

# Supercritical Fluid Extraction on Semibatch Mode for the Removal of Terpene in Citrus Oil

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Supercritical carbon dioxide extraction of a mixture of limonene and linalool was carried out with a rectification column in the semibatch operation mode. For the simple semibatch extraction where the column was controlled at the uniform temperature without an internal reflux, the Rayleigh equation, developed for the simple batch distillation, was applied to express the dynamic extraction behavior. In this paper the Peng–Robinson equation of state was used to estimate the ternary phase equilibria. The semibatch extraction with internal reflux induced by a temperature gradient of the rectification column increased the separation selectivity. The internal reflux ratio was calculated by the measurement of the extraction rates at the top and bottom of the column, and it was 7.6 for the column having a temperature gradient from 313 K at the bottom to 333 K at the top at 8.8 MPa. Behavior in the rectification column was discussed by means of estimated physical properties.

## Introduction

Citrus oil is a mixture of high volatile components such as terpenes and oxygenated compounds and non-volatiles such as pigments and waxes. Terpenes in citrus oil must be removed to stabilize the product and dissolve it in aqueous solution. They are conventionally processed by distillation or solvent extraction, resulting in the thermal degradation of the compounds. Supercritical fluid extraction with carbon dioxide as the solvent has been focused upon for the terpeneless citrus oil processing as an alternative process. It is possible to operate this process at lower temperatures than the conventional processes.

However, simple extraction with supercritical carbon dioxide has not been successful since it is difficult to optimize the operating conditions in terms of both the extraction yield and separation selectivity. Namely, a lower pressure led to a higher selectivity but a lower extraction yield, whereas a higher pressure gave a higher extraction yield but a lower selectivity. Extensive research to overcome this problem has been carried out in the last decade. Yamauchi and Saito (1990) and Barth et al. (1994) introduced adsorbent into a supercritical fluid system to achieve higher selectivity. They successfully fractionated lemon oil, bergamot oil, and orange oil, by a silica gel as the adsorbent. However, in these adsorptive separation processes, a considerably high pressure is required to desorb the solutes, since the oxygenated compounds which are desired components are strongly adsorbed, resulting in the requirement of higher energy and higher instrumental cost.

In the extraction process, a more effective separation can be established by increasing the number of equilibrium stages for a continuous countercurrent extraction as well as multistage operation. Perre et al. (1994) successfully developed the countercurrent extraction process, which obtained concentrated terpeneless oil to 5- or 10-fold with the column of 0.25 m<sup>3</sup> of feed oil/day on the ECOSS pilot plant (125 mm i.d. × 8 m height). On the other hand, Gerard (1984) suggested that

internal reflux induced by a temperature gradient was advantageous in the enriching section for the production of terpeneless essential oil by supercritical carbon dioxide.

For a semibatchwise extraction, pioneering works on a fractionation using a rectification column with an axial temperature gradient were carried out by Eisenbach (1984). He used an internal hot finger to reflux solutes dissolved in supercritical carbon dioxide and fractionated fatty acid ethyl esters. Nilsson et al. (1988) and Suzuki et al. (1989) investigated the fractionation of a urea-crystallized fish oil ester by supercritical carbon dioxide using a rectification column with an axial temperature profile. Concentrated EPA and DHA with purities higher than 90% were obtained by using a rectification column. Shibuya et al. (1993) and Sato et al. (1995) studied supercritical fluid fractionation of a model orange oil mixture with a column having a linear temperature gradient. They showed that the separation selectivity obtained for a column with a temperature gradient was higher than that for a column without a temperature gradient.

Although it is well-known that fractionation and purification by a rectification column with a temperature gradient increase the separation selectivity, only a qualitative explanation has been given. Our objective is to make quantitative analysis for the rectification phenomena induced by internal reflux. For this purpose, a Peng–Robinson equation of state (PR-EOS) was applied to estimate high pressure equilibria for the ternary system of carbon dioxide, limonene, and linalool, where limonene and linalool are principal constituent of terpenes and oxygenated compounds in orange oil. Experimental and thermodynamical approaches were developed to understand the rectification phenomena with internal reflux in semibatch supercritical fluid extraction.

## Experimental Section

A model mixture of limonene and linalool (Kanto Chem. Ltd.) was used as the feed. Liquefied carbon dioxide from a cylinder with a siphon attachment (Uchimura Sanso Ltd.) was used as the extraction solvent. A schematic diagram of the bench-scale ex-

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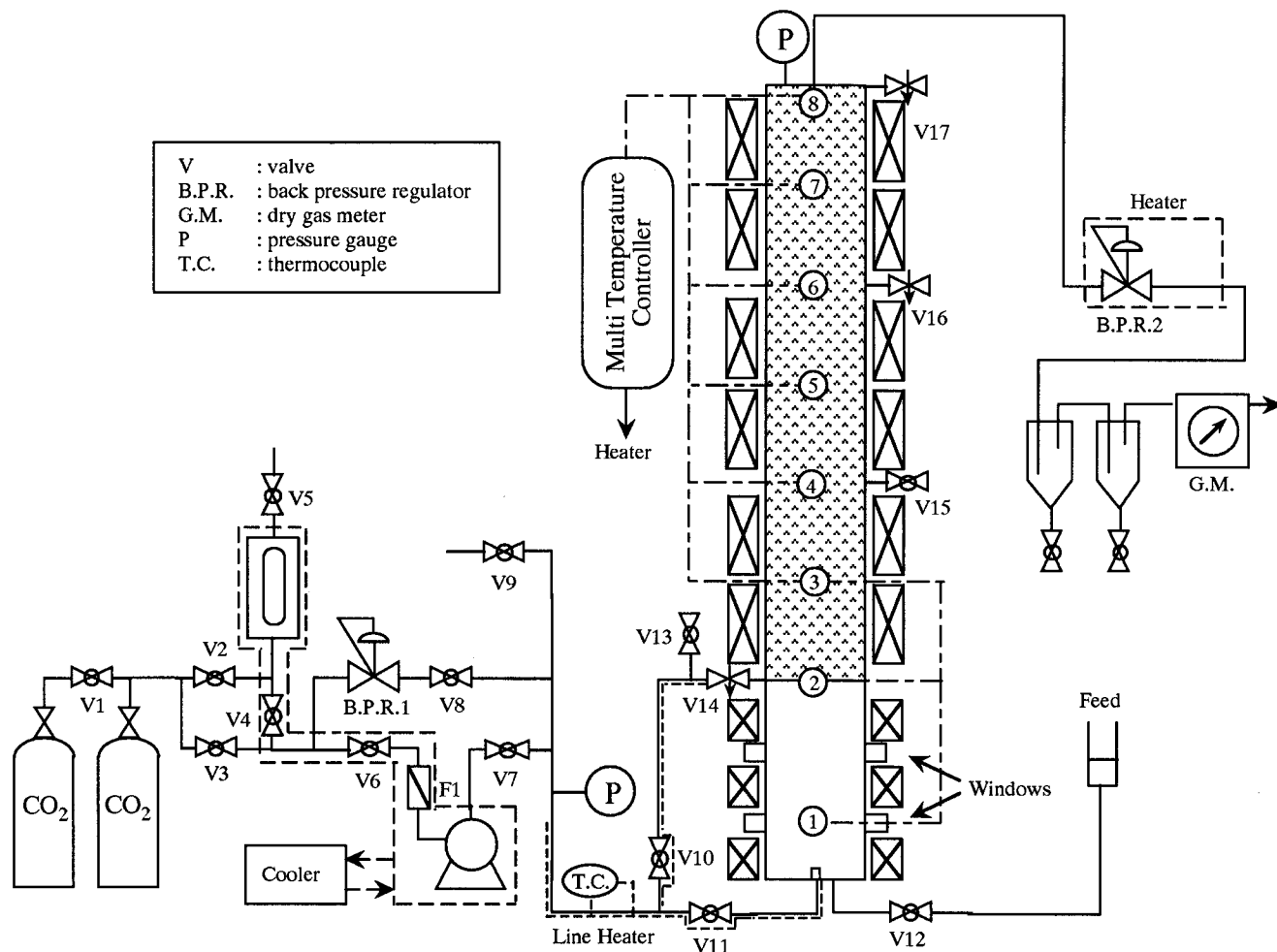


Figure 1. Experimental apparatus for the semibatch extraction.

perimental apparatus is illustrated in Figure 1. The column has a 20 mm internal diameter, and the total column length is 2400 mm. The rectification part is packed with stainless steel 3 mm Dixon packing in a length of 1800 mm. Two pairs of 10 mm diameter windows are located at the bottom of the column to permit visual observation of the phenomena. The temperature of the column is controlled by eight PID controllers.

Carbon dioxide was passed through a cooled line and compressed to the operating pressure by a high-pressure pump. The CO<sub>2</sub> flow rate was adjusted by the stroke of the piston of the pump. The compressed CO<sub>2</sub> was passed through the line heater in order to reach the desired temperature. The fluid exiting from the top of the column was expanded to ambient pressure through a back-pressure regulator which was heated by a ribbon heater to prevent it from freezing. The pressure was controlled by the back-pressure regulator.

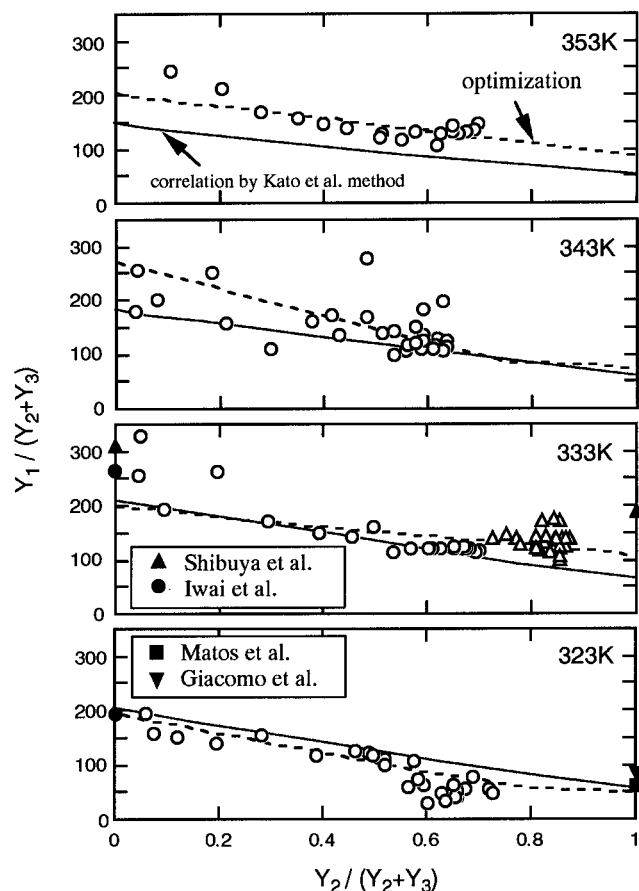
A feed was charged into the bottom of the column through valve 12 up to a level of the lower window. At the beginning, valve 11 was closed and valve 14 was opened, so that the CO<sub>2</sub> flowed to the rectification column by passing by the feed. After the temperature, pressure, and flow rate reached the desired value, valve 11 was opened and valve 14 was closed, so that CO<sub>2</sub> bubbled into the feed to start the extraction. The extraction was continued until complete extraction of the feed.

The CO<sub>2</sub> flow rate used ranged from 0.09 to 0.60 g/s. The extract might be in equilibrium in this flow-rate region, because no influence of flow rate on the extract

was observed. For example, the symbols  $\Delta$  and  $\circ$  in the plots at 333 K in Figure 2 are results at flow rates of 0.09 and 0.60 g/s, respectively.

The extract trapped in the separator was collected into sampling tubes in a certain interval of time, weighed, and analyzed by a capillary gas chromatograph. A dry test meter was used to measure the amount of CO<sub>2</sub> in the extract. The GC analysis was performed with a Shimadzu GC-14A instrument equipped with a J&W DB-WAX (30 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film) fused-silica capillary column and FID.

**Fluid Properties.** In this paper the estimated phase equilibria were used to understand the outline of the fluid properties, because only a few experimental data concerning the binary system are available. High-pressure phase equilibria for ternary system (1) CO<sub>2</sub>–(2) limonene–(3) linalool were estimated by using PR-EOS (Peng and Robinson, 1976). In the calculation, the critical parameters of limonene and linalool were estimated by the Lydersen method (Reid et al., 1987). A conventional mixing rule, including the binary interaction parameters, was used to calculate ternary phase equilibria. The binary interaction parameters were obtained by two methods. One was from a correlation method of Kato et al. (1981) to calculate the interaction parameters between (1) CO<sub>2</sub> and (2) limonene and between (1) CO<sub>2</sub> and (3) linalool, where those between (2) limonene and (3) linalool were assumed to be zero. Another method was optimization with experimental data obtained in this work. In the optimization, the binary interaction parameters between (1) CO<sub>2</sub> and (3)



**Figure 2.** Estimated saturated vapor lines and comparison of the extract on semibatch operation on the Janecke diagram at 8.8 MPa. Lines are estimated by PR-EOS, which includes the binary interaction parameters as shown in Table 1. Open symbols are experimental values in this work, and solid symbols are the reported binary equilibrium data.

linalool,  $k_{13}$ , at 323 and 333 K were adopted from the fitting value in the binary system (Iwai et al., 1994).

The density of pure CO<sub>2</sub> is available in the literature (IUPAC, 1976), and the density of a mixture was calculated by PR-EOS, including the binary interaction parameters obtained from the correlation method of Kato et al. (1981), for both vapor and liquid phases at the supercritical condition.

The viscosity of pure CO<sub>2</sub> was calculated by the Chung et al. method (Reid et al., 1987). The viscosities of pure liquid limonene and linalool at atmospheric pressure estimated by the Orrick and Erbar method (Reid et al., 1987) were extrapolated to the operating pressures by means of the Lucas correlation (Reid et al., 1987). The vapor and liquid phase viscosities were estimated from the pure components with the method of Gunberg and Nissan (Reid et al., 1987).

## Results and Discussion

**Simple Batch Extraction (without Reflux).** In this batch extraction, a liquid feed is charged to the extractor cell and is extracted by supercritical carbon dioxide with continuous flow. The extract is continuously withdrawn from the system, and the solutes are condensed by vaporizing CO<sub>2</sub> at the separator. The column was kept at a uniform temperature on the mode of this simple batch extraction. Consequently, there is no reflux and a single stage, where the extract leaving the extractor cell is assumed to be in equilibrium with the liquid in the extractor cell.

**Table 1.** Binary Interaction Parameters,  $k_{ij}$ <sup>a</sup>

temp (K)	correlation method of Kato et al.			optimization		
	$k_{12}$	$k_{13}$	$k_{23}$	$k_{12}$	$k_{13}$	$k_{23}$
323	0.116	0.101	0.000	0.098	0.046	0.079
333	0.117	0.099	0.000	0.274	0.051	-0.026
343	0.119	0.097	0.000	-0.027	0.226	0.011
353	0.121	0.095	0.000	0.290	0.222	-0.006

<sup>a</sup> The subscripts 1, 2, and 3 correspond to CO<sub>2</sub>, limonene, and linalool, respectively.  $k_{i=j} = 0$  and  $k_{ij} = k_{ji}$ .

Figure 2 shows the composition in the extracts for each fraction for our semibatchwise operation on the Janecke diagram at 8.8 MPa. Open symbols are the experimental data of the composition in the extracts for each fraction. In these plots, however, the compositions of the liquid phase are not shown because of the difficulty in measurement of the liquid phase for the batch operation. Phase equilibrium data for the binary system measured by Matos et al. (1989), Giacomo et al. (1989), Iwai et al. (1994), and Shibuya et al. (1993) are also shown in Figure 2 for comparison.

The data for the ternary phase equilibrium, CO<sub>2</sub>–limonene–linalool system, are not available in the literature. Phase equilibria in the ternary system were calculated by PR-EOS with the binary interaction parameters. The binary interaction parameters used in this work are summarized in Table 1. The binary interaction parameters were obtained from two methods. One was applied from a correlation method of Kato et al. (1981), which yields a good correlation between CO<sub>2</sub> and *n*-paraffins systems. In this correlation, the binary interaction parameter between limonene and linalool,  $k_{23}$ , was assumed to be zero. Another method was optimization with experimental data. In the optimization, the binary parameters,  $k_{13}$ , at 323 and 333 K were adopted from the value of the binary system (Iwai et al., 1994). Figure 2 indicates that the estimated equilibrium lines are considerably influenced by the binary interaction parameters. The lines from the correlation method of Kato et al. (1981) deviated from the experimental data. On the other hand, the lines from the optimization setting the binary parameter as the fitting parameter expressed well the saturated vapor lines. Although the binary interaction parameters from the optimization were more suitable than those from the correlation, however, the correlation method might be helpful for understanding the properties of the system, when we would not have any information about it.

Compositions in vapor phase extracted and liquid phase remaining in the extractor are shown in Figure 3 in the *X*–*Y* equilibrium diagram on a solvent-free basis. Experimental data were compared with the estimated phase equilibrium at 333 K and 8.8 MPa. The compositions of liquid in the extractor cell were calculated from the material balance of the charged feed and the extracts. The average values of the separation selectivity obtained from the experimental results and the estimated phase equilibrium are listed in Table 2. The separation selectivity was defined by eq 1

$$\beta = \frac{Y_2/X_2}{Y_3/X_3} \quad (1)$$

where subscripts 2 and 3 correspond to limonene and linalool, respectively. The values in parentheses in Table 2 were obtained by using the optimized binary interaction parameters with the experimental data of the extracts. Although the saturated lines from estima-

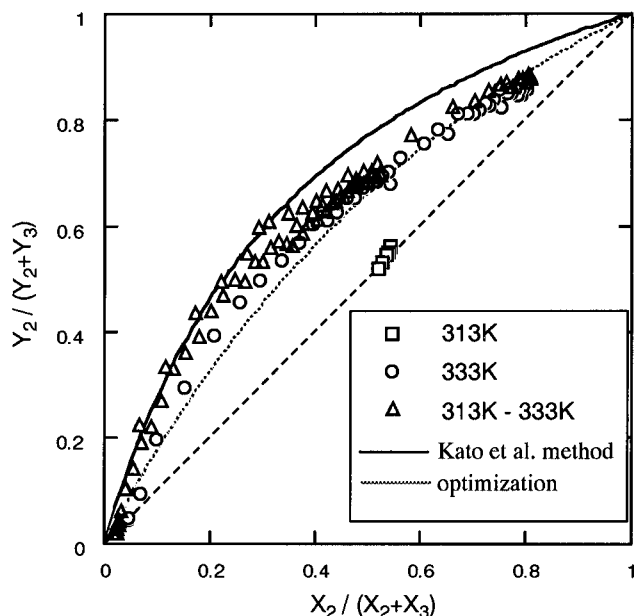


Figure 3.  $X$ - $Y$  relation of limonene concentration.

Table 2. Separation Selectivity between Limonene and Linalool

temp (K)		selectivity, $\beta$	
		PR-EOS	experiments
8.8 MPa	353	2.96 (2.68)	1.98
	343	3.22 (8.96)	2.30
	333	3.44 (1.95)	2.05
	323	3.47 (4.34)	2.26
	313	1.97	1.03
9.8 MPa	333	2.97 (1.45)	1.88
	313		

tion with PR-EOS were in good agreement with experimental data, the large difference in selectivities between experimental results and calculation was observed.

The difference in selectivity may be caused by the lack of the liquid phase data to optimize the binary interaction parameters. In our batch system, the compositions of extracts,  $Y_1$ ,  $Y_2$ , and  $Y_3$ , and the concentrations of limonene and linalool in the liquid phase on a solvent-free basis,  $X_2$  and  $X_3$ , were obtained by analyzing each fraction and subtracting the extracts from the initially charged feed. However, the concentration of  $\text{CO}_2$  in the liquid phase,  $X_1$ , in the extractor could not be obtained. The lack of the tie line data, that is, the liquid phase data and the vapor phase data in equilibrium, caused the large deviation of selectivity, although PR-EOS expressed well the vapor phase data as shown in Figure 2. However, the optimized lines at 323 and 333 K are more reliable than those of 343 and 353 K. Because the binary interaction parameter between (1)  $\text{CO}_2$  and (3) linalool,  $k_{13}$ , was used, the fitting value with a lot of experimental data in the binary system includes not only the vapor phase composition, that is, solubility, but also the liquid phase composition. Especially, the calculation in parentheses at 333 K and 8.8 MPa was in good agreement with both the vapor phase data and the selectivity.

For this simple batch extraction without reflux, the Rayleigh equation (Henley et al., 1981) developed for a batch distillation could be applied to the extraction on

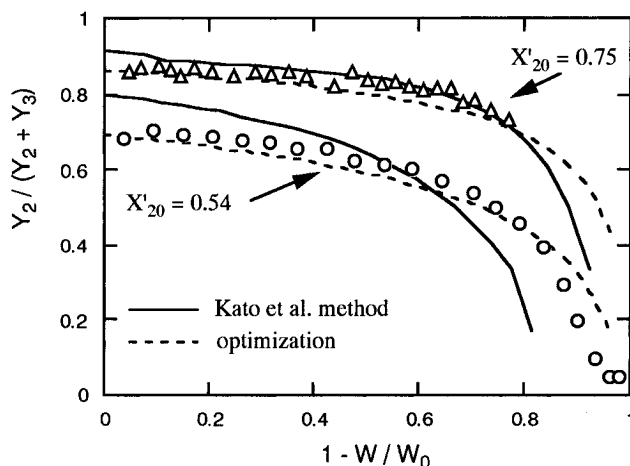


Figure 4. Dynamic changes in composition of limonene in the extract at 333 K and 8.8 MPa.

the composition of a  $\text{CO}_2$ -free basis

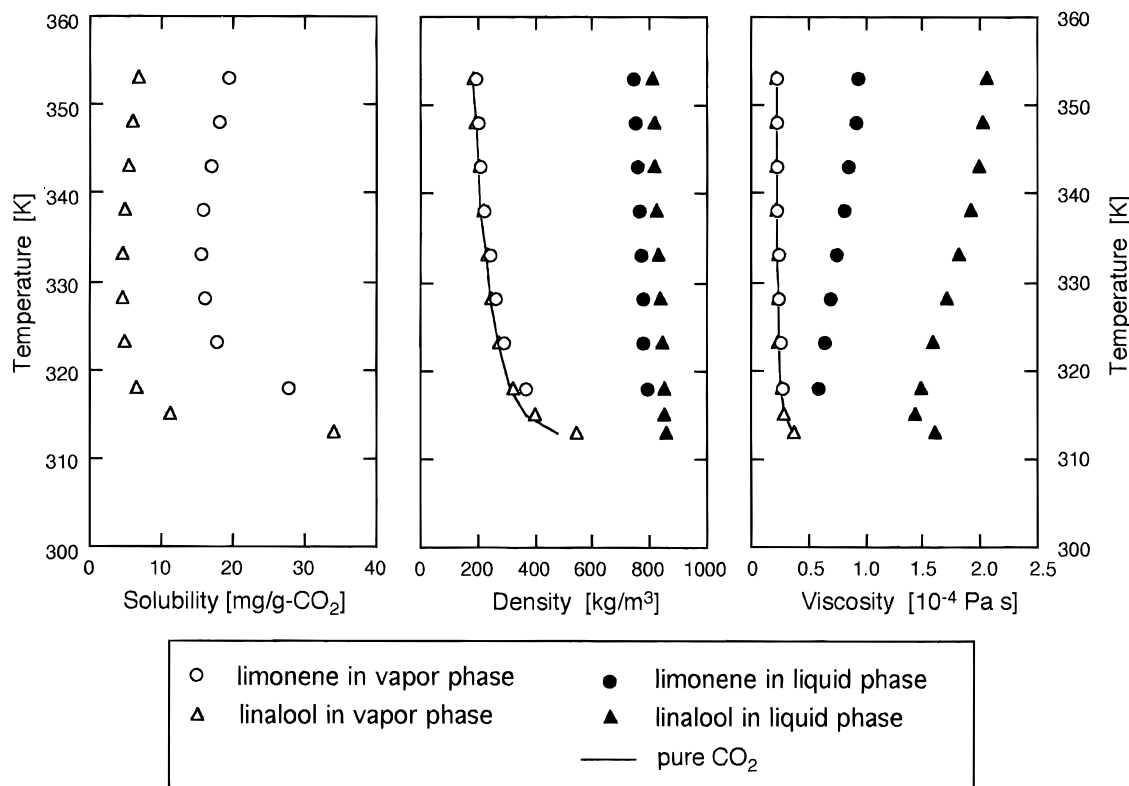
$$d(WX'_i) = Y'_i dW \quad (2)$$

where  $W$  is the amount of feed in the extractor. This equation was numerically integrated by the Runge-Kutta method. The equilibrium relationship was interpolated by the Lagrange method. Figure 4 shows the composition change of limonene in the extract on the semibatch operation at 333 K and 8.8 MPa for two runs of different initial composition. Calculated lines for the initial composition of  $X'_{20} = 0.75$  in the feed agreed well with the experimental data. Extraction behavior for the initial composition of  $X'_{20} = 0.54$  had a larger deviation than that of  $X'_{20} = 0.75$ .

This deviation must be reduced by using more accurate phase equilibria. Iwai et al. (1994) correlated the experimental data of the vapor-liquid phase equilibrium for the  $\text{CO}_2$ -linalool system by PR-EOS with two binary interaction parameters,  $k_{ij}$  and  $l_{ij}$ . Introduction of another interaction parameter,  $l_{ij}$ , is required to correlate not only the vapor phase but also the liquid phase. Consequently, it could be possible to correlate our experimental results by PR-EOS with six fitting parameters, where the binary interaction parameters,  $k_{ij}$  and  $l_{ij}$ , among different size molecules are six for the ternary system as well as for our experimental system. By these methods, the selectivity and dynamic extraction behavior could be expressed accurately. However, the lack of equilibrium data in the liquid phase prevents an accurate estimation of the phase equilibrium and then an accurate simulation of the extraction behavior.

Since our final objective is to separate terpenes and oxygenated compounds for citrus oil processing, which is a much more complicated multicomponent system including over 200 components, it is important to predict the tendency of separation behavior. The dynamic simulation by the Rayleigh equation may be advantageous for the design of supercritical fluid extraction in the semibatch operation mode.

**Batch Extraction with Internal Reflux.** The temperature dependence of solubility of solutes in supercritical fluid can be effectively utilized in rectification. A rectification column with a temperature gradient is connected in series with an extractor in a semibatch operation. The temperature at the top of the column is usually held higher than that at the bottom and extractor. When the supercritical fluid containing dissolved solutes flows into a higher temperature zone

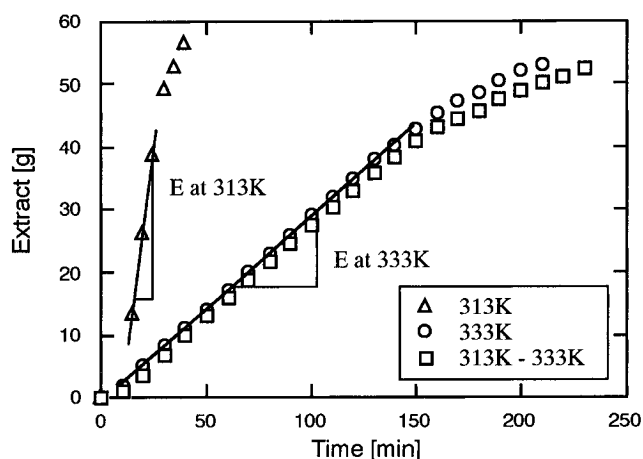


**Figure 5.** Effect of temperature on solubility, density, and viscosity of a mixture in CO<sub>2</sub> at 8.8 MPa.

in the column, less volatile components condense and drop back because of a decrease in the solubility of the solutes.

The concentration change of limonene when the rectification column had a temperature gradient from 313 K at the bottom to 333 K at the top is shown in Figure 3. The separation with a temperature gradient was more selective than the column with a uniform temperature at 333 K. It indicates that the temperature gradient in the rectification column improved the fractional extraction due to the internal reflux and countercurrent contact between liquid solute and solute in CO<sub>2</sub>. The average selectivities obtained from the rectification column with a temperature gradient are listed in Table 2. In this table the arrows show the temperature gradient in the rectification column from a lower temperature at the bottom to a higher temperature at the top of the column. The column having the temperature gradient from 313 at the bottom to 333 K at the top at a pressure of 8.8 MPa was most selective.

Figure 5 shows the estimated solubilities of limonene and linalool in CO<sub>2</sub> at 8.8 MPa, densities, and viscosities for both vapor and liquid phases. Below a temperature of 318 K at 8.8 MPa in the vicinity of the critical point, pure limonene was completely miscible in CO<sub>2</sub>. A remarkable turning point of properties is 310–320 K at 8.8 MPa. The temperature dependence of physical properties at a temperature over 320 K is not large. These physical properties may give information to understand the behavior in the column with a temperature gradient. Since the solubility remarkably decreased from 313 to 333 K, the internal reflux drop may be mainly formed in this temperature gradient region. However, since both density and viscosity between vapor and liquid phases were close in this region, we could imagine the difficulty of falling down of the reflux drop and the difficulty of the formation of the droplet. The extremely small droplet like a state of mist seems to stay in the rectification column with a temperature gradient. Consequently, dispersion behavior in the



**Figure 6.** Extraction curves of a mixture at 8.8 MPa and a CO<sub>2</sub> flow rate of 0.600 g/s.

rectification column may be quite better than the usual countercurrent contacting system, because of the large contacting area between the small droplet of the solutes and the vapor phase.

Because of the the fine dispersion of the liquid phase in the rectification column, attention must be paid to avoid flooding phenomena. Our rectification column was long enough to prevent the flooding. The extract leaving the column is in equilibrium at the top of the column at 8.8 MPa. Figure 6 shows the cumulative extraction curves of a mixture of limonene and linalool at 8.8 MPa. Extraction behaviors for the column with a temperature gradient from 313 to 333 K almost agreed with the curves for the uniform temperature column at 333 K.

The slope of the extraction curve for the uniform temperature column at 333 K corresponds to the leaving rate of the solutes at the top of the column with a temperature gradient. On the other hand, the slope of the curve for the uniform temperature column at 313

K is sharper and corresponds to the extraction rate at the extractor cell, where limonene and linalool were not separated as shown in Table 2 and Figure 3.

Consequently, the internal reflux ratio can be calculated by the following relation:

$$R_1 = \frac{L}{E} = \frac{E_{\text{bottom}} - E_{\text{top}}}{E_{\text{top}}} \quad (3)$$

$E_{\text{bottom}}$  and  $E_{\text{top}}$  are the extraction rates at the temperature at the bottom and at the top of the column having a temperature gradient and correspond to the extraction rate at the uniform temperature column on the simple semibatch operation. At a constant flow rate of  $\text{CO}_2$ , the internal reflux ratio can be obtained from the experiment as shown in Figure 6. The internal reflux ratios calculated are 7.6, 7.7, and 1.5, for the operation at 313–333, 313–343, and 323–343 K, respectively, at 8.8 MPa. The reflux ratio for the column having a temperature gradient from 323 K at the bottom to 343 K at the top of the column was smaller than the others, because of a slight change in solubility induced by temperature as shown in Figure 5.

## Conclusion

Supercritical fluid extraction of a mixture of limonene and linalool was carried out in the semibatch operation mode. On the simple semibatch extraction, which means the uniform temperature column without an internal reflux, the Rayleigh equation, developed for the simple batch distillation, was applied to express the dynamic extraction behavior. Prediction of the extraction behavior may be improved by the measurement of the ternary phase equilibrium of the  $\text{CO}_2$ –limonene–linalool.

The semibatch extraction with internal reflux induced by a temperature gradient of the rectification column increased the separation selectivity. The internal reflux ratio was calculated by the measurement of the extraction rate at a temperature at the top and bottom of the column. The column having the temperature gradient from 313 K at the bottom to 333 K at the top at a pressure of 8.8 MPa was most selective, because the properties such as solubility, density, and viscosity were remarkably changed in this temperature gradient.

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## Nomenclature

$E$  = extraction rate [kg/h]

$L$  = rate of internal reflux drop [kg/h]

$R_1$  = internal reflux ratio

$X_i$  = composition of solutes in the liquid phase

$X_i$  = composition of solutes in liquid on a  $\text{CO}_2$ -free basis

$Y_i$  = composition of solutes in the vapor phase

$Y_i$  = composition of solutes in extract on a  $\text{CO}_2$ -free basis

$W$  = amount of liquid in the extractor cell [kg]

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