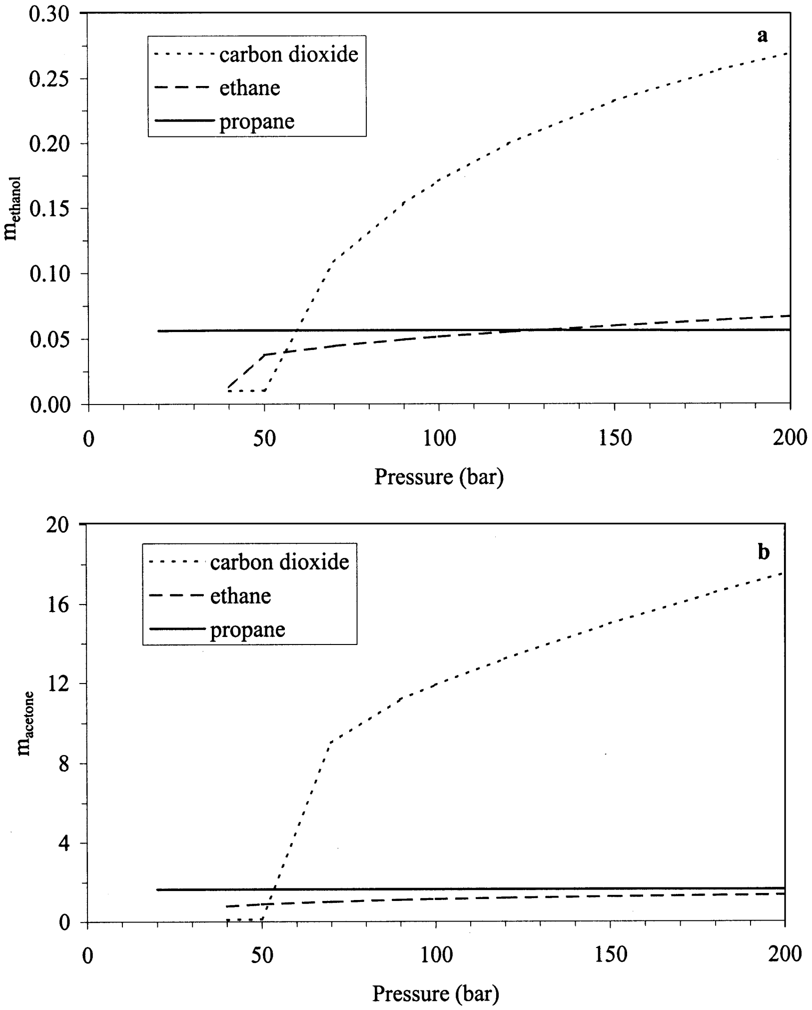

Fig. 3. The predicted equilibrium distribution coefficient (GCA–EOS) between an equimolar compressed solvent phase/aqueous phase is shown as a function pressure for (a) aqueous ethanol and (b) aqueous acetone at 10 wt.% solute and 298 K.

respectively, for a 10 wt.% solution of ethanol in an equimolar mixture of water and solvent (Fig. 3a). Small changes in ethanol concentration had little affect on m_i for the compressed gases, as determined by the GCA–EOS (data not shown).

Within an aqueous phase, acetone has a much higher affinity for the compressed solvents than ethanol. Compressed propane is a liquid at 298 K over the pressure range used for prediction (20–200 bar, Fig. 3b); the acetone partitioning from the aqueous phase is essentially constant for a 10 wt.% solution of acetone in an equimolar mixture of water and solvent ($m_{acetone} = 1.63$). At 69 bar and 298 K, corresponding to liquid conditions of CO_2, $m_{acetone}$ is approximately 9.5 (Fig. 3b) for a 10 wt.% solution of acetone in an equimolar mixture of water and CO_2.

Ethanol and acetone were successfully extracted from aqueous solution within an HFC using compressed propane and CO_2 at ambient temperatures for a range of aqueous flows and molar solvent to feed ratios (Tables 3–5). No significant extraction of ethanol by ethane was observed for aqueous flowrates ranging from 0.15 to 1.0 ml/min

Table 3
Extraction of aqueous ethanol (10 wt.%) with compressed propane and CO_2 at ambient temperature

Compressed solvent		Aqueous feed	
Fluid (pressure, bar)	S/F [a]	Flowrate (ml/min)	Extraction (% ± standard deviation, S.D.)[b]
	1	0.15	6.8 ± 0.3
		0.25	6.4 ± 0.4
		0.50	9.0 ± 0.4
		0.75	11.3 ± 0.6
		1.0	9.2 ± 1.1
		1.5	13.7 ± 0.9
		2.0	11.0 ± 1.2
Propane (34.5 bar)	2	0.15	7.6 ± 0.2
		0.25	6.6 ± 0.1
		1.0	9.5 ± 1.3
		1.5	13.1 ± 1.2
		2.0	9.9 ± 0.6
	3	0.15	7.4 ± 1.4
		0.25	10.4 ± 1.0
		1.0	14.0 ± 1.1
		1.5	13.4 ± 1.1
		2.0	14.3 ± 0.4
	10	0.10	9.7 ± 1.6
CO_2 (69 bar)	3	0.15	15.2 ± 0.5
		0.25	10.4 ± 0.5
		0.50	4.7 ± 1.8
		1.0	9.9 ± 0.5
	10	0.10	31.9 ± 1.4

[a] Molar solvent to feed ratio (S/F).
[b] S.D. based on GC analysis.

at $S/F = 3$. For these experiments, we were unable to differentiate between ethanol extraction and the uncertainty associated with GC analysis. The ranges of the flow variables were limited by the need to maintain steady-state in a single fiber HFC at a given pressure.

Successful extraction suggests that the transmembrane pressure was sufficient to prevent aqueous/solvent breakthrough and maintain the interface at or within the fiber wall. In addition, potential swelling of the polymeric membrane by the compressed solvent did not compromise the separation. Although polymer swelling by compressed CO_2 is observed in many amorphous systems, swelling is negligible in most semicrystalline polymers including isotactic polypropylene [50]. Reproducible results after extended use suggest that the physical properties of the membrane remained unchanged. Consistent with successful extraction, no noticeable aqueous breakthrough on the shellside was observed in our investigations. However, the reported extent of extraction within the HFC may be overestimated based on the presence of an aqueous and solvent interface within the static equalizing vessel. While not included in our interpretation of the results, this vessel likely act as an addition extraction stage.

The interpretation of the efficiency of HFC-based extractions using compressed solvents is based on both thermodynamic driving forces and mass transfer characteristics of the process. Thus, a simplified, preliminary mass transfer analysis has been performed based on the theory of solvent extraction within a continuous counter-current mass transfer device. The Colburn equation can be used to predict the extraction efficiency ($\phi_{\mathrm{predicted}}$) of the HFC:

Table 4
Extraction of aqueous acetone (10 wt.%) with compressed propane and CO_2 at ambient temperature

Compressed solvent		Aqueous feed	
Fluid (pressure, bar)	S/F [a]	Flowrate (ml/min)	Extraction (%±S.D.)[b]
	1	0.15	38.9±1.6
		0.25	36.6±0.9
		0.50	21.8±1.0
		1.0	22.6±0.9
Propane (34.5 bar)	2	0.50	30.4±1.3
		1.0	22.1±1.1
	3	0.15	64.6±1.4
		0.25	63.9±0.9
		0.50	33.5±1.2
		1.0	23.9±1.0
	10	0.10	90.6±0.9
CO_2 (69 bar)	3	0.15	96.1±1.8
		0.25	89.6±1.8
		0.5	68.9±1.8
		1.0	67.9±1.9

[a] Molar solvent to feed ratio (S/F).
[b] S.D. based on GC analysis.

$$\phi_{\text{predicted}} = 1 - \frac{1 - 1/S_F}{e^{N_{OL}(1-1/S_F)} - 1/S_F} \tag{1}$$

where S_F represents the extraction factor, which is the distribution coefficient of species i multiplied by the molar solvent to feed ratio ($S_F = m_i S/F$), and N_{OL} is the number of theoretical liquid phase transfer units. The required length of the HFC can be determined from the following relationship:

$$L = N_{OL} H_{OL} = \left[\frac{q_{aq}}{K_L a}\right] N_{OL} \tag{2}$$

Table 5
Extraction of aqueous ethanol (5 wt.%) and acetone (5 wt.%) from a ternary aqueous feed solution with compressed propane and CO_2 at ambient temperature

Compressed solvent			Aqueous feed	
Fluid (pressure, bar)	S/F [a]	Flowrate (ml/min)	Ethanol Extraction (%±S.D.)[b]	Acetone extraction (%±S.D.)[b]
	1	0.25	4.6±0.4	26.6±0.4
		0.50	6.9±0.2	35.2±0.1
		1.0	8.9±0.8	14.2±0.8
Propane (34.5 bar)	3	0.15	5.2±0.7	53.3±0.6
		0.25	9.5±0.3	50.3±0.1
		0.50	10.5±0.4	25.8±0.3
		1.0	11.8±0.3	27.7[c]
	10	0.1	8.1±0.6	87.4±0.1
CO_2 (69 bar)	3	0.15	17.5±0.9	97.3±1.1
		0.25	24.3±0.9	92.9±7.0
		0.50	21.0±1.0	78.8±6.0
	10	0.10	35.9±0.9	99.7±0.8

[a] Molar solvent to feed ratio (S/F).
[b] S.D. based on GC analysis.
[c] S.D. < 0.05.

where L is the length of the HFC lumen and H_{OL} is the theoretical height of the transfer unit. For a countercurrent contacting scheme, H_{OL} is further expressed as $q_{aq}/K_L a$, where K_L is the overall mass transfer coefficient, a is the lumen inner-area to volume ratio, and q_{aq} is the specific molar aqueous flowrate per unit cross section.

The overall mass transfer resistance ($1/K_L$) can be expressed as the summation of the individual mass transfer coefficients on the aqueous (k_w), membrane (k_m), and shell sides (k_s) according to the following equation:

$$\frac{1}{K_L} = \frac{1}{k_w} + \frac{d_i}{m_i d_o k_s} + \frac{d_i}{m_i d_{lm} k_m} \tag{3}$$

where d represents the inner (i), outer (o), and log-mean (lm) diameters of the fiber, and m_i is the distribution coefficient. Laminar flow prevails on both sides of the membrane; therefore, the Sherwood numbers ($k_w d_i/D_{AB}\rho_w$) and ($k_s d_o/D_{AB}\rho_s$) for both fluids are assumed to be constant ($\mathrm{Sh} \approx 4$) where ρ_w and ρ_s are the aqueous and solvent molar densities, respectively. This assumption is based on a mass transfer analogy of the limiting solutions of the classic Nusselt–Graetz heat transfer problem. Hence, K_L can be assumed independent of the individual flowrates on the tube and shell sides.

The membrane resistance ($1/k_m$) is assumed to be constant for a given system and is described as a function of solute diffusion through the solvent filled membrane pores [35]. The membrane mass transfer coefficient (k_m) is computed by relating the unhindered diffusion coefficient of the solute within the compressed solvent (D_{AB}) to the membrane thickness (t), porosity (ε), and tortuosity (τ).

$$k_m = \frac{D_{AB}\varepsilon}{t\tau} \tag{4}$$

Given these assumptions regarding mass transfer on either side of the membrane, N_{OL} can be predicted as a function of q_{aq} (Eq. (2)) and used to predict extraction efficiency ($\phi_{predicted}$; Eq. (1)). The predicted extraction efficiency is compared with the experimentally determined extraction efficiency (ϕ_{exp}) in Table 6. A more detailed analysis of the HFC mass transfer characteristics is currently being conducted to test the applicability of these assumptions for compressed solvent systems.

3.1. Aqueous ethanol extraction

Compressed propane (34.5 bar and 298 K) was used to extract aqueous ethanol (10 wt.%) within the HFC as a function of aqueous flowrate (Q_{aq}; 0.1–2 ml/min) and molar solvent to feed ratio (S/F; 1, 2, 3, and 10) (Table 3). A relatively small change in ethanol extraction (6.4–14.3%) was measured over the experimental range of Q_{aq} and S/F (Fig. 4). Furthermore, the values of the extraction factor for ethanol ($S_F = m_i S/F$) at the conditions studied in the present work range from 0.065 to 0.65, based on an ethanol distribution coefficient ($m_{ethanol} = 0.065$). The extractions observed experimentally are consistent with a countercurrent extraction at very low values of the extraction factor (Table 6).

The low value of $m_{ethanol}$ suggests that the dominant mass transfer resistance is within the solvent phase. This resistance is made up of the individual resistances of both the solvent-filled membrane wall and of the solvent flowing outside the fiber. Considering the low value of $m_{ethanol}$ and assuming that laminar flow prevails on both the tube and shell sides, the membrane is expected to offer the greatest mass transfer resistance. This is supported by Fig. 4, which shows only small changes in extraction efficiency as Q_{aq} and S/F increase.

Experimental extraction efficiencies (ϕ_{exp}) ranging from 4.7 to 31.9% were obtained when compressed CO_2 (69 bar and 298 K) was used to recover aqueous ethanol (10 wt.%) as a function of Q_{aq} (0.1–1 ml/min) and S/F (3 and 10) (Table 3). A previous study has demonstrated 20% ethanol extraction using compressed CO_2 (100 bar, 297 K) at a molar solvent to feed ratio of roughly 1, within an HFC module containing 120 of the same polypropylene fibers [45]. An increase in the aqueous flowrate from 0.15 to 1.0 ml/min at $S/F = 3$ decreased extraction from 15.2 to 9.9%. As in the case with compressed propane, the partitioning of ethanol within compressed CO_2 is

Table 6
Comparing predicted extraction efficiencies ($\phi_{predicted}$) with experimentally determined extraction (ϕ_{exp})

Solvent	Solute	Q_{aq} (ml/min)	N_{OL} (predicted)	S_F (m_iS/F)	$\phi_{predicted}$ (%)	ϕ_{exp} (%)
		0.15	1.47	0.065	6.5	6.8
		0.25	0.88	0.065	6.5	6.4
		0.5	0.44	0.065	6.5	9.0
		0.75	0.29	0.065	6.4	11.3
		1.0	0.22	0.065	6.2	9.2
		1.5	0.15	0.065	5.8	13.1
		2.0	0.11	0.065	5.2	11
	Ethanol ($m = 0.065$)	0.15	1.47	0.13	13.0	7.6
		0.25	0.88	0.13	13.0	10.4
		1.0	0.22	0.13	10.3	9.5
		1.5	0.15	0.13	8.6	13.1
		2.0	0.11	0.13	*12*	9.9
Propane		0.15	1.47	0.2	19.5	4.7
		0.25	0.88	0.2	19.1	10.4
		1.0	0.22	0.2	12.7	14.0
		1.5	0.15	0.2	9.9	13.4
		2.0	0.11	0.2	8.2	14.3
		0.1	2.20	0.65	56.3	9.7
		0.15	9.93	1.63	99.2	38.9
		0.25	5.95	1.63	95.9	36.6
		0.5	2.98	1.63	84.8	21.8
		1.0	1.49	1.63	66.8	22.6
.	Acetone ($m = 1.63$)	0.5	2.98	3.26	90.8	30.4
		1.0	1.49	3.26	72.3	22.1
		0.15	9.93	4.89	100	64.6
		0.25	5.95	4.89	99.3	63.9
		0.5	2.98	4.89	92.4	33.5
		1.0	1.49	4.89	74.0	23.9
		0.1	14.88	16.9	100	90.6
CO_2	Ethanol ($m = 0.1$)	0.15	1.54	0.3	29.4	15.2
		0.25	0.92	0.3	27.5	10.4
		0.5	0.46	0.3	22.0	4.7
		1.0	0.23	0.3	15.1	6.9
		0.1	2.31	1	69.5	31.9
	Acetone ($m = 9.5$)	0.15	19.46	28.5	100	96.1
		0.25	11.42	28.5	100	89.6
		0.5	6.20	28.5	100	68.9
		1.0	3.10	28.5	95.1	67.9

relatively low ($m_{ethanol} = 0.1$). Under these conditions, N_{OL} decreases with the aqueous flowrate. This is in agreement with the experimentally observed decrease in extraction with an increase in aqueous flowrate at a given extraction factor.

The membrane mass transfer coefficient, a function of membrane properties and the diffusion coefficient, is constant for a given system. Mass transfer within compressed fluids can be manipulated with temperature and pressure and is typically enhanced relative to conventional organic solvents, suggesting that lower membrane resistances may be obtained. This is evident when comparing the kinematic viscosity (v/ρ, cm^2/s) of compressed propane (2.2×10^{-3}) and CO_2 (2.4×10^{-4}) to that of tri-*n*-butylphosphate (3×10^{-2}) [38] or *n*-octanol (9×10^{-3}) [41], solvents that have been used previously for HFC extraction of ethanol.

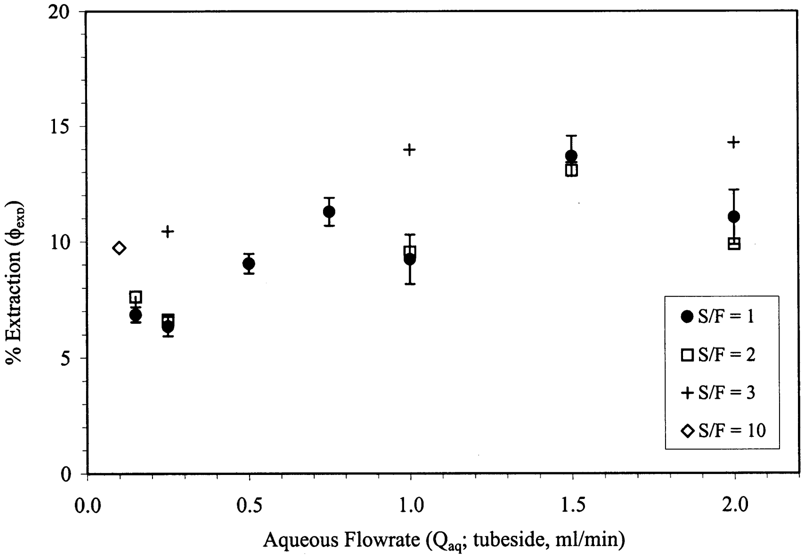

Fig. 4. Extraction of ethanol (10 wt.%) from binary aqueous feed solutions is shown for compressed propane (34.5 bar) at ambient temperature. Error bars represent standard error associated with GC analysis.

3.2. Aqueous acetone extraction

Acetone was extracted with compressed propane at 34.5 bar and 298 K ($m_{acetone} = 1.63$) as a function of Q_{aq} (0.1–1.0 ml/min) and S/F (1, 2, 3, and 10). Extraction ranged from 14.2 to 90.6% (Table 4). A decrease in extraction was observed with increasing aqueous flowrate. Increasing the solvent to feed ratio or the extraction factor improves acetone extraction, with an exception at $Q_{aq} = 1.0$ ml/min, in which the extraction at a S/F of 1, 2, and 3 was approximately equal.

The experimental trends are consistent with the trends predicted from the analysis of N_{OL} and the predicted extraction efficiency ($\phi_{predicted}$) (Table 6). At the conditions investigated, N_{OL} decreases with Q_{aq}. Therefore, at the highest flowrate ($Q_{aq} = 1$), the low values of N_{OL} limit acetone extraction to similar low values. These low extraction efficiencies are observed in spite of extraction factors greater than one, which suggests that the aqueous residence times may not be sufficient. At low Q_{aq} (0.1 ml/min) and high S/F ($S/F = 10$) conditions, N_{OL} is greatest for this system (14.88), resulting in 90.6% acetone extraction.

Compressed CO_2 (69 bar and 298 K) was also used to extract aqueous acetone ($m_{acetone} = 9.5$). Extraction also decreased from 96.1 to 67.9% for aqueous flowrates ranging from 0.1 to 1 ml/min at $S/F = 3$, respectively (Table 4). Previous studies have reported 98.8% acetone extraction from a 10 wt.% aqueous feed solution with compressed CO_2 at similar operating conditions [45]. Extraction took place in a HFC module containing 120 polypropylene fibers of the same dimension as the single fiber used in our investigations. In this previous investigation, the aqueous flowrate in each fiber was equivalent to 0.02 ml/min and the molar solvent to feed ratio was approximately 6.

The trends observed for the extraction of acetone as a function of Q_{aq}, aqueous flowrate, and solvent to feed ratio provide an interesting comparison to ethanol extraction. The equilibrium distribution of acetone is significantly greater than that of ethanol in the compressed solvents. Thus, the experimental observation of increased percentage extraction of acetone relative to ethanol is expected. In addition, mass transfer of solutes that exhibit high distribution coefficients ($m_i > 1$), such as acetone, is limited by the aqueous phase mass transfer resistance. The membrane mass transfer resistance that was dominant in ethanol extraction is less significant in acetone extraction with propane, and even less in the case of CO_2, both of which exhibit high distribution coefficients. While a reduction in the aqueous phase resistance is expected as Q_{aq} increases (improving extraction), the subsequent decrease in N_{OL} resulted in limited acetone extraction for propane and CO_2.

3.3. Aqueous ethanol/acetone extraction

Aqueous mixtures containing both ethanol (5 wt.%) and acetone (5 wt.%) were extracted with compressed propane and CO_2 to determine the effect of an additional solute on extraction within the HFC (Table 5). The hydrophobic nature within the membrane may be reduced if solute concentration is too high, resulting in aqueous breakthrough to the solvent side. Therefore, solutions of 10 wt.% total solute were used. The percentage extraction of ethanol and acetone with compressed propane was similar in the binary (10 wt.% ethanol or acetone) and ternary (5 wt.% ethanol and 5 wt.% acetone) mixtures (Tables 3 and 4). The percentage of ethanol extracted with propane at an aqueous flowrate of 0.1 ml/min and a S/F ratio of 10 was 9.7 ± 1.6 and $8.1 \pm 0.6\%$ for the binary solution and ternary mixture, respectively. Increasing Q_{aq} from 0.15 to 1 ml/min at $S/F = 3$ increased ethanol extraction from 5.2 to 11.8% (Fig. 5). The percentage of acetone extracted with compressed propane from the ternary mixture decreased with increasing aqueous flowrate and increased with increasing an S/F ratio (1 to 3). These trends are consistent with those obtained for the binary solutions.

The percentage of ethanol extracted using compressed CO_2 was $31.9\% \pm 1.4$ and $35.9\% \pm 0.9$ for the binary and ternary solutions at $Q_{aq} = 0.1$ ml/min and $S/F = 10$, respectively (Tables 3 and 5). In general, an increase in percentage of ethanol extraction was observed in the ternary feed solution (ethanol/acetone/water/CO_2) relative to the binary feed (ethanol/water/CO_2). Ethanol extraction as a function of Q_{aq} (0.15–0.5 ml/min) at $S/F = 3$ remained somewhat constant at approximately 21% (Fig. 6). This is a considerable increase when compared with the percentage of ethanol extracted from the binary solution, which ranged from 15.2 to 4.7% at the same conditions. However, a more appropriate criterion for comparing the extraction may be the amount extracted; 20% ethanol extraction from a 5 wt.% solution removes an amount of ethanol equivalent to 10% ethanol extraction from a 10 wt.% solution. Therefore, the amount of ethanol removed is comparable for 5 and 10 wt.% ethanol solutions extracted at the same aqueous and compressed CO_2 flowrates at an S/F of 3, meaning that the loading in the compressed solvent was similar.

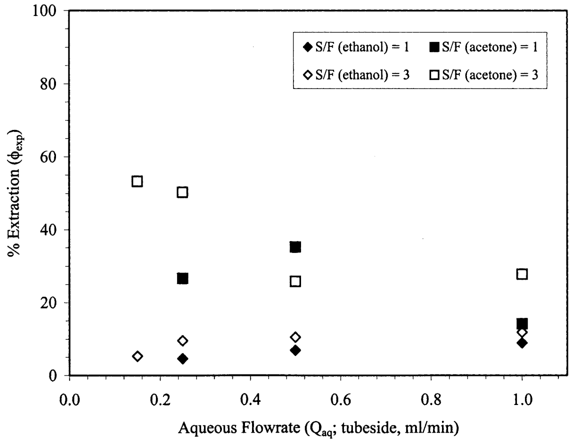

Fig. 5. The extraction of aqueous ethanol (5 wt.%) and acetone (5 wt.%) from ternary feed solutions with compressed propane at ambient temperature. Error bars associated with GC analysis are smaller than symbols.

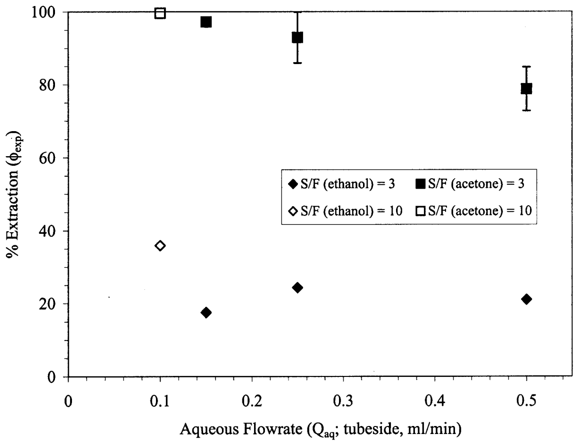

Fig. 6. The extraction of aqueous ethanol (5 wt.%) and acetone (5 wt.%) from ternary feed solutions with compressed CO_2 at ambient temperature. Bars represent standard error for GC analysis. Error bars are smaller than symbols for the remaining points.

The percentage of acetone extracted by CO_2 from the ternary solution was greater than the binary, however, was not as significant as the increase in the ethanol extraction. The acetone distribution coefficients at the conditions of extraction are much higher than the ethanol distribution coefficient in compressed propane or CO_2. Thus, the system may be exhibiting a cosolvent effect, where the solvent power of the compressed phase toward ethanol is enhanced due to the presence of dissolved acetone.

4. Conclusions

Compressed fluid solvents may be employed in bioprocessing applications where expensive separation steps and residual solvents hinder product recovery. These solvents can be tuned with temperature and pressure to enhance extraction and provide a basis for selective extraction. The feasibility of extracting aqueous solutes within an HFC using a compressed solvent has been demonstrated and extended to compressed hydrocarbons as extractive solvents. The ability to extract model fermentation products, aqueous ethanol and acetone, with largely differing affinities for the compressed solvent relative to water, suggests the versatility of this technique. The effect of choice of solvent and process flowrates on the extraction of volatile fermentation products was consistent with the descriptions of thermodynamic and mass transfer driving forces applied to non-pressurized systems. Combining the tunability of compressed solvents and the high surface area to volume ratios of HFCs could also lead to the economical replacement of hexane by compressed solvents for the extraction of a variety of natural products, including essential fats [51].

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