Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Supercritical Carbon Dioxide Extraction of Caffeine from Korean Green Tea

Wan-Joo Kim[ab]; Jae-Duck Kim[a]; Seong-Geun Oh[b]
[a] Energy and Environment Research Division, Korea Institute of Science and Technology, Seoul, Korea
[b] Department of Chemical Engineering and Center of Ultramicrochemical Process System, Hanyang University, Seoul, Korea

To cite this Article Kim, Wan-Joo , Kim, Jae-Duck and Oh, Seong-Geun(2007) 'Supercritical Carbon Dioxide Extraction of Caffeine from Korean Green Tea', Separation Science and Technology, 42: 14, 3229 — 3242
To link to this Article: DOI: 10.1080/01496390701513008
URL: http://dx.doi.org/10.1080/01496390701513008

Separation Science and Technology, 42: 3229–3242, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701513008

Supercritical Carbon Dioxide Extraction of Caffeine from Korean Green Tea

Wan-Joo Kim
Energy and Environment Research Division, Korea Institute of Science and Technology, Seoul, Korea and Department of Chemical Engineering and Center of Ultramicrochemical Process System, Hanyang University, Seoul, Korea

Jae-Duck Kim
Energy and Environment Research Division, Korea Institute of Science and Technology, Seoul, Korea

Seong-Geun Oh
Department of Chemical Engineering and Center of Ultramicrochemical Process System, Hanyang University, Seoul, Korea

Abstract: Extract caffeine from Korean green tea using supercritical carbon dioxide as an extracting solvent carried out in a 230 mL extractor at extraction temperatures of 313–353 K and pressures of 10–40 MPa with water contents of 15.8–23.8 wt% and flow rate of 5.04–28.08 kg CO_2/kg green tea per hour. The result showed that 66% of caffeine was removed under the condition of 323 K, 40 MPa with water contents of 20.8% and a flow rate of 28.08 kg CO_2/kg green tea per hour. The experimental results were compared with Goto's mass transfer model in supercritical fluid extraction. It was found to be fit with regression $R^2 = 0.95$. It was shown that the extraction yields were dependant on the temperature, pressure, water contents, and carbon dioxide flow rate.

Keywords: Caffeine, decaffeination, green tea leaves, supercritical carbon dioxide

Received 12 December 2006, Accepted 30 April 2007

Address correspondence to Jae-Duck Kim, Energy and Environment Research Division, Korea Institute of Science and Technology, Seoul, Korea 136-791. Fax: +82-958-5879; E-mail: jdkim@kist.re.kr

INTRODUCTION

Numerous epidemiological and pharmacological studies demonstrate that green tea extract possesses strong antioxidant, antimutagenic, antivarcinogenic, and anticlastogenic effects (1). In addition, green tea contains catechin, caffeine (1–5%) and other components. Caffeine typically is used as a stimulant which can affect the central nervous system. However, caffeine has significant effects on the cardiovascular system, gastric acid secretion and can cause nervousness, dizziness, headaches, and interfere with sleep (2). Decaffeination processes including extraction with methyl chloride (3) and ethyl acetate can obtain caffeine-free products of green tea. The quality of decaffeinated material obtained with these solvents is different according to the amount of isolated caffeine, remaining catechin, and solvent residue (4).

Conventional production methods such as solvent extraction and soxhlet according to EPA SW 846 method, although effective for extraction, can lead to degradation of heat sensitive compounds as well as leave traces of toxic solvents in the extracts (5). Decaffeination research activity on supercritical fluid extraction of stimulants from coffee, tea, and cocoa has continued, indicated by several numbers of patents (6–10). The advantages of supercritical carbon dioxide are that they are environmentally friendly, readily available, easily removed, without evaporation or heating, and this will save electricity. $SCCO_2$ could be adjusted for selective separation and enhancement in separation rate, due to the low viscosity and high diffusivity. In this work, characteristics of caffeine extraction from green tea using $SCCO_2$ was investigated with variables of pressure, temperature, CO_2 flow rate, and water contents. Also, experimental results were compared with mathematical models.

MATHEMATICAL MODELING

The extraction of natural substances from solid matrices in packed beds forms the basis of most present day commercial scale, supercritical fluid extraction. Extraction phenomena entails a series of sequential steps comprising diffusion of CO_2 into the pores adsorption of CO_2 on the solid surface, formation of an external liquid film around the solid particles, dissolution and convective transport of the solute in the bulk fluid phase, desorption of the solute to the fluid phase in the pores, diffusion through the pores, and finally transport to the bulk CO_2. Therefore, there have been many reports measuring and modeling the rates of mass transfer from beds of organic material. Most studies have concentrated on the extract quality and the influence of the operating parameters (pressure and temperature) on the yield of the extract, its quality, and its solubility in the solvent. The general equations for the process of supercritical fluid extraction (SFE) are similar to mass transport operations involving solids and fluids such as leaching and adsorption/desorption processes (11). Those models contain two differential solute mass balances in fluid and solid phase, in addition to a local equilibrium adsorption that describes the relation between solute and solid. The extraction model in this study was first developed by Goto et al. to predict concentrations of the solute in both the fluid and, the solid phase (12). Further modifications to the model were made by Dunford, Goto, and Temelli (13) and Goto, Roy, and Kodana (14). The following assumptions are first made.

1. Axial dispersion is negligible,
2. Radial dispersion is also neglected because of small column diameter,
3. Isothermal process,
4. The packed column is isobaric,
5. No interaction among solutes in the fluid phase or solid phase,
6. Local equilibrium adsorption between solute and solid in pore of green tea,
7. Assumed differential bed is gradientless bed in solid and fluid phase,
8. Physical properties of the supercritical fluid are constant.

The extractor was assumed to be a fixed bed of the green tea particle containing caffeine as the fluid phase with flowing supercritical carbon dioxide as the mobile phase. The mass balance for the solute on the fluid phase in the extractor is

$$\alpha\frac{\partial C}{\partial t}+U_s\frac{\partial C}{\partial Z}=-k_f a_p(1-\alpha)(C-C_{ps}) \tag{1}$$

here C, C_p, and C_{ps} are solute concentration in the fluid phase, in pores within particle and solute concentration in pore at the surface of the particle, respectively. D_{ab} is an axial dispersion coefficient and k_f in an external mass transfer coefficient of particle. The specific surface area, a_p is defined by $a_P = 6/d_P$

The mass balance for the solute on the solid phase is

$$\beta\frac{\partial C_p}{\partial t}=D_e\frac{\partial C_P^2}{\partial r^2}-(1-\beta)\frac{\partial C_s}{\partial t} \tag{2}$$

The local extraction rate, which is equivalent to the desorption rate, is assumed to be reversible and linear.

$$\frac{\partial C_s}{\partial t}=k_a\left(C_p-\frac{C_s}{K}\right) \tag{3}$$

For a relatively fast adsorption-desorption rate (large value of k_a), the adsorption equilibrium condition holds

$$C_s = KC_p \tag{4}$$

At the beginning of the supercritical run, the solute is inside the solid and distributed between the adsorbed and desorbed states. For the case of adsorption equilibrium, the total solute concentration is given by

$$C_0 = \beta C_{so} + (1 - \beta)KC_{so} \tag{5}$$

It is assumed here that the combined internal and external mass transfer processes are described by a linear driving-force approximation (15). The overall mass transfer coefficient for sphere geometry is given by

$$k_p = \frac{k_f}{1 + Bi/5} \tag{6}$$

Here, the Biot number, $Bi = k_f\, r/D_e$.

The mathematical model used here was based on the work of Goto et al. (12). The cumulative fraction of caffeine extracted up to dimensionless time θ is given by

$$\begin{aligned} F(\theta) &= \frac{1}{(1-\alpha)}\int_0^\theta x d\theta \\ &= \left[\frac{A}{1-\alpha}\right] \times \left\{\left[\frac{\exp(a_1\theta) - 1}{a_1}\right] - \left[\frac{\exp(a_2\theta) - 1}{a_2}\right]\right\} \end{aligned} \tag{7}$$

here,

$$\begin{aligned} a_1 &= \frac{(-b + (b^2 - 4c)^{1/2})}{2} \\ a_2 &= \frac{(-b - (b^2 - 4c)^{1/2})}{2} \\ b &= \frac{\phi}{[\beta + (1-\beta)K]} + \frac{1}{\alpha} + \frac{\phi(1-\alpha)}{\alpha} \\ c &= \frac{\phi}{[\beta + (1-\beta)K\alpha]} \\ A &= \frac{(1-\alpha)\phi}{[\beta + (1-\beta)K]\alpha(a_1 - a_2)} \end{aligned}$$

Dimensionless quantities are defined as

$$x = C/C_0, \quad x_s = C_s/C_0, \quad \theta = t/\tau, \quad \phi = K_p a_p \tau$$

The quality of data fitting was evaluated by R^2 shown below.

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(F_i - F_i')^2}{\sum_{i=1}^{n}(F_i - \overline{F_i})^2} \tag{8}$$

EXTRACTION EXPERIMENTS

Green tea leaves were cultivated at Bosong (Korea) and were ground to an average particle size of 520 μm. The bed void fraction was approximately 0.84 for extractors. Commercial grade carbon dioxide (Sinyang Sanso 99.5%) was used as the solvent. The mean particle sizes reported in the experiments were calculated as the average of sieve sizes to be 212, 425, 710, 1400, and 1680 μm, respectively. A typical particle size distribution is presented in Table 1. Water concentration in the green tea was determined according to ORION AF8 volumetric Karl Fischer Titrator and the water content was 15.8 wt/wt%.

The experiments were conducted in a lab-scale extractor system. The system consisted of an extractor with an internal volume of 230 mL (90 mm outer diameter (O.D.) × 280 mm height (H)), a one separators (50 mm O.D. × 210 mm H), a heat exchanger, and a carbon dioxide recycle storage tank (258 mm O.D. × 870 mm H) as shown in Fig. 1. Ground green tea leaves of 50 g and water contents of 15.8–23.8% were put into a cylindrical extractor. CO_2 from the storage tank was delivered by a Miton Roy pump (model MCP13D10BIM) into the extraction vessel. The extraction pressure was varied from 10 to 40 MPa and temperature was varied from 313 to 353 K. Solvent flow rates were adjusted to 28.08, 5.04 kg CO_2/kg green tea per hour by varying pump stroke. The pressure in the extractor was controlled by a back pressure regulator. The caffeine dissolved in the supercritical carbon dioxide was separated from the carbon dioxide by pressure reduction and collected in the separator. The caffeine-free carbon dioxide was cooled and recycled to the carbon dioxide recycle storage tank.

ANALYSES

The caffeine contents of green tea were quantified by a high pressure liquid chromatography (HPLC) with an U6K injector (from Waters Associates). The system's pump is a Model 930, the absorbance detector is M720 from Young Lin (Korea). The HPLC column is C_{18} (15 cm × 3.9 mm, 5 μm)

Table 1. Size distribution of green tea leaves

Sieve Size (μm)	Mass fraction (%)
1680	1.8
1400	5.3
710	30.3
425	31.8
212	30.8
Average: 520	

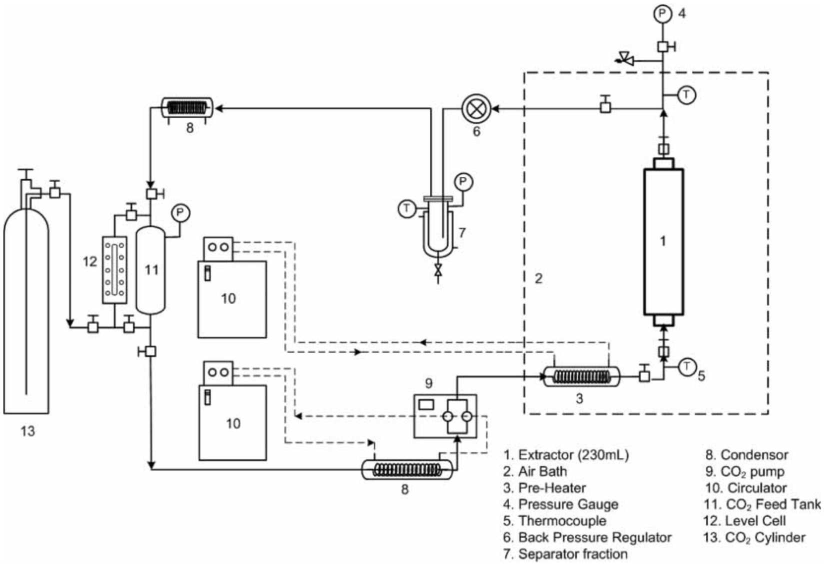

Figure 1. Schematic diagram of supercritical extraction apparatus.

from μ-Bondapak (USA). A mobile phase composed of 40% methanol in 60% water were used at flow rate of 1.0 mL/min. The detector wavelength was UV-254 and injection amount is 10 μL. For grinding, the whole green tea leaves were introduced into an electric mixer. D.I water was poured over the leaves and the tea was steeped for 5 h at room temperature and in the dark. The tea brew is filtered through a 0.45 μm membrane filter and analyzed immediately.

RESULTS AND DISCUSSION

The powder particle density, ρ_p, of the green tea leaves was measured using a pycnometer and found to be 1.643 g/cm^3. The porosity of the green tea powder was estimated from $\beta = 1 - (\rho_b/\rho_P)$. The bed void fraction, α, was obtained from the volume of green tea and bulk volume of bed ($\beta = 0.61$ and $\alpha = 0.84$). The density of CO_2 was calculated by using EOS. The residual viscosity correlation of Stiel and Thodos using low-pressure gas viscosity estimated by Chung et al. (16) were used to calculate the viscosity of CO_2. The effective intraparticle diffusion coefficient was estimated to be $D_e = D\beta^2$ and the binary diffusion coefficient, D of caffeine was using Takahashi's correlation, Rei et al. (16). The external mass transfer coefficient, k_f, was estimated by the Wakao and Kaguei (17) correlation. The most common approach for determining the mass transfer coefficient, k_f, and the equilibrium constant, K, is to regress experimental data (18).

The combined mass transfer coefficient, k_p, calculated from theory, increases with increasing temperature, solvent flow rate, and decreasing pressure. However, k_p are independent water contents. Equilibrium constant, K, decreases with higher pressure, water contents, and temperature and is independent of the flow rate.

Table 2 lists the physical properties of CO_2 as well as a comparison of experimental conditions and the parameters of theoretical model at various conditions.

The Effect of Temperature

The first set of SFE experiments was designed to investigate the effect of extraction temperature on the extraction rate. Extraction was carried out at a constant pressure of 40 MPa, water contents of 20.8%, and flow rate of 28.08 kg CO_2/kg green tea/h over a temperature range from 313 to 353 K. The results are presented in Fig. 2 and the mathematical model fitted the experimental results well. The maximum caffeine extraction yields were 66% under the extraction condition of 353 K, 40 MPa, water contents of 20.8% and 28.08 kg CO_2/kg green tea/h. However, it was found out that at temperature higher than 323 K, the catechin is also extracted with caffeine. Thus, further experiments were done at the extraction temperature 323 K. As shown in Fig. 2 the extraction yield was increased with higher temperature as indicated by other works reported in the literature (19). At higher pressure, the solute volatility and diffusivity were increased as the temperature rise, whereas the CO_2 density does not depend so markedly on the temperature, so the increase in the vapor pressure of solute prevails and the solubility rise, Similar solubility behavior has been reported for other vegetable and seed oils (20, 21). Mass transfer coefficient, k_f and k_p, increased with higher temperature due to low transfer resistance, as a result of high diffusivity of caffeine in $SCCO_2$ (Table 2).

The Effect of Pressure

The influence of pressure on the extraction yield was investigated at constant 323 K, water contents of 20.8% and 28.08 kg CO_2/kg green tea/h. As shown in Fig. 3, the larger extraction yield at high pressure is due to the increment of caffeine solubility at CO_2. This is attributed to the increasing of the CO_2 density, which results in the increment of its dissolving ability. Again the mathematical model is able to fit the experimental results.

Mass transfer coefficient, k_f and k_p, decreased with higher pressure and the diffusivity of caffeine in $SCCO_2$ decreases at higher pressure.

Table 2. Experimental condition and process parameters in the theoretical model at various conditions. ($\alpha = 0.84$, $\beta = 0.61$, *dp*: 520 μm, C_0: 34.832 mg/g of green tea, *w*: 50 g)

P (MPa)	T (K)	ρ (g/cm^3)	Q (kg/hr)	Water cons. (%)	τ (sec)	Re	SC (*10^2)	k_f (*10^3) cm/sec	Bi	k_p (*10^3) cm/sec	D_{ab} (*10^4) cm^2/sec	D_e(*10^5) cm^2/sec	ø	K	R^2
Effect of temperature															
40	313	0.96	28.08	19.6	566.15	0.18	2.65	2.89	2.8	1.84	0.71	2.64	1.04	564	0.97
40	323	0.92	28.08	19.6	542.56	0.19	1.79	4.16	2.83	2.66	1.03	3.83	1.44	229	0.97
40	353	0.82	28.08	19.6	483.59	0.22	0.78	9.39	2.85	6.01	2.34	8.71	2.91	210	0.98
Effect of pressure															
10	323	0.39	28.08	19.6	227.64	0.32	0.32	29.66	2.81	19.00	7.36	27.50	4.32	3181	0.92
20	323	0.79	28.08	19.6	462.95	0.23	1.16	6.31	2.83	4.03	1.56	5.80	1.87	784	0.91
40	323	0.92	28.08	19.6	542.56	0.19	1.79	4.16	2.83	2.66	1.03	3.83	1.44	229	0.97
Effect of water															
40	323	0.92	28.08	14.6	542.56	0.19	1.79	4.16	2.83	2.66	1.03	3.83	1.44	981	0.94
40	323	0.92	28.08	19.6	542.56	0.19	1.79	4.16	2.83	2.66	1.03	3.83	1.44	229	0.97
40	323	0.92	28.08	22.6	542.56	0.19	1.79	4.16	2.83	2.66	1.03	3.83	1.44	157	0.95
Effect of flow rate															
40	323	0.92	28.08	19.6	542.56	0.19	1.79	4.16	2.83	2.66	1.03	3.83	1.44	229	0.97
40	323	0.92	5.04	19.6	3022.9	0.03	1.79	4.03	2.73	2.6	1.03	3.83	7.87	201	0.94

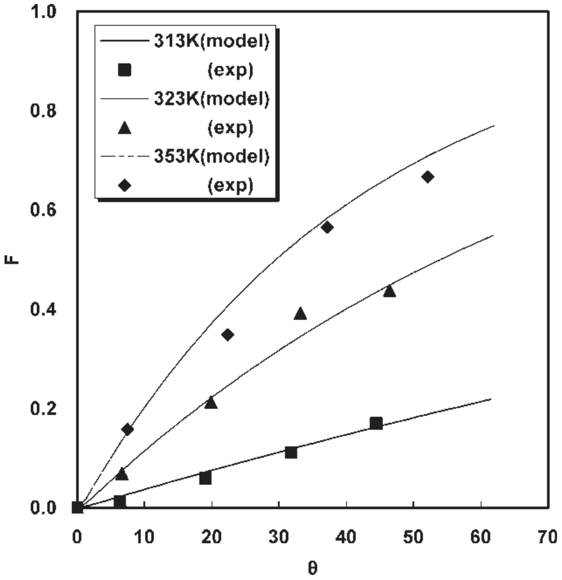

Figure 2. Effect of temperature on extraction yield and dimensionless time at 40 MPa, 20.8 % water contents, and 28.08 kg CO_2/kg green tea/h.

Consequently, the mass transfer resistance increased resulting in decrease in the extraction rate.

The Effect of Water Contents

The final set of experiments was carried out at a constant temperature of 323 K, a pressure of 40 MPa, using $SCCO_2$ at a flow rate of 28.08 kg CO_2/kg green tea/h and water contents varying in weight from 15.8 to 23.8%, as shown in Fig. 4. As the water contents increased, the extraction yield increased. The mathematical model fit the experimental results well.

Caffeine is rarely soluble in $SCCO_2$ (ca. 1 mg/g at 20 MPa and 313 K) (5). So, $SCCO_2$ is ineffective at extracting caffeine from coffee or tea leaves. The addition of water to the green tea facilitates higher extraction yield of the caffeine. This may be due to two different mechanisms, both representatives of reasons to employ waters. First, the addition of water serves to sell the matrix and facilitates diffusion of the caffeine out of the plant tissue. The second mechanism may involve the hydrolysis of caffeine–tannin complexes within the plant cellular structure. Water added to a sample can favor extraction of the caffeine. The enhancing effect of a certain amount of moisture on the extraction yield by $SCCO_2$ was also observed by Charest et al. and Leeke et al. (22).

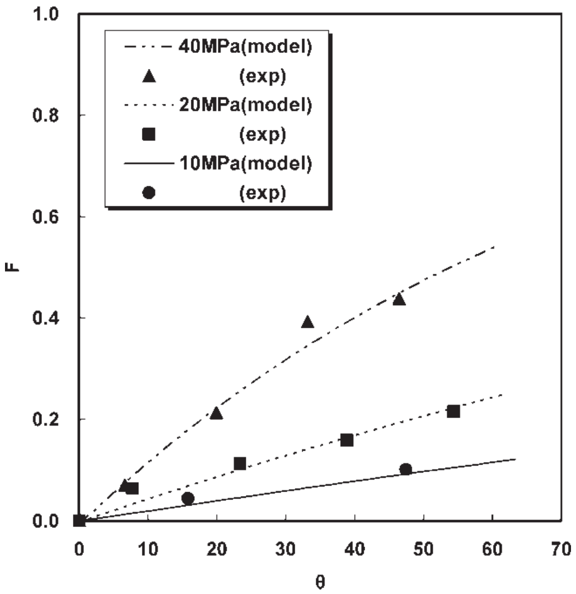

Figure 3. Effect of pressure on extraction yield and dimensionless time at 323 K, 20.8% water contents, and 28.08 kg CO_2/kg green tea/h.

The Effect of Solvent Flow Rate

Several experiments were done to examine the effect of solvent flow rate on extraction yields at an extractor temperature of 323 K, a constant pressure of 40 MPa and water contents of 20.8%. The CO_2 flow rates ranging from 5.04 kg CO_2/kg green tea/h to 28.08 kg CO_2/kg green tea/h. The results of the experiments reveal that the amount of caffeine extracted versus time increased with increasing the CO_2 flow rate. This indicates that a large amount of $SCCO_2$ contacting the green tea at a higher CO_2 flow rate brought out larger amount of caffeine during the some duration of extraction. The cumulative fraction for lower flow rates indicates a need for long extraction time at these conditions. By plotting the extraction results at various flow rates versus dimensionless time θ, one can determine if the rate-controlling step had been an internal mass transfer, the curves have been the same pattern with the plotting of the extraction results at various flow rates versus time (23, 24). However, our result indicated the reverse pattern. This implies that the external mass transfer was the controlling step of this process (25). Mass transfer coefficients, k_f and k_p, increased with increase in CO_2 flow rate. This was due to the decrease in mass transfer resistance as a result of increase in convection.

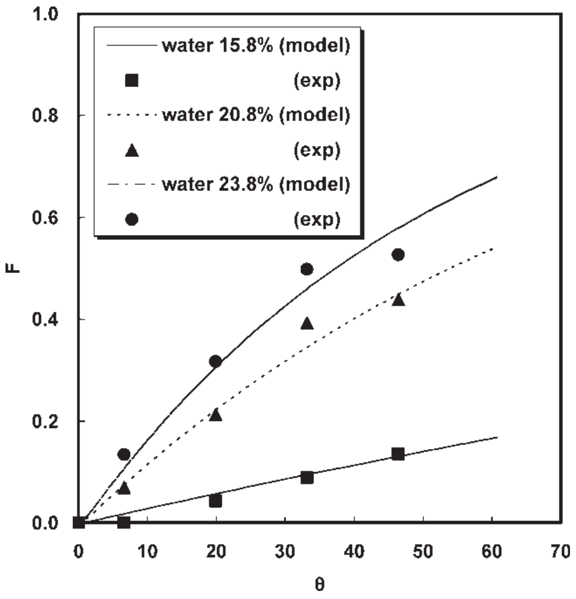

Figure 4. Effect of water contents on extraction yield and dimensionless time at 323 K, 40 MPa, and 28.08 kg CO_2/kg green tea/h.

CONCLUSION

An experimental study for the caffeine extraction from Korean green tea was performed by supercritical CO_2. Experimental data showed that caffeine extraction yields increased with increasing pressure, temperature, CO_2 flow rate, and water contents. Based on Goto's mass transfer model, the external mass transfer was proven to be the controlling step of this process. The maximum caffeine extraction yields were 66% under extractions condition of 353 K, 40 MPa, water contents of 20.8% and 28.08 kg CO_2/kg green tea/hour. However it should be considered that at temperature higher than 323 K, the catechin is also extracted with caffeine.

NOMENCLATURE

a_p	Specific surface area (cm^{-1})
B_i	Biot number
C	Concentration of solute in the fluid phase surrounding the particle (g/cm^3)
C_p	Concentration of solute in pore fluid in annulus (g/cm^3)
C_{ps}	Concentration of solute in the pore space at the surface of the particle (g/cm^3)

C_s	Concentration of solute in solid phase expressed as mass of solute per unit mass of solid (g/cm^3)
C_0	Total initial solute concentration (g/cm^3)
D_{ab}	Binary diffusion coefficient for solute in fluid (cm^2/s)
D_e	Effective intraparticle diffusion coefficient for solute in the solid (cm^2/s)
d_p	Particle diameter(cm)
F	Cumulative fractional yield of solute extracted (–)
F_i	Experimented fractional yield (–)
F_i'	Calculated fractional yield (–)
$\bar{\mathrm{F}}_i$	Mean value of experimented fractional yield (–)
K	Equilibrium constant (–)
k_a	Adsorption rate constant (–)
k_f	External mass transfer coefficient (cm/s)
k_p	Combined mass transfer coefficient (cm/s)
Q	Volumetric flow rate (cm^3/min)
r	Particle radius (cm)
Re	Reynolds number (–)
Sh	Sherwood number (–)
U_s	Superficial velocity (cm/s)
Z	Bed height co-ordinate (cm)

Greek Letters

α	Void fraction in bed (–)
β	Particle porosity (–)
ρ_P	Particle density (g/cm^3)
ρ_f	Fluid density (g/cm^3)
ρ_b	Bulk density in bed
ϕ	Dimensionless mass transfer coefficient
θ	Dimensionless time
τ	Total bed volume/volumetric flow rate (s)

ACKNOWLEDGMENT

This work was supported by the Korea Institute of Science and Technology for the supercritical fluid project.

REFERENCES

1. Gupta, S., Saha, B., and Giri, A.K. (2002) Comparative antimutagenic and anticlastogenic effects of green tea and black tea: a review. *Mutation Research*, 512: 37.

2. Nehlig, A., Daval, J.L., and Debry, G. (1992) Caffeine and the central nervous system: Mechanisms of action, biochemical, metabolic, and psychostimulant effects. *Brain Res. Rev.*, 17 (2): 139.
3. Hartmann, M. and Baumberger, F. (2000) Good reasons to drink tea; the healthy components are not extracted during decaffeination. *CHIMIA*, 54 (5): 325.
4. Amra Perva-Uzunalić, Mojca Škerget, Željko Knez, Bernd Weinreich, Frank Otto, and Sabine Grüner. (2006) Extraction of active ingredients from green tea (Camellia sinensis): Extraction efficiency of major catechins and caffeine. *Food Chemistry*, 96 (4): 597.
5. Luque de Castro, M.D., Valcarcel, M., and Tena, M.T. (1994) *Analytical Supercritical Fluid Extraction*; Spinger-Verlag: Germany.
6. Peter, S. and Brunner, G. (1982) Process for the decaffeinating of raw coffee. U. S. Patent 4,322,445, March 30.
7. General Food Corporation (1984). Decaffeination process. U. S. Patent 4,472,442, September 18.
8. Theissing Peter, Saamer Peter, and Korner. (1991). Decaffeinating coffee and tea. U. S. Patent 5,153,015, December 31.
9. Sun Chuanjing, Sun Yunpeng, and Chen Bin. (2003). Supercritical CO_2 back extraction process for extraction catechin from tea extract. C. N. Patent 1,304,919, May 21.
10. Greentech 21 Corporation. (2006). Supercritical fluid extraction method of caffeine. K.R. Patent 0,119,032, November 24.
11. Erkey, C.T., Guo, Y., Erkey, C., and Akgernam, A. (1996) Mathermatical modeling of adsorption and desorption of volatile constaminants from soil; influence of isotherm shape on adsorption and desorption profiles. *Environmental Science and Technology*, 30: 2127.
12. Goto, M., Sato, M., and Hirose, T. (1993) Extraction of peppermint oil by supercritical carbon dioxide. *J. Chem. Eng. Jpn.*, 26 (4): 401.
13. Duford, N.T., Goto, M., and Temelli, F. (1998) Modeling of oil extraction with supercritical CO_2 from Atlantic mackerel (*Scomber scombrus*) at different moisture contents. *J. Supercrit Fluids*, 13: 303.
14. Goto, M., Roy, B.C., Kodana, A., and Hirose, T. (1998) Modeling supercritical fluid extraction process involving solute-solid interaction. *J. Chem. Eng. Jpn.*, 3 (2): 171.
15. Goto, M., Smith, J.M., and McCoy, B.J. (1990) Parabolic profile approximation (linear driving-force model) for chemical reactions. *Chemical Engineering Science*, 45 (2): 443.
16. Bruce, E. Poling, John, M. Prausnitz, and John P. O'Connell. (2000) *The Properties of Gases and Liquids*, 5th Edn.; McGraw-Hill: U.S.
17. Wakao, N. and Kaguei, S. (1985) *Heat and Mass Transfer in Packed Beds*; Gordon and Breach Science Publishers: Yokohama National University, Japan.
18. Ronyai, E., Simandi, B., Tomoskozi, S., Deak, A., Vigh, L., and Weinbrenner, Zs. (1998) Supercritical fluid extraction of corn germ with carbon dioxide-ethyl alcohol mixture. *J. Supercrit. Fluids*, 14: 75.
19. Bozan, B. and Temelli, F. (2003) Extraction of poppy seed oil using supercritical CO_2, Food. *Chem. Toxicol.*, 66: 422.
20. Ozkal, S.G., Salgin, U., and Yener, M.E. (2005) Supercritical carbon dioxide extraction of hazelnut oil. *J. Food Eng.*, 69: 217.
21. Marleny, D.A. Saldana., Carsten Zetzl, Rahoma S. Mohamed, and Brunner, G. (2002) Decaffeination of guarana seeds in a microextraction column using water-saturated CO_2. *J. Supercrit. Fluid*, 22: 119.

22. Leeke, G., Gaspar, F., and Santos, R. (2002) Influence of water on the extraction of essential oils from a model herb using supercritical carbon dioxide. *Ind. Eng. Chem. Res.*, 41: 2033.
23. Reverchon, E. and Marrone, C. (2001) Modeling and simulation of the supercritical CO_2 extraction of vegetable oils. *J. Supercrit. Fluids*, 19: 161.
24. Wu, W. and Hou, Y. (2001) Mathematical modeling of extraction of egg yolk oil with supercritical CO_2. *J. Supercrit. Fluids*, 19: 145.
25. Pathumthip Tonthubthimthong, Peter L. Douglas, and Supaporn Douglas, S. (2004) Extraction of nimbin from neem seeds using supercritical CO_2 and a supercritical CO_2-methanol mixture. *J. Supercrit. Fluids*, 30: 287.