Supercritical Fluid Fractionation for Citrus Oil Processing

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Introduction

Citrus oils generally contain terpenes, oxygenated compounds, and nonvolatiles such as waxes and pigments. Since terpenes 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. The process to remove terpens is called deterpenation and has been carried out by vacuum distillation or solvent extraction.

Fractionation with supercritical carbon dioxide ($SC-CO_2$) is a prominent candidate for the deterpenation process. We have developed two processes by using $SC-CO_2$, counter current extraction process and pressure swing adsorption process. We have studied supercritical fluid extraction of orange oil and its model mixtures with a column having a temperature gradient in a semi-batch operation mode and continuous mode. We also proposed a new extraction process having a side-stream withdrawal to separate citrus oil into simultaneously terpenes, oxygenated compounds, and waxes rich fractions. We applied $SC-CO_2$ extraction with a rectification column to the fractionation of citrus oil such as orange oil[1-3], lemon oil[4], and bergamot oil[5]. Process simulator was applied to simulate the extraction behavior[6].

On the other hand, $SC-CO_2$ adsorption and/or desorption could be an alternative process for the citrus oil processing. Chouchi and Barth[7] proposed the $SC-CO_2$ desorption technique for the bergamot oil to obtain the terpeneless oil. We have applied the concept of the simple two-bed pressure swing adsorption (PSA) cycle into $SC-CO_2$ to make the adsorption/desorption process continuous[8,9]. Silica gel was used to adsorb the oxygenated compounds selectively. A simple mass transfer model with a multicomponent Langmuir isotherm was used to simulate the process.

Experimental

1) Extraction process

Cold-pressed bergamot oil (InouePerfumery MFG. Co., Ltd.) was used as a feed. In 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% of terpenes (25 wt% limonene) and 60 wt% oxygenated compounds (25 wt% linalyl acetate). The other oils used are orange oil (Givaudan-Roure Flav. Ltd.) with 95 wt% terpenes, <5 wt% oxygenated compounds (mainly linalool) and lemon oil (Givaudan-Roure Flav. Ltd.) with 96 % terpenes and 3% oxygenated compounds (0.3% linalool, 0.7% neral, 1.3% geranial).

The column used was 20 mm internal diameter and the total column length was 2400 mm. The rectification part was packed with stainless steel 3 mm Dixon Packing in a length of 1800 mm. The temperature of the column was controlled by eight PID controllers. The fluid exiting from the column is cyclonically introduced to the separator kept at a pressure of 5 MPa and a temperature of 303 K. In the semi-batch operation, the feed oil was charged into the bottom of the column, whereas in the continuous countercurrent operation the feed oil was flowed continuously from the top of the column.

2) Pressure swing adsorption process

The experimental apparatus is shown in Fig. 1. The extraction column was equipped before the adsorption column in order to dissolve the raw oil completely in supercritical carbon dioxide and to remove waxes and pigments. A pair of adsorption columns (500 mm long and 9 mm i.d.) packed with silica gel were used for adsorber. Sets of 10 air-regulated valves were used for switching flows in the adsorption-desorption cycle. Feed oil dissolved in CO_2 is supplied continuously to column 1 in the

adsorption step, while column 2 is pressurized, desorbed and de-pressurized in the reverse flow direction. The two columns are switched between the adsorption and the other steps in turn for the cyclic continuous operation. Temperature of the system was kept at 313 K.

Results and Discussion
1) Extraction process

The temperature dependence of solutes solubility in $SC-CO_2$ can be effectively utilized in a rectification column. Figure 2 shows the extraction curves for bergamot oil and the changes in composition of each fraction at 9.8 MPa in semi-batch mode. The cumulative extraction curve for the column with the axial temperature gradient of 20 K almost agreed with the curve for the uniform temperature column at 333 K. Therefore, the fluid leaving the column was in equilibrium with the liquid phase at the top of the column. Terpenes (solid symbols) was 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. 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 concentration of linalyl acetate in 9th fraction came up to 46.12 wt%.

The operating cost of a continuous process depends on the S/F (Solvent-to-Feed) ratio. The following results were observed for the citrus oil processing by continuous operation as a function of S/F ratio[5,6]. The extraction ratio of terpenes, defined by the mass of terpenes in the extract to that in the feed, increased with the increase in the S/F ratio and pressure. The selectivity also increased with the increase in the S/F ratio. There is an intimate relation 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.

For the continuous countercurrent operation, the effect of pressure on the separation selectivity was investigated as a function of S/F ratio. Since the temperature profile did not
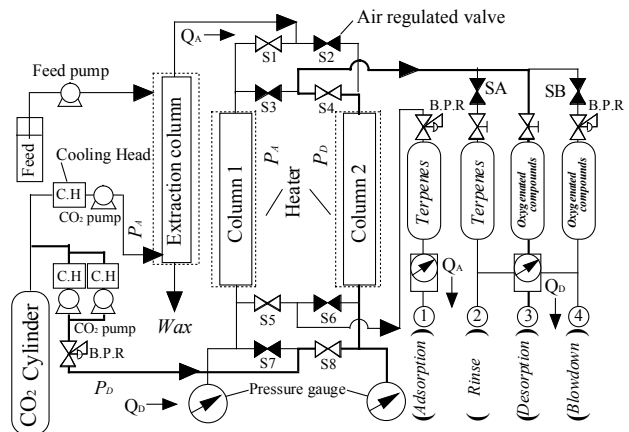

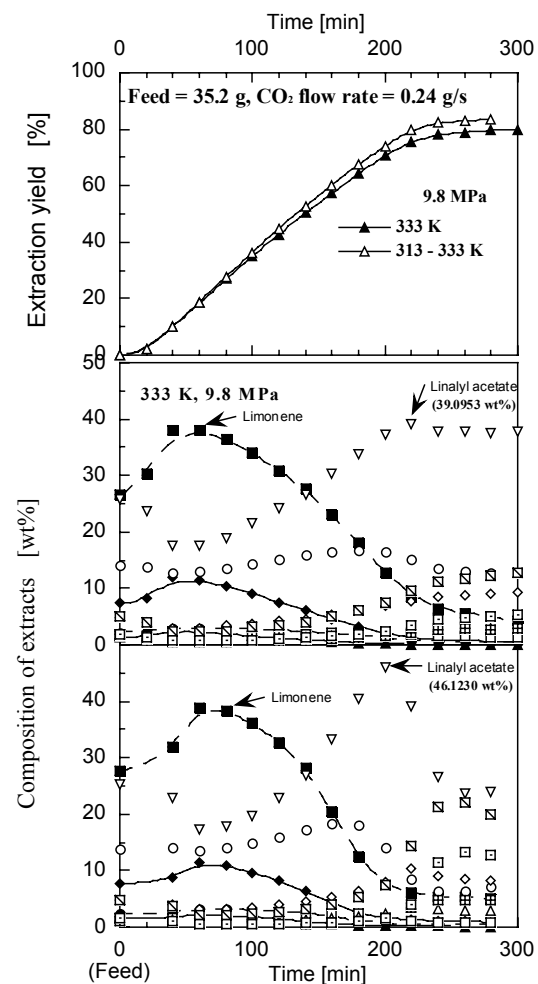Figure 1. Experimental setup of supercritical PSA process.

Figure 2. Effect of temperature profile for the semi-batch extraction process of bergamot oil.
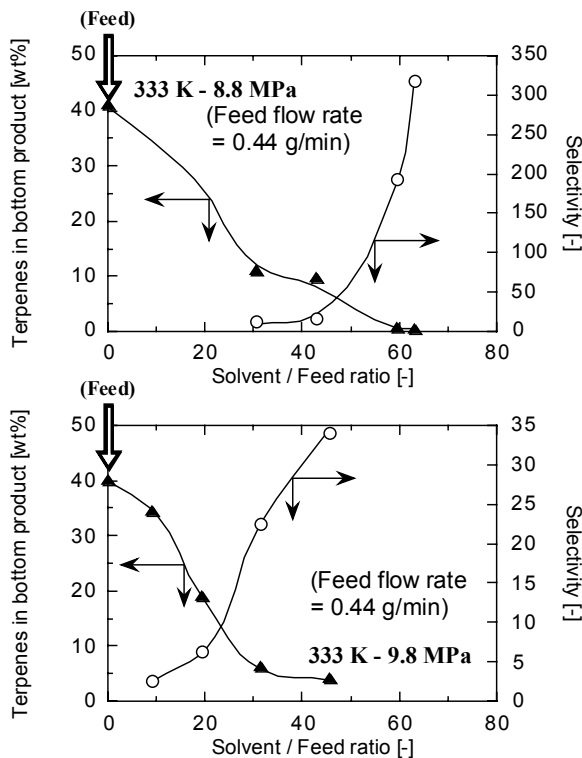
Figure 3. Effect of extraction pressure for the continuous countercurrent extraction process of bergamot oil.
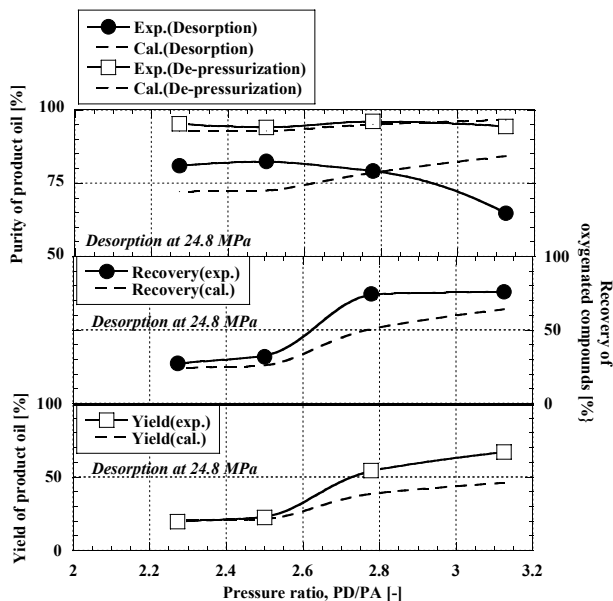

Figure 4. Effect of pressure ratio for supercritical PSA process: (a) purity of product oil, (b) recovery of oxygenated compounds, and (c) yield of product oil for desorption step.
(Q_A=3.49x10^{-5} kg/s, Q_D=2.12x10^{-5} kg/s, C_F=0.0404)

improved the selectivity significantly for the semi-batch extraction, the continuous operation was carried out without temperature gradient.

Figure 3 shows the separation selectivity between terpenes and oxygenated compounds for the extract and the raffinate product for bergamot oil processing. The results at 8.8 and 9.8 MPa are compared. In either condition, the selectivity was increased with an increase in S/F ratio. The operation at 8.8 MPa, however, has much larger selectivity than the operation at 9.8 MPa. This is owing to the difference in the density of SC-CO_2 and/or solubility of solutes in SC-CO_2 depending on the pressure. When bergamot oil was processed at 333 K, 8.8 MPa and S/F ratio of 63.2, the concentration of terpenes in the bottom product reduced lower than 1 wt% and high selectivity up to 300 was obtained.

2) Pressure swing adsorption process

The continuous apparatus had run 13 half cycles (13 hours). The samples collected from 9 to 13 half cycles. Following definitions were used to discuss the results. The effect of desorption-to-adsorption pressure ratio (P_D/P_A) on the purity of product oil, the recovery of oxygenated compounds and the yield of product oil at a constant P_D for the desorption step are shown in Fig. 4-(a). An increase in the (P_D/P_A) ratio increased the purity of product oil for desorption step. The purity of 82.49 % was obtained at a (P_D/P_A) ratio of 2.5. However, further increase in (P_D/P_A) ratio over 2.5 made the purity of product oil decreased.

The recovery of oxygenated compounds and the yield of product oil for desorption step are shown in Fig. 4-(b) and (c). An increase in (P_D/P_A) ratio increased the recovery of oxygenated compounds and the yield of product oil for desorption step. The purity of product oil, the recovery of oxygenated compounds and the yield of product oil for desorption step had optimum value on the (P_D/P_A) ratio.

An isothermal model was developed to simulate a two-bed cycle pressure swing adsorption in supercritical fluid. In order to

develop a mathematical model[6] for this system, the following assumptions are made: (1) The system is isothermal, (2) Pressure drop in the bed is negligible, (3) Axial and radial dispersions are negligible, (4) Equilibrium relationships for both terpenes and oxygenated compounds are represented by the competitive Langmuir isotherms, (5) The mass transfer rates are expressed by the linear driving force approximation and the rate coefficients are taken to be the same for both high pressure and low pressure, (6) During the pressurization and de-pressurization the profile of adsorbed amounts in the beds are frozen.

Model calculations agreed roughly with the experimental results, although the mathematical model was simple. The calculated purity, recovery and yield are smaller than the experimental data. There difference may be owing to the inaccurate adsorption isotherm and mass transfer coefficient. Simulation results also showed that the approach to the cyclic steady state was fast and required 3 full cycles at a half cycle time of 120 min.

Conclusion

Supercritical fluid extraction of citrus oil was carried out in the semi-batch operation and continuous countercurrent operation. For the semi-batch 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, the selectivity was increased with an increase in S/F ratio. At the S/F ratio of 63.2, the concentration of terpenes in the raffinate reduced lower than 1 wt%, that is, terpeneless oil was obtained. In PSA process, an increase in the (P_D/P_A) ratio, purity, recovery and yield were increased in the desorption step. The purity of 82.5 % was obtained in the desorption step at a (P_D/P_A) ratio of 2.5.

$$purity\ [\%] = weight\ fraction\ of\ oxy.\ comp.\ in\ effluent\ oil\ for\ desorption\ step$$

$$recovery\ [\%] = \frac{amounts\ of\ oxy.\ comp.\ obtained\ for\ the\ desorption\ step}{amounts\ of\ oxy.\ comp.\ supplied\ for\ the\ desorption\ step}\ \sim 100$$

$$yield\ [\%] = \frac{amounts\ of\ product\ oil\ obtained\ for\ the\ desorption\ step}{feed\ flow\ rate}\ \sim 100$$

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