

MODELING OF SOYBEAN OIL BED EXTRACTION WITH SUPERCRITICAL CARBON DIOXIDE

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Abstract—Dry-milled soybeans are extracted with supercritical carbon dioxide at pressures 270 to 375 atm, temperature 50 to 70°C, solvent flow rates 0.025 to 0.16 cm/sec as a linear velocity in the bed at supercritical state, and three types of soybean particle size in the range 0.05 to 0.2828 cm.

Under these conditions, extraction rates of soybean oil from solid substrates in a fixed bed (1.1 mm I.D.×200 mm Height) have been determined.

The extraction rates were constant during the initial extraction period where the film resistance controls the rates, and then, the rates shifted to time-dependent diffusion controlling mass transfer mode. To correlate these features, mass transfer calculations were carried out for the constant rate period and the subsequent unsteady mass transfer rate period, respectively.

INTRODUCTION

During recent years the principles and practice of supercritical fluid (SCF) technology have experienced a resurgent interest and rapid advances. The motivation for the development of SCF technology as a viable alternative is a result of increased cost of energy, scrutiny of industrial solvents by the government, awareness about pollution control, and the performance demands of specialized new materials.

Especially the energy shortage in the 1970s was largely responsible for considerable research and effort on the SCF processes. Presently, SCF technology may be a replacement to current extraction and distillation methods. SCF technology becomes a useful process for upgrading heavy crude petroleum residuals, for extracting polymer blends, or for purifying natural products such as edible oils [1-4].

While a great deal of information about SCF technology can be obtained from several recently published review papers and symposium books, a large portion of the information available is limited to high pressure fluid phase equilibrium data and patent-oriented feasibility studies. It is not easy to find any literature dealing with engineering-oriented process operation data for the practical design of the candidate SCF process.

To find a type of engineering data for seed oil bed

extraction this paper deals with the mass transfer operation from solid matrix of dry-milled soybean solid in supercritical fluid extraction with carbon dioxide.

Recently, petroleum-free extraction of oil from soybeans with supercritical carbon dioxide has been reported by the United States Department of Agriculture's Northern Regional Research Center [5,6]. They considered supercritical carbon dioxide as a replacement for hexane in soybean-oil extraction. By comparing oil qualities such as color, iron, phosphorus, unsaponifiable contents, odor and flavor, they concluded that supercritical carbon dioxide, an ideal solvent for extraction of food products. The carbon dioxide is low in cost and readily available from fermentation processes.

Data on the extraction and oil composition have been described in a number of papers [7-9]. Also, Brunner [10] has been reported separation of substances from solid substrates by supercritical gases for coffee beans and for rapeseed oil seeds.

The time required for the supercritical extraction usually determines the engineering design of the extraction plant. It is therefore, important to calculate the extraction rate process for the optimization of process parameters. Beside the knowledge of phase equilibria, the knowledge of mass transfer rates is essential for the designing of process equipment.

Such engineering data are provided in the present study for the mass transfer from fixed bed charged with powdered soybeans in supercritical carbon dioxide.

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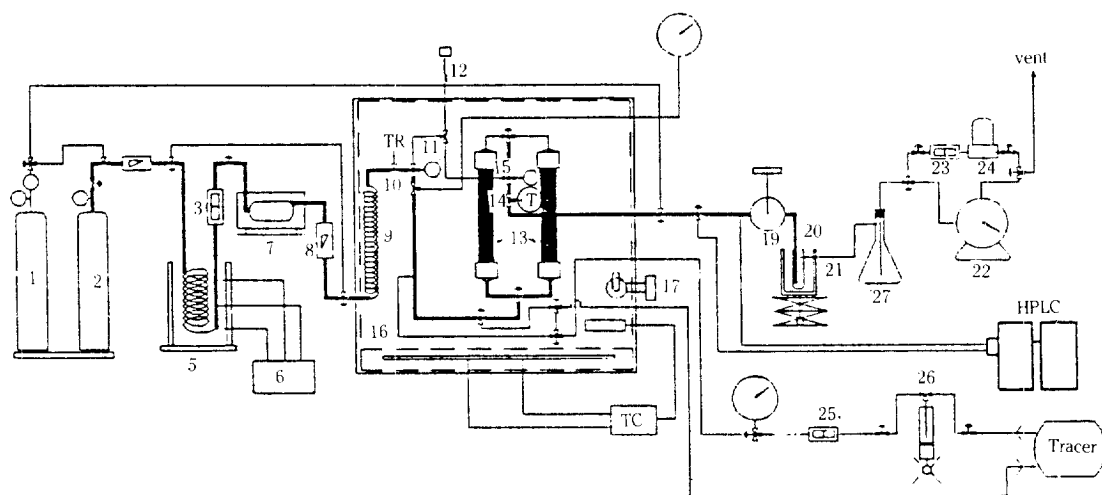


Fig. 1. Prototype mass transfer experimental apparatus for the extraction of soybean oil.

- | | | | |
|---------------------------------|--------------------------------------|-----------------------------|---------------------|
| 1. CO ₂ gas cylinder | 2. N ₂ gas purge cylinder | 3. Solid filter | 4. Check valve |
| 5. Liquefaction tank | 6. Flow cooler | 7. Solvent pump | 8. Check valve |
| 9. Preheater | 10. Thermocouple | 11. Rupture disc | 12. Emergency vent |
| 13. Extractor | 14. Thermocouple | 15. Rupture disc | 16. Air-Bath |
| 17. Fan | 18. Pressure gauge | 19. Back pressure regulator | 20. Sampling bottle |
| 21. Cold trap | 22. Wet test meter | 23. Filter | 24. Mass flowmeter |
| 25. Solid filter | 26. Hand pump | 27. Flow stabilizer | |

ide extraction.

EXPERIMENTAL

Soybeans were obtained commercially from domestic food market. The sample beans used in the experiment were washed with water, dried for 24 hours at 50°C, dehulled and prepared as the three types of sample powders; sample particles in mean particle size 0.05 cm, 0.154 cm, and 0.2828 cm by sieve test respectively.

The flow diagram of the extraction apparatus which is originally designed and constructed in the present study is shown in Figure 1. The extraction section consists of two identical fixed bed (11 mm I.D. and 260 mm height). While one of extractors is used to carry out rate experiment, the other extractor is disassembled, charged with a new bean sample, and assembled in order to save experimental time. Commercial-grade carbon dioxide from a cylinder is cooled, liquefied, and pumped to preheater which is located in air-bath and converted to carbon dioxide into its supercritical state. After measurement of pressure and temperature, the supercritical carbon dioxide solvent was passed through one of the extractor beds charged with 10 gram sample. The SCF solvent stream with extracted soybean oil is expanded to atmospheric pressure by a

back pressure regulator. The amount of separated soybean oil is collected into a preweighed sampling bottle which is located in a flow cooler. The sampling bottle contained extracted oil is detached and weighed at a given time interval. The solute-free carbon dioxide stream pass through a wet test meter and/or a mass flow meter in order to measure the flow rate.

Hardware for the extraction system described above was purchased from the following manufactures: 450 atm double-ended diaphragm pump (Milton Roy Constametric III); High pressure on-off valves, unions, metering valves, 1/4 inch tube, thermocouples and pressure gauge (HIP Instrument); 0-500 ml/min mass flow meter (Techmax Co.); a cooling bath at -40°C (Techne Co.). The air-bath (800 mmH × 650 mmW × 310 mmT) is specially designed and constructed in order to maintain the temperature accurately by using a controller with electric heater and air circulation fan. The accuracy of the air-bath is within ±0.1°C up to 120°C.

EXTRACTION RATE MODELING

In searching for an extraction rate model it may be found that the observed data are well fitted by a combined model of steady state mass transfer at high oil concentrations in soybean solid matrix, but by un-

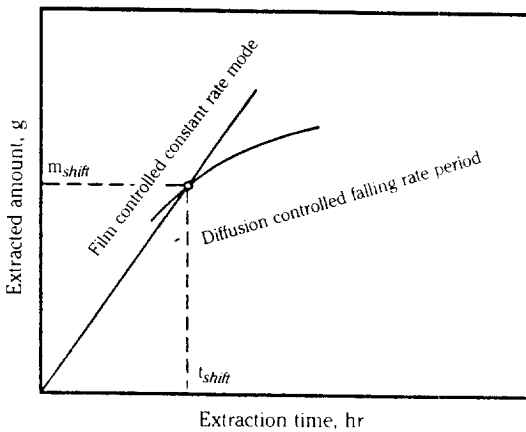


Fig. 2. Characteristics of extraction of soybean oil fitted by film and diffusion controlled mass transfer coefficients.

steady state at low concentrations as schematically shown in Fig. 2. Thus, we assumed that the extraction region controlled by constant rate follows a film controlling mass transfer and the region by falling rate follows a diffusion controlling mass transfer and the two types of mass transfer calculations were carried out individually and the results were combined to the observed mass transfer data. The boundary regions, m_{shift} and t_{shift} , where the constant rates shifted to falling rates are found from experimental data.

1. Constant Rate Mass Transfer

During the constant rate period steady state mass transfer prevails. The extracted oil quantity is expressed as;

$$m = k_g A_s V_t \Delta C_m \quad (1)$$

$$A_s = 6(1 - \phi) / d \quad (2)$$

where k_g represents the external mass transfer coefficient, A_s the specific mass transfer area, V_t the volume of the fixed bed, and ΔC_m the concentration difference of oil between the mass transfer interface and mean bulk concentration, ϕ the void volume fraction and d the mean particle diameter of the soybeans.

To find external mass transfer coefficient, Brunner [10] introduced a correlation valid for a fixed bed of spheres for a wide range of Reynolds number (Re). However, due to the limited low range of Re of our experimental conditions, we proposed a modified correlation based on the observed data as the form;

$$Sh \{1 + 1.15(1 - \phi)\} = 0.035 Re^{1/2} Sc^{1/3} \quad (3)$$

where Sh represents Sherwood's number, $k_g d / D_g$, Re the Reynold's number, $\rho u d / \mu$, and Sc the Schmit's number, $\mu / \rho D_g$. Also, k_g the external mass transfer coefficient, D_g the binary diffusion coefficient, ϕ the

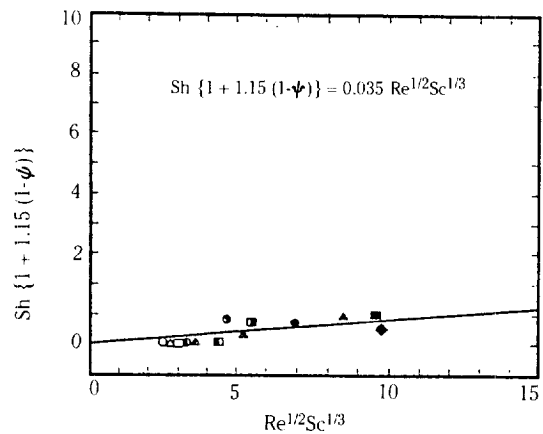


Fig. 3. Mass transfer correlation for constant extraction rate period.

Hydrodynamic conditions;

$$\circ \bar{d} = 0.05 \text{ cm}, \quad U_\infty = 0.0263 \text{ cm/sec}, D_g = 7.07 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\bullet \bar{d} = 0.05 \text{ cm}, \quad U_\infty = 0.0329 \text{ cm/sec}, D_g = 8.00 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\odot \bar{d} = 0.154 \text{ cm}, \quad U_\infty = 0.0276 \text{ cm/sec}, D_g = 7.07 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\bullet \bar{d} = 0.154 \text{ cm}, \quad U_\infty = 0.0534 \text{ cm/sec}, D_g = 7.07 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\triangle \bar{d} = 0.05 \text{ cm}, \quad U_\infty = 0.0288 \text{ cm/sec}, D_g = 8.00 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\blacktriangle \bar{d} = 0.05 \text{ cm}, \quad U_\infty = 0.0462 \text{ cm/sec}, D_g = 8.00 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\triangle \bar{d} = 0.154 \text{ cm}, \quad U_\infty = 0.0336 \text{ cm/sec}, D_g = 8.95 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\blacktriangle \bar{d} = 0.154 \text{ cm}, \quad U_\infty = 0.0909 \text{ cm/sec}, D_g = 8.95 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\square \bar{d} = 0.05 \text{ cm}, \quad U_\infty = 0.0288 \text{ cm/sec}, D_g = 7.07 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\blacksquare \bar{d} = 0.05 \text{ cm}, \quad U_\infty = 0.0625 \text{ cm/sec}, D_g = 7.07 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\blacksquare \bar{d} = 0.2828 \text{ cm}, \quad U_\infty = 0.0171 \text{ cm/sec}, D_g = 7.07 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\blacksquare \bar{d} = 0.2828 \text{ cm}, \quad U_\infty = 0.0538 \text{ cm/sec}, D_g = 7.07 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\blacklozenge \bar{d} = 0.2828 \text{ cm}, \quad U_\infty = 0.0562 \text{ cm/sec}, D_g = 7.07 \times 10^{-5} \text{ cm}^2/\text{sec}$$

void fraction. The factor $\{1 + 1.15(1 - \phi)\}$ is the term to extend Sh for single spheres to the fixed bed as introduced by Schlünder [12].

The viscosity(μ), density(ρ) and diffusion coefficient(D_g) for binary CO_2 -soybean triglyceride are estimated according to the recommendations of Reid et al. [12]. The correlation of experimental data to find the parameters in Eq. (3) is shown in Fig. 3.

2. Unsteady Mass Transfer

When we assume that the diffusion inside the solid phase controls the unsteady mass transfer from the boundary of shifting region (m_{shift} , θ_{shift}), the Ficks' second law of diffusion can be applied. As the usual case, the diffusion equation can be written for the diffusion of solute from the infinite slab with thickness of $2L$ and the initial concentration, C_o as;

$$\frac{\partial C}{\partial \theta} = D_s \frac{\partial^2 C}{\partial x^2} \quad (4)$$

$$\text{I. C.} \quad C = C_o \quad \text{at } L \leq x \leq L, \theta = 0$$

$$\text{B. C. 1} \quad C = 0 \quad \text{at } x = L \quad \theta > 0$$

$$\text{B. C. 2} \quad \partial C / \partial x = 0 \quad \text{at } x = 0 \quad \theta > 0$$

Also, the analytical solution can be expressed as;

$$\frac{C(x, \theta)}{C_o} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left\{ -\frac{D_s (2n+1)^2 \pi^2 \theta}{4L^2} \right\} \cos \frac{(2n+1) \pi x}{2L} \quad (5)$$

Eq. (5) can be converted to average extraction rate, $m(\theta)$, in stead of concentration $C(x, \theta)$ as the form;

$$\frac{m(\theta)}{m_o} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left\{ -\frac{D_s (2n+1)^2 \pi^2 \theta}{4L^2} \right\} \quad (6)$$

Where $m(\theta)$ and m_o is the amount of soluble remained in the solid and the initial amount of solute respectively after the shift time, θ_{shift} , in the case of

present study.

It is possible that when we use Eq. (6), the diffusivity in the solid phase can be obtained. However, it is very difficult to use the rigorous expression such as Eq. (6) to the case of mass transfer from natural substances since the morphology and mass transport mechanism are significantly complicate. Thus, in the present study, the experimental data are analysed by the simplified unsteady extraction rate expression of the form;

$$\frac{m(\theta)}{m_o} = \exp(-K\theta),$$

$$K \cong F_o / \theta, \quad F_o = D_s \theta / d^2 \quad (7)$$

where K is defined as a parameter and F_o represents Fourier's number and D_s the diffusivity in the solid phase. The values of parameter K are obtained from the observed rate data and from which the approximate values of diffusivity are obtained.

RESULTS AND DISCUSSION

The operating conditions adopted in the present study and the external mass transfer coefficients obtained by Eq. (3) are summarized in Table 1.

For the constant rate mass transfer calculations, the concentration of the extracted oil at the mass transfer interface was assumed to be constant as the 95% of the equilibrium concentration during the period of constant extraction rate. The amount of oil extracted, m_o , in the region that the constant rate mass transfer shifts

Table 1. Operating and hydrodynamic conditions for the mass transfer experiments

Run No.	T (°C)	P (atm)	d (cm)	U (cm/s)	C_{sat} (g/cm ³)	Re	Sc	Sh	K_g (cm/s)
1	50	272.11	0.05	0.02888	0.00717	1.562	11.56	0.0471	7.63E-5
2	50	272.11	0.05	0.04632	0.00717	2.5	11.56	0.05322	8.52E-5
3	50	374.15	0.05	0.02629	0.01877	1.327	14.01	0.02653	3.65E-5
4	50	374.15	0.05	0.0625	0.01877	3.145	14.02	0.04363	6.17E-5
5	70	272.11	0.05	0.0329	0.0065	1.919	10.71	0.03742	5.99E-5
6	70	374.15	0.05	0.02877	0.0202	1.599	12.277	0.03385	4.79E-5
7	50	204.08	0.154	0.03356	0.00247	5.757	10.03	0.2316	1.35E-4
8	50	204.08	0.154	0.09092	0.00247	15.60	10.03	0.5174	3.01E-4
9	50	204.08	0.154	0.1458	0.00247	25.01	10.03	4.739	2.75E-3
10	50	374.15	0.154	0.02758	0.01877	4.287	14.01	0.5274	2.42E-4
11	50	204.08	0.2828	0.15328	0.00247	48.28	10.03	3.8	1.20E-3
12	50	374.15	0.2828	0.0538	0.01877	15.36	14.01	0.5123	1.28E-4
13	50	374.15	0.2828	0.01706	0.01877	4.869	14.01	0.4208	1.05E-4
14	50	374.15	0.2828	0.0562	0.01877	16.04	14.01	0.4471	1.12E-4
15	50	374.15	0.154	0.0534	0.01877	8.3	14.01	0.4039	1.85E-4

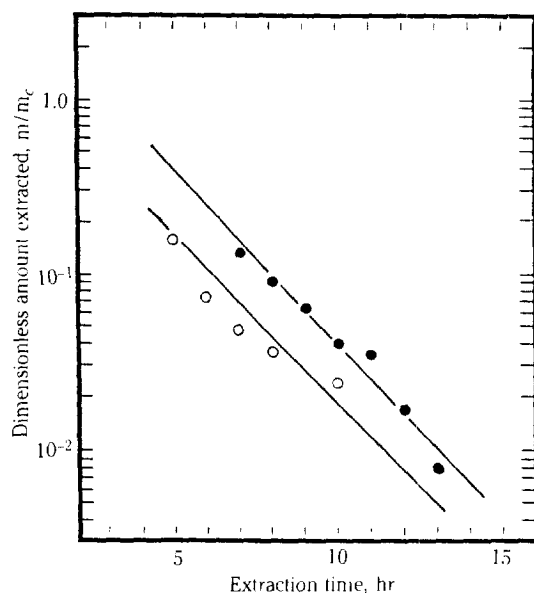


Fig. 4. Correlated mass transfer coefficients for the diffusion controlled period.

Extraction conditions;

● $T = 50^{\circ}\text{C}$, $P = 270$ atm

$U_{\infty} = 0.0288$ cm/sec, $\bar{d} = 0.05$ cm

○ $T = 50^{\circ}\text{C}$, $P = 270$ atm

$U_{\infty} = 0.0460$ cm/sec, $\bar{d} = 0.05$ cm

to unsteady rate is slightly scattered with respect to extraction conditions.

The parameter, K , in Eq. (7) for the unsteady diffusional mass transfer is fitted by experimental data as shown in Fig. 4-6. It is found that the diffusion resistance inside the solid particle is almost independent with respect to extraction pressures and flow rates, however, highly sensitive to the extraction temperature and particle size.

The diffusivities estimated by the fitted parameter K are summarized in Table 2. These results show similar trend in the order of magnitude of the values with the literature data [10].

Finally the overall amounts of extracted oil with respect to extraction time, $m(\theta)$, by using the estimated correlation parameters, k_x and D_s are shown in Fig. 7-8. It is believed that the mass transfer rate for the high pressure supercritical soybean extraction is similar to the case of drying.

There are two distinct relations between drying and SCF process. The solution equilibrium is mainly dependent on the thermodynamic properties of the solvent and mass transfer is divided into two regions. In the first region the substances to be extracted are

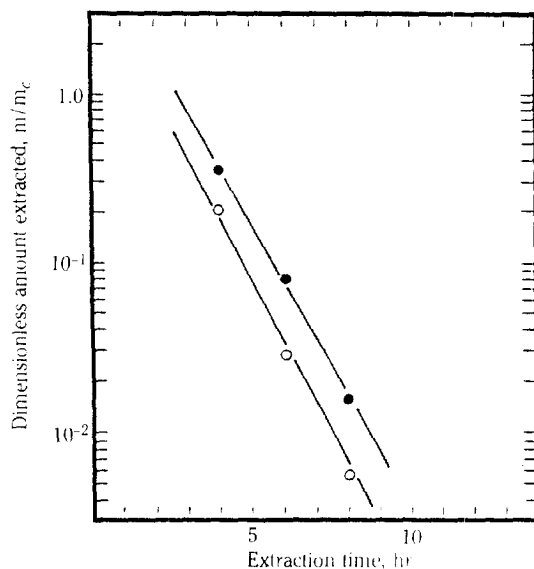


Fig. 5. Correlated mass transfer coefficients for the diffusion controlled period.

Extraction conditions;

● $T = 70^{\circ}\text{C}$, $P = 270$ atm

$U_{\infty} = 0.0330$ cm/sec, $\bar{d} = 0.05$ cm

○ $T = 70^{\circ}\text{C}$, $P = 375$ atm

$U_{\infty} = 0.0288$ cm/sec, $\bar{d} = 0.05$ cm

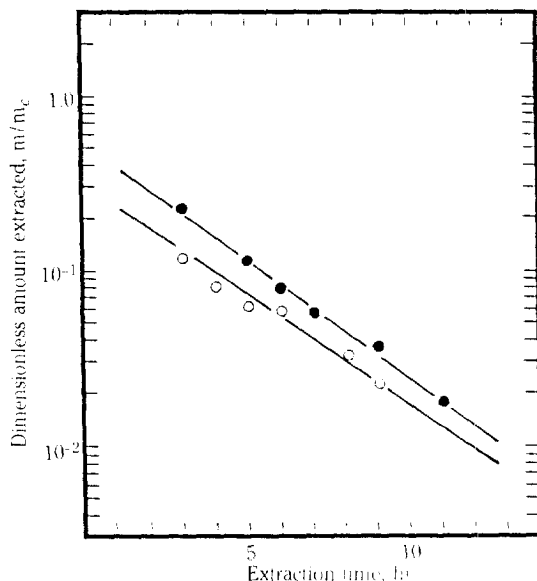


Fig. 6. Correlated mass transfer coefficients for the diffusion controlled period.

Extraction conditions;

● $T = 50^{\circ}\text{C}$, $P = 205$ atm

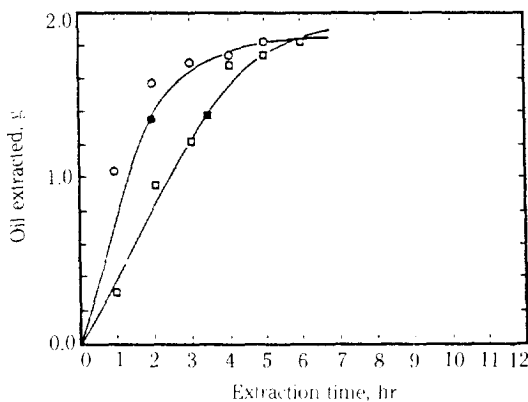
$U_{\infty} = 0.1458$ cm/sec, $\bar{d} = 0.154$ cm

○ $T = 50^{\circ}\text{C}$, $P = 375$ atm

$U_{\infty} = 0.0275$ cm/sec, $\bar{d} = 0.154$ cm

Table 2. Estimated diffusivities with respect to experimental condition

T (°C)	P (atm)	d (cm)	U (cm/s)	D_s (cm ² /s)
50	272.11	0.05	0.0288	3.20E-7
50	272.11	0.05	0.0460	3.02E-7
70	272.11	0.05	0.0330	5.71E-7
70	374.15	0.05	0.0288	6.15E-7
50	204.08	0.154	0.1458	2.02E-6
50	374.15	0.154	0.0275	1.92E-6

**Fig. 7. Extraction of soybean oil fitted by the combined mass transfer models at the constant pressure, 375 atm.**

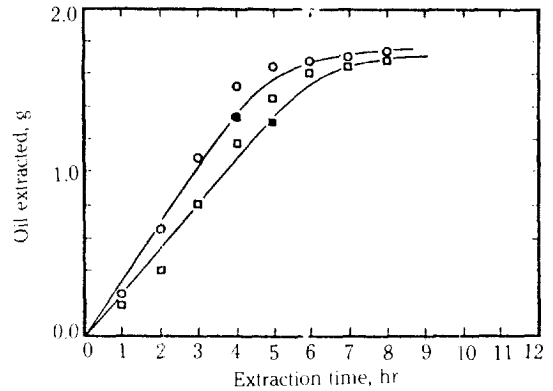
Extraction conditions;
 ○ T = 50°C, P = 375 atm
 d = 0.05 cm, U_{∞} = 0.0625 cm/sec
 □ T = 70°C, P = 375 atm
 d = 0.05 cm, U_{∞} = 0.0288 cm/sec

removed from the macropores and the particle surfaces comparable to the constant rate drying section. In the second part mass transfer is controlled by the diffusion of extractants from the micropores of the solid and other unknown properties which reduce the mass transfer rate as the type of falling rate of drying.

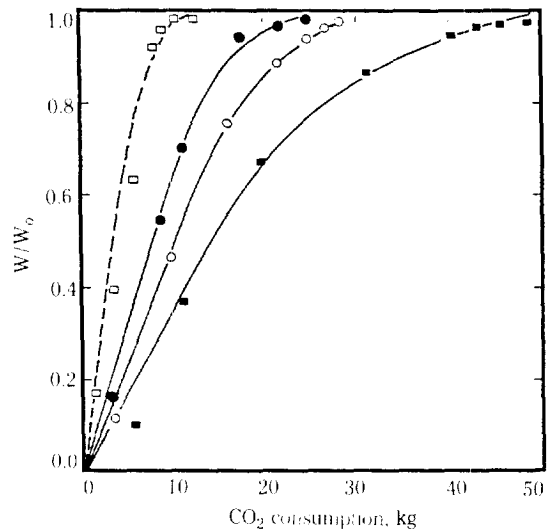
Finally, the extraction rate of soybean with respect to solvent consumptions is shown in Fig. 9 with data of Christianson et al. [7], the rate of extraction increased with increased supercritical pressure of the solvent.

CONCLUSIONS

Using a combined mass transfer calculations of film and diffusion controlled mass transport models, the extraction rate of crude oil from the dry-milled soy-

**Fig. 8. Extraction of soybean oil fitted by the combined mass transfer models at the constant temperature, 50°C.**

Extraction conditions;
 ○ T = 50°C, P = 375 atm
 d = 0.05 cm, U_{∞} = 0.0263 cm/sec
 □ T = 50°C, P = 270 atm
 d = 0.05 cm, U_{∞} = 0.0462 cm/sec

**Fig. 9. Extraction curves for the extraction of crude oil from dry-milled soybeans with supercritical carbon dioxide at a solvent flow rate 340 ml/min and a temperature, 50°C.**

Present study:
 ■ 272 atm
 ● 374 atm
 Data reported by Christianson et al. (1984):
 □ 544 atm
 ○ 340 atm

bean charged in a small size of fixed bed are carried out. The results of the calculation show a good corre-

spondence to experimental results.

The hydrodynamic correlation [Eq. (3)] of constant rate mass transfer coefficient proposed in the present study was obtained for a fixed geometry, eg., the fixed bed diameter and height. When it taking into account this limitation, the mass transfer correlation proposed for the constant rate period can be used for the purpose of process calculations.

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NOMENCLATURE

A_s	: specific mass transfer area, [m^2/m^3]
C_i	: solute concentration in solid surface, [g/m^3]
C_∞	: solute concentration in the supercritical solvent, [g/m^3]
ΔC_m	: concentration difference of oil between the mass interface and mean bulk concentration, [g/m^3]
d	: mean particle diameter of soybean solid, [mm]
D_g	: binary diffusion coefficient for binary CO_2 -soybean triglyceride, [cm^2/s]
D_s	: diffusivity in the solid phase, [cm^2/s]
F	: flow rate of carbon dioxide at standard state, [m^3/min]
F_o	: Fourier's number
k_g	: external mass transfer coefficient, [m/sec]
$m(\theta)$: amount of solute remained in the solid, [g]
m_o	: initial amount of solute in the solid, [g]
P	: pressure, [atm]
T	: temperature, [$^\circ\text{C}$]
U	: superficial velocity, [cm/sec]
V_t	: total effective volume of soybean bed, [m^3]

Greek Letters

ϕ	: void volume of bed
θ	: extraction time, [hr]

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