# CAFFEINE AND CHLOROGENIC ACID SEPARATION FROM RAW COFFEE BEANS USING SUPERCRITICAL $CO_2$ IN WATER

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## Abstract

The aim of this work was to develop new process for extracting and separating hydrophilic and hydrophobic compounds from coffee beans using supercritical $CO_2$ in water. In this work, experiments and simulation of the process has been conducted. Chlorogenic acid and caffeine from coffee beans were used as model compounds of hydrophilic and hydrophobic compounds, respectively. Experiment was conducted in the semi-continuous flow extractor at various densities and ratios of coffee mass and water mass (C/W). Extracted compounds in SC-$CO_2$ and in water were analyzed by HPLC-PDA detector, respectively. As expected, the extracted compound in SC-$CO_2$ was containing 100% purity of caffeine. However, the extracted compound in water was containing caffeine and chlorogenic acid. It was due to the solubility of caffeine in water is higher than that in SC-$CO_2$. Recovery of caffeine in SC-$CO_2$ increased with increasing density and decreasing ratio of coffee mass and water mass (C/W).

In addition, this process was also simulated using model based on mass transfer balance to estimate recovery of caffeine and to describe concentration profile inside of the extractor (both in SC-$CO_2$ phase and water phase). Simulation was conducted using Visual Basic in Excel 2003. As in the experimental result, the recovery of caffeine in SC-$CO_2$ increased with the increase in density. However, the effect of C/W on the recovery of caffeine in SC-$CO_2$ yielded adversative result. In the simulation result, the recovery of caffeine in SC-$CO_2$ decreased with decreasing C/W. The result can be explained that increasing mass of water caused increasing mass transfer rate of caffeine in water, thus the increasing mass transfer resistance in SC-$CO_2$. Concentration profile of caffeine in SC-$CO_2$ phase and in water phase inside of the extractor have also been simulated.

## Introduction

Coffee is believed to be the most popular beverage in the world. Caffeine (1,3,7-trimethylxanthine) is an alkaloid generally responsible for ~0.9–2.5% of coffee dry matter composition [1]. Even though caffeine has been widely consumed and studied for centuries, research results are inconclusive about both adverse and beneficial relations of caffeine to several health outcomes. Low to moderate caffeine intake is generally associated with improvements in alertness, learning capacity, exercise performance, and perhaps mood [2].Caffeine is also often used as an additive in pain medications [3]. However, its stimulatory effects may also adversely affect sensitive individuals by causing tachycardia, increase of blood pressure, anxiety, and insomnia [4]. According to Shlonsky et al. [5], the research for a healthier lifestyle by some people and the effects of caffeine on various

illnesses may account for the increasing demand for decaffeinated coffee throughout the world. Today, decaffeinated coffee makes up ~10% of the coffee market [6].

Decaffeination is performed prior to the roasting process. The most common and least costly caffeine extraction methods in the coffee industry employ an organic solvent associated with the used of water/vapor prior to and after extraction. Water alone has also been used to replace organic solvents in the process. By using the process, caffeine content is usually reduced to $0.02 - 0.3\%$ [7]. Supercritical fluid, particularly carbon dioxide, is an alternative to be applied in the decaffeination process. More recent commercial application was the decaffeination of coffee and tea [8]. The decaffeination process advantageously eliminates residual solvent.

Chlorogenic acids (CGA) are water-soluble phenolic components of coffee and other plants formed by the esterification of certain trans-cinnamic acids, such as cafeic (CA), ferulic (FA), and p-coumaric acids (CoA), with (-)-quinic acid [9]. CGA not only contribute to coffee flavor, but also may be of potential bio-pharmacological importance in humans. The most studied pharmacological activities of phenolic compounds such as CGA have been related to their antioxidant properties, because they are thought to have positive effects on chronic degenerative diseases [10, 11]. In the decaffeination process with water, CGA is usually extracted together with caffeine and their related compounds.

In order to eliminate CGA from caffeine in the decaffeination process, both supercritical $CO_2$ and water were used as solvents in this study. Concept of the separation process is shown in **Figure 1**, where both water and $SCCO_2$ flow continuously. Target component of hydrophobic compound (caffeine) and small amount of hydrophilic compound (chlorogenic acid) are directly extracted or dissolved from the surface of raw material into $SCCO_2$ or dissolved into $SCCO_2$ after dissolved in water from the surface of raw material. On the other hand, target component of hydrophilic compound (chlorogenic acid) is dissolved in water and collected in water phase. Simulation of the process was also conducted in order to describe solvent behavior in the extractor.



**SCCO$_2$** + hydrophobic compound

**H$_2$O**

**SCCO$_2$**

**H$_2$O** + hydrophilic compound
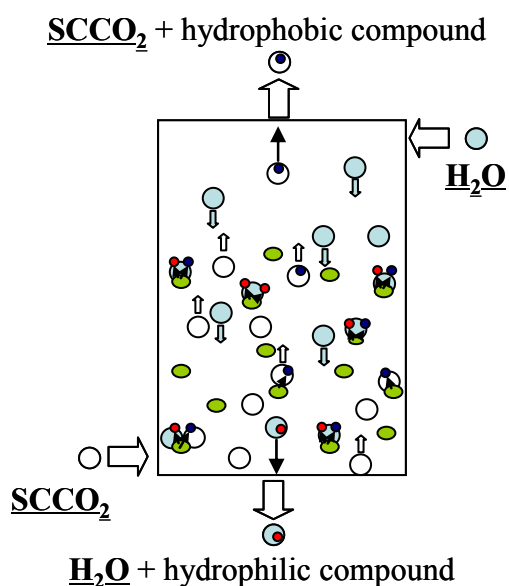
**Figure 1**. Concept of proposed separation process

## Materials and Methods

### *Materials and Chemicals*

In this work, raw Arabica coffee beans from Costa Rica purchased from local market was used as starting material. Caffeine and chlorogenic acid standards and HPLC grade of acetonitrile and phosphoric acid were provided by Wako Chemical Ltd. $CO_2$ was obtained from Uchimura Co., Japan.

### *Experimental Method*

Experiment was conducted in semi continuous extractor with volume of 50 and 250 ml. In this work, coffee beans were used as starting material, while chlorogenic acid and caffeine were used as model compounds. $SCCO_2$ and water were used as solvents to extract caffeine and chlorogenic acid, respectively. Two types of separation mode were used, those are $SCCO_2$ and water in flow and batch mode, respectively, and both $SCCO_2$ and water in flow mode. Schematic diagrams of two types of

separation apparatus are shown in **Figure 2** and **3** for first and second types of separation, respectively. The apparatus includes a chiller (Cooling Unit CLU-33, Iwaki Asahi Techno Glass, Japan), two pumps (Syringe pump Model 260D, ISCO, Japan, and Intelligent Prep. Pump. PU-2086 Plus, Jasco, Japan, for $CO_2$ and water, respectively), a heating chamber (ST-110, ESPEC Corp., Japan), an extractor (Taikiatsu, Japan, 50 and 250 ml in volume), back pressure regulators (SCF-Bpg, Jasco, Japan and AKICO, Japan), collection vials, and a wet gas meter (Sinagawa Co., Japan). In the first type of separation, glass beads and coffee beans were put in the 50 ml of extractor and soaked with water, while $SCCO_2$ bubbling was flowed from the top of extractor. In the second type of separation, $SCCO_2$ and water were flowed from the top and bottom side of 250 ml of extractor, respectively. Separation and extraction were carried out at various temperatures of $40 - 60^{\circ}C$, pressures of $15 - 25$ MPa, particle sizes, water volumes and height of glass beads. The extracts from the $CO_2$ and water phases were collected in the vial at every 60 min for 6 hours, and weighed immediately after the collection.
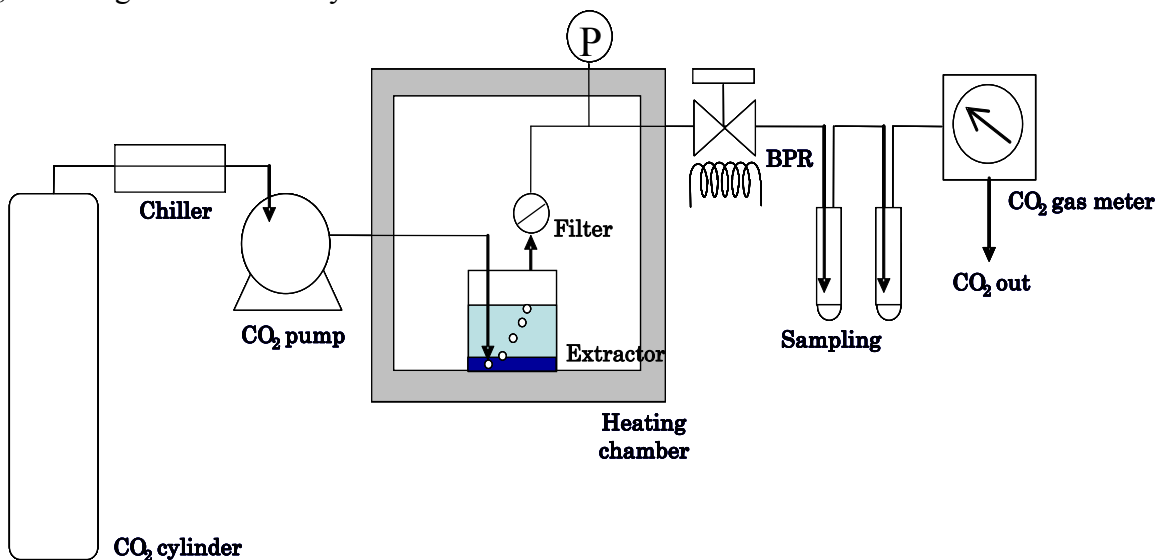


**Figure 2**. Schematic diagram of separation apparatus for $SCCO_2$ in flow and water in batch modes
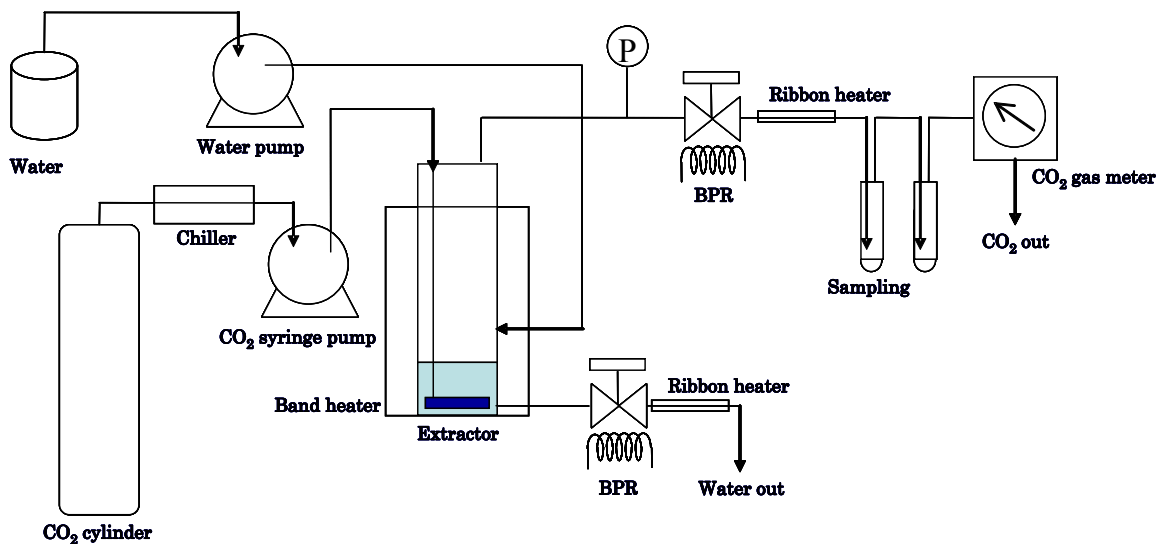


**Figure 3**. Schematic diagram of separation apparatus for both $SCCO_2$ and water in flow modes

*Analytical Method*

Caffeine and chlorogenic acid extracted from $CO_2$ and water phases were analyzed by using a High Performance Liquid Chromatograph LC-10AD gradient system, equipped with Diode Array Detector SPD-M10A (Shimadzu, Japan). 10 μl of extract dissolved in methanol was injected by SIL-10AF auto-sampler (Shimadzu, Japan) and separated with a STR ODS II column (5μm; 4.6x250 mm; Shinwa Chemical Industries, Ltd., Japan) at $40^{\circ}$C. The mobile phase consisted of eluent A (10 mM phosphoric acid) and eluent B (acetonitrile). Separation of caffeine and chlorogenic acid were achieved by the following gradient procedure: 10% of B for 5 min; a linear gradient from 10 to 70% of B within 10 min; 70% of B for 3 min; 10% of B for 13 min, at a flow rate of 1.0 ml/min. The absorption spectra of caffeine and chlorogenic acid were displayed between 190 and 800 nm. Peaks were measured at wavelength of 270 and 325 nm to facilitate the detection of caffeine and chlorogenic acid, respectively.

### Simulation

Simulation of the process was conducted using model based on mass transfer balance to estimate recovery of caffeine and to describe concentration profile inside of the extractor (both in SC-$CO_2$ phase and water phase). As assumption, particle is arranged as packed bed and soaked by water. Solute (caffeine and chlorogenic acid) is distributed among the fluid phase. Fluid (water and SCCO$_2$) penetrates into the particle and solute is transferred from particle into water and SCCO$_2$, where a part of solute in water is transferred into SCCO$_2$.

The following model equations were derived based on the assumptions.

- Mass balance of solute on the SCCO$_2$ phase:

$$\rho_f.\varepsilon.\left(\frac{\partial C}{\partial t}+u.\frac{\partial C}{\partial Z}\right)=-\rho_f.k_f.a.(1-\alpha).(C-C^*)-\rho_L.k_L.a.(C_L-C_L^*) \qquad (1)$$

- Mass balance of solute on the water phase:

$$\rho_L.\varepsilon.\frac{\partial C_L}{\partial t}=\rho_L.k_L.a.(C_L-C_L^*)-\alpha\rho_f.k_f.a.(C-C^*) \qquad (2)$$

- Mass balance of solute on the solid phase:

$$(1-\varepsilon).\rho_s.\frac{\partial C_s}{\partial t}=\rho_f.k_f.a.(C-C^*) \qquad (3)$$

$$C_s=f(C^*) \qquad (4)$$

Initial and boundary conditions used in the model were:

$$t=0 \rightarrow C=C^*, C_s=C_{s0}, C_L=C_{L0}=C_L^* \qquad (5)$$
$$Z=0 \rightarrow C=0 \qquad (6)$$
$$Z=L \rightarrow \frac{\partial C}{\partial Z}=0 \qquad (7)$$

Yield of extract was calculated using the following equation:

$$Yield=Q\int_0^t C|_{Z=L}\, dt \qquad (8)$$

Where:
- $C$ = concentration of caffeine in SCCO$_2$ phase
- $C_L$ = concentration of caffeine in water phase
- $C_s$ = concentration of caffeine in solid phase
- $k_f.a$ = volumetric mass transfer in SCCO$_2$ phase
- $k_L.a$ = volumetric mass transfer in water phase
- $\rho_f$ = density of SCCO$_2$

- $\rho_L$ = density of water
- $\rho_s$ = density of solid
- $Q$ = solvent flow rate

The model equations are transformed into dimensionless form using dimensionless variables:

$$X_s = \frac{C_s}{C_{s0}} \qquad X = \frac{C}{C_0} \qquad X^* = \frac{C^*}{C_0} \qquad X_L^* = \frac{C_L^*}{C_{s0}}$$

$$X_L = \frac{C_L}{C_{s0}} \qquad H = \frac{Z}{L} \qquad \theta = \frac{u.t}{L}$$

Equation (1), (2) and (3) become:

$$\frac{\partial X}{\partial \theta} + \frac{\partial X}{\partial H} = -\frac{(1-\alpha)}{\psi_L}.(X - X^*) - \frac{1}{\psi_e.\phi_L}.(X_L - X_L^*) \tag{9}$$

$$\frac{\partial X_L}{\partial \theta} = \frac{1}{\psi_e}.(X_L - X_L^*) - \frac{\phi_L.\alpha}{\psi_L}.(X - X^*) \tag{10}$$

$$\frac{\partial X_s}{\partial \theta} = \frac{\phi_s}{\psi_i}.(X - X^*) \tag{11}$$

Where:

$$\psi_i = \frac{(1-\varepsilon).u}{k_f.a.L} \qquad \psi_e = \frac{\varepsilon.u}{k_L.a.L} \qquad \psi_L = \frac{\varepsilon.u}{k_f.a.L}$$

$$\phi_s = \frac{\rho_f.C_0}{\rho_s.C_{s0}} \qquad \phi_L = \frac{\rho_f.C_0}{\rho_L.C_{L0}}$$

The differential equations coupled with initial and boundary conditions were solved numerically by Crank Nicholson's method and computational programming using Visual Basic 6.0.
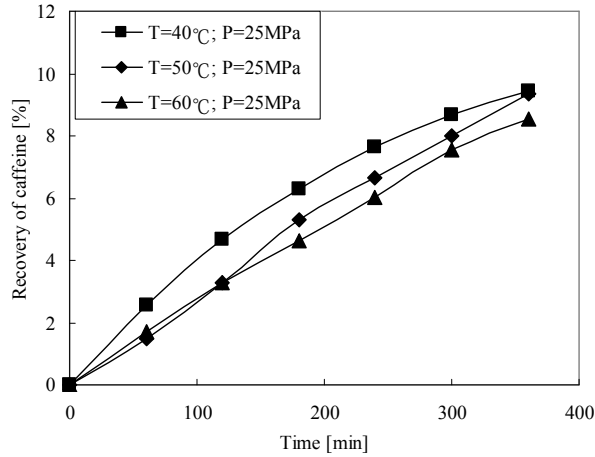
## Results and Discussions

### Separation using SCCO₂ in Flow and Water in Batch Modes

Effect of temperature and pressure on the recovery of caffeine and chlorogenic acid in $SCCO_2$ and water phases will be presented below. Recovery of caffeine and chlorogenic acid were defined as weight of caffeine and chlorogenic acid extracted divided by weight of caffeine and chlorogenic acid extracted by soxhlet extraction, respectively.
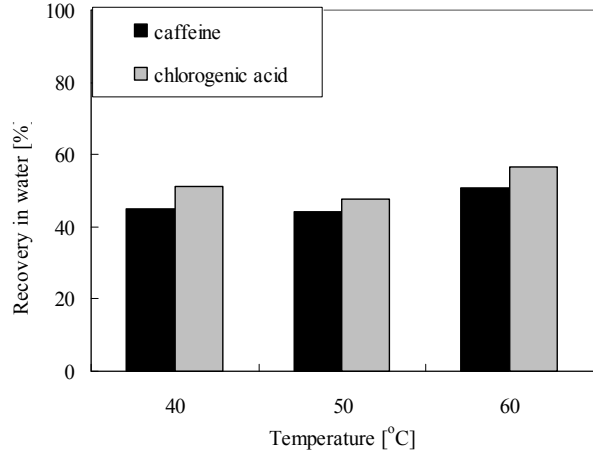
The effect of temperature on the recovery of compounds in $SCCO_2$ and water phases was studied at pressure of 25 MPa, $CO_2$ flow rate of 3 ml/min, water volume of 30 ml with 4 g of raw coffee beans. Recoveries of compounds in $SCCO_2$ and water phases are expected containing caffeine and chlorogenic acid in high purity, respectively. **Figure 4** and **5** show the effect of temperature on the recovery of compounds in $SCCO_2$ and water phases, respectively. As expected, the extracted compound in $SCCO_2$ was containing 100% purity of caffeine. However, the extracted compound in water was containing caffeine and chlorogenic acid. As shown in the figures, recovery of caffeine in $SCCO_2$ significantly decreased with increasing temperature due to decreasing $SCCO_2$ density. However, the increasing temperature almost had no effect on the composition of caffeine and chlorogenic acid in water phase. It might be caused the change of temperature could not increase temperature of water, and as the result the composition of extract was not changed.

**Figure 6** and **7** show the effect of pressure on the recovery of caffeine and chlorogenic acid in $SCCO_2$ and water phases, respectively. Increasing pressure promoted the increasing recovery of caffeine and chlorogenic acid in $SCCO_2$ and water phases, respectively, due to increasing $SCCO_2$ density. This result indicated that caffeine might be separated from chlorogenic acid by increasing pressure of the
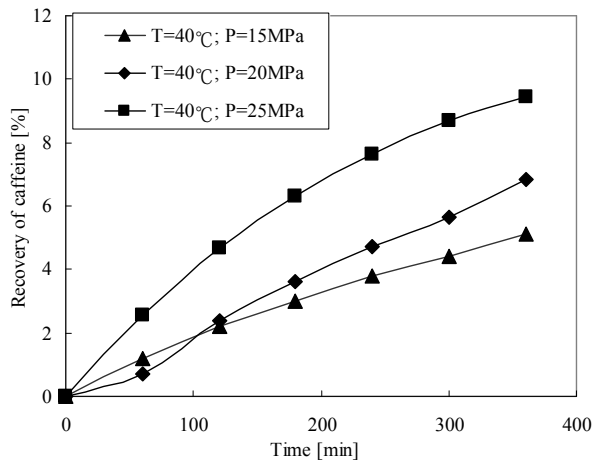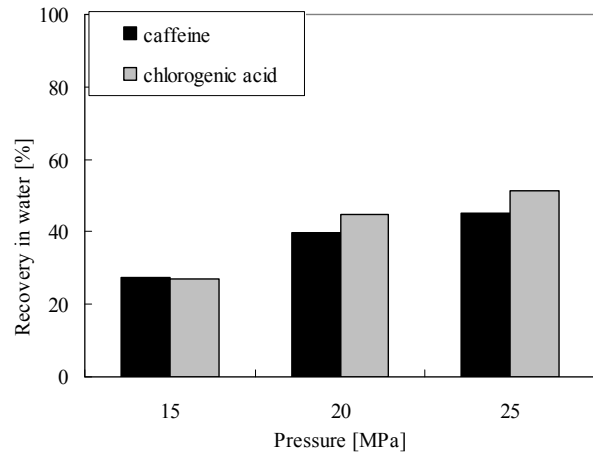
process.



**Figure 4**. Effect of temperature on the recovery of caffeine in $SCCO_2$ phase



**Figure 5**. Effect of temperature on the recovery of caffeine and chlorogenic acid in water phase



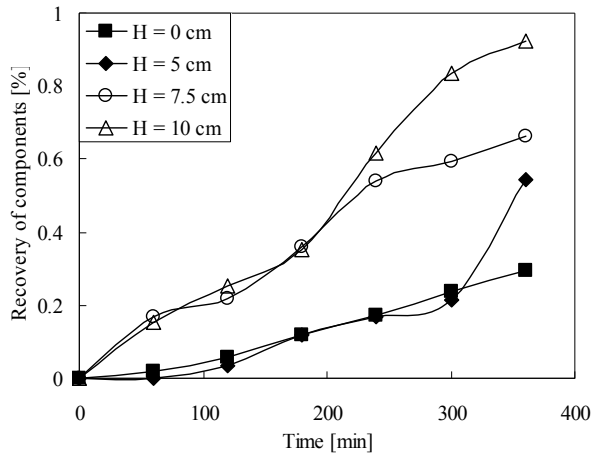**Figure 6**. Effect of pressure on the recovery of caffeine in $SCCO_2$ phase



**Figure 7**. Effect of pressure on the recovery of caffeine and chlorogenic acid in water phase

### *Separation using SCCO₂ and Water in Flow Modes*

To improve extraction efficiency of caffeine and chlorogenic acid, glass beads as hydrophobic substance collection part were loaded into the bottom of extractor. Effect of height of hydrophobic substance collection part on the recovery of caffeine and chlorogenic acid in $SCCO_2$ and water phase, and on the separation factor were studied. The separation factor was defined as weight of caffeine extracted in $SCCO_2$ phase divided by weight of caffeine in $SCCO_2$ and water phases.

**Figure 8** and **9** show the effect of height of hydrophobic substance collection part on the recovery of caffeine and chlorogenic acid in $SCCO_2$ and water phase, respectively. As shown in **Figure 8**, initially increasing height of hydrophobic substance collection part didn't affect on the recovery of caffeine, however at longer extraction time recovery of caffeine significantly increased with increasing height of hydrophobic substance collection part. It evidenced that hydrophobic substance collection part is necessary to enhance the extraction efficiency. In **Figure 9**, higher hydrophobic substance collection part caused higher selectivity of caffeine to chlorogenic acid.
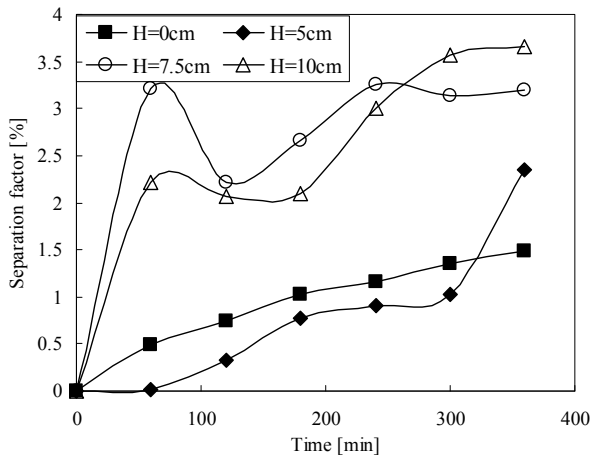
**Figure 8**. Effect of height of hydrophobic substance collection part on the recovery of caffeine in $SCCO_2$ phase
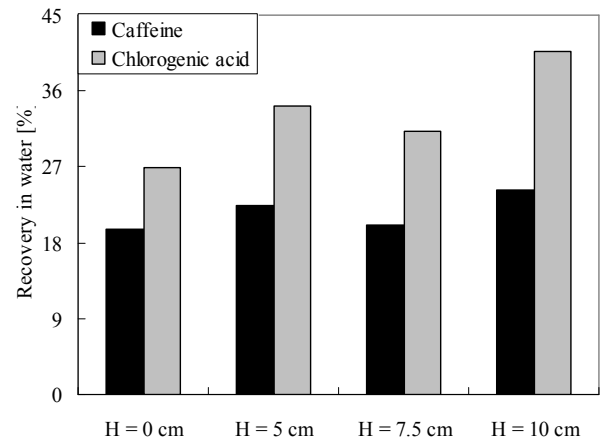


**Figure 9**. Effect of height of hydrophobic substance collection part on the recovery of caffeine and chlorogenic acid in water phase

The effect of height of hydrophobic substance collection part on the separation factor is shown in **Figure 10**. The separation factor tended to be increased with increasing height of hydrophobic substance collection part. It can be explained that at higher hydrophobic substance collection part, amount of water stored in the extractor was large, and as the result amount of caffeine dissolved in the water was large and easy to be extracted by $SCCO_2$.



**Figure 10**. Effect of height of hydrophobic substance collection part on the separation factor
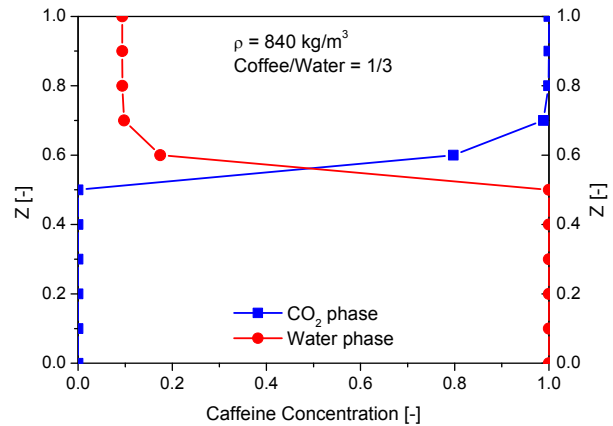


**Figure 11**. Profile of caffeine concentration in SC-$CO_2$ and water along extractor height

### Simulation Result

In the simulation work separation was conducted in first type separation, $SCCO_2$ and water in flow and batch mode, respectively. Effects of $SCCO_2$ density, ratio of mass of coffee and water, and ratio of extractor height and diameter on the recovery of caffeine in $SCCO_2$ phase were studied. Concentration profile of caffeine in $SCCO_2$ and water phases along the extractor height was also determined. However, in this paper only concentration profile of caffeine will be presented.

**Figure 11** shows concentration profile of caffeine in $SCCO_2$ and water phases along the extractor height. Caffeine concentrations in $SCCO_2$ and water phases at the top of extractor were 1 and 0.09, respectively. It indicated that 0.09 caffeine in water phase might be extracted together with caffeine in

SCCO$_2$ phase. This calculation result is in agreement with the experimental result. As observation in the experiment, sometimes extract in SCCO$_2$ phase was including small amount of water.

## Conclusion

Separation of caffeine and chlorogenic acid from raw coffee beans using SCCO$_2$ and water has been studied. Two types of separation mode were used in the experimental work. The effect of temperature and pressure in the separation mode using SCCO$_2$ in flow and water in batch mode has been reported. Recovery of caffeine in SCCO$_2$ phase increased with decreasing temperature and increasing pressure. However, only the increasing pressure could promote the increasing recovery of caffeine and chlorogenic acid in water phases. The change of height of hydrophobic substance collection part on the recovery of caffeine and chlorogenic acid in SCCO$_2$ and water phases and on the separation factor has been studied using SCCO$_2$ and water in flow mode. Recovery of caffeine and separation factor of caffeine from chlorogenic acid significantly increased with increasing height of hydrophobic substance collection part. Simulation work was also conducted in order to estimate concentration of caffeine both in SCCO$_2$ and water phases.

## References

1. Ky, C., J. Louarn, S. Dussert, B. Guyot, S. Hamon and M. Noirot (2001), "Caffeine, trigonelline, chlorogenic acids and sucrose diversity in wild *Coffee Arabica* L. and *C. canephora* P. accessions", *Food Chemistry*, 75, pp. 223–230.
2. Flores, G.B., F. Andrade and D.R. Lima (2000), "Can coffee help fighting the drug problem? Preliminary results of a Brazilian youth drug study", *Acta Pharmacologica Sinica*, 21 (12), pp. 1059–1070.
3. De Paulis, T., P. Commers, A. Farah, J. Zhao, M.P. McDonald, R. Galici and P.R. Martin (2004), "4-Caffeoyl-1,5-quinide in roasted coffee inhibits [$^3$H]naloxone binding and reverses antinociceptive effects of morphine in mice", *Psychopharmacology*, 176, pp. 146–153.
4. Ramalakshmi, K. and B. Bhagavan (1999), "Caffeine in coffee: its removal. Why and how?" *Critical Reviews in Food Science and Nutrition*, 39, pp. 441–456.
5. Shlonsky, A.K., A. Klatsky and A. Armstrong (2003), "Traits of persons who drink decaffeinated coffee", *Annals and Epidemiology*, 13 (4), pp. 273–279.
6. Silvarola, M.B., P. Mazzafera and L.C. Fazioli (2004), "A naturally decaffeinated arabica coffee", *Nature*, pp. 249, 826.
7. Balyaya, K.J. and M.N. Clifford (1995), "Individual chlorogenic acids and caffeine contents in commercial grades of wet and dry processed Indian green robusta coffee", *Journal of Food Science and Technology*, 32, pp. 104-108.
8. McHugh, M. and V. Krukonis (1994), "Supercritical Fluid Extraction Principles and Practice", 2$^{nd}$ ed., Butterworth-Heinemann.
9. Farah, A., T. de Paulis, D.P. Moreira, L.C. Trugo and P.R. Martin (2006), "Chlorogenic acids and lactones in regular and water-decaffeinated Arabica coffees", *Journal of Agricultural and Food Chemistry*, 54, pp. 374-381.
10. Daglia, M., A. Papetti, C. Gregotti, F. Berte and G. Gazzani (2000), "*In vitro* antioxidant and *ex vivo* protective activities of green and roasted coffee", *Journal of Agricultural and Food Chemistry*, 48, pp. 1449-1454.
11. Del Castilho, M.D., J.M. Ames and M.H. Gordon (2002), "Effect of roasting on the antioxidant activity of coffee brews", *Journal of Agricultural and Food Chemistry*, 50, pp. 3698-3703.