

Supercritical CO₂ Extraction of Ethanol

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Extraction of ethanol was studied from both synthetic ethanol solution and fermentation broth using supercritical CO₂ in an extraction apparatus in ranges of 313 to 333 K and 80 to 160 atmospheres, for varying extraction times. The experimental system consists mainly of four parts: a CO₂ storage system, a high-pressure liquid pump, an extractor and a product collection unit. Samples were analyzed by gas chromatography. Effects of temperature, pressure, extraction time, initial ethanol concentration and consecutive solvent feeding on extraction yield were investigated. It was found that increasing the initial ethanol concentration and extraction pressure and decreasing the extraction temperature increased the extraction yield. In addition, it was observed that consecutive solvent feeding affected the extraction yield positively. With the Box-Wilson experimental design method, optimum extraction conditions in a batch system for 15% (v/v) ethanol solution were found to be 313 K, 133 atmospheres and 30 minutes. Extraction yields were found to be 5.8 % for one-step and 19.2 % for three-step extraction of fermentation broth.

Key Words: Ethanol, Supercritical Fluid Extraction, Supercritical CO₂

Introduction

In biotechnology, most production processes take place in aqueous media and generally yield dilute solutions of the valuable products. This poses a challenge in achieving higher efficiencies at minimum cost of energy without degrading the quality of the product.

As is well known, fermentation processes generally produce aqueous solutions of ethanol, the separation of which necessitates a series of distillation processes. Distillation, however, is a very expensive operation and, in addition, an ethanol-water mixture forms an azeotrope, which further increases the cost of purification. Therefore, novel separation methods must be investigated to make the process more feasible and economical.

Supercritical Fluid Extraction (SFE), proposed in recent years, appears to be a promising technique since it requires low energy for separation. Wilson¹ showed that, although the initial capital cost for a SFE process is about 40% higher than that for distillation, the cost of compression for the supercritical (SC) fluid is one seventh of the cost of cooling water and steam required for distillation processes. Serra et al.² investigated the energy costs (kJ/L product ethanol) of various ethanol recovery processes. It was found that energy costs for recovery of ethanol for two-column conventional distillation, conventional + azeotropic

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distillation with pentane and supercritical fluid extraction with carbon dioxide are 4730 kJ/L, 8100 kJ/L and 2500 kJ/L, respectively. This showed that the energy consumption of the supercritical fluid extraction process is more than that of distillation process.

There are several studies in the literature about the phase equilibria of the ternary system of ethanol-water-CO₂³⁻¹⁴ and only one study exists for the quaternary system of ethanol-water-CO₂-entrainer¹⁵. In general, these studies showed that extract concentration was positively influenced by increasing extraction pressure and by increasing the initial ethanol concentration and by decreasing extraction temperature. In addition, some researchers found that the azeotropic composition (89.5 mole%) of ethanol-water could be exceeded at various temperatures and pressures with or without the addition of entrainer^{7,9,13,14,15}. Exceeding azeotropic composition also depend on the initial ethanol concentration of the feed solution. For example, Furuta et al⁹. used concentrated feed solution (88.1 mole%, CO₂ free basis) to exceed the azeotropic composition in their studies.

Thibault et al.¹⁶ attempted to produce ethanol by fermentation under CO₂ pressure, but they were unsuccessful because of the negative effect of pressure on the microorganisms used. L'Italien et al.¹⁷ attempted to improve the ethanol fermentation under hyperbaric conditions, with limited success. The separation of ethanol from fermentation broth, however, was not investigated thoroughly.

In many of the previous studies, ethanol extraction utilizing CO₂ was investigated using synthetic ethanol solutions, concentrations of which were higher than those in the fermentation broth. The extraction conditions were not also optimized.

In present study, ethanol extraction with SC CO₂ was achieved from (v/v) synthetic ethanol solutions of 15-75% and also from fermentation broth. The effects of temperature, pressure, extraction time and initial ethanol concentration on extraction yield were investigated in the ranges of 313 to 333 K and 80 to 160 atmospheres. Optimum conditions for the batch extraction of 15%(v/v) ethanol solution were found by the Box-Wilson experimental design method in a linear form. In addition, the effect of consecutive solvent feeding on extraction yield was investigated, with both 15%(v/v) ethanol solution and fermentation broth.

Experimental

The experimental apparatus is schematically shown in Figure 1. It consists mainly of four parts: the CO₂ storage system (1), the HPLC pump (4) and its cooling unit (5), the extractor (100 mL stainless steel cell) (6) and the extract collection unit (7).

The CO₂ was passed through a drier (2) and a filter (3). It was compressed to the operating pressure by the HPLC pump. Then the CO₂ was heated up and sent into the high-pressure cell containing the ethanol solution. Ethanol extracted by CO₂ was captured by water in a flask immersed into a water-ice bath (8).

The high-pressure cell was heated to the desired extraction temperature by a heating tape attached to a temperature controller. In addition, the valve and the tubes at the exit of the cell were heated to 373 K to vaporize the liquid sample and to avoid condensation .

Extraction experiments were carried out with 15-75% (v/v) ethanol solutions and also with fermentation broth in the pressure range of 80 to 160 atmospheres at temperatures of 313-333K. Production of ethanol was carried out with *Saccharomyces cerevisiae* (Y-567, obtained from the National Regional Research Center, Peoria, USA) immobilized in Ca-alginate gel. Yeast growth medium and ethanol production media were previously reported in the literature¹⁸. The fermentation broth was centrifuged before use in the extraction experiments.

Table 1. The effect of initial ethanol concentration on extraction yield T=313 K, P=120 atm, t=60 min

$C'_{E,I}$ (%,v/v)	$C_{E,I}$ (g/L)	$C_{E,R}$ (g/L)	$C_{E,E}$ (g/L)	Y_E (%)
15	123	115	8	6.5
30	269	230	39	14.5
60	534	485	49	9.2
75	762	698	64	8.4

As is shown, Y_E (extraction yield, %) first increased then decreased in spite of $C_{E,E}$ (amount of extracted ethanol from 1L feed solution, g/L) continuously increased when the feed solution concentration increased from 15% to 75% by volume. This change in extraction yield is a natural result because the amount of ethanol, that can be extracted by CO₂ is limited for 60 minutes at 120 atmospheres. The data in the literature also agrees with these results^{3,4,10,11,13}.

The effects of temperature and pressure on extraction yield

At high ethanol concentration

Experiments were carried out with a solution containing 60%(v/v) ethanol in the batch extraction system in the pressure range of 80-160 atmospheres and at temperatures of 313 and 333 K for 60 minutes. Experimental results are given in Table 2. As can be seen, extraction yield rose from 4.7% to 8.6% , when temperature decreased from 333 K to 313 K at 80 atmospheres. Similarly, decreasing temperature increased the extraction yield both at 120 and 160 atmospheres. At 313 K, extraction yield rose from 8.6% to 11.2% with increasing pressure from 80 to 160 atmospheres. At 333 K, the effect of pressure was not as obvious.

As a result, extraction yield increased with increasing pressure and decreasing temperature. These observations agree with the results of previous researchers who worked with high ethanol concentrations^{4,5,6,9,10,12,13}.

Table 2. The effects of temperature and pressure on extraction yield (60%(v/v) ethanol solution, t=60 min)

P (atm)	T (K)	$C_{E,B}$ (g/L)	$C_{E,R}$ (g/L)	$C_{E,E}$ (g/L)	Y_E (%)
80	313	534	488	46	8.6
	333	534	509	25	4.7
120	313	534	485	49	9.2
	333	534	519	15	2.8
160	313	534	474	60	11.2
	333	534	513	21	3.9

At low ethanol concentrations

The solution containing 15%(v/v) ethanol was used to simulate the fermentation broth in these experiments. Experiments were carried out in the batch system at conditions of 80 and 160 atmospheres, 313 and 333 K and for 30 and 90 minutes.

In the literature, there are inconsistent results with respect to the effect of temperature and pressure on extraction yield at low ethanol concentrations^{5,8,13}. For this reason, an experimental design was performed with the Box-Wilson method to observe this effect more clearly and for the optimization of the experimental conditions.

Experimental design and optimization by the Box-Wilson experimental design method

The experimental design was made with three independent variables¹⁹. Thus, the total number of experiments is $2^n=2^3=8$. These independent variables are extraction temperature (U_1), extraction pressure (U_2) and extraction time (U_3); the dependent variable (Y_E) is extraction yield (%). Maximum and minimum values for the temperature, pressure and time were selected as 333 and 313 K, 160 and 80 atmospheres, and 90 and 30 minutes, respectively. Experimental designs based on these conditions and experimental results obtained are given in Table 3.

Table 3. Experimental design by Box-Wilson experimental design method and experimental results obtained (15%(v/v) ethanol solution)

Exp.no	1	2	3	4	5	6	7	8
U_1	60	60	60	60	40	40	40	40
U_2	160	160	80	80	160	160	80	80
U_3	90	30	90	30	90	30	90	30
$C_{E,E}$	5.9	9.4	4.7	8.2	7.0	12.8	10.5	8.2
Y_E	4.8	7.6	3.8	6.6	5.7	10.4	8.5	6.6

The equation formed utilizing this method is as follows:

$$Y_{E,P} = 6.75 - 1.05Z_1 + 0.37Z_2 - 1.05Z_3 + 1.55Z_1 - Z_2 - 0.35Z_1Z_3 - 0.83Z_2Z_3 \quad (1)$$

$$\text{where } Z_i = (U_i - U_{i,ave})/\Delta U_i; U_{i,ave} = [(U_i^+) + (U_i^-)]/2; \Delta U_i = [(U_i^+) - (U_i^-)]/2$$

For the batch extraction with 15%(v/v) ethanol solution, the optimum conditions obtained from this equation were 313 K, 133 atmosphere and 30 minutes²⁰.

The effect of consecutive solvent feeding on extraction yield

15%(v/v) ethanol solution and fermentation broth (7%(v/v) ethanol) were used as solutions in the experiments conducted at 313 K and 120 atmospheres. The first batch extraction experiment was carried out for 60 minutes. After the CO₂ was bled down to the atmospheric pressure, the system pressure was risen again to 120 atmospheres with fresh CO₂. This operation was repeated at the end of 30 minutes. Thus, the feed solution had contact with fresh SC CO₂ at three consecutive steps.

Table 4. The effect of consecutive solvent feed on extraction yield

T=313 K	P=120 atm.	Ethanol solution (15%, v/v)		Ferment. broth (7%, v/v)	
Ext.time (min.)	Number of step	$C_{E,E}$ (g/L)	Y_E (%)	$C_{E,E}$ (g/L)	Y_E (%)
60	1	8	6.5	3	5.8
60+30	2	21	17.1	-	-
60+30+30	3	27	21.9	10	19.2

As can be seen, consecutive solvent feeding increased extraction yield. Extraction yield rose from 6.5% to 21.9% at the end of 3 steps for 15%(v/v) ethanol solution. Also, the extraction yield of fermentation broth increased from 5.8% to 19.2% at the end of the three steps. This shows that consecutive extraction is superior to batch extraction .

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Nomenclature

$C_{E,I}$	Initial ethanol concentration (g/L)
$C'_{E,I}$	Initial ethanol concentration (% , v/v)
$C_{E,R}$	Ethanol concentration in the raffinate solution (g/L)
$C_{E,E}$	Amount of extracted ethanol from 11 feed solution (g/L)
$C_{E,P}$	Predicted extracted ethanol concentration (g/L)
Y_E	Extraction yield (%)
$Y_{E,P}$	Predicted extraction yield (%)

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