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A MASS TRANSFER MODEL FOR SUPER- AND NEAR-CRITICAL CO_2 EXTRACTION OF SPEARMINT LEAF OIL

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ABSTRACT

For the dynamic behavior in the super- or near-critical CO_2 extraction of essential oil components (carvone and limonene) from spearmint leaves, a mass transfer model was developed on the basis of intraparticle diffusion and external mass transfer. The effects of temperature, pressure, and CO_2 mass flow-rate on the model parameters which are the intraparticle effective diffusion and the external mass transfer coefficients, were investigated. Good agreement between the prediction by the model and the experimental data was obtained. When increasing the CO_2 pressure, the intraparticle effective diffusion coefficients mostly increased and the external mass transfer coefficients significantly increased by showing the enhanced mass transfer at an increased CO_2 density at a higher pressure. The effects of CO_2 flow rate on the extent of the extraction rate and external mass transfer

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coefficient were negligible. Also, the Biot numbers determined for the extraction runs were generally much larger than 5, which indicates the predominance of the internal mass transfer resistance over the external mass transfer resistance. The intraparticle effective diffusion coefficients estimated from the extraction data were markedly smaller than the molecular diffusivities determined by empirical estimation methods. Therefore, this study suggests the significance of the intraparticle mass transfer resistance in the CO_2 extraction of spearmint leaves, which implies that the complex matrix structure of the herbaceous spearmint leaf hinders the mass transfer inside leaf particles during the extraction process.

Key Words: Carbon dioxide; Near-critical; Supercritical; Extraction; Intraparticle diffusion; Spearmint oil

INTRODUCTION

Supercritical CO_2 has been considered as a clean solvent and is being used for various purposes, especially including extraction or pretreatment of plant materials (1,2). Studies on the mathematical models for supercritical fluid extraction (SFE) for the extraction of plant seed oils have been well documented (3–15). The plant seed oil extraction using supercritical fluids (SCFs) is characterized by the high oil yield of a predominant single oil component (16).

In comparison with the plant seed oil extraction, fewer studies have been carried out on the SFE of oil from herbaceous substrates. The supercritical CO_2 extraction of herbaceous materials generally results in a lower oil yield and a more complex final product profile (16–19) than that of plant oil seeds. The herbaceous plant oil extraction may be more dependent on the interactions between multi-components and the complex inner matrix structure of herbaceous substrates that hampers the internal mass transfer of oil components than the plant seed oil extraction.

The objective of this study is to model the dynamic behavior in the super- or near-critical CO_2 extraction of the two major components of spearmint oil including carvone and limonene (20) from the herbaceous material, spearmint leaves. By employing a mass transfer model based on the intraparticle effective diffusion and external mass transfer, the intraparticle effective diffusion coefficients and external mass transfer coefficients were estimated at various extraction conditions.

EXPERIMENTAL

Materials

Spearmint leaves, a local product obtained from southern California, were washed with deionized water to remove dirt and were air-dried at room temperature. They were then ground into particles having an average radius of 0.15 mm. CO_2 at 99.6 or 99.9% purity was used for extraction. Methanol (99.9% purity) was used as a collection solvent for the extracted essential oil.

Experimental Apparatus

All the extraction experiments were performed on the apparatus depicted in Fig. 1. The extraction system consisted of a SCF controller and delivery system (CCS, Unionville, NJ) and an extraction vessel (inner diameter 2.54 cm and height 9 cm, Valco, Houston, TX). The extraction vessel was heated with heating tape, and the internal temperature of the extractor was measured by a thermocouple inserted into the extraction vessel and was regulated by a temperature controller. Stainless-steel frits were placed at both ends of the extraction vessel. The restriction valve and nearby tubing were kept at

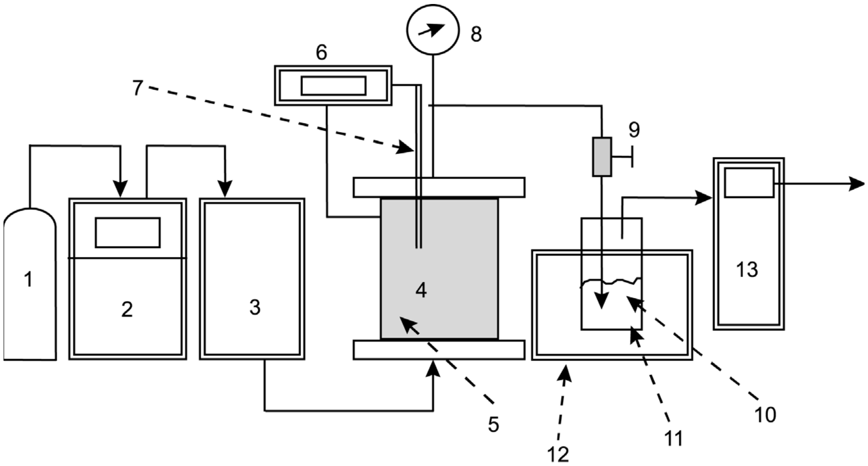

Figure 1. Schematic diagram of the experimental apparatus: (1) CO_2 cylinder, (2) fluid delivery system, (3) valve oven, (4) extraction vessel, (5) heating tape, (6) temperature controller, (7) thermocouple, (8) pressure gauge, (9) flow restriction valve, (10) collection solvent, (11) collection vessel, (12) ice bath, (13) flow meter.

approximately 250°C to prevent freezing and clogging of the exit tubing during extraction. The flow rate of the exiting fluid was measured and monitored by a digital flow meter (J&W Scientific, Folsom, CA). A gas chromatograph (Model 3350, Varian, Sugarland, TX) equipped with a packed column (3% OV101 on Chromosorb) and a thermal conductivity detector (TCD) was used in the analysis of extract samples.

Experimental Procedures

Two grams of ground spearmint leaves were loaded with 40 mL of glass beads (diameter 2 mm) in the extraction vessel to increase the contact area between leaf particles and CO_2 during extraction. The extraction vessel was wrapped with heating tape and was connected to the fluid delivery system. Immediately after the pressure and temperature of the extraction vessel reached the desired values, the heated flow-restriction valve was opened and this marked the start of extraction.

The exiting CO_2 stream laden with essential oil, which was continuously exiting from the extraction vessel at a constant flow rate, was depressurized through the restriction valve to atmospheric pressure. The expanded vapor stream was bubbled in the methanol collection solvent so that the essential oil could be captured and dissolved by methanol. For the determination of the cumulative mass of CO_2 used in extraction, the gas flow rate of the depressurized CO_2 leaving the methanol collection solvent was measured by the gas flow meter. The extracted oil dissolved in the methanol collection solvent was taken at specific time intervals to obtain extraction curves with time. The analysis of carvone and limonene dissolved in the methanol solvent was performed by using the gas chromatograph.

The procedures for measuring the apparent density and the solid density of the leaf particles to determine the porosity of leaf particles (Table 1) are described in detail in a previous study (21).

MODELING

Description of Mass Transfer Model

The short bed-length, low fluid flow rates, and low-solute concentration changes through the packed-bed extractor enable the assumption of a well-mixed reactor (22). In this study, the extraction vessel loaded with large size glass beads (diameter 2 mm) compared to spearmint leaf particles was not a true packed-bed system since the glass beads were used to reduce the volume

Table 1. Physical Parameters Used in Modeling

Parameter	Value
Average radius of leaf particle (R)	1.5×10^{-2} cm
Solid density of leaf particle (ρ_p)	1.11 g/cm^3
Porosity of leaf particle (α)	0.333
Initial concentration of carvone in pores of leaf particles (c_0)	8.25×10^{-3} g/cm^3
Initial concentration of limonene in pores of leaf particles (c_0)	3.60×10^{-3} g/cm^3
Total void volume of the packed extractor (V)	16.2 cm^3
Mass of leaf particles per extraction (W)	2.0 g

of the extraction vessel and disperse the leaf particles. Furthermore, the total void volume of the extraction vessel (16.2 cm^3) shown in Table 1 was much larger than the loading size of leaf particles (2 g and 1.8 cm^3) in the extraction vessel. All of these facts made this extraction system different from normal packed-bed systems, which generally are compacted of materials to be extracted. In addition, the CO_2 flow rates were slow relatively to the large void volume of the extraction vessel. Therefore, we suggest that the slow flow-rate of CO_2, large void-volume of extraction vessel, and short length of extraction vessel compared to its diameter are reasonable for assuming a well-mixed vessel to simplify the mathematical modeling.

Pure supercritical CO_2 continuously enters the extractor at a constant flow rate, q. Carvone and limonene, which are known to be the major components of spearmint oil, are taken into account in the modeling. The leaf particles contain oil components in their leaf pores at the initial concentration, c_0. The oil components in pores diffuse from the pores to the surfaces of leaf particles through the solid leaf matrix. Then, the oil components diffuse into the bulk CO_2 phase through the external film covering the leaf particles.

The mass balance of the oil components in the bulk CO_2 of the extractor is:

$$-qC + \left(-\frac{3W\alpha}{\rho_p R} D_e \frac{\partial c}{\partial r}\bigg|_{r=R} \right) = V\frac{dC}{dt} \tag{1}$$

where C is the oil concentration in the bulk fluid, c the oil concentration in the pores of leaf particles, D_e the intraparticle effective diffusion coefficient, R the average radius of leaf particles, t the extraction time, V the total void volume of the packed-bed extractor, W the total weight of leaf particles, α the porosity of leaf particles, and ρ_p is the solid density of leaf particles.

The mass balance of the oil components in the pores of leaf particles becomes:

$$D_{\mathrm{e}}\left(\frac{\partial^2 c}{\partial r^2}+\frac{2}{r}\frac{\partial c}{\partial r}\right)=\frac{\partial c}{\partial t} \tag{2}$$

At the surface of leaf particles, both the intraparticle diffusion and external mass transfer rates of the oil components are equal. Hence, this boundary condition is expressed as:

$$-D_{\mathrm{e}}\left(\frac{\partial c}{\partial r}\right)_{r=R}=k_{\mathrm{f}}(c-C) \quad \text{at } r=R \tag{3}$$

where k_{f} refers to the external mass transfer coefficient.

The intraparticle effective diffusion and the external mass transfer coefficients can be related by dimensionless Biot number Bi as follows, to compare the effects of internal and the external mass transfer resistances involved in the extraction process.

$$Bi=\frac{k_{\mathrm{f}}R}{D_{\mathrm{e}}} \tag{4}$$

The initial conditions for the oil concentration in leaf particles and in the bulk fluid are given as Eqs. (5) and (6), respectively.

$$c=c_0 \quad \text{at } t=0 \tag{5}$$

$$C=0 \quad \text{at } t=0 \tag{6}$$

For the simplicity of mathematical manipulations, the following combined parameters, Eq. (7), and dimensionless variables Eqs. (8)–(11) are introduced as follows:

$$\frac{V}{\alpha}=n, \quad \frac{3W}{\rho_{\mathrm{p}}}=P, \quad \frac{qR^2}{\alpha D_{\mathrm{e}}}=m, \quad \frac{k_f R}{D_{\mathrm{e}}}=l \tag{7}$$

$$U=\frac{C}{c_0} \tag{8}$$

$$u=\frac{(c_0-c)r}{Rc_0} \tag{9}$$

$$y = \frac{r}{R} \tag{10}$$

$$\tau = \frac{D_e t}{R^2} \tag{11}$$

Equation (1), the mass-balance equation for the oil components in the bulk fluid, is rearranged by using the dimensionless variable as:

$$-mU - n\frac{\partial U}{\partial \tau} + P\left(\frac{\partial u}{\partial y} - u\right)_{y=1} = 0 \tag{12}$$

Equation (2), the mass-balance equation for the oil components in leaf particles, is obtained in dimensionless form as:

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial y^2} \tag{13}$$

The boundary condition can be converted to the following dimensionless form:

$$\frac{\partial u}{\partial y} + (l-1)u = l(1-U), \quad y = 1 \tag{14}$$

The initial conditions become in the dimensionless form as:

$$U = 0, \quad \tau = 0 \tag{15}$$

$$u = 0, \quad \tau = 0 \tag{16}$$

By employing the Laplace transform, the following analytical solution Eq. (17) is obtained.

$$U\left(=\frac{C}{c_0}\right) = -\sum_{n=1}^{\infty} \frac{2(m+ns_n)[\sqrt{-s_n}\cos\sqrt{-s_n} + (l-1)\sin\sqrt{-s_n}]}{G_n P_{n1} + F_n P_{n2} + n P_{n3}} \exp(s_n \tau) \tag{17}$$

where

$$G_n = m + ns + Pl$$

$$F_n = (m + ns_n)(l - 1) - Pl$$

$$P_{n1} = \sqrt{-s_n}\cos\sqrt{-s_n} - \frac{s_n\cos\sqrt{-s_n}}{2\sqrt{-s_n}} + \frac{s_n\sin\sqrt{-s_n}}{2}$$

$$P_{n2} = \sin\sqrt{-s_n} - \frac{s_n\cos\sqrt{-s_n}}{2\sqrt{-s_n}}$$

$$P_{n3} = s_n\sqrt{-s_n}\cos\sqrt{-s_n} + (l - 1)s_n\sin\sqrt{-s_n}$$

where each s_n is found from the following transcendental equation:

$$\sqrt{-s}\cot\sqrt{-s} = \frac{(m + ns)(1 - l) + Pl}{(m + ns + Pl)} \tag{18}$$

Parameter Estimation

The model parameters, k_f and D_e, were estimated by using the experimental data. The parameter estimation was carried out by FORTRAN programming using a nonlinear least square method with an IMSL subroutine UNLSF. To obtain the best fit for the experimental data, the objective function to be minimized is:

$$\frac{1}{N}\sum_{i=1}^{N}\left(\frac{U_{\text{cal}} - U_{\text{exp}}}{U_{\text{cal}}}\right)^2 \tag{19}$$

where N is the number of experimental data, U_{cal} the calculated value of U, and U_{exp} the experimental data of U. All physical parameters used in the modeling are shown in Table 1.

Molecular Diffusivities of Carvone and Limonene

To compare the experimentally estimated intraparticle effective diffusion coefficients of the oil components by the mass transfer model and the molecular diffusivities of the pure compounds, the molecular diffusivities of carvone and limonene were determined by combining the empirical methods of Fuller et al. (23) and Takahashi (23). The empirically determined molecular diffusivities of carvone and limonene in CO_2 at the extraction temperatures and pressures are listed in Table 4.

RESULTS AND DISCUSSION

Effect of Temperature

The effect of temperature at pressures of 69.0 (near-critical) and 84.5 bar (supercritical) are shown in Figs. 2 and 3, respectively. The concentrations of carvone and limonene in the bulk CO_2 of the extractor (referred to as "Conc." in figures) were plotted against the extraction time. The cumulative extracted oil masses (referred to as "Cum." in figures), for each oil component with respect to time, were also presented.

The extraction rates of carvone at both 69.0 and 84.5 bar were higher at 39°C than at 49°C. The carvone concentrations in the bulk CO_2 decreased more rapidly at 39°C than at 49°C. In contrast, in the limonene extraction at both 69.0 and 84.5 bar, the extraction rate was higher at 49°C than at 39°C. As shown in

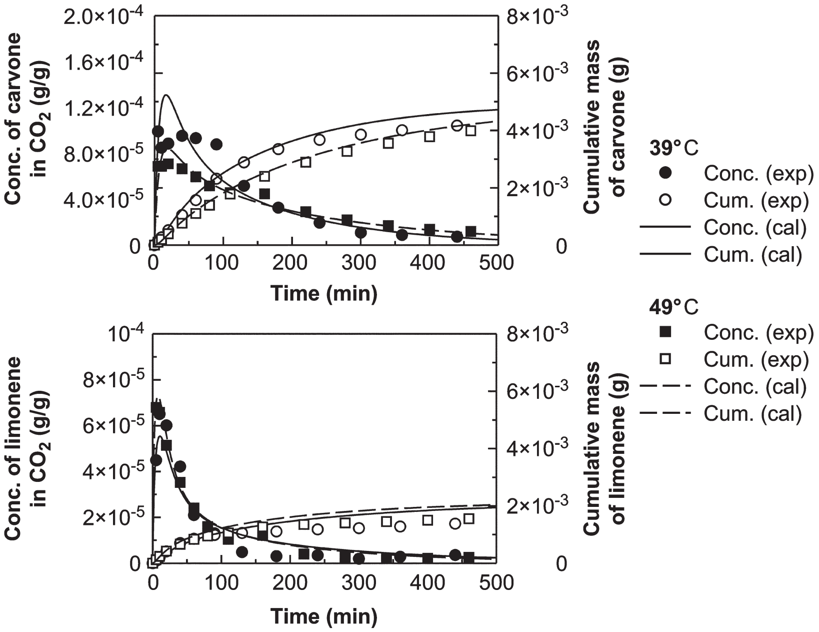

Figure 2. Effect of temperature on the extraction of carvone and limonene at 69.0 bar when the CO_2 mass flow rates were 0.351 and 0.353 g/min for 39 and 49°C, respectively.

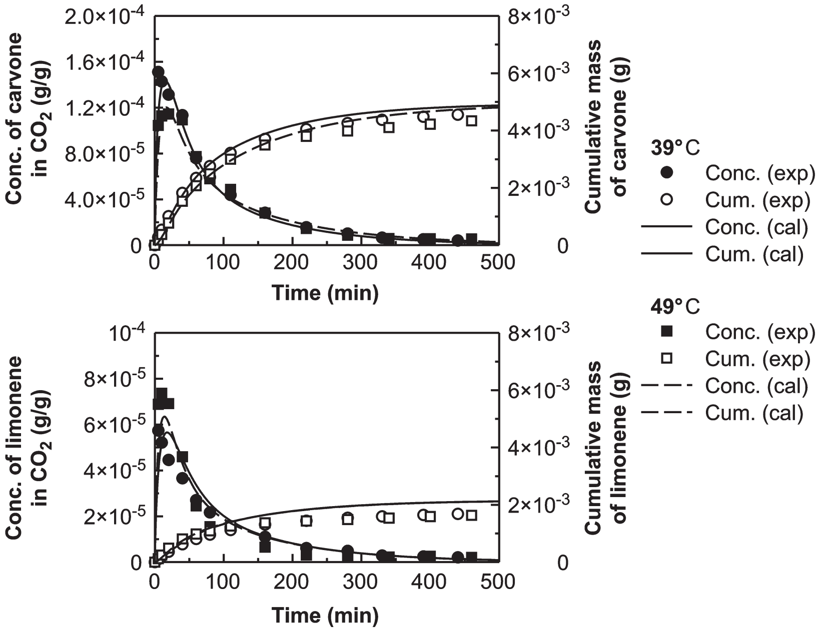

Figure 3. Effect of temperature on the extraction of carvone and limonene at 84.5 bar when the CO_2 mass flow rates were 0.352 and 0.353 g/min for 39 and 49°C, respectively.

Table 2, there was no strong dependence of the intraparticle effective diffusion and external mass transfer coefficients on the extraction temperature.

Effect of Pressure

The pressure effect on the extraction at 49°C is shown in Fig. 4. The extraction was carried out at three different pressures including 69.0, 84.5, and 103.4 bar at the same temperature 49°C. The concentrations of carvone and limonene in the bulk fluid decreased with time more rapidly at a higher pressure. In other words, the cumulative masses of the extracted carvone and limonene increased more quickly at a higher pressure. Accordingly, higher extraction rates were obtained at higher pressures for both oil components.

At a higher pressure, CO_2 density increases and the increase in CO_2 density may enhance the solubility of solute in supercritical CO_2. However, higher CO_2 viscosity at the increased pressure can decrease the binary diffusivity in the CO_2 phase. Therefore, the higher extraction rates resulting from increasing the extraction pressure can be attributed to the predominance of the density effect over the viscosity effect.

Table 2. Effect of Temperature and Pressure on Model Parameters

			D_e (cm^2/min)		k_f (cm/min)		Bi ($= k_fR/D_e$)	
T (°C)	P (bar)	CO_2 Mass Flow Rate (g/min)	Carvone	Limonene	Carvone	Limonene	Carvone	Limonene
39	69.0	0.351	1.87×10^{-7}	9.41×10^{-8}	8.16×10^{-5}	2.43×10^{-4}	6.6	38.7
39	84.5	0.352	1.90×10^{-7}	1.90×10^{-7}	6.97×10^{-4}	3.15×10^{-4}	55.0	24.9
39	103.4	0.346	1.43×10^{-7}	1.57×10^{-7}	2.93×10^{-3}	1.21×10^{-2}	307.3	1156.1
49	69.0	0.353	1.54×10^{-7}	1.17×10^{-7}	3.91×10^{-5}	5.16×10^{-4}	3.8	66.2
49	84.5	0.353	1.90×10^{-7}	1.90×10^{-7}	1.31×10^{-4}	2.40×10^{-4}	10.3	19.0
49	103.4	0.358	1.98×10^{-7}	3.07×10^{-7}	3.00×10^{-3}	2.89×10^{-2}	227.3	1412.1

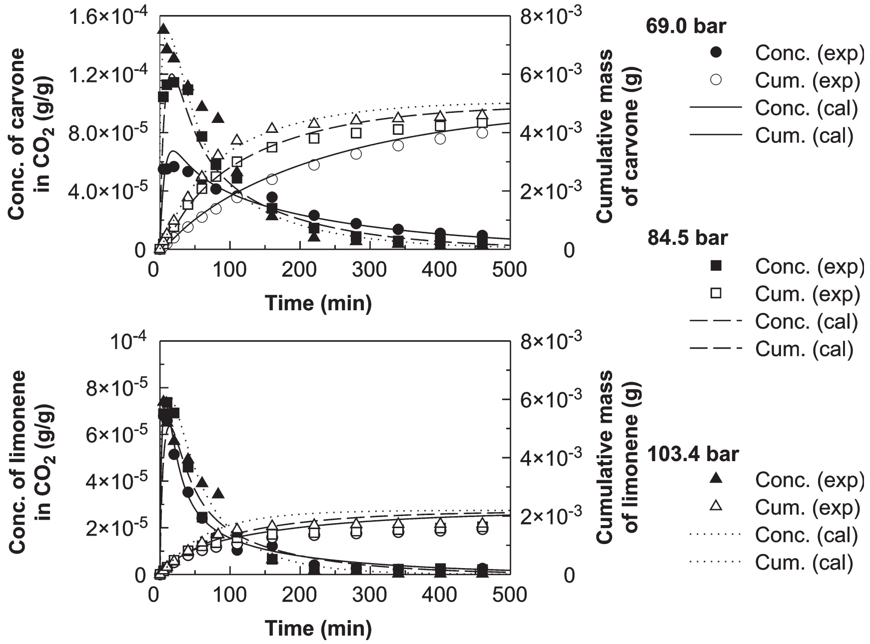

Figure 4. Effect of pressure on the extraction of carvone and limonene at 49°C when the CO_2 mass flow rates were 0.353, 0.353, and 0.358 g/min for 69.0, 84.5, and 103.4 bar, respectively.

The internal effective diffusion coefficient in the leaf particles was not significantly affected by pressure as seen in Table 2. The external mass transfer coefficient increased with an increase in pressure and was found to be more dependent on the extraction pressure than the intraparticle effective diffusion coefficient. The magnitudes of Biot numbers shown in Table 2, which are mostly larger than 5, indicate that in the extraction process, the intraparticle mass transfer resistance either existed or the external mass transfer resistance was negligible compared to the internal mass-diffusion resistance (22).

Effect of CO_2 Mass Flow Rate

To study the effect of CO_2 mass flow rate, three different mass flow rates were tested at the same extraction condition of 84.5 bar and 39°C. As seen in Fig. 5, the time-dependent concentration profile of carvone and limonene in the bulk CO_2 were highly dependent on the CO_2 mass flow rate. The external mass

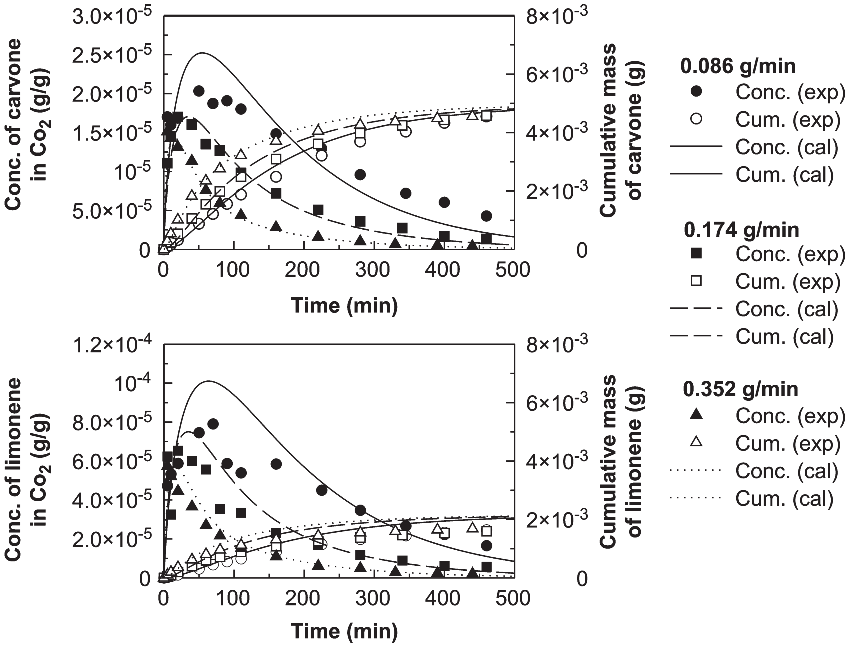

Figure 5. Effect of CO_2 mass flow rate on the extraction of carvone and limonene at 39°C and 84.5 bar.

transfer coefficient generally increased by a small extent with an increase in CO_2 flow rate as listed in Table 3. According to the cumulative masses of extracted oil components, the almost complete extraction of oil components occurred within 500 min at all three CO_2 flow rates. These results suggest that the external mass transfer resistance was not significant at the CO_2 flow rates tested in this study. This agrees with the assessment of the internal and external mass transfer resistances by the Biot numbers, which are comparable to 5 (22). Therefore, higher CO_2 flow rates appear to be unnecessary for reducing the extraction time required for the complete extraction of spearmint oil.

Comparison of Intraparticle Effective Diffusion Coefficient and Molecular Diffusivity

As seen in Table 4, the molecular diffusivities of pure carvone and limonene were obtained by the empirical methods (23). The order of magnitude

Table 3. Effect of CO_2 Mass Flow Rate on External Mass Transfer Coefficient at 39°C and 84.5 bar

CO_2 Mass Flow Rate (g/min)	D_e (cm^2/min)		k_f (cm/min)		Bi ($= k_f R/D_e$)	
	Carvone	Limonene	Carvone	Limonene	Carvone	Limonene
0.086	1.90×10^{-7}	1.90×10^{-7}	2.56×10^{-4}	1.41×10^{-4}	20.2	11.1
0.174	1.90×10^{-7}	1.90×10^{-7}	1.8510^{-4}	1.94×10^{-4}	14.6	15.3
0.352	1.90×10^{-7}	1.90×10^{-7}	6.97×10^{-4}	3.15×10^{-4}	55.0	24.9

Table 4. Molecular Diffusivities of Carvone and Limonene in CO_2 Determined by Using Empirical Methods at Various Extraction Conditions

Temperature (°C)	Pressure (bar)	Molecular Diffusivity (cm^2/min) Carvone	Molecular Diffusivity (cm^2/min) Limonene
39	69.0	2.81×10^{-2}	2.86×10^{-2}
39	84.5	1.65×10^{-2}	1.67×10^{-2}
39	103.4	9.40×10^{-3}	9.52×10^{-3}
49	69.0	3.12×10^{-2}	3.17×10^{-2}
49	84.5	1.90×10^{-2}	1.93×10^{-2}
49	103.4	1.33×10^{-2}	1.34×10^{-2}

of the molecular diffusivities of carvone and limonene is 10^{-2} in cm^2/min, which is the same as that of self-diffusivity of supercritical CO_2 reported in the literature (24). However, the effective diffusion coefficients estimated by fitting the model to the experimental data are much smaller than the molecular diffusivities of carvone and limonene. The order of magnitude of the internal effective diffusion coefficients (D_e) obtained in this study is 10^{-7} cm^2/min. This value is close to intraparticle effective diffusion coefficients reported by others who carried out the supercritical CO_2 extraction of vanillin oil (25), basil oil (16,18), rosemary oil (16), marjoram oil (16), and evening primrose oil (26). Except vanillin oil, these essential oils are from herbaceous substrates showing the high internal mass-diffusion resistance in SFE due to the complex matrix structure (16). Likewise, the intraparticle diffusion resistance appears to be substantially affected by the complex matrix structure of spearmint leaves. For the industrial application of this SFE process using CO_2, appropriate pretreatment of herbaceous materials, such as particle size reduction or soaking in a proper benign solvent, is desired prior to the extraction process in order to reduce the internal mass transfer resistance.

CONCLUSIONS

The prediction by a mass transfer model having intraparticle effective diffusion and external mass transfer terms showed good agreement with the experimental data for the dynamic extraction of essential oil components (carvone and limonene) from spearmint leaves using CO_2 at super- or near-critical conditions. In general, the intraparticle effective diffusion coefficients and the external mass transfer coefficients increased with increasing the extraction pressure, probably due to the increased CO_2 density at the increased pressure. The mere effects of CO_2 flow rate on the extraction rate and external mass transfer coefficient as well as the Biot numbers indicate that the external mass transfer resistance was negligible during the extraction. The intraparticle effective diffusion coefficients obtained by fitting the model to the experimental data were significantly smaller than the molecular diffusivities determined by empirical estimation methods. This suggests the importance of the internal mass transfer resistance during extraction, which is presumed to be related to the complex matrix structure of the herbaceous spearmint leaf.

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REFERENCES

1. Kim, K.H.; Hong, J. Supercritical CO_2 Pretreatment of Lignocellulose Enhances Enzymatic Cellulose Hydrolysis. Bioresour. Technol. **2001**, *77*, 139–144.
2. Kim, K.H.; Hong, J. Dynamic Extraction of Spearmint Oil Components by Using Supercritical CO_2. Sep. Sci. Technol. **2000**, *35* (2), 315–322.
3. Bernardo-Gil, M.G. Extraction of Rape-Seed Oil Using Compressed CO_2: Evaluation of Mass Transfer Coefficients, *Proceedings of the International Symposium on Supercritical Fluids, Nice, France, Oct 17–19, 1988*; Perrut, M., Ed.; Institut National Polytechnique de Lorraine: Paris, 1988.
4. Bully, N.R.; Fattori, M.; Meisen, A.; Moyls, L. Supercritical Fluid Extraction of Vegetable Oil Seeds. J. Am. Oil Chem. Soc. **1984**, *61* (8), 1362–1365.
5. Cocero, M.J.; Calvo, L. Supercritical Fluid Extraction of Sunflower Seed Oil with CO_2–Ethanol Mixtures. J. Am. Oil Chem. Soc. **1996**, *73* (11), 1573–1578.
6. Cuperus, F.P.; Boswinkel, G.; Muuse, B.G.; Derksen, J.T.P. Supercritical Carbon Dioxide Extraction of *Dimorphoteca pluvialis* Oil Seeds. J. Am. Oil Chem. Soc. **1996**, *73* (12), 1675–1679.
7. Gomez, A.M.; Ropez, C.P.; de la Ossa, E.M. Recovery of Grape Seed Oil by Liquid and Supercritical Carbon Dioxide Extraction: A Comparison with Conventional Solvent Extraction. Chem. Eng. J. **1996**, *61*, 227–231.

8. Lancas, F.M.; Queiroz, M.E.C.; da Silva, I.C.E. Seed Oil Extraction with Supercritical Carbon Dioxide Modified with Pentane. Chromatography **1994**, *39* (11–12), 687–692.
9. Lee, A.K.K.; Bulley, N.R.; Fattori, M.; Meisen, A. Modelling of Supercritical Carbon Dioxide Extraction of Canola Oilseed in Fixed Beds. J. Am. Oil Chem. Soc. **1986**, *63* (7), 921–925.
10. Lee, B.-C.; Kim, J.-D.; Hwang, K.-Y.; Lee, Y.Y. Extraction of Oil from Evening Primrose Seed with Supercritical Carbon Dioxide. In *Supercritical Fluid Processing of Food and Biomaterials*; Rizvi, S.S., Ed.; Blackie Academic & Professional: London, 1994; 168–180.
11. Manninen, P.; Parkarianen, J.; Kallio, H. Large-Scale Supercritical Carbon Dioxide Extraction and Supercritical Carbon Dioxide Countercurrent Extraction of Cloudberry Seed Oil. J. Agric. Food Chem. **1997**, *45*, 2533–2538.
12. Perrut, M.; Clavier, J.Y.; Poletto, M.; Reverchon, E. Mathematical Modeling of Sunflower Seed Extraction by Supercritical CO_2. Ind. Eng. Chem. Res. **1997**, *36*, 430–435.
13. Reverchon, E.; Osseo, L.S. Comparison of Processes for the Supercritical Carbon Dioxide Extraction of Oil from Soybean Seeds. J. Am. Oil Chem. **1994**, *71* (9), 1007–1012.
14. So, G.C.; Macdonald, D.G. Kinetics of Oil Extraction from Canola (Rapeseed). Can. J. Chem. Eng. **1986**, *64*, 80–86.
15. Tolboe, O.; Hansen, I.R.; Shukla, V.K.S. Extraction of Oil from Evening Primrose Seed. *Proceedings of the International Symposium on Supercritical Fluids, Nice, France, Oct 17–19, 1988*; Perrut, M., Ed.; Institut National Polytechnique de Lorraine: Paris, 1988;.
16. Reverchon, E.; Donsi, G.; Osseo, L.S. Modeling of Supercritical Extraction from Herbaceous Matrices. Ind. Eng. Chem. Res. **1993**, *32*, 2721–2726.
17. Goto, M.; Sato, M.; Hirose, T. Extraction of Peppermint Oil by Supercritical Carbon Dioxide. J. Chem. Eng. Jpn **1993**, *26* (4), 401–407.
18. Reverchon, E.; Osseo, L.S.; Gorgoglione, D. Supercritical CO_2 Extraction of Basil Oil: Characterization of Products and Process Modeling. J. Supercrit. Fluids **1994**, *7*, 185–190.
19. Ozer, E.O.; Platin, S.; Akman, U.; Hortacsu, O. Supercritical Carbon Dioxide Extraction of Spearmint Oil from Mint-Plant Leaves. Can. J. Chem. Eng. **1996**, *74*, 920–928.
20. Kim, K.H.; Hong, J. Equilibrium Solubilities of Spearmint Oil Components in Supercritical Carbon Dioxide. Fluid Phase Equilib. **1999**, *164*, 107–115.
21. Kim, K.H.; Hong, J. Desorption Kinetic Model for Supercritical Fluid Extraction of Spearmint Leaf Oil. Sep. Sci. Technol. **2001**, *36* (7), 1433–1446.

22. Srinivasan, M.; Smith, J.M.; McCoy, B.J. Supercritical Fluid Desorption from Activated Carbon. Chem. Eng. Sci. **1990**, *45* (7), 1885–1895.
23. Reid, R.C.; Prausnitz, J.M.; Poling, B.E., *The Properties of Gases and Liquids*, 4th Ed.; McGraw-Hill Book Co.: New York, 1988.
24. Luque de Castro, M.D.; Valcarcel, M.; Tena, M.T. *Analytical Supercritical Fluid Extraction*; Spring-Verlag: Berlin, 1994.
25. Nguyen, K.; Barton, P.; Spencer, J.S. Supercritical Carbon Dioxide Extraction of Vanilla. J. Supercrit. Fluids **1991**, *4*, 40–46.
26. King, J.W.; Cygnarowicz-Provost, M.; Favati, F. Supercritical Fluid Extraction of Evening Primrose Oil Kinetic and Mass Transfer Effects. Ital. J. Food Sci. **1997**, *9* (3), 193–204.

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