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Simultaneous Extraction and Separation Process for Coffee Beans with Supercritical CO$_2$ and Water

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ABSTRACT: The aim of this work was to develop a new process for extraction and separation of polar and nonpolar compounds from natural materials using supercritical CO$_2$ (SCCO$_2$) in water. In this work, chlorogenic acid and caffeine from coffee beans were used as model compounds of polar and nonpolar compounds, respectively. Extraction and separation were conducted in three types of semicontinuous extractors with different sizes and flow types of CO$_2$ and water. 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 the 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 the nonpolar recovery section 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 co-current and counter-current flow modes. Recovery of caffeine and separation factor of caffeine from chlorogenic acid significantly increased with increasing height of nonpolar recovery section. The effect of temperature in counter-current type of separation on the recovery of caffeine and chlorogenic acid in SCCO$_2$ and water phases exhibited different trend with batch type of separation. The counter-current type of separation was more effective compared to both batch and co-current types of separation. On the basis of the results of this work, it is suggested to design longer extractor columns with a higher nonpolar recovery section in the counter-current type in order to increase separation efficiency.

1. INTRODUCTION

Supercritical fluids extraction (SFE) has immediate advantages over conventional extraction techniques: it is a flexible process due to the possibility of adjustment of the solvent power or selectivity of the SCF, it allows protection of polluting organic solvents, and it eliminates the expensive cost of postprocessing of the extract for solvent reduction. Even though several compounds have been examined as SFE solvents, the most popular one is carbon dioxide (CO$_2$). CO$_2$ is an inert, inexpensive, easily available, odorless, tasteless, environment-friendly, and generally regarded as safe (GRAS) solvent. CO$_2$ offers supercritical operations at relatively low pressures and at near-room temperatures. Recently, water has also been used as supercritical solvent for extraction, especially in the field of food application. Water is a polar component that is a environmentally friendly solvent, especially for non-heat-sensitive compounds.[1]

Supercritical CO$_2$ (SCCO$_2$) is a nonpolar solvent and usually used for extraction of nonpolar compounds. Extraction of polar compounds is conducted using SCCO$_2$ with the addition of a polar solvent, such as ethanol, methanol, and water. Separation and extraction of nonpolar and polar compounds simultaneously from natural products are necessary to simplify the separation process. In this work, a simultaneous extraction and separation process was proposed using SCCO$_2$ and water as solvent to extract nonpolar and polar compounds from natural products,

respectively. Caffeine and chlorogenic acids from coffee beans are used as nonpolar and polar model compounds, respectively.

Coffee is one of the most popular beverages in the world. Coffee beans contain around 20 wt % of water-soluble substances, including caffeine and chlorogenic acids.[2] Caffeine (1,3,7-trimethylxanthine) is an alkaloid generally responsible for about 0.9—2.5% of coffee dry matter composition.[3] Even though caffeine has been widely consumed and studied for centuries, research results are inconclusive about both adverse and beneficial effects 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.[4] Caffeine is also often used as an additive in pain medications.[5] However, its stimulatory effects may also adversely affect sensitive individuals by causing tachycardia, increase of blood pressure, anxiety, and insomnia.[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 use of water/vapor prior to and after extraction. Water alone has also

been used to replace organic solvents in the process. By using water, the 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.[2,8] The decaffeination process advantageously eliminates residual solvent. The decaffeination process with $SCCO_2$ can be improved by adding water as a cosolvent.[9] Soaking the raw beans in water prior to decaffeination enhanced the rate of extraction, which increased markedly with water content. Using CO_2 saturated with water also increased the rate of extraction.

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.[10] CGA not only contributes to coffee flavor but also may be of potential biopharmacological 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.[11,12] In the decaffeination process with water, CGA is usually extracted together with caffeine and their related compounds. Azevedo et al. has reported that CGA might be extracted by $SCCO_2$ with polar solvents, such as ethanol and isopropyl alcohol.[13] CO_2 is a nonpolar solvent with low affinity for polar substances. So, the solubility of substances in supercritical CO_2 decreases with the increase in the number of polar functional groups (e.g., hydroxyl, carboxyl, amino, and nitro). Thus, the solubility of CGA molecules is expected to be low, particularly as the molecular weight increases.[14−16]

To extract both CGA and caffeine, and to separate CGA from caffeine in the decaffeination process, a simultaneous extraction process was developed in this work. Both supercritical CO_2 and water were used as solvents in this process to extract caffeine and CGA, respectively. The CGA was expected to be isolated from caffeine in the water phase. The concept of the extraction process will be explained in detail in the next section. In this work, the extraction and separation process was proposed experimentally to study the effect of extraction conditions and type of extractors on the recovery of CGA and separation of caffeine from the coffee beans and extracted compounds in the water phase.

2. CONCEPT OF SIMULTANEOUS EXTRACTION PROCESS

Concept of the simultaneous extraction and separation process is shown in Figure 1, where both water and $SCCO_2$ flow counter-currently through the extractor or only $SCCO_2$ flows while water is steady in the extractor. In this case, $SCCO_2$ is dispersed in water. Target component of nonpolar compound is directly extracted or dissolved from the surface and inside of the raw material into $SCCO_2$. A part of nonpolar compounds is initially dissolved in water from the surface or inside of the raw material, and then it is dissolved into $SCCO_2$. The nonpolar compounds are expected to be collected in the $SCCO_2$ phase. On the other hand, the target component of the polar compound is dissolved in water and collected in the water phase. In $SCCO_2$ extraction of natural products, water may play an important role, and extraction of caffeine from coffee beans is as an example. Caffeine is extracted by $SCCO_2$ from coffee beans wetted and swollen by water. In this case, coffee beans were saturated with water prior to $SCCO_2$ extraction. Water penetrated and diffused
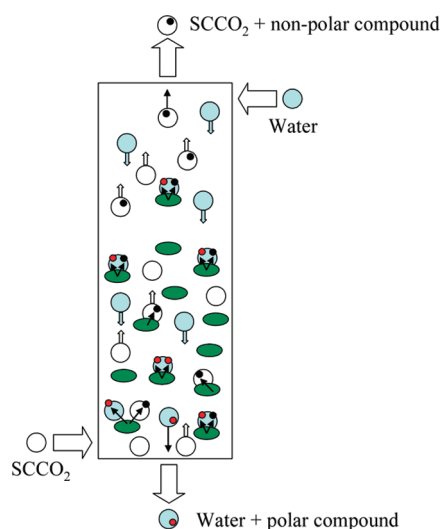
Figure 1. Concept of simultaneous extraction and separation process. Blue circle = water; ○ = $SCCO_2$; red circle = polar compound; ● = nonpolar compound.

into the beans and as a result caffeine is dissolved in water and transferred from inside to the surface of the beans' matrix. Furthermore, caffeine on the surface of the beans is directly dissolved in $SCCO_2$. The extraction is efficient if all caffeine contained in the beans is dissolved and extracted in the water, then the caffeine existing in the water is expected to be transferred and dissolved in $SCCO_2$. In addition, water may act as an entrainer that can enhance the solubility of caffeine in $SCCO_2$.[8]

CGA is one of the polar compounds contained in coffee beans, which has pharmaceutical importance in humans. CGA can be decomposed in the roasting process, and as a result small amount of CGA remained in the coffee beans. Therefore, it is necessary to extract both caffeine and CGA from coffee beans before roasting process for collecting the valuable compound (in this case CGA) and removing the unnecessary compound (in this case caffeine). In the case of CGA, it will be recovered in the water phase due to its polarity and can be added again into the coffee drink or coffee beans after the roasting process by dispersing the CGA into the beans. In this extraction process, recoveries of compounds in $SCCO_2$ and water phases are expected to contain caffeine and CGA in high purity, respectively.

3. MATERIALS AND METHODS

3.1. Materials and Chemicals. In this work, green Arabica coffee beans from Costa Rica with a moisture content of less than 5% purchased from a local market were used as starting material. Caffeine (purity: 99.0%) and CGA (purity: 99.5%) standards and HPLC grade of methanol, acetonitrile, and phosphoric acid were provided by Wako Chemical Ltd. CO_2 with purity of 99.9% and glass beads for experiments were obtained from Uchimura Co., Japan, and As One Co., Japan, respectively.

3.2. Experimental Method. The experiments were conducted in three types of semicontinuous extractors made of SUS316. The first type of extractor had an inside diameter of 40 mm, length of 50 mm, and volume of 60 mL. The second type of extractor had an inside diameter of 40 mm, length of 200 mm, and volume of 250 mL. The third type of extractor had an inside diameter of 21.4 mm, length of 697 mm, and volume of 250 mL. In this work, whole coffee beans were used as the starting

material, while CGA and caffeine were used as model compounds of polar and nonpolar compounds, respectively. $SCCO_2$ and water were used as solvents to extract caffeine and CGA, respectively. Three types of extraction and separation were used. They are extraction and separation with $SCCO_2$ and water in flow and batch, respectively, and extraction and separation with both $SCCO_2$ and water in flow co-currently and counter-currently, respectively. Schematic diagrams of each type of separation apparatus are shown in Figure 2a—c. The apparatus includes a chiller (cooling unit CLU-33, Iwaki Asahi Techno Glass, Japan), two pumps (syringe pump model 260D, ISCO, USA, for CO_2, and Intelligent Prep. pump PU-2086 Plus, Jasco, Japan, for water), a heating chamber (ST-110, ESPEC Corp., Japan), an extractor (Taiatsu, Japan), 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 extraction and separation, glass beads and coffee beans were put in the extractor and soaked with water, while bubbling $SCCO_2$ was flowed and exhausted from the top of the extractor. Extract in the CO_2 phase was collected every hour for 6 h, while extract in the water phase was collected at the end of the extraction process. In the co-current type of extraction and separation, $SCCO_2$ was flowed from the top and bubbled at the bottom of the extractor while water was flowed from the middle of the extractor. Extract in the CO_2 and water phase was collected at the top and bottom of the extractor every hour for 6 h, respectively. In the counter-current type, $SCCO_2$ and water were flowed from the bottom and top of the extractor, respectively. Extract in the CO_2 and water phase was collected every hour for 6 h from the top and bottom of the extractor, respectively. Separation and extraction were carried out at a constant water flow rate (1 mL/min) and various temperatures of 40—60 °C, pressures of 15—30 MPa, ratios of coffee and water mass of 1/30—4/30, height of glass beads of 0—40 cm, and CO_2 flow rates (at the pump) of 3—5 mL/min. In the batch, co-current and counter-current, the amount of whole coffee beans with an average diameter of 0.8 cm used in the extraction was 4, 12, and 25 g, respectively. The extracts from the CO_2 and water phases were weighed immediately after the collection and stored in a refrigerator for a day.

Coffee beans were also extracted by Soxhlet extraction with methanol as the solvent to determine the maximum amount of extractable caffeine and CGA. Methanol with 150 mL of volume was used to extract caffeine and chlorogenic acid from 7 g of coffee beans. Extract was then analyzed by HPLC to determine the caffeine and CGA content.

3.3. Analytical Method. Caffeine and CGA 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). Ten microliters of extract dissolved in methanol was injected by SIL-10AF autosampler (Shimadzu, Japan) and separated with a STR ODS II column (5 μm; 4.6 × 250 mm; Shinwa Chemical Industries, Ltd., Japan) at 40 °C. The mobile phase consisted of eluent A (10 mM phosphoric acid) and eluent B (acetonitrile). Separation of caffeine and CGA was 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 CGA were displayed between 190 and 800 nm. Peaks were measured at a wavelength of 270 and 325 nm to facilitate the detection of caffeine and CGA, respectively.

3.4. Statistical Analysis. To determine the interaction of extraction variables and their effect on the components recovery, an analysis of variance (ANOVA) was carried out according to the Excel Statistics 2004 program. The significance level was stated at 95%, with a p-value 0.05.

4. RESULTS AND DISCUSSION

On the basis of the Soxhlet extraction, maximum extractable caffeine and CGA from green coffee beans were 32.39 ± 0.2 and 54.94 ± 0.3 mg/g of coffee beans, respectively. Collected extract in the $SCCO_2$ and water phase were a white solid and dark brownish-green solution, respectively.

4.1. Extraction and Separation Using $SCCO_2$ in Flow and Water in Batch Modes. In the first type of extraction and separation, the effect of temperature, pressure, and water mass on the recovery of caffeine and CGA in $SCCO_2$ and water phases was investigated to determine of optimum condition for the separation process. Recovery of caffeine or CGA was defined as the weight of caffeine or CGA extracted divided by the weight of caffeine or CGA extracted by Soxhlet extraction, respectively.

The effect of extraction conditions on the recovery of caffeine and CGA in $SCCO_2$ and water phases was investigated. Recovery of caffeine and CGA in $SCCO_2$ and water phases at various extraction conditions is shown in Table 1. The effect of temperature on the recovery of compounds in $SCCO_2$ and water phases was studied at a maximum extractor pressure of 25 MPa, CO_2 flow rate of 3 mL/min, and water volume of 30 mL with 4 g of raw coffee beans. As expected, the extracted compound in $SCCO_2$ contained 100% purity of caffeine. Even though in some experimental conditions $SCCO_2$ that came out from the extractor was saturated in water, the extract did not contain CGA. In this case, water may act as an entrainer to increase the solubility of caffeine in $SCCO_2$. On the other hand, the extracted compound in water contained both caffeine and CGA. On the basis of the HPLC chromatogram, the contents of caffeine and CGA in the water phase varied from 20 to 30 and from 35 to 40%, respectively, depending on the extraction condition. It can be noticed that both caffeine and CGA are well soluble in water (2.71 g/100 mL and 25 mg/mL at 25 °C, respectively[17]). On the other hand, caffeine is also soluble in $SCCO_2$ with a solubility of 0.138 g/100 mL at 40 °C and 30 MPa,[18] while CGA is almost not soluble in $SCCO_2$.[14–16] Thus, a high concentration of caffeine was found both in the $SCCO_2$ and water phases. However, the caffeine concentration was higher in the water phase compared to the $SCCO_2$ phase. As shown in Table 1, recovery of caffeine in $SCCO_2$ significantly decreased with increasing temperature due to the decrease in $SCCO_2$ density, resulting in decreasing mass transfer and solubility of caffeine in $SCCO_2$. The temperature interaction with the caffeine recovery was also confirmed by ANOVA with a significance level of more than 95%. This result is in agreement with other reports[19,20] that the solubility of caffeine in $SCCO_2$ increased with decreasing temperature at pressures lower than 30 MPa. However, the increasing temperature almost had no effect significantly on the composition of caffeine and CGA in the water phase. It might be because the increasing extractor temperature could not increase the temperature of the water, and as a result water properties and composition of extract did not change significantly.

The effect of pressure on the recovery of compounds in $SCCO_2$ and water phases was investigated at a temperature of 40 °C, CO_2 flow rate of 3 mL/min, and water volume of 30 mL

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dx.doi.org/10.1021/ie101252w |*Ind. Eng. Chem. Res.* 2011, 50, 2227–2235

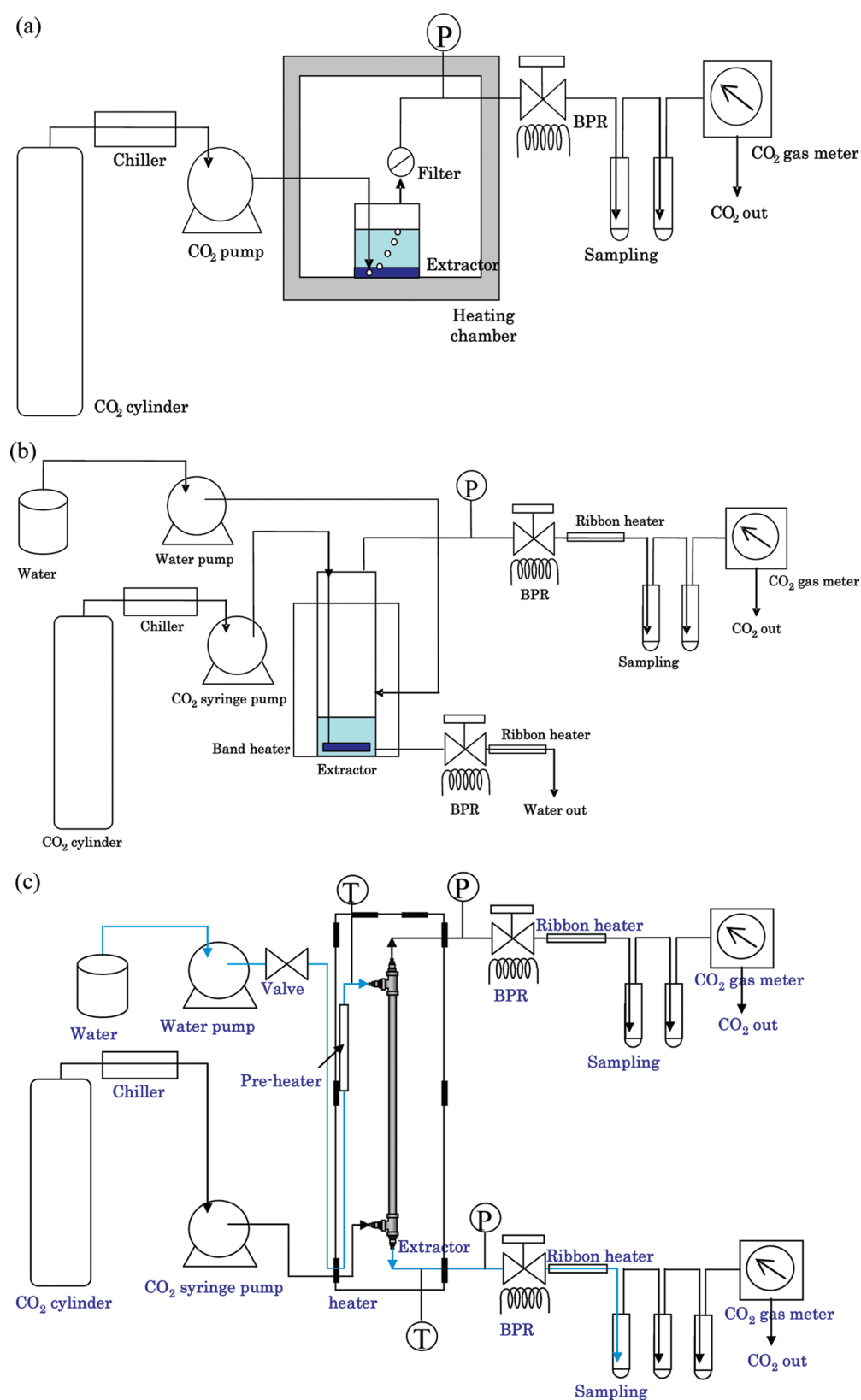**Figure 2.** Schematic diagram of simultaneous extraction and separation apparatus with $SCCO_2$ and water as solvent. (a) Batch type; (b) co-current type; (c) counter-current type.

with 4 g of raw coffee beans. In Table 1, increasing pressure promoted increasing recovery of caffeine in the $SCCO_2$ phase

due to the increasing $SCCO_2$ density. The increasing pressure also caused easy penetration of $SCCO_2$ into the coffee beans,

Table 1. Recovery of Caffeine in SCCO$_2$ and Recovery of Caffeine and CGA in the Water Phase at Various Extraction Conditions for Batch Type

accumulation recovery (%)	time (min)	temperature (°C)[a]			pressure (MPa)[b]			ratio of coffee and water mass (mc/mw)[c]		
		40	50	60	15	20	25	1/30	2/30	4/30
caffeine in SCCO$_2$	60	2.55 ± 0.04	1.50 ± 0.02	1.72 ± 0.02	1.18 ± 0.02	0.72 ± 0.01	2.55 ± 0.04	3.67 ± 0.04	2.13 ± 0.03	2.55 ± 0.04
	120	4.67 ± 0.05	3.30 ± 0.03	3.28 ± 0.04	2.19 ± 0.02	2.38 ± 0.04	4.67 ± 0.05	6.62 ± 0.07	5.34 ± 0.06	4.67 ± 0.05
	180	6.30 ± 0.05	5.31 ± 0.06	4.64 ± 0.05	3.02 ± 0.04	3.61 ± 0.04	6.30 ± 0.05	9.42 ± 0.10	7.33 ± 0.07	6.30 ± 0.05
	240	7.64 ± 0.06	6.66 ± 0.07	6.02 ± 0.06	3.79 ± 0.04	4.73 ± 0.06	7.64 ± 0.06	11.6 ± 0.12	9.70 ± 0.11	7.64 ± 0.06
	300	8.69 ± 0.09	8.01 ± 0.08	7.53 ± 0.08	5.63 ± 0.08	5.83 ± 0.09	8.69 ± 0.09	13.6 ± 0.14	11.2 ± 0.11	8.69 ± 0.09
	360	9.44 ± 0.12	9.34 ± 0.11	8.55 ± 0.10	5.10 ± 0.13	6.84 ± 0.11	9.44 ± 0.12	15.2 ± 0.14	12.4 ± 0.10	9.44 ± 0.12
caffeine in H$_2$O	360	45.0 ± 0.21	44.2 ± 0.20	50.7 ± 0.20	27.4 ± 0.20	39.7 ± 0.23	45.0 ± 0.21	52.1 ± 0.20	40.1 ± 0.20	45.0 ± 0.21
CGA in H$_2$O	360	51.3 ± 0.25	47.7 ± 0.22	56.6 ± 0.30	26.9 ± 0.19	44.8 ± 0.20	51.3 ± 0.25	79.3 ± 0.31	55.0 ± 0.30	51.3 ± 0.25

[a] P = 25 MPa, mc/mw = 4/30, CO$_2$ flow rate = 3 mL/min. [b] T = 40 °C, mc/mw = 4/30, CO$_2$ flow rate = 3 mL/min. [c] T = 40 °C, P = 25 MPa, CO$_2$ flow rate = 3 mL/min.

thus increasing the mass transfer of caffeine and resulting in increasing solubility of caffeine in SCCO$_2$.[17] The increasing pressure also promoted increasing recovery of both caffeine and CGA in the water phase. High pressure of CO$_2$ in water caused easy penetration of both CO$_2$ and water into the coffee beans to extract both caffeine and CGA. In addition, the increasing pressure also causes the increasing water properties related to the mass transfer rate of solute to the solvent, such as density, ion product, and dielectric constant.[21] Moreover, a part of caffeine dissolved in water was transferred to the SCCO$_2$ phase that resulted in increasing recovery of caffeine in the SCCO$_2$ phase. Separation of caffeine from CGA in the water phase seems to be higher with increasing pressure. This result indicated that caffeine might be separated from CGA by increasing the pressure of the process.

To understand the effect of water used in the process, the ratio of coffee and water mass (mc/mw) was changed to a temperature of 40 °C and a pressure of 25 MPa. The effect of ratio of coffee and water mass used for extraction on the recovery of caffeine and CGA in SCCO$_2$ and water phases is shown Table 1. In the SCCO$_2$ phase, the increasing water mass caused an increased caffeine recovery. It indicated that a larger amount of water in the extractor caused decreasing mass transfer resistance of caffeine into both SCCO$_2$ and water, thus increasing mass transfer of caffeine from water to SCCO$_2$, and as a result an increasing recovery of caffeine in SCCO$_2$. A larger amount of water might also swell the coffee beans matrix and favor penetration of SCCO$_2$ inside the matrix, leading to enhancement of the solute diffusion out of the plant tissue. A similar enhancement in extraction recovery with an addition of water was observed in the caffeine and epigallocatechin gallate extraction from green tea[22] and in bioactive compounds extraction from *Helianthus annuus* L.[23] In the water phase, recovery of CGA dramatically increased with increasing water mass, while recovery of caffeine slightly increased with increasing water mass, and as a result the increasing separation of caffeine from CGA. It can be explained that water is a polar solvent that induces changes in the structure of the cellular matrix via intracrystalline and osmotic swelling and breaks solute−matrix bindings by competing with polar interactions between the matrix and the compounds, in this case CGA, to be extracted.[24]

For all conditions, recovery of caffeine in the SCCO$_2$ phase was much lower than that in the water phase. Caffeine recovery in the SCCO$_2$ phase was also still low for 6 h extraction; however, the recovery tends to increase with increasing extraction time. It indicated that a longer extraction time may increase the recovery and separate the caffeine from the coffee beans.

4.2. Co-current Extraction and Separation using SCCO$_2$ and Water in Flow Modes. In section 4.1, extraction and separation using water in batch mode, a larger amount of water yielded high caffeine recovery and separation efficiency. Furthermore, it is necessary to design continuous flow extractor column with longer residence time of water to collect caffeine prior to the extraction with SCCO$_2$. For this purpose, glass beads were installed in the bottom of the extractor to accommodate water, which has contact with the coffee beans and extracted a part of the caffeine and/or CGA. Furthermore, the installation of glass beads was called nonpolar recovery section. The higher nonpolar recovery section indicates the larger amount of water loaded into the extractor. The height of the nonpolar recovery section was changed to study the effect of nonpolar recovery section height on the recovery of caffeine and CGA in SCCO$_2$ and water phases, and on the separation factor. The separation factor was defined as the weight of caffeine extracted in the SCCO$_2$ phase divided by the weight of caffeine in SCCO$_2$ and water phases.

Table 2 shows the effect of nonpolar recovery section height on the recovery of caffeine and CGA in SCCO$_2$ and water phases. The effect of nonpolar recovery section was investigated using 12 g of coffee beans and various glass beads weights from 0 to 168 g depending on the height of the nonpolar recovery section. As shown in Table 2, initially the increase in height of the nonpolar recovery section from 0 to 5 cm had no effect on the recovery of caffeine; however, at a longer extraction time the recovery of caffeine significantly increased with increasing nonpolar recovery section. Furthermore, higher nonpolar recovery section could improve caffeine recovery, especially from 5 to 7.5 cm. However, the increasing nonpolar recovery section height from 7.5 to 10 cm slightly increased caffeine recovery at the initial extraction time, and then dramatically increased at longer extraction times. It showed that the nonpolar recovery section is necessary to enhance extraction efficiency in the SCCO$_2$ phase for longer extraction time. The recovery of caffeine and CGA in the water phase is also displayed in Table 2. As expected, higher nonpolar recovery section could enhance recovery of both caffeine and CGA because a larger amount of water was available for transferring both compounds from the beans.

Table 2. Effect of Nonpolar Recovery Section Height on the Recovery of Caffeine in $SCCO_2$ and Recovery of Caffeine and CGA in Water Phase for Co-current Type at 60 °C and 25 MPa

accumulation recovery (%)	time (min)	height of nonpolar recovery section (cm)			
		0	5	7.5	10
caffeine in $SCCO_2$	60	0.02 ± 0.00	0.00 ± 0.00	0.17 ± 0.01	0.15 ± 0.01
	120	0.06 ± 0.01	0.04 ± 0.01	0.22 ± 0.03	0.25 ± 0.03
	180	0.12 ± 0.02	0.12 ± 0.01	0.36 ± 0.05	0.35 ± 0.04
	240	0.17 ± 0.03	0.17 ± 0.02	0.54 ± 0.06	0.62 ± 0.06
	300	0.24 ± 0.04	0.22 ± 0.03	0.60 ± 0.05	0.84 ± 0.06
	360	0.30 ± 0.05	0.54 ± 0.05	0.66 ± 0.05	0.92 ± 0.09
caffeine in H_2O	60	3.49 ± 0.08	7.04 ± 0.10	5.05 ± 0.20	6.79 ± 0.25
	120	7.64 ± 0.15	11.1 ± 0.31	9.67 ± 0.25	12.0 ± 0.25
	180	11.4 ± 0.50	15.2 ± 0.50	13.2 ± 0.60	16.5 ± 0.70
	240	14.6 ± 0.56	18.3 ± 0.42	16.1 ± 0.45	20.0 ± 0.50
	300	17.4 ± 0.45	20.7 ± 0.60	18.4 ± 0.40	22.6 ± 0.60
	360	19.6 ± 0.41	22.5 ± 0.62	20.2 ± 0.42	24.31 ± 0.60
CGA in H_2O	60	2.84 ± 0.05	6.70 ± 0.10	5.94 ± 0.15	7.29 ± 0.25
	120	7.42 ± 0.12	12.2 ± 0.50	12.5 ± 0.30	14.7 ± 0.50
	180	12.7 ± 0.50	18.9 ± 0.43	18.4 ± 0.40	22.7 ± 0.60
	240	17.9 ± 0.46	25.0 ± 0.75	23.5 ± 0.45	29.9 ± 0.70
	300	22.6 ± 0.65	29.9 ± 0.72	28.0 ± 0.50	35.8 ± 0.65
	360	26.8 ± 0.50	34.2 ± 0.96	31.2 ± 0.52	40.6 ± 0.75
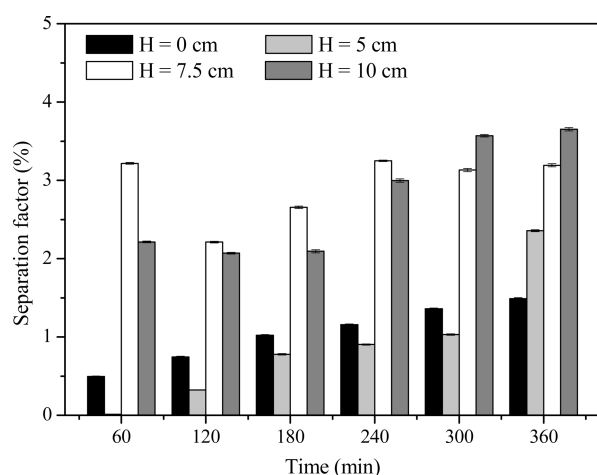
Figure 3. Effect of nonpolar recovery section height on the separation factor for co-current type at 60 °C and 25 MPa.

Moreover, a larger amount of water might decrease mass transfer resistance and enhance the mass transfer rate due to the influence of both intraparticle diffusion in water-soaked beans and external mass transfer.[9] Because the migration of caffeine from water into $SCCO_2$ either increased with increasing nonpolar recovery section height, selectivity of caffeine to CGA in the water phase might increase for higher nonpolar recovery section.

The effect of nonpolar recovery section height on the separation factor is shown in Figure 3. High separation factor indicates high separation efficiency of caffeine from coffee beans and the water phase. Even though a small difference in the separation factor was observed, the separation factor has a tendency to be increased with increasing height of nonpolar recovery section. It can be explained that at a higher nonpolar recovery section, the amount of water accommodated in the extractor was large, and as

the result the amount of caffeine dissolved in the water was large and easy to be extracted by $SCCO_2$. Furthermore, it is suggested to apply a longer extractor column to increase the separation factor. In addition, the observation of a small difference in the separation factor might be caused by the irregularity of the water flow rate during the process. In this case, it is necessary to design level control in the system to control the flow rate.

For all experimental results using co-current extraction type, caffeine recovery in the $SCCO_2$ phase was lower than that in batch type. It might be caused by water stored in the extractor. In co-current extraction type, fresh water flowed continuously to replace water containing extract collected every 60 min. While in batch type, a certain amount of water was used for one extraction process and coffee beans was soaked in the water during the extraction. Thus, the content of extracted compounds in water increased with progressing time and longer contacting time of water with $SCCO_2$ to dissolve extracted caffeine from the water. Furthermore, it resulted in a higher caffeine recovery in the batch type.

4.3. Counter-Current Extraction and Separation Using $SCCO_2$ and Water in Flow Modes. In this type of extraction and separation, a longer extractor column was used in order to improve extraction and separation efficiency. Effect of temperature, height of nonpolar recovery section and CO_2 flow rate on the recovery of caffeine and CGA in $SCCO_2$ and water phases, and separation factor was investigated. Maximum pressure used for the extraction was 30 MPa based on the maximum pressure of the extractor.

Table 3 shows the effect of temperature on the recovery of caffeine and CGA in $SCCO_2$ and water phases at 3 mL/min of CO_2 flow rate, 1 mL/min of water flow rate, and 0 cm of nonpolar recovery section height. Recovery of caffeine both in $SCCO_2$ and water phases, and recovery of CGA in water phase increased with an increase in temperature. The increasing temperature might cause increasing temperature of water and vapor pressure of both

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Table 3. Recovery of Caffeine in SCCO$_2$ and Recovery of Caffeine and CGA in the Water Phase at Various Extraction Conditions for Counter-Current Type

accumulation recovery (%)	time (min)	temperature (°C)[a]			nonpolar recovery section height (cm)[b]				CO$_2$ flow rate (mL/min)[c]	
		40	60	80	0	20	30	40	3	5
caffeine in SCCO$_2$	60	0.12 ± 0.01	0.55 ± 0.03	0.70 ± 0.02	0.55 ± 0.03	0.65 ± 0.02	0.47 ± 0.02	0.66 ± 0.03	0.28 ± 0.02	0.27 ± 0.02
	120	0.34 ± 0.03	1.12 ± 0.07	1.42 ± 0.10	1.12 ± 0.07	1.13 ± 0.05	1.31 ± 0.04	1.74 ± 0.04	0.54 ± 0.04	0.70 ± 0.05
	180	0.57 ± 0.05	1.83 ± 0.07	2.22 ± 0.09	1.83 ± 0.07	1.96 ± 0.06	1.96 ± 0.04	2.84 ± 0.09	0.80 ± 0.06	1.07 ± 0.07
	240	0.91 ± 0.10	2.32 ± 0.10	2.85 ± 0.10	2.32 ± 0.10	2.66 ± 0.08	2.89 ± 0.06	3.47 ± 0.08	1.25 ± 0.08	1.54 ± 0.09
	300	1.07 ± 0.09	3.15 ± 0.15	3.42 ± 0.14	3.15 ± 0.15	3.28 ± 0.75	3.48 ± 0.09	3.95 ± 0.10	1.64 ± 0.05	2.00 ± 0.08
	360	1.16 ± 0.07	3.61 ± 0.09	3.50 ± 0.10	3.61 ± 0.09	3.84 ± 0.08	3.74 ± 0.10	4.25 ± 0.13	1.85 ± 0.07	2.41 ± 0.09
caffeine in H$_2$O	60	1.59 ± 0.08	5.10 ± 0.10	7.69 ± 0.20	5.10 ± 0.10	3.52 ± 0.10	2.64 ± 0.05	2.61 ± 0.06	2.55 ± 0.05	1.99 ± 0.07
	120	4.04 ± 0.15	11.8 ± 0.35	16.0 ± 0.70	11.8 ± 0.35	8.94 ± 0.12	7.64 ± 0.12	5.91 ± 0.13	9.14 ± 0.07	7.25 ± 0.09
	180	6.27 ± 0.25	18.4 ± 0.50	20.7 ± 0.55	18.4 ± 0.50	14.4 ± 0.32	12.8 ± 0.25	10.6 ± 0.20	14.9 ± 0.10	13.4 ± 0.11
	240	8.29 ± 0.32	22.2 ± 0.55	23.1 ± 0.60	22.2 ± 0.55	18.0 ± 0.45	16.4 ± 0.30	14.5 ± 0.40	19.0 ± 0.25	17.9 ± 0.20
	300	10.1 ± 0.25	22.7 ± 0.60	24.3 ± 0.50	22.7 ± 0.60	21.3 ± 0.50	19.0 ± 0.40	16.8 ± 0.40	21.8 ± 0.50	20.9 ± 0.50
	360	11.8 ± 0.30	24.3 ± 0.40	24.9 ± 0.45	24.3 ± 0.40	22.8 ± 0.60	20.6 ± 0.55	18.4 ± 0.50	23.6 ± 0.50	22.7 ± 0.45
CGA in H$_2$O	60	1.54 ± 0.09	6.69 ± 0.10	12.7 ± 0.50	6.69 ± 0.10	5.41 ± 0.15	4.67 ± 0.12	4.06 ± 0.07	4.06 ± 0.07	2.74 ± 0.05
	120	4.32 ± 0.11	18.1 ± 0.60	29.8 ± 0.85	18.1 ± 0.60	16.4 ± 0.40	15.6 ± 0.30	13.6 ± 0.25	16.0 ± 0.10	12.5 ± 0.12
	180	7.32 ± 0.35	30.8 ± 0.90	41.7 ± 0.92	30.8 ± 0.90	28.2 ± 0.80	26.7 ± 0.90	25.4 ± 0.88	28.0 ± 0.50	25.1 ± 0.50
	240	10.6 ± 0.50	39.7 ± 0.85	49.4 ± 0.90	39.7 ± 0.85	37.1 ± 0.90	36.2 ± 1.05	34.5 ± 0.90	37.0 ± 1.2	35.9 ± 1.50
	300	13.7 ± 0.45	46.2 ± 0.80	54.9 ± 1.05	46.2 ± 0.80	43.2 ± 1.25	43.4 ± 1.20	42.2 ± 1.10	43.5 ± 1.30	43.9 ± 1.60
	360	16.8 ± 0.50	51.7 ± 1.70	57.9 ± 1.75	51.7 ± 1.70	47.8 ± 1.50	48.9 ± 1.20	47.7 ± 1.10	48.8 ± 1.50	49.7 ± 1.20

[a] P = 30 MPa, CO$_2$ flow rate = 5 mL/min, H$_2$O flow rate = 1 mL/min, nonpolar recovery section height = 0 cm. [b] T = 60 °C, P = 30 MPa, CO$_2$ flow rate = 5 mL/min, H$_2$O flow rate = 1 mL/min. [c] T = 60 °C, P = 30 MPa, H$_2$O flow rate = 1 mL/min, nonpolar recovery section height = 30 cm.
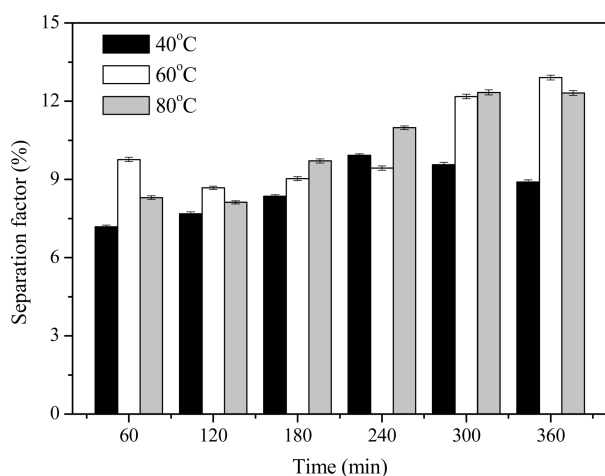
Figure 4. Effect of temperature on the separation factor for counter-current type at 30 MPa, 3 mL/min of CO$_2$ flow rate, 1 mL/min of water flow rate, and 30 cm of nonpolar recovery section.

caffeine and CGA that resulted in increasing recovery of caffeine in SCCO$_2$ and both components in water. Moreover, high temperature might break the plant cells of the coffee beans that caused easy penetration of SCCO$_2$ and water into the cells. Because high concentration of caffeine was available in water, caffeine was easily transferred into the SCCO$_2$ phase.

Evaluation of temperature effect on the separation factor is shown in Figure 4. The separation factor slightly increased with increasing temperature; however, the highest separation factor was obtained at 60 °C for 6 h of extraction time. As explained before, the increasing temperature caused increasing dissolved

caffeine in SCCO$_2$ and resulted in higher separation of caffeine from CGA in the water phase.

As resulted in the co-current type, at a higher nonpolar recovery section, higher separation efficiency was obtained. In the counter-current type, nonpolar recovery section height was changed to obtain a higher separation efficiency. The nonpolar recovery section height was changed from 0 to 40 cm by installation of glass beads in the bottom of the extractor. The effect of nonpolar recovery section height on the recovery of caffeine in the SCCO$_2$ phase and the recovery of caffeine and CGA in water phase are shown in Table 3. Recovery of caffeine in the SCCO$_2$ phase significantly increased with increasing height of nonpolar recovery section. As expected, the increasing nonpolar recovery section height could increase caffeine recovery because caffeine dissolved in water was easily transferred to the SCCO$_2$ phase. On the contrary, caffeine recovery in the water phase significantly decreased with increasing nonpolar recovery section height due to migration of caffeine from water to SCCO$_2$ phase. The same trend either could be observed for CGA recovery; however, CGA recovery did not significantly change by changing the nonpolar recovery section height from 20 to 40 cm. It might be because the coffee beans were not soaked well with water on the glass beads installed at the bottom of extractor. As a comparison with the co-current type, recovery of caffeine in SCCO$_2$ increased more than five fold, while recovery of caffeine in the water phase decreased about 25% at the highest nonpolar recovery section. It indicates that the counter-current type is more effective than the co-current type for separation of caffeine from CGA. The effect of nonpolar recovery section height on the separation factor is shown in Figure 5. Separation factor of the process dramatically increased with the increasing nonpolar recovery section height, especially from 30 to 40 cm. It is suggested that higher nonpolar
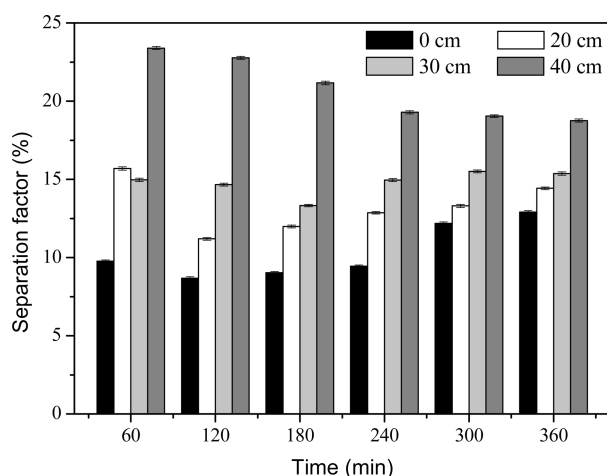
Figure 5. Effect of nonpolar recovery section height on separation factor for counter-current type at 60 °C and 30 MPa.
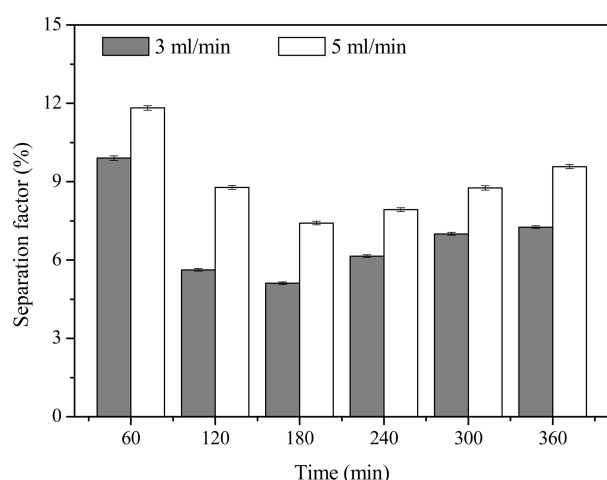

Figure 6. Effect of CO_2 flow rate on the separation factor for counter-current type at 60 °C and 30 MPa.

recovery section resulted in higher separation efficiency of caffeine from the coffee beans. Moreover, higher nonpolar recovery section caused a higher concentration of CGA to remain in the coffee beans. The separation factor of counter-current type was 5-fold higher than the co-current type due to the longer contacting time between $SCCO_2$ and water in the higher nonpolar recovery section and longer extractor column.

In order to obtain a higher separation efficiency, the CO_2 flow rate was changed from 3 to 5 mL/min. As shown in Table 3, caffeine recovery in the $SCCO_2$ phase significantly increased with an increase in the CO_2 flow rate, especially at the end of extraction. It can be explained that the increasing CO_2 flow rate caused an increasing number of CO_2 molecules to penetrate and diffuse into beans to extract caffeine. On the other hand, the change of CO_2 flow rate had no significant effect on the recovery of both caffeine and CGA in the water phase. It indicated that the number of CO_2 molecule did not effect the interaction between caffeine and CO_2 molecules. Because caffeine recovery in the $SCCO_2$ phase increased, the separation factor of the process increased (Figure 6), which indicated the increasing separation efficiency of caffeine from the coffee beans.

5. CONCLUSION

Extraction and separation of caffeine and CGA from raw coffee beans using $SCCO_2$ and water were studied. Three types of extraction and separation modes were used in this work. Extraction and separation were conducted in three types of extractor columns with different sizes and flow types of CO_2 and water. The effect of temperature and pressure in the separation mode using $SCCO_2$ in flow and water in batch mode was reported. Recovery of caffeine in the $SCCO_2$ phase increased with decreasing temperature and increasing pressure. However, only the increasing pressure could promote the increasing recovery of caffeine and CGA in the water phases. The change of height of the nonpolar recovery section on the recovery of caffeine and CGA in the $SCCO_2$ and water phases and on the separation factor was studied using $SCCO_2$ and water in co-current and counter-current flow modes. Recovery of caffeine and separation factor of caffeine from CGA significantly increased with increasing height of the recovery section. The effect of temperature in counter-current type of separation on the recovery of caffeine and CGA in $SCCO_2$ and water phases exhibited different trends with the batch type of separation. Even though the recovery of caffeine in $SCCO_2$ and separation efficiency obtained in this work was very low (less than 10%), the proposed simultaneous extraction and separation process can be developed further to obtain maximum efficiency. In addition, it is necessary to employ another substance as a nonpolar model compound. On the basis of the results of this work, it is suggested to design longer extractor columns with higher nonpolar recovery sections in counter-current type in order to increase the separation efficiency. Moreover, it is better to employ substances from natural materials with high polarity and nonpolarity in this process.

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