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SEPARATION PERFORMANCE OF SUPERCRITICAL CARBON DIOXIDE EXTRACTION COLUMN FOR THE CITRUS OIL PROCESSING: OBSERVATION USING SIMULATOR

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ABSTRACT

Phase behavior of limonene and linalyl acetate, which are principal constituents of terpenes and oxygenated compounds, respectively, in bergamot oil, with supercritical carbon dioxide (SC-CO_2) was observed by use of process simulator (SIMSCI PRO/II). Solubility of each pure component in SC-CO_2 was calculated by the Peng–Robinson equation of state. For a given calculating condition, the solubility of limonene was 2–5 times higher than that of linalyl acetate. Process flow diagram for the citrus oil processing by SC-CO_2 extraction column was successfully constructed to evaluate the separation performance.

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The effects of feed composition, feed inlet position, reflux ratio, and stage number on the extraction ratio of limonene, separation selectivity, and recovery of linalyl acetate were studied at 333K and 8.8 MPa.

Key Words: Citrus oil; High-pressure vapor–liquid equilibrium; Linalyl acetate; Process simulator; Supercritical carbon dioxide

INTRODUCTION

Citrus oils are widely used for flavor, beverage, food, cosmetics, pharmaceuticals, and chemical industries. The citrus oil mainly contains volatiles such as terpenes and oxygenated compounds. Between these compounds, 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. Terpenes such as limonene do not contribute much to the flavor or fragrance of the oil, though they are recently praised as superior solvent for polystyrol in chemical recycling processes. Since they are unstable to heat and light, and rapidly degrade to produce undesirable off-flavor compounds, terpenes must be removed to stabilize the product.

Fractionation of citrus oil by supercritical carbon dioxide (SC-CO_2) is a prominent candidate for the removal of thermosensitive natural compounds such as terpenes, since the separation can be performed at low temperature. In fact, the extraction of essential oil by SC-CO_2 has been largely studied to minimize thermal degradation and organic solvent pollution in the conventional processes. We have studied supercritical fluid extraction for the fractionation of both model mixtures and raw oils with SC-CO_2 extraction column in a semi-batch and/or a continuous countercurrent operation mode.[1–5] In the semi-batch extraction mode, high-pressure phase equilibria for the quasi-ternary system of CO_2–terpenes–oxygenated compounds have been measured to observe the extraction behavior of the feed oil. For the semi-batch extraction of bergamot oil, the separation selectivity increased with an increase in temperature and with a decrease in pressure.[5] The highest selectivity was obtained at 333K and 8.8 MPa.

In the continuous countercurrent extraction process for the fractionation of citrus peel oil, on the other hand, the effective separation can be established by increasing the number of the equilibrium stages as well as multistage operation.[3] In this process, terpenes in feed oil were selectively removed into the extract and oxygenated compounds were selectively fractionated into the raffinate. The extraction process operated at a higher solvent-to-feed ratio and with a longer stripping column would 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. Finally, we proposed a new extraction process to separate citrus oil into simultaneously terpenes, oxygenated compounds, and high-viscous waxes-rich fractions.[4]

The correlations and estimation procedures have been widely developed to predict physical properties, phase equilibria, and phase behaviors for the model mixtures of citrus oil. Giacomo et al.[6,7] have measured the solubility of pure limonene and citral in SC-CO_2. The solubilities of pure essential oil components and their binary mixtures in SC-CO_2 were correlated with an equation of state using density-dependent mixing rules. The phase behavior of the ternary system of CO_2–limonene–citral was also calculated in their study. Iwai et al.[8,9] measured the high-pressure vapor–liquid equilibria (VLE) for the CO_2–limonene and CO_2–linalool systems, then those results were correlated by the Peng–Robinson equation of state (PR-EOS) using conventional mixing rules with two interaction parameters, k_{ij} and l_{ij}. They also measured high-pressure VLE for the CO_2–limonene–linalool ternary system.[10] Furthermore, Akgun et al.,[11] Viera de Melo et al.,[12] and Chang and Chen[13] reported the VLE calculation focused on modeling high-pressure phase behavior for CO_2–limonene and CO_2–linalool using several different mixing rules. Further, an isothermal flash calculation was applied to investigate selectivity and yield for the ternary system CO_2–limonene–linalool in order to understand the process parameters for the citrus oil processing by SC-CO_2.

In this work, phase behavior of limonene and linalyl acetate with SC-CO_2 was predicted by the use of the process simulator SIMSCI PRO/II (Version 4.15; Simulation Sciences Inc., Brea, California). Solubility of each pure component in SC-CO_2 was calculated by the PR-EOS. Furthermore, process flow diagram (PFD) for the citrus oil processing with SC-CO_2 extraction column was constructed to evaluate the separation performance. The effects of feed composition, feed inlet position, reflux ratio, and stage number on extraction ratio of limonene, separation selectivity, and recovery of linalyl acetate were studied at 333K and 8.8 MPa.

PROCESS SIMULATOR

Fundamentals

SIMSCI PRO/II is useful for observation of phase behaviors in chemical process in a steady state since one can rapidly conduct theoretical calculation of unit operations. For the correlation of binary system, phase equilibrium is calculated more easily by selection of the components from database library. If they do not exist in library, the physical properties such as critical parameters can be estimated based on Joback's method with the input of chemical structure. The procedures for the PFD design are as follows:

1. Components are selected from database library or filled from chemical structure.
2. Unit operations are added on the flow sheet and connected by the streams.
3. Conditions of unit operations and streams are supplied.
4. Calculation.

Calculating Condition

Limonene and linalyl acetate, which are principal constituents of terpenes and oxygenated compounds in bergamot oil, respectively were used as a feed material. Their chemical formulae are shown in Fig. 1. In order to observe the separation behavior of citrus oils widely, four types of model mixtures were tested (limonene–linalyl acetate; 20–80, 40–60, 60–40, and 80–20 wt%).

The PFD for the citrus oil processing by SC-CO_2 extraction column is shown in Fig. 2. The column was operated in the countercurrent flow, where feed stream (S1) was the dispersed phase entering at a certain inlet position of the column (theoretical tray) and SC-CO_2 solvent stream (S2) was the continuous phase entering at the bottom of the column. For the product streams from extraction column, top stream (S3) was introduced in the separator as vapor phase, and bottom product (S4) was obtained as a liquid phase. Flash drum was used as a separator operated at 303K and 5 MPa, where same condition was set in our previous experiment.[5] After the isothermal flash calculation, vapor phase

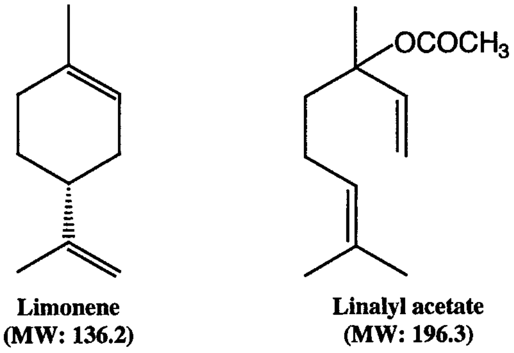

Figure 1. Chemical formulae of model components.

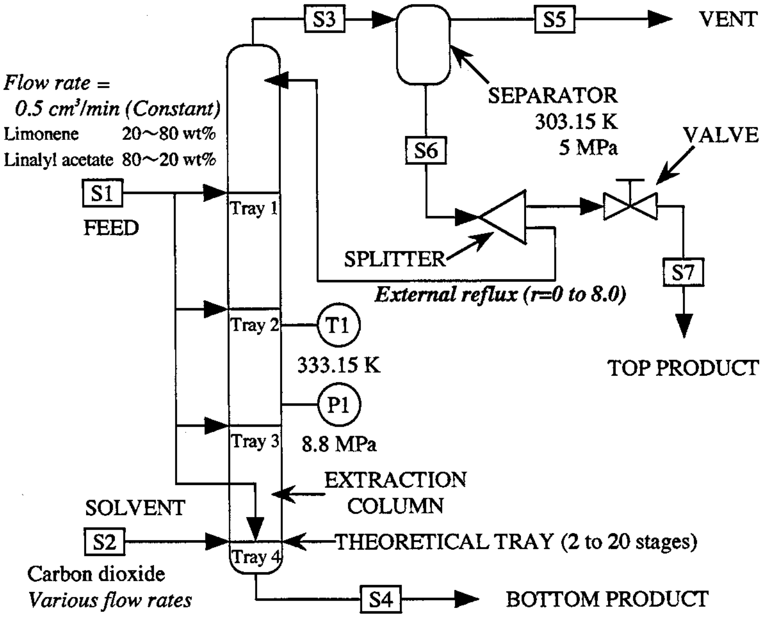

Figure 2. PFD for the citrus oil processing by SC-CO_2 extraction column.

stream (S5), which highly consists of CO_2 separated from model oil mixture was vented. On the other hand, liquid phase stream (S6) from the separator was depressurized to atmospheric pressure by a valve, so that top product (S7) was obtained. When the process was operated with external reflux, a part of S6 was returned to the top of the column (Tray 1) by adjusting flow rate of two streams from splitter. Reflux ratios, defined by ratio of S7 to refluxed flow, of 0 (no reflux) to 8.0 were given in this work. For the unit operation, distillation model was used as an extraction column having theoretical trays (stage number) of 2–20 without condenser and reboiler. In any calculation, extraction column was operated at 333K and 8.8 MPa, where the highest selectivity was obtained in our previous experiment.[5]

Analytical Factor

The flow rate of SC-CO_2 solvent is an important factor to design the extraction process. Solvent-to-feed (*S*/*F* ratio) was used as a flow-rate factor, as used in the evaluation of our previous experimental results.[3–5] The calculation was carried out at a constant feed flow rate of 0.5 cm^3/min with various CO_2 flow rates. The extraction ratio of limonene, separation selectivity, and recovery of linalyl acetate in the bottom product were calculated as a function of the *S*/*F* ratio. These factors are defined as;

$$\text{Extraction ratio}\,(-) = \frac{\text{Limonene (Top) (g mol/min)}}{\text{Limonene (Feed) (g mol/min)}} \tag{1}$$

$$\text{Recovery}\,(\%) = \frac{\text{Linalyl acetate (Bottom) (g mol/min)}}{\text{Linalyl acetate (Feed) (g mol/min)}} \times 100 \tag{2}$$

$$\text{Separation selectivity}\,(-) = \frac{Y_{\text{Limonene}}/X_{\text{Limonene}}}{Y_{\text{Linalyl acetate}}/X_{\text{Linalyl acetate}}} \tag{3}$$

where, Y and X are mass fractions in the top and the bottom product, respectively, calculated from flow rate of each component (CO_2-free basis).

RESULTS AND DISCUSSION

Phase Equilibrium of Binary System

The VLE for the binary systems CO_2–limonene and CO_2–linalyl acetate were calculated by use of physical properties. The critical parameter of linalyl acetate was estimated by Joback's method since it was not available in the database library. The calculated parameters for linalyl acetate are listed in Table 1. The parameters for limonene obtained from database are also shown in

Table 1. Parameters for Limonene and Linalyl Acetate

	Value	
Parameter	Limonene[a]	Linalyl Acetate[b]
Normal boiling point (K)	450.6	529.7
Critical temperature (K)	653.0	719.9
Critical pressure (MPa)	2.820	1.981
Critical volume (cm^3/g mol)	470.0	684.5
Acentric factor (–)	0.3809	0.5551
Enthalpy of formation (kJ/g mol)	−6.400	−384.2
Gibbs energy of formation (kJ/g mol)	246.0	−97.86

[a] Parameters were obtained from database library.
[b] Parameters were calculated.

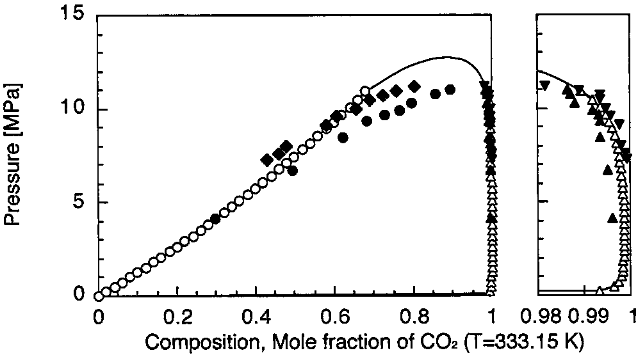

Figure 3. VLE for CO_2–limonene at 333K calculated from PR-EOS without fitting parameter.

Table 1. Figures 3 and 4 show the VLE descriptions for CO_2–limonene and CO_2–linalyl acetate, respectively. Any fitting parameter was not used in the calculation. At a low pressure, calculated results and previous experimental values[11,13] were in good agreement for CO_2–limonene system as shown in Fig. 3. However, it could not determine the bubble point pressure and vapor composition in the vicinity of mixture critical point with enough accuracy. On the other hand, excellent convergence was obtained for CO_2–linalyl acetate system as shown in Fig. 4. A comparison could not be made for VLE of this system since

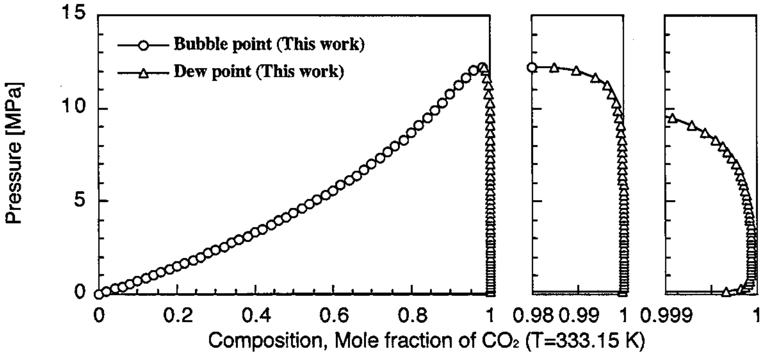

Figure 4. VLE for CO_2–linalyl acetate at 333K calculated from PR-EOS without fitting parameter.

Table 2. Estimated Solubility Data of Each Pure Component in SC-CO_2 at 333K

Limonene		Linalyl Acetate	
Pressure (MPa)	Solubility (mg/g CO_2)	Pressure (MPa)	Solubility (mg/g CO_2)
7.447	7.327	7.643	1.403
7.806	8.144	7.976	1.674
8.170	9.144	8.324	2.031
8.539	10.378	8.686	2.512
8.914	11.922	9.064	3.167
9.295	13.878	9.458	4.099
9.682	16.383	9.871	5.442
10.080	20.416	10.302	7.424
10.488	25.361	10.751	10.914
10.915	33.358	11.213	16.002
		11.675	26.765
		12.089	45.870
		12.226	68.056

no data were reported in the literature. Therefore, the solubility of linalyl acetate in SC-CO_2 at 333K based on VLE calculations is reported in Table 2 with that of limonene. Furthermore, Fig. 5 shows the effect of temperature on the solubility of each component in SC-CO_2 at 8.8 MPa. At given calculating conditions, the solubility of limonene was 2–5 times higher than that of linalyl acetate. Both

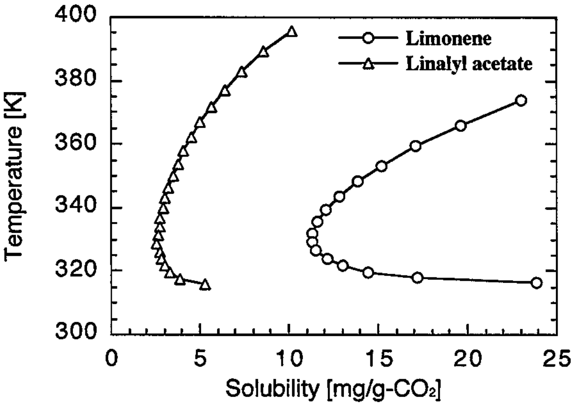

Figure 5. Effect of temperature on the solubility of each component in SC-CO_2 at 8.8 MPa.

solubilities of limonene and of linalyl acetate in SC-CO_2 at 8.8 MPa were minimum in the vicinity of 333K.

Evaluation of Separation Performance

In this section, extension to the ternary system of CO_2–limonene–linalyl acetate will be discussed as a separation performance. To evaluate the performance of SC-CO_2 extraction column with/without reflux for the removal of limonene in model mixture, various parameters are supplied for the PFD.

Effects of Feed Composition and Feed Inlet Position

Countercurrent extraction without reflux was operated for the model mixtures of citrus oil using four-stage column. For each operation, feed was introduced into the top of the column (Tray 1). Figure 6 shows the effect of feed composition on the separation behavior as a function of S/F ratio at 333K and 8.8 MPa. Extraction ratio of limonene increased with an increase in the S/F ratio and with an increase in the limonene content in the feed (Fig. 6a), whereas recovery of linalyl acetate decreased (Fig. 6b). These results imply that an increase in the solubility of model mixture in SC-CO_2 induced by the high limonene contents resulting in the decrease in the flow rate of linalyl acetate in the bottom product. For a model mixture of 80 wt% limonene and 20 wt% linalyl acetate, in particular, the recovery dramatically decreased at higher S/F ratio. For a given calculation, it is concluded that effective separation is achieved by removal of limonene from the bottom product with higher S/F ratio, since separation selectivity increased with an increase in limonene content in feed (Fig. 6c). However, optimal condition in terms of both the selectivity and the recovery could not be decided easily.

On the other hand, operation with reflux was also carried out for the model mixtures of citrus oil using the four-stage column at 333K and 8.8 MPa. For each operation, refluxed stream was introduced into the top of the column (Tray 1) at a reflux ratio of 1.0. Calculating results at the S/F ratio of 92 are listed in Table 3. The highest values at each feed composition are shown in *italic* style. For a given calculation, optimal condition was found in terms of extraction ratio of limonene, separation selectivity, and recovery of linalyl acetate against certain feed inlet positions. These results show that optimal feed inlet position for the operation with reflux is predicted by the use of the simulator. Separation performance would be improved by information

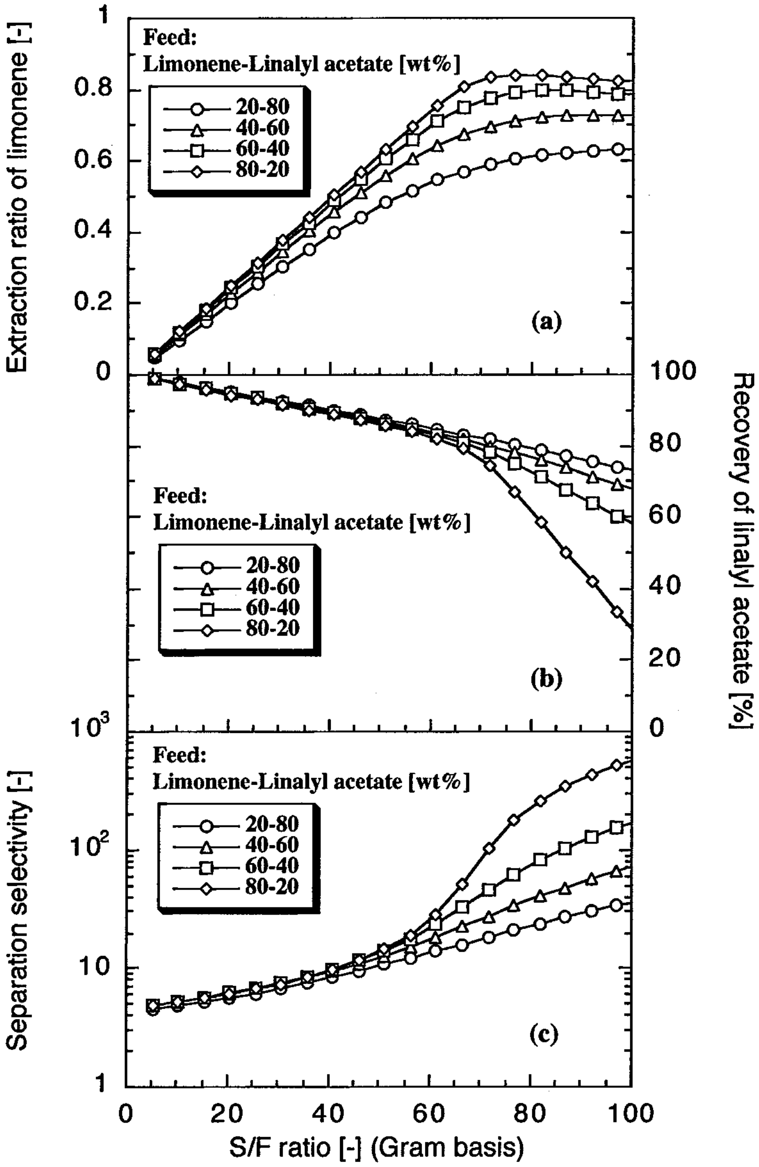

Figure 6. Effect of feed composition on the separation behavior as a function of *S*/*F* ratio at 333K and 8.8 MPa.

Table 3. Effect of Feed Composition and Feed Inlet Position on the Separation Behavior at *S*/*F* Ratio of 92

Feed Composition (wt%)					
Terpene	Oxy.	Feed Inlet Position	Extraction Ratio (−)	Separation Selectivity (−)	Recovery of Oxy. (%)
20	80	*Tray 1*	*0.4638*	*23.15*	*88.58*
		Tray 2	0.4631	22.93	88.57
		Tray 3	0.4107	13.53	88.21
		Tray 4	0.3090	5.815	87.48
40	60	Tray 1	0.5664	29.67	88.96
		Tray 2	*0.5868*	*37.17*	*89.29*
		Tray 3	0.5324	21.05	88.37
		Tray 4	0.4108	7.827	86.32
60	40	Tray 1	0.6053	30.69	89.74
		Tray 2	*0.6494*	*55.40*	*91.46*
		Tray 3	0.6150	34.57	90.11
		Tray 4	0.5020	10.71	85.78
80	20	Tray 1	0.6033	26.73	90.28
		Tray 2	0.6409	62.82	94.40
		Tray 3	*0.6419*	*64.88*	*94.55*
		Tray 4	0.5852	19.50	88.43

[a] Note: Terpene = limonene, Oxy. = linalyl acetate.

for such a concentration profile in column obtaining from the calculation results.

Effect of Reflux Ratio

Figures 7 and 8 show the effects of reflux ratio on the separation behavior for the model mixture of bergamot oil (40 wt% limonene and 60 wt% linalyl acetate) at 333K and 8.8 MPa. For each operation, refluxed stream was also introduced into the top of the four-stage column (Tray 1). Description for extraction ratio of limonene is omitted because it decreases obviously with an increase in the reflux ratio. Recovery of linalyl acetate increased in the reflux ratio, whereas it decreased with increase in the *S*/*F* ratio (Fig. 7). Therefore, distribution for the top and the bottom products would be determined by competition between the amounts of solute refluxed and that extracted. Figure 8 shows the effect of reflux ratio on the composition of products and the separation selectivity at *S*/*F* ratio of 92. The selectivity and linalyl acetate content in the bottom product decreased with increase in the reflux ratio, even though

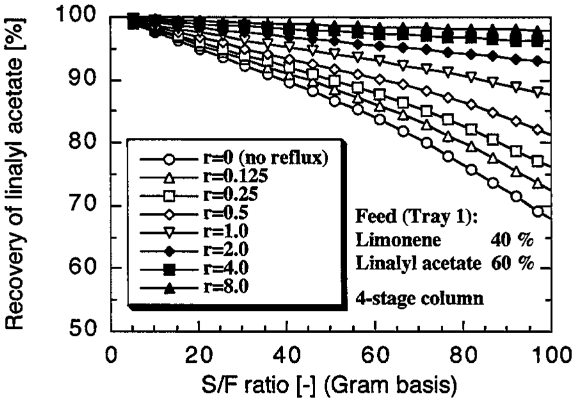

Figure 7. Effect of reflux ratio on the recovery of linalyl acetate as a function of *S*/*F* ratio at 333K and 8.8 MPa.

limonene content in the top product increased. These results show that the reflux of the top product is a rewarding technology not for the fractionation of citrus oil but for the concentration of light component such as limonene.

Effect of Stage Number

Figure 9 shows the effect of stage number on the separation behavior without reflux for the model mixture of bergamot oil (40 wt% limonene and

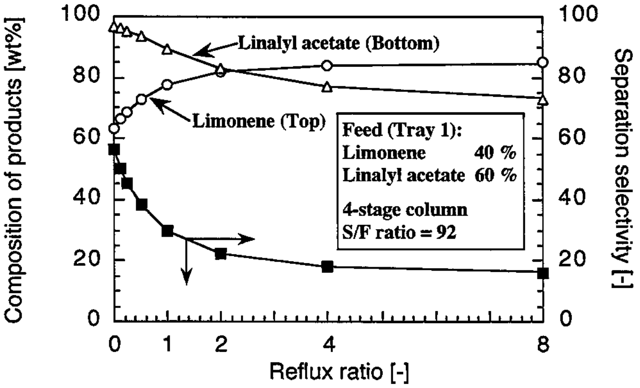

Figure 8. Effect of reflux ratio on the composition of products and the separation selectivity at 333K and 8.8 MPa with *S*/*F* ratio of 92.

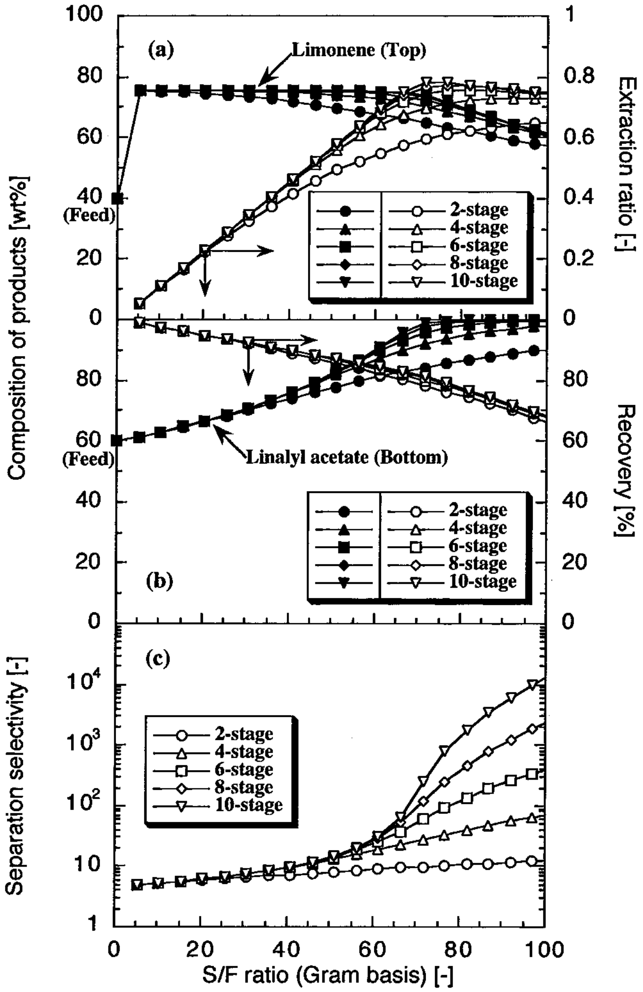

Figure 9. Effect of stage number on the separation behavior as a function of *S/F* ratio at 333K and 8.8 MPa.

60 wt% linalyl acetate) as a function of *S/F* ratio at 333K and 8.8 MPa. For operation with each stage number, feed was introduced into the top of the column (Tray 1). Extraction ratio of limonene increased with increase in the *S/F* ratio, whereas limonene in the top product decreased. Then, the extraction ratio was found gradually decreasing since excess top stream would flow into vent stream as vapor phase from separator (Fig. 9a). Recovery of linalyl acetate decreased

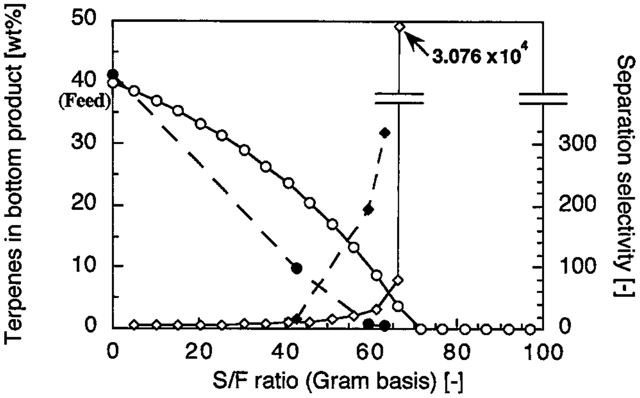

Figure 10. Comparison between simulation and experiment in terms of the limonene (terpenes) in bottom product and the separation selectivity at 333K and 8.8 MPa.

with increase in the *S/F* ratio, even though linalyl acetate content increased (Fig. 9b). Such a behavior must have resulted from a decrease in the flow rate of the bottom product. For a given operation, the separation performance is improved with increase in the stage number, that is, extraction column becomes longer. Consequently, removal of limonene was achieved without decrease in the recovery. As shown in Fig. 9c, separation selectivity increased dramatically with increase in stage number. At the *S/F* ratio of 92, the selectivity was about 5 times higher as it increases at every 2-stage.

These separation behaviors agreed with the previous experiment for the bergamot oil processing.[5] Figure 10 shows the comparison between simulation and experiment in terms of the limonene (terpenes) in bottom product and separation selectivity. For the extraction column, 20-stage was used in the simulation and a column of length 2400 mm was used in the experiment. As shown in this figure, separation performance for experimental results was greater than that for simulation at a given *S/F* ratio. Therefore, it was estimated that HETS (height equivalent to theoretical stage) for extraction column in our previous experiment was less than 120 mm.

CONCLUSIONS

Phase behavior of limonene and linalyl acetate with SC-CO_2 was observed using the process simulator (SIMSCI PRO/II). The high-pressure VLE for the binary systems CO_2–limonene and CO_2–linalyl acetate was calculated by use of physical properties. Solubility of each pure component in SC-CO_2 was calculated by PR-EOS. For a given calculating condition, the solubility of limonene was 2–5 times higher than that of linalyl acetate. Both solubilities of limonene and of linalyl acetate in SC-CO_2 at 8.8 MPa were minimum in the vicinity of 333K.

The PFD for the citrus oil processing by SC-CO_2 extraction column with/without reflux was successfully constructed to evaluate the separation performance. For the calculation at 333K and 8.8 MPa, the effects of operating conditions on extraction ratio of limonene, separation selectivity, and recovery of linalyl acetate could be observed as a function of *S*/*F* ratio. However, it was difficult to optimize the operating conditions in terms of both the selectivity and the recovery.

Consequently, reflux of the top product was not a rewarding technology for the fractionation of citrus oil; the performance was improved with increase in the stage number at higher *S*/*F* ratio. HETS for extraction column could be approximately estimated through the comparison between simulation and experiment.

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