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A Supercritical Carbon Dioxide Extraction from Mackerel (Scomber Japonicus) Powder: Experiment and Modeling

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The extraction of some organic substances from freezed-dried mackerel powder was performed using supercritical carbon dioxide (SC-CO_2) at 4.9—24.5 MPa and 313 K in a fixed-bed flow extractor. It was found that the rate of extraction was enhanced by raising the pressure. The overall yield of the SC-CO_2 extraction was comparable to that of a hot-hexane-extraction from the same material. The SC-CO_2 extraction produced glycerides of pharmacologic significance such as icosapentaenoic acid (IPA) and docosahexaenoic acid (DHA) from mackerel. In addition, a kinetic model for extraction with supercritical fluids is described, and is applied to correlate our results obtained in the SC-CO_2 extraction of mackerel. This model could express the transport within the solid in the supercritical fluid extraction process.

Recently much attention has been drawn to the separation process using a supercritical fluid (SCF). As compared with usual extraction procedure performed at relatively high temperature, the SCF extraction has several advantages. For example, it can yield thermolabile materials without denaturalization because of its low operating temperature. The feature of SCF techniques has previously been described and discussed in detail.[1-4] In some industries, the SCF has effectively separated the desired materials from natural products.[5-8]

We have been studying supercritical carbon dioxide (SC-CO_2) extraction of mackerel powder to obtain unsaturated fatty acids of pharmacologic value such as icosapentaenoic acid (IPA) and docosahexaenoic acid (DHA). These two acids have recently been reported to be efficacious against arteriosclerois.[9,10] The present study concerns the effective utilization of natural resources rich in our area where over one million tons of mackerel are caught every year for domestic use. Therefore, it should make possible the extraction of such high-valued substances as IPA and DHA from this inexpensive material.

In the present work, we carried out SC-CO_2 extraction from freezed-dried mackerel powder in a fixed bed extractor at pressures of 4.9—24.5 MPa and a temperature of 313 K. The pressure dependence of the extraction effectiveness of SC-CO_2 is discussed. The composition of the SC-CO_2-extracted oil is analyzed and compared with that of a hot hexane-extracted oil. We also present a kinetic model for the SCF extraction and attempt to use it to correlate our results of the SC-CO_2 extraction. For the practical design of SCF extraction plants, it is highly desirable to kinetically express the extraction process in order to optimize process parameters. For this not only knowledge of phase equilibria but also a kinetic analysis of the processes involved is essential. For the latter, however, little consideration has been made so far in the literature.

A Model of SCF Extraction

A mass transfer model is used to express the SCF extraction process. We regard the extraction process as a reaction such that one molecule of a solute, B, associates with j molecules of a SCF, A, with the formation of a complex, BA_j, $B+jA \rightarrow BAj$, and use a kinetic and diffusional model of solid-gas reaction. In the application of this model to the extract of mackerel, we will suppose the oils to be extracted to consist of a single component, as described later.

At first, the mass transfer for a single spherical extract is considered. Then the results are applied to a fixed bed of spheres. The model for solid-gas reactions proposed by Ishida and Wen[11] is used for a single spherical extract. Ishida et al. presented a kinetic and diffusional model for solid-gas reaction occurring in a spherical particle. We apply this model for the extraction of a solute from a solid with SCF. In applying this model to a fixed bed of spheres in the extractor, we make some modifications as mentioned later. The extraction process in a single spherical particle with SCF will be described in the following manner. Since the extraction near the surface is faster, the solute in this region is completely extracted after a certain time. That is to say, as the extraction progresses, a so-called raffinate layer is formed in the outside of the extract. Here, the stage of extraction prior to the formation of the raffinate layer is regarded as the first stage and the following stage as the second stage. Two models, 1

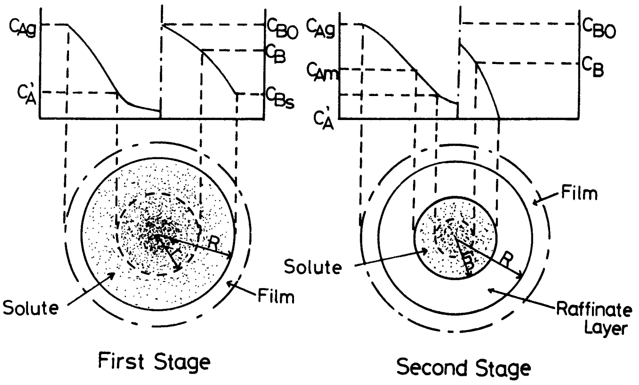

Fig. 1. Schematic diagram of the concentration profile in the first and second stage.

and 2, are presented for the first and second stages, respectively. Schematic diagram for these two stages are shown in Fig. 1. The following assumptions are employed:

—A steady state approximation for the transfer of SCF,A, holds.

—The rate of extraction is independent of the extract concentration in the solid.

—The fixed bed consists of spherical particles of uniform size which remain unchanged during the extraction.

Model 1: The mass balance and boundary conditions for gas A and solute B are given by

$$0 = D'(\mathrm{d}^2C_A'/\mathrm{d}r^2 + 2/r\,\mathrm{d}C_A'/\mathrm{d}r) - jk_V C_{B0}(C_A' - C_A^*), \tag{1}$$

$$\mathrm{d}C_B/\mathrm{d}t = -\,k_V C_{B0}(C_A - C_A^*), \tag{2}$$

$$D'\mathrm{d}C_A'/\mathrm{d}r = k_g(C_{Ag} - C_A^*) \qquad \text{at } r = R, \tag{3}$$

$$\mathrm{d}C_A'/\mathrm{d}r = 0 \qquad \text{at } r = 0, \tag{4}$$

where C_A' is the concentration of component A in solid B, C_A^* is C_A' at equilibrium, C_{Ag} is the concentration of component A in gas, C_B is the concentration of solid extract B, C_{B0} is the initial concentration of solid extract B, D' is the effective diffusivity of component A in the extraction layer, j is a stoichiometric coefficient, k_g is the mass transfer coefficient of component A, k_V is the extraction rate constant based on volume, r is a distance from the center of the sphere, R is a particle radius, t is a time.

The concentration profile of solute B can be obtained

$$C_B = C_{B0} - \int_0^t k_V C_{B0}(C_A' - C_A^*)\mathrm{d}t \tag{5}$$

as

$$C_B/C_{B0} = 1 - (\sinh(\phi'\xi)/(\xi \sinh\phi')(\theta_V/\theta_{VC}), \tag{6}$$

where ξ is a dimensionless radius, $\phi'$is a Thile modulus based on D', θ_v is a dimensionless time, θ_{vc} is θ_v at the end of the first stage as defined respectively by

$$\xi = r/R, \tag{7}$$

$$\phi' = R(jk_V C_{B0}/D')^{1/2}, \tag{8}$$

$$\theta_V = k_V(C_{Ag} - C_A')t, \tag{9}$$

$$\theta_{Vc} = 1 + (\phi' \coth\phi' - 1))/N_{sh}', \tag{10}$$

$$N_{sh}' = k_g R/D', \tag{11}$$

where N_{sh}' is a Sherwood number. Further, the degree of extraction X is given as follows.

$$X = 1 - \left[\int_0^R 4\pi r^2 C_B \mathrm{d}r \Big/ \int_0^R 4\pi r^2 C_{B0}\mathrm{d}r\right] \tag{12}$$

as

$$X = 3/(\phi')^2[\phi'\coth\phi' - 1]\theta_V/\theta_{VC} \tag{13}$$

At the end of the first stage, the degree of extraction X can be obtained upon substituting $\theta_v = \theta_{vc}$ in Eq 13 as follows.

$$X = 3/(\phi')^2[\phi'\coth\phi' - 1] \tag{14}$$

The concentration profile of gas A in the solid is obtained from Eqs. 1, 3, and 4 as

$$(C_A' - C_A^*)/(C_{Ag} - C_A^*) = \sinh(\phi'\xi)/\theta_{Vc}\xi \sinh\phi', \tag{15}$$

Model 2: As the extraction progresses, the solute is completely extracted at an outer layer, the raffinate layer is gradually formed as a new diffusion resistance for the gaseous solvent, but the extraction still occurs inside the raffinate layer. The mass balance and boundary conditions for gas A and solute B are then given as follows. In the inner core (extraction region), the mass balance and boundary conditions are identical to Eqs. 1, 2, and 4. In the raffinate layer, as extraction dose not occur, the mass balance for gas A can be obtained by

$$0 = D(\mathrm{d}^2C_A/\mathrm{d}r^2 + r/2\,\mathrm{d}C_A/\mathrm{d}r), \tag{16}$$

$$C_B = 0 \qquad \text{at } r = R, \tag{17}$$

$$D\mathrm{d}C_A/\mathrm{d}r = k_g(C_{Ag} - C_A) \qquad \text{at } r = R, \tag{18}$$

where D is the effective diffusivity of component A in raffinate layer. Further, at the boundary between the extraction region and the raffinate layers,

$$C_A' = C_A \tag{19}$$

$$D'\mathrm{d}C_A'/\mathrm{d}r = \mathrm{D}\mathrm{d}C_A/\mathrm{d}r. \tag{20}$$

The concentration profile of the solid extract can be obtained from

$$C_B = C_{Bm} - \int_{tc}^t k_V C_{B0}(C_A' - C_A^*)\mathrm{d}t \tag{21}$$

as

$$\begin{aligned} C_B/C_{B0} = 1 &- \sinh(\phi'\xi)/\xi \sinh\phi' - \\ &\sinh(\phi'\xi)/\xi\left[\int_{\theta_{Vc}}^{\theta_V}[\xi_m/\sinh(\phi'\xi_m)]\mathrm{d}\theta_V/[1 + D'/D\right. \\ &\left.[1 - \xi_m + \xi_m/N_{sh}][\phi'\xi_m \coth(\phi'\xi_m) - 1]]\right], \end{aligned} \tag{22}$$

where C_{Bm} is C_B at the end of the first stage, $N_{sh} = k_g R/D$, $\xi_m = r_m/R$, r_m is r at the boundary between the extraction region and the raffinate layer. The time required for the raffinate layer to reach r_m is obtained as

$$\theta_V = \theta_{Vc} + \int_1^{\xi_m}(\mathrm{d}\theta_V/\mathrm{d}\xi_m)\mathrm{d}\xi_m \tag{23}$$

θ_v can be obtained from Eqs. 22 and 23 as follows.

$$\begin{aligned} \theta_V = 1 &+ (1 - D'/D)\ln[\xi_m \sinh\phi'/\sinh(\phi'\xi_m)] + \phi^2 \\ &(1 - \xi_m)^2(1 + 2\xi_m)/6 + D'/D(1 - \xi_m)[\phi'\xi_m \coth(\phi'\xi_m) - 1] \\ &+ \phi^2(1 - \xi_m{}^3)/3N_{sh} + \xi_m[\phi'\xi_m \coth(\phi'\xi_m) - 1]/N_{sh}'. \end{aligned} \tag{24}$$

When we substitute Eq. 24 into Eq. 22, the concentration profile for the solid extract is obtained as

$$1 - C_B/C_{B0} = \xi_m \sinh(\phi'\xi)/\xi \sinh(\phi'\xi_m). \tag{25}$$

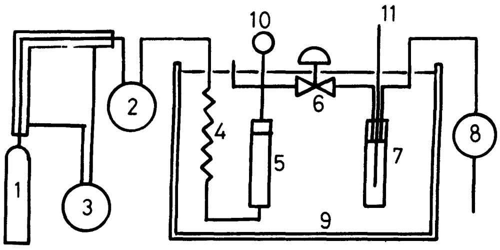

Fig. 2. Schematic diagram of supercritical CO_2 extraction apparatus. 1: CO_2 Cylinder, 2: High pressure pump, 3: Cooling circulator, 4: Preheater, 5: Extractor, 6: Back pressure regulator, 7: Receiver, 8: Flow totalizer, 9: Constant temperature bath, 10: Pressure gauge, 11: Thermocouples.

Thus, the degree of extraction X_2 can be obtained from Eq. 25 as

$$X_2 = 1 - \xi_m^3 + 3\xi_m[\phi'\xi_m \coth(\phi'\xi_m) - 1]/(\phi')^2. \tag{26}$$

Experimental

Materials. Mackerel were obtained commercially. They were freezed-dried and sieved in the range of about 32 to 64 mesh. The average diameter of the mackerel particles was 10^{-5} m. The amount of water contained was 7.3 wt%. Commercial-grade carbon dioxide was used as solvent.

Extraction Procedures. A flow diagram of the extraction apparatus used is shown in Fig. 2. Liquid carbon dioxide is charged into a Hitachi high pressure liquid pump through a 1/16 inch tube and a check valve, and compressed to the desired pressure. The pump can deliver the solvent at a constant flow rate of 1 $NL\,min^{-1}$ (1 NL=1 L of gas at 293 K and 101.3 kPa). The pressure is controlled by a back pressure regulator. The extraction pressure is measured with a Bourdon-type pressure gauge. Fluctuations in pressure due to the pump are less than ±1 $Kg\,cm^{-2}$ below 300 $Kg\,cm^{-2}$. The temperature is controlled within ±0.1 K.

A 25 g sample of mackerel particles is placed in a 0.1 L extractor and extracted at pressures of 4.9—24.5 MPa and 313 K. The extracted solution is flashed to atmospheric pressure across a heated back pressure regulator and the component is collected in a receiver. The amount collected is determined by weighing and the corresponding total volume of CO_2 used is measured with a flow totalizer.

Further, mackerel particles were extracted with hexane for 5 h in a Soxhlet for comparison.

Analytical Methods. Extracted glycerides were changed into methyl esters of fatty acids according to the usual method. The esters were identified by GC-MS and gas chromatography. Phosphorus was analyzed colorimetrically.[12]

Results and Discussion

In Fig. 3, the yield of extracted oil is plotted against the total amount of CO_2 consumed under the conditions that carbon dioxide was forced to flow at a rate of 1 $NL\,min^{-1}$ at 19.6 MPa and 313 K. The linear portion of the curve indicates that steady-state extraction conditions are readily established at the beginning of the extraction. The extraction rate is maintained at about 0.27 $g\,h^{-1}$ until an oil yield of 6.7 g is obtained. The overall yield is comparable to 85% of that obtained by the hot hexane extraction.

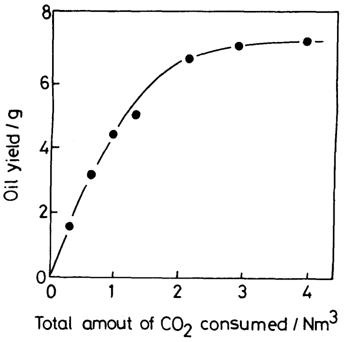

Fig. 3. Oil yield from freezed-dried mackerel powder during supercritical CO_2 extraction at 19.6 MPa and 313 K.

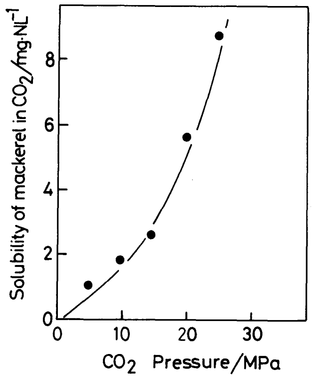

Fig. 4. Effect of pressure on the solubility of mackerel in CO_2 during the initial 6 h at 313 K.[13]

The solubility at 313 K between 4.9—24.5 MPa is given in Fig. 4. The initial solubility of mackerel oil in CO_2 was determined from the slope of the plot of oil yield-to-total amount of CO_2 consumed (as shown in Fig. 3, for example).[13] The solubility at 313 K increased greatly with the pressure. For example, the amount of the oil extracted at 24.5 MPa is about 4.6 times that at 9.8 MPa. This is considered to be associated with an increased solute holding power. Previously, Yamaguchi[14] reported that 14.4 g of oil per 100 g of mackerel could be extracted at 39.2 MPa, 313 K and a flow rate of 10 $kg\,h^{-1}$.

Table 1 provides an analytical characterization of SC-CO_2-extracted and hot hexane-extracted oils from the same mackerel particles. In this Table are listed the kinds of fatty acid components and the amounts of phosphorus contained in both SC-CO_2- and hexane-extracted mackerel oils. Under these conditions, the oils obtained by SC-CO_2 extraction contains both IPA and DHA and the amounts of fatty acid components compete with those obtained by the hot hexane extraction.[13] Furthermore, SC-CO_2-extracted oil has significantly less phosphorus than hexane-extracted oil. The hexane-extracted oil is red brown and turbid whereas the SC-CO_2-extracted oil is yellow and clear. The method used to estimate the phosphatide content is to multiply the percent elemental phosphorus by 25.4.[12] The phosphatide content calculated on this basis is 1% for the hexane-extracted oil and 0.023% for the SC-CO_2-extracted oil. These values are reflected in a significant difference in the refining loss on the removal of the phosphatide content in the purification process between the SC-CO_2- and hexane-extracted oils. Therefore, the oil extracted with SC-CO_2 has the advantage of being essencially comparable to a degummed, hexane-extracted crude oil. In addition, it was reported[15] that oil extracted from soybeans with SC-CO_2 had less phosphorus than hexane-extracted oil. That is to say, with SC-CO_2, phosphatide free oil not only from plant seed but from fish is shown to be extracted.

The Application of the Kinetic Models. The results obtained for a single sphere in the models 1 and 2 using the Ishida's model[11] are transfered to a fixed bed of spheres by correcting the Sherwood number. In the model 1, we present the modification of the Sherwood number N_{sh}' as follows.

$$N_{sh}^* = N_{sh}'\psi, \tag{27}$$

where N_{sh}^* is the Sherwood number for a fixed bed of spheres. In the model 2, we regard the correction factor ψ as a function of the dimensiomless radius ξ_m of the extraction region as follows.

$$\psi = \exp(-K/\xi_m), \tag{28}$$

where K is a constant, which is treated here as an adjustable parameter.

The results calculated from the above two models employing Eqs. 27 and 28 are compared with the experimental results in Fig. 5. Table 2 summarizes the parameters used in the present calculations. The stoichiometric coefficient was estimated from the components of each fatty acids of the SC-CO_2-extracted mackerel oils shown in Table 1 and the solubility constant of triglycerides in SC-CO_2 studied by Chrastll.[16] The initial concentration of the mackerel oil was determined as follows. The weight of the mackerel oil obtained from 25 g of mackerel powder with n-hexane in a Soxhlet was 8.8 g. We assumed that it was the total yield contained in the powders and that the oil consisted of triglycerides. From the analytical results shown in Table 1, 25 g of mackerel powder contained 9.9×10^{-3} mol (=0.01 mol) of the oil. Since the bulk density of the mackerel powder was 0.25, the initial concentraion was about 100 mol m^{-3}. The effective diffusivity D' and D were estimated in the following manner. First, for D', we applied the equation of Grigull.[17]

$$m/m_c = C_q(1-\exp(-EF_o)), \tag{29}$$

where F_o is the Fourier number, C_q and E are coefficients (C_q=0.6079, E=9.8696), m is the remaining quantity of SC-CO_2-extracted oil, m_c is the initial quantity of mackerel oil. Further, F_o was defined as

$$F_o = D't/R^2, \tag{30}$$

where R is the radius of the sphere. D' was determined from Eqs. 29 and 30. Next, in the second stage, the mass transfer coefficient k_g was considered as follows.

$$1/k_g = 1/\beta_i + 1/\beta_a, \tag{31}$$

where β_i is the mass transfer coefficient in the extraction layer, β_a is the mass transfer coefficient in the raffinate layer. Since $\beta_a \gg \beta_i$,

Table 1. Compositions of SC-CO_2- and Hexane-Extracted Mackerel Oils[13]

Fatty acid	Hexane	SC-CO_2
	%	%
Myristoreic	4.8	6.3
Palmitic	20.4	21.8
Palmitoleic	5.7	7.3
Stearic	2.3	1.1
Oleic	33.4	32.2
Linoleic	—	1.9
Icosenoic	5.4	2.0
Icosapentaenoic	7.8	5.8
Erucic	0.5	0.6
Docosahexaenoic	11.7	8.1
Lignoceric	0.4	—
	Hexane	SC-CO_2
	ppm	ppm
Phoshorous	405	3
	Hexane	SC-CO_2
Oil description	Yellow oil	Red brown oil

Table 2. Parameters Used in the Model Calculations for Extraction of Mackerel Oil with SC-CO_2

Diameter of the equivalent sphere	$d=10^{-4}$/m
Initial concentration of the solute	$C_{BO}=100$/mol Nm^{-3}
Effective diffusivity of the solvent in the extraction region	$D'=4\times10^{-7}$/m^2 h^{-1}
Effective diffusivity of the solvent in the raffinate layer	$D=9\times10^{-5}$/m^2 h^{-1}
Pressure	$P=19.6$/MPa
Temperature	$T=313$/K
Volumetric flow of the solvent	$F=60$/NL h^{-1}
Stoichiometric coefficient	$j=4$
Thiele modulus	$\phi'=2.5$, $\phi'=0.17$
Correction constant	$K=3.2$

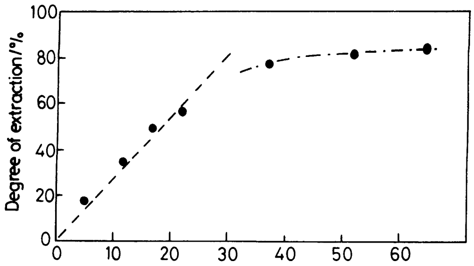

Fig. 5. Degree of extraction of mackerel oil at 19.6 MPa and 313 K.
●: Exp., ——: Model 1, —·—: Model 2.

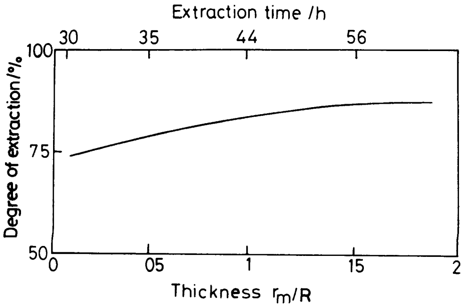

Fig. 6. Calculated relation between the degree of extraction and the thickness of raffinate layer in the second stage.

$$k_g \simeq \beta_1. \tag{32}$$

Schlunder proposed the following equation.[18)]

$$\beta_1 R/D = (10.82^2+4/\pi F_o)^{1/2}. \tag{33}$$

In addition, Brauer[19)] assumed that if F_o was larger than 0.4,

$$\beta_1 \sim 1/t. \tag{34}$$

Therefore, D was estimated from Eqs. 32, 33, and 34. The optimal Thile modulus and the correction constant K were determined so as to minimize the difference between the experimental results in Fig. 3 and the estimates using the models.

As shown in Fig. 5, the overall extraction process can be represented by these models well, the initial stage being by model 1 while the latter stage by model 2. Furthermore, using the parameters in Table 2 and the results in Fig. 5, the overall yield in the first stage from Eq. 14 and the duration for it is shown to be about 74% and 28 h, respectively. This means that beyond this extraction region, the solvent CO_2 rapidly becomes more difficult to diffuse into the particle because under these conditions, the raffinate layer begins to form.

In model 2, the ralationship between the thickness of the raffinate layer and the degree of extraction derived from Eqs. 24 and 26 is shown in Fig. 6. The formation rate of the raffinate layer decreases with the extraction time. As the raffinate layer thickens, the degree of extraction gradually decreases and attains a steady value such that the thickness of the raffinate layer is over about 10% of the whole extraction region. That is to say, the raffinate layer acts as a diffusion resistance for the extraction and decrease the degree of extraction. Estimating from the above calculated results, the extraction occurs near the surface of the mackerel particle and large amounts of the materials contained remain unextracted. Therefore, the diffusion of the gas in the particle must progress in order to improve the degree of extraction. This may be attained by the adjustment of the extraction pressure and temperature. Finally, we would like to note that the addition of a suitable third substance to the CO_2 enhances the extraction efficiency.[20,21)]

References

1) L. G. Randall, *Sep. Sci. Tech.*, **17**, 1 (1982).

2) S. Saito, *Petrotech*, **5**, 115 (1982).

3) K. Nagahama, *Bunrigizyutsu*, **11**, 23 (1981).

4) S. Peter and S. G. Brunner, "Extraction with Supercritical Gases," ed by G. M. Schneider, E. Stahl, and G. Wilke, Verlag Chemie, Weinheim (1980).

5) Brit. Patent, 133651.

6) U. S. Patent, 3843824.

7) Brit. Patent, 1388581.

8) Japan Patent, 55-45391.

9) T. O. Lossonczy, *Am. J. Clin. Nutr.*, **31**, 1340 (1978).

10) A. Hirai, T. Hamazaki, T. Terano, T. Nishikawa, A. Tamura, A. Kumagai, and J. Sajiki, *Lacent*, **11**, 1132 (1980).

11) M. Ishida and C. Y. Wen, *AIChE, J.*, **14**, 311 (1968).

12) "Kizjun Yushi Bunseki Shikenho," The Japan Oil Chemists' Society (1981).

13) N. Saito, *Shokuhin Kogyo*, **28**, 1 (1985).

14) K. Yamaguchi, 8th Technical Seminar, The Society of Chemical Engineering, Japan (1985), p. 59.

15) J. P. Friedrich, G. R. List, and A. J. Heakin, *J. Am. Oil Chem. Soc.*, **59**, 288 (1982).

16) J. Chrastll, *J. Phys. Chem.*, **86**, 3016 (1982).

17) U. Grigull, "Temperaturausgleich in Einfachen Korpern, Springer," Berlin (1964).

18) E. U. Schlunder, "Einfuhrung in die Warmeubettertragung, Vieweg," Braunschweig (1981).

19) H. Brauer, Stoffaustausch einschlieβlich Chemischer Reaktion, Sauelander," Aaraw (1971).

20) Y. Ikushima, N. Saito, K. Hatakeda, S. Ito, T. Asano, and T. Goto, *Chem. Lett.*, **1985**, 1789.

21) To be submitted.