Fractional Extraction by Supercritical Carbon Dioxide for the Deterpenation of Bergamot Oil

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Supercritical fluid extraction of bergamot oil was carried out in the semibatch operation and continuous countercurrent operation to improve the oil quality through selective separation between terpenes and oxygenated compounds. Vapor-phase equilibria for the quasi-ternary system were measured by a semibatch extraction with a uniform temperature column at the temperature range from 313 to 353 K and the pressure range from 7.8 to 10.8 MPa. Internal reflux induced by the temperature gradient along the column improved the separation selectivity. For a continuous operation, the effect of pressure on the separation selectivity was investigated.

Introduction

Citrus oils are widely used for flavor, beverage, food, cosmetics, pharmaceutical, and chemical industries. The citrus oil generally contains over 90% terpenes, about 5% oxygenated compounds, and less than 1% nonvolatiles such as waxes and pigments. Among these compounds, terpenes such as limonene do not contribute much to the flavor or fragrance of the oil, despite its high content. Because they are unstable to heat and light and rapidly degrade to produce undesirable off-flavor compounds, terpenes must be removed to stabilize the product. Furthermore, nonvolatiles such as waxes and pigments must be eliminated because of turbidity in the oil and phototoxic activity. It is the oxygenated compounds that provide much of the characteristic flavor of citrus oil. This flavor fraction consists of alcohols, aldehydes, and esters such as linalool, citral, and linalyl acetate, respectively.

Fractionation with supercritical carbon dioxide (SC-CO_2) is a prominent candidate for the removal of thermosensitive compounds such as terpenes, because the separation can be performed at low temperature. Gerard[1] suggested a continuous countercurrent extraction process for the production of the terpeneless essential oil, where an internal reflux induced by the temperature gradient was used in the enriching section. Shibuya et al.[2] and Sato et al.[3,4] studied supercritical fluid extraction for the fractionation of model orange oil mixtures with a column having a linear temperature gradient in a semibatch operation mode. The semibatch extraction with internal reflux induced by the temperature gradient along the rectification column improved the separation selectivity between terpenes and oxygenated compounds.

Sato et al.[5] developed the continuous extraction process. In the continuous countercurrent extraction process for the fractionation of orange peel oil, the effective separation can be established by increasing the number of the equilibrium stages as well as multistage operation. In this process, terpenes in the feed oil were selectively removed into the extract and oxygenated compounds were selectively fractionated into the raffi-nate. They suggested that the extraction process operated at a higher solvent-to-feed ratio and with a longer stripping column will make the products with higher quality. The operation at total reflux including an internal and an external reflux was also carried out to find out the limiting operating condition. Sato et al.[6] proposed a new extraction process to separate simultaneously citrus oil into fractions rich in terpenes, oxygenated compounds, and waxes.

On the other hand, SC-CO_2 adsorption and/or desorption could be an alternative process for the citrus oil processing. Chouchi et al.[7] proposed the SC-CO_2 desorption technique for the bergamot oil to obtain the terpeneless oil and to eliminate phototoxic activity compounds such as coumarins and psoralens. They obtained the high flavor content at the end of the isobaric desorption step.

In this work, we applied SC-CO_2 extraction with a rectification column to the fractionation of bergamot oil. At first, high-pressure phase equilibria for the quasi-ternary system were measured by semibatch extraction experiments. In the continuous countercurrent extraction at 333 K, the effect of pressure on the selectivity was studied.

Experimental Section

Cold-pressed bergamot oil (Inoue Perfumery Mfg. Co., Ltd., Yamagata, Japan) was used as a feed. In gas chromatographic (GC) analysis, oxygenated compounds were defined as components having a higher retention time than limonene. According to this definition, the feed oil contained about 40 wt % terpenes (25 wt % limonene) and 60 wt % oxygenated compounds (25 wt % linalyl acetate). The GC analysis for weight percent calculation was performed with a percentage method by use of a J&W DB-WAX (30 m × 0.25 i.d., 0.25 μm film) fused-silica capillary column (GC-14B; Shimadzu Corp., Kyoto, Japan). Temperature program for the oven was as follows; from 343 to 488 K at 3 K min^{-1}; 10 min constant (injector and detector: 523 K). Peak identification has made in reference to the results of Chouchi et al.[7]

The fractionation column used was 20 mm i.d., and the total column length was 2400 mm. The rectification part was packed with stainless steel 3 mm Dixon Packing (Naniwa Special Wire Netting Co., Ltd., Tokyo,

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Japan) in a length of 1800 mm. The temperature of the column was controlled by eight proportional−integral−differential (PID) controllers. The fluid exiting from the column is cyclonically introduced to the separator. The separator was 40 mm i.d., and the total volume was 600 mL. The separator was kept at a pressure of 5 MPa and a temperature of 303 K. Both the dry and wet test meters were used to measure the flow rate of CO_2. In the semibatch operation, the feed oil of 35.2 g (40 mL) was charged into the bottom of the column. In the continuous countercurrent operation, on the other hand, the feed oil flowed continuously from the top of the column at 0.44 g/min (0.5 mL/min). The details of the experimental setup and the procedure for semibatch or continuous operation are given in our previous paper.[3,4] The extract and the raffinate were collected into sampling tubes, weighed, and analyzed by GC.

Semibatch Operation

(1) Phase Equilibrium. When the column is kept at a uniform temperature on the simple semibatch extraction, it is considered to be a single stage with no reflux, where the extract leaving the column is assumed to be in equilibrium with the liquid in the column. The extract trapped in the separator was collected into sampling tubes in a certain interval of time.

The extraction data gave phase equilibria for the quasi-ternary system (1) CO_2−(2) terpenes−(3) oxygenated compounds. The compositions of the liquid phase were not obtained because of the difficulty in measurement of the liquid phase for the semibatch experiment. The composition of liquid phase in the extractor was calculated from the material balance of the charged feed and the extracts. Furthermore, an empirical relationship (eq 1) for the CO_2 content of the liquid phase, X_1, was used,[8] with $A_x = 120.725 − 0.43613 T$ (T in K) and $B_x = 7.76422 − 0.03455 T$ (T in K).

$$X_1 = A_x/(B_x + P^{0.5}) \text{ [wt \%] } (P \text{ in MPa}) \qquad (1)$$

As an example, the phase equilibria on the Janecke diagram and distribution curve for terpenes at 333 K and 9.8 MPa are shown in Figure 1. In the simple batch extraction, a sufficiently high terpene content could not be obtained in each fraction. The average and maximum values of the separation selectivity obtained from the experimental results were calculated. The separation selectivity is defined by

$$\alpha = \frac{Y_2/X_2}{Y_3/X_3} \qquad (2)$$

where Y = mass fraction in the extract (CO_2 free), X = calculated mass fraction in the raffinate (CO_2 free), and subscripts 2 and 3 correspond to terpenes and oxygenated compounds, respectively.

The operation using the column with a uniform temperature at 333 K and 8.8 MPa, as shown in Table 1, gave the highest selectivity. For given semibatch extraction, the selectivity increased with an increase in the temperature at fixed pressure and with a decrease in the pressure at fixed temperature. Operation with the temperature gradient from the bottom to the top of the column, furthermore, gave slightly higher selectivity than operation with a uniform temperature at fixed pressure of 9.8 MPa.
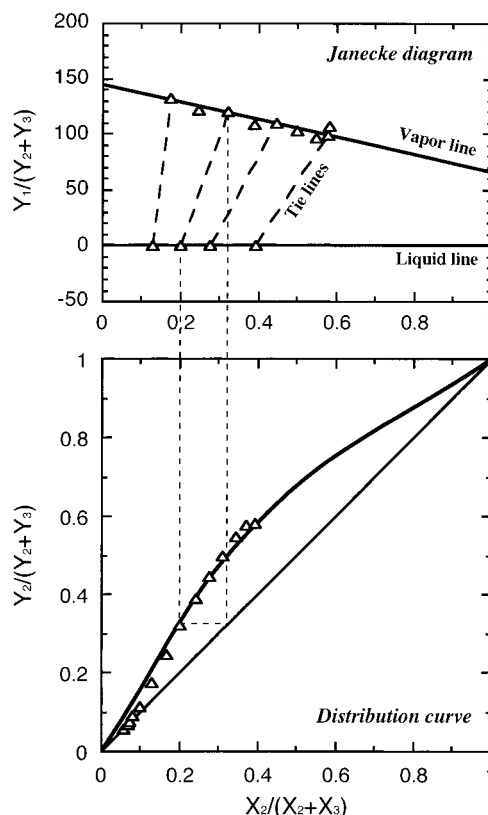

Figure 1. Phase equilibria for the quasi-ternary system of (1) CO_2−(2) terpenes−(3) oxygenated compounds at 333 K and 9.8 MPa.

Table 1. Separation Selectivity between Terpenes and Oxygenated Compounds

		separation selectivity	
pressure [MPa]	temp [K]	average	max
7.8	313	1.9981	2.7807
8.8	313	1.2091	1.4262
	323	1.8114	2.4325
	333	2.1006	3.0760
9.8	313	0.9714	1.0165
	323	1.4473	1.7489
	333	1.7287	2.3127
	343	1.8974	2.5646
	353	1.8867	2.8120
	313−333	1.8510	2.6402
	313−343	1.8823	2.7315
	313−353	1.8957	2.7578
	323−343	1.9808	2.8816
	323−353	1.9861	2.8880
	333−353	1.8333	2.3424
10.8	333	1.4843	1.8590

(2) Rectification by the Temperature Gradient. The temperature dependence of solubility of solutes in SC-CO_2 can be effectively utilized in the rectification column. The temperature at the top of the column is usually held higher than that at the bottom.

Figure 2 shows the effect of the CO_2 flow rate on the changes in the composition of the extracts for operation with a linear temperature gradient at 9.8 MPa. Terpenes (solid symbols) are extracted selectively at the beginning of the extraction, and the oxygenated compounds (open symbols) followed. This separation is due to the difference in solubility among terpenes and oxygenated compounds. There is no change in the performance of the concentration of each component, which increased in the CO_2 flow rate, whereas the extraction rate was increased. Therefore, the used
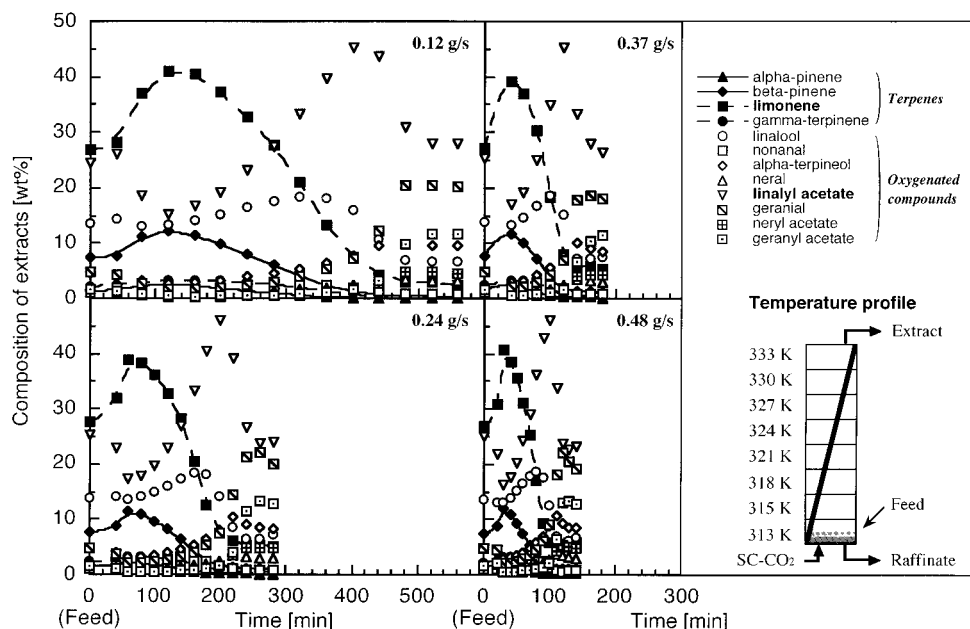
Figure 2. Changes in the composition of each extract for the semibatch operation with a linear temperature gradient at 9.8 MPa and various CO_2 flow rates.

column was long enough to prevent the hold-up, and the fluid leaving the column with an axial temperature gradient was in equilibrium at the top of the column within CO_2 flow rate from 0.12 to 0.48 g/s.

The cumulative extraction curve and the changes in composition of each fraction at 9.8 MPa and CO_2 flow rate of 0.24 g/s are shown in Figure 3. The curve for the column with an axial temperature gradient of 20 K almost agreed with the other curve. For the operation with a linear temperature gradient, the separation of oxygenated compounds is more selective than the operation with a uniform temperature of 333 K. The concentrations of oxygenated compounds having higher retention times than linalyl acetate are selectively increased. Particularly, the concentration of linalyl acetate in the ninth fraction came up to 46.12 wt %. When the supercritical fluid containing dissolved solutes flows into a higher temperature zone in the column, less volatile components (mainly oxygenated compounds) condense and drop back to the bottom of the column. The liquefied drops countercurrently contact with the SC-CO_2 flowing up in the column, resulting in the rectification. However, the internal reflux for the column with the temperature gradient was less efficient at pressures greater than 10.8 MPa.

Continuous Operation

The operating cost of a continuous process depends on the S/F (solvent-to-feed) ratio. In our previous work,[5,6] the following results were observed for the citrus oil processing by continuous operation as a function of the S/F ratio.

The extraction ratio of terpenes, defined by the mass of terpenes in the extract to that in the feed, increased with an increase in the S/F ratio and pressure. The selectivity also increased with an increase in the S/F ratio. There is an intimate relationship between the reflux ratio and the extraction ratio at constant S/F ratio. The extraction ratio of terpenes is reduced by external reflux, resulting in lower selectivity. The external reflux for the citrus oil processing is economically difficult for the deterpenation.
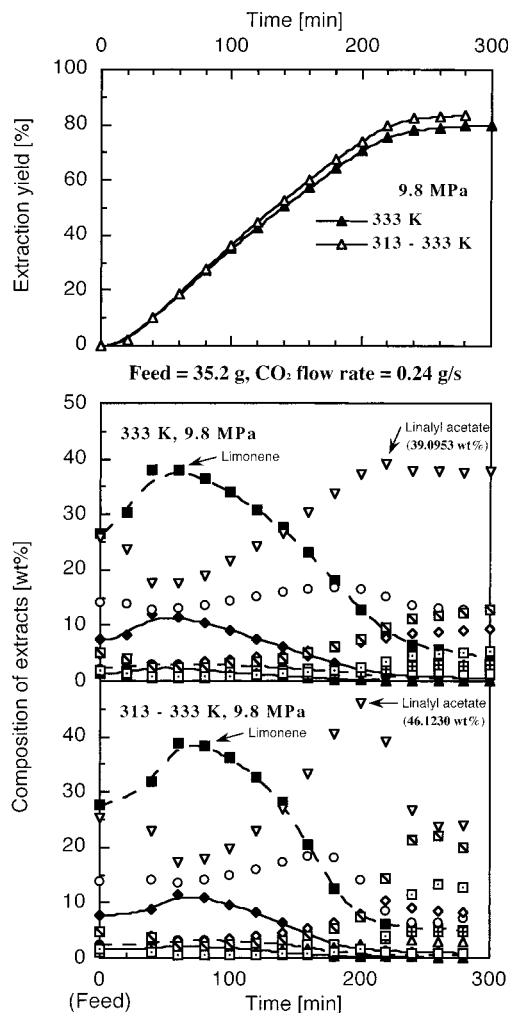

Figure 3. Effect of the temperature profile on the extraction curve and the composition of extracts for a SC-CO_2 fractionation of raw bergamot oil at 9.8 MPa.

For the continuous countercurrent operation, the effect of the pressure on the separation selectivity was investigated as a function of the S/F ratio, where the
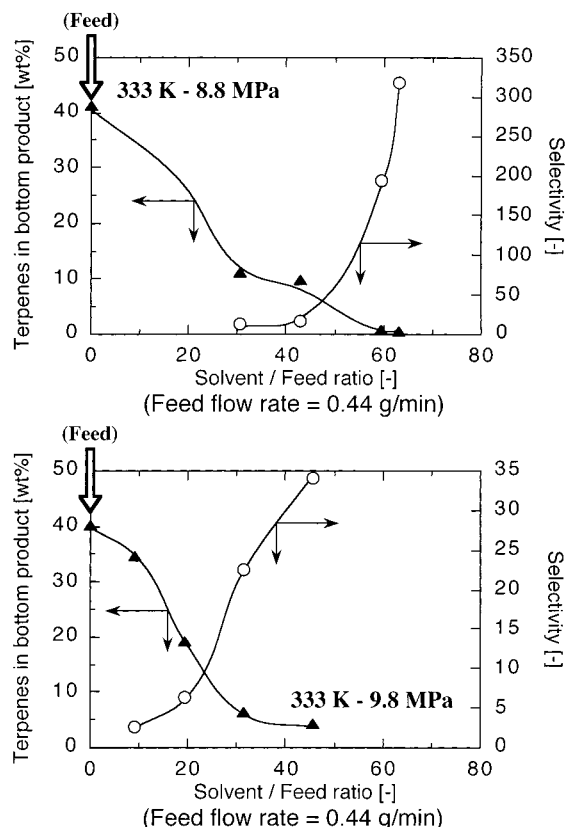
Figure 4. Effect of the extraction pressure on the selectivity for continuous operation at 333 K as a function of the S/F ratio.

continuous operation was carried out without the temperature gradient. Figure 4 shows the separation selectivity between terpenes and oxygenated compounds for the extract and the raffinate product. The results at 8.8 and 9.8 MPa are compared. In either condition, the selectivity was increased with an increase in the S/F ratio. The operation at 8.8 MPa, however, has a much larger selectivity than the operation at 9.8 MPa. This is because of the difference in the density of SC-CO_2 and/or the solubility of solutes in SC-CO_2 depending on the pressure. When bergamot oil was processed at 333 K, 8.8 MPa, and a S/F ratio of 63.2, the concentration of terpenes in the bottom product was reduced lower than 1 wt % and a high selectivity of up to 300 was obtained.

Conclusion

Supercritical fluid extraction of bergamot oil was carried out in the semibatch operation and continuous countercurrent operation. Vapor−liquid-phase equilibria for the quasi-ternary system of CO_2−terpenes−oxygenated compounds were calculated from the semibatch experiments. For the operation with a uniform temperature column, the highest selectivity was obtained at 333 K and 8.8 MPa. The selectivity increased with an increase in the temperature and with a decrease in the pressure for the semibatch extraction.

For the semibatch operation with a linear temperature gradient, oxygenated compounds were separated more selectively, as compared with the operation with a uniform temperature column. For the continuous countercurrent extraction at 333 K, the operation at 8.8 MPa is a rewarding strategy for the bergamot oil processing, as compared with operation at 9.8 MPa. At the S/F ratio of 63.2, the concentration of terpenes in the raffinate was reduced lower than 1 wt %; that is to say, terpeneless oil was obtained.

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