PAPER

SUPERCRITICAL FLUID EXTRACTION OF EVENING PRIMROSE OIL KINETIC AND MASS TRANSFER EFFECTS

ESTRAZIONE CON FLUIDI SUPERCRITICI DELL'OLIO DI ENAGRO STUDIO DELLA CINETICA E DEL TRASPORTO DI MATERIA

J. W. KING*, M. CYGNAROWICZ-PROVOST[1], and F. FAVATI[2]

Food Quality & Safety Research Unit - National Center for Agricultural
Utilization Research - Agricultural Research Service, U.S. Department
of Agriculture - 1815 N. University Street - 61604 Peoria, IL, USA
[1]Office of Device Evaluation - Center for Device and Radiological Health -
U.S. Food & Drug Administration - 20850 Rockville, MD, USA
[2]Dipartimento di Biologia DBAF - Università della Basilicata - 85100 Potenza, Italy
*Corresponding author: J. W. King - Tel: (309) 681-6203 - Fax: (309) 681-6686 -
E-Mail: KINGJW@NCAUR1.NCAUR.GOV

ABSTRACT

For processing utilization, super-critical fluid extraction requires a thorough understanding of the relevant phase equilibria, mass balance, and kinetic factors that impact on the successful recovery of extracts. In this study, we have determined the factors contributing to the kinetics and mass transfer of evening primrose oil (EPO) from its ground seed matrix, to supplement previously determined solu-

RIASSUNTO

L'utilizzazione a livello industriale del processo di estrazione con fluidi allo stato supercritico richiede una approfondita conoscenza dei pertinenti equilibri di fase, dei bilanci di materia e delle cinetiche che influenzano il recupero degli estratti. Al fine di integrare i dati di solubilità ed alcuni dati analitici precedentemente determinati sull'olio di enagro estratto con CO_2 supercritica, in questo lavoro sono stati

- Key words: evening primrose, extraction, kinetics, mass transfer, oilseed, supercritical fluid. -

bility data and chemical characterization of this oil moiety. The effect of extraction pressure, temperature, fluid density, and flow rate (over a threefold range) have been ascertained; the flow rate effect being correlated in terms of the extracted seed mass and similar data from the literature performed on a pilot and production plant scale. Using a dual mass transfer model, we have correlated the theory with extraction experiments conducted over a pressure range from 20-70 MPa, temperatures from 40°-60°C, and carbon dioxide flow rates in the interval from 9-27 g/min. The agreement between the model calculations and experimental data is excellent allowing potential use of the data in process design.

studiati i fattori che influenzano il trasporto di materia e la cinetica di estrazione di tale olio estratto con CO_2 supercritica a partire da semi macinati. In questo ambito sono stati valutati gli effetti causati dalla pressione e dalla temperatura di estrazione, nonché quelli causati dalla variazione della densità e della portata del fluido estraente. L'effetto della variazione della portata è stato studiato in relazione alla quantità di estratto recuperata ed alla massa di semi estratta; i dati sperimentali sono stati anche confrontati con dati simili riportati in letteratura per estrazioni condotte su impianti pilota o di produzione. Utilizzando un modello duale di trasporto di materia, i dati teorici sono stati messi in relazione con i dati sperimentali ottenuti operando a pressioni e temperature comprese negli intervalli 20-70 MPa e 40°-60°C, e con portate di CO_2 comprese nell'intervallo 9-27 g/min. La concordanza fra i dati della modellazione e quelli ottenuti sperimentalmente è risultata eccellente, e ciò potrebbe consentire l'uso di tali dati nella progettazione del processo di estrazione su scala industriale.

INTRODUCTION

Supercritical fluid extraction (SFE) has matured considerably as a processing technique over the last two decades due to fundamental thermodynamic, phase equilibria, and mass transfer studies, which have provided a basis for design of industrial scale extraction processes. For the extraction of oils from seeds and other natural products, SFE provides the processor with the ability to alter the solvent power of the fluid, and hence its selectivity, by varying the fluid's density as a function of extraction pressure and temperature. This factor, coupled with the superior mass transport properties exhibited by solutes dissolved in supercritical media, assures rapid removal of solutes from natural product matrices.

Studies on the solubility of seed oils in our laboratory (FRIEDRICH et al., 1982; SNYDER et al., 1984) as well as others (STAHL et al., 1980; 1983) have provided a basis on which to design processes for the rapid and efficient removal of oil from a variety of seed and natural product matrices (KING and LIST, 1996). Other investigators in the 1980's (FATTORI, et

al., 1988; EGGERS et al., 1985; EGGERS and SIEVERS, 1989a) provided preliminary information on the kinetics of oil extraction, which, along with basic mass transfer data for solutes in supercritical fluids (KING et al., 1983; LAHIERE and FAIR, 1987; BARTOLOMEO et al., 1990; GOTO et al., 1990; LIM et al., 1990; ZEHNDER and TREPP, 1993), are required for the successful design of a supercritical fluid extraction process (RIZVI et al., 1986).

In the absence of the latter data, modelling studies of the SFE process become important since they provide the basis of optimizing the extraction process as well as a guide to process scaleup. Early research by BRUNNER (1984) explored the fundamental variables that influenced the mass transfer of solutes from solid substrates and provided the basis for several other modelling studies involving oilseed substrates (HONG et al., 1990; SAKAKI et al., 1990; FAVATI and FLORENTINI, 1993; SOVOVA, 1994; COELHO et al., 1995; STASTOVA et al, 1996) which were to follow. More recently, SFE kinetics have been interpreted in terms of a more fundamental physicochemical approach (BARTLE et al., 1990; GOTO et al., 1996) or have employed chromatographic models to describe oil depletion from packed beds of seed (GOODRUM et al., 1996). REVERCHON (REVERCHON, 1992; REVERCHON and OSSEO, 1993; POLETTO and REVERCHON, 1996), in particular, has been very active in testing alternative models for the SFE of oilseeds and other natural product matrices.

Previously, we have reported on the solubility of evening primrose oil (EPO) in supercritical carbon dioxide (SC-CO$_2$) and characterized its extraction from the seed (FAVATI et al., 1991a,b). Others have also employed SC-CO$_2$ for the extraction of EPO (LEE et al., 1994) and further characterized the resultant oil with respect to its thermal stability (ANDRICH et al., 1994). The importance and commercial value of EPO is related to its gamma-linolenic acid content (HUANG and MILLS, 1996) and use as a nutraceutical and curative agent (FAVATI et al, 1991a,b; FANTOZZI et al., 1993); hence it is a seed oil of high value whose economic value is well matched with the attendant costs of conducting SFE.

In this paper, we have extended our previous studies to determine the kinetic and mass transfer dependency of the extraction of EPO with SC-CO$_2$, and modelled the extraction rates using the methods of HONG, et al. (1990) and BRUNNER (1984). Interpretation of the SFE rate of EPO from the seed matrix can be facilitated with the aid of concepts advanced by EGGERS (EGGERS et al, 1985; EGGERS and SIEVERS, 1989b), and these have been utilized to generalize the extraction rate dependency on CO$_2$ pressure and flow rate. Extraction models such as those advocated here, have been employed by others for the SFE of fungal lipids (CYNAROWICZ-PROVOST et al., 1995; CYNAROWICZ-PROVOST, 1996), algae lipids (MENDES et al., 1996), and commodity seed oils (YOO and HONG, 1996). As we shall subsequently show, they work equally well for modelling the SFE of EPO.

MATERIALS AND METHODS

Experimental

The experimental apparatus used in these extraction studies has been previously described (FAVATI et al., 1991a,b) and will not be repeated here. The extraction vessel consisted of a 316 SS tube, pressure rated to 76 MPa, having dimensions of 1.75 cm i.d. x 30 cm. in length. Tests were conducted on 50 grams of evening primrose seeds that had been ground to pass a 0.355 mm sieve. The evening primrose seeds were obtained from Efamol Ltd. (Guilford, England). Their oil content was 26.1% by weight on a dry basis; gamma-linolenic acid represented 10% by weight of the total fatty

acid content. Both oil and moisture content of the seeds were determined using standard AOCS methods (AOCS, 1989).

Extractions were performed at 20, 30, 50 and 70 MPa, over a temperature range of 40°-60°C. A fixed quantity of CO_2 (2.5 kg) was used for each experiment with extracts being collected after 125, 250, 375, 500, 750, 1,000, 1,500, 2,500 g of CO_2 had passed through the seed bed. Different CO_2 flow rates were also employed during this study: 9, 18, 27 g/min. The CO_2 flow rate was determined with the aid of a Micro Motion Model D6 (Boulder, CO, USA) mass flow meter placed immediately before the gas booster pump. These CO_2 mass values were also checked by measuring the gas volume utilized with a dry test meter (Singer Model DTM-115, American Meter Division, Philadelphia, PA, USA), placed after the receiver vessel, and then converting the differential volume of CO_2 that was measured to a mass basis.

Since a small amount of water was coextracted with the EPO, the collected extracts were diluted with anhydrous ethyl ether (J.T. Baker, Phillipsburg, NJ, USA), and dried over sodium sulfate (EM-Science, Gibbstown, NJ, USA). The extraction yields were then determined by gravimetry after removing the solvent under vacuo.

Calculations

The calculation of the theoretical extraction curves utilized the models developed by HONG et al. (1990) and BRUNNER (1984), in which the SFE is partitioned into two sectors: one in which the rate of oil extraction is constant, followed by a second sector where the oil extraction is governed by diffusion out of the seed matrix. The first part of the model assumes that steady state mass transfer is applicable and that it can be used to represent values obtained during the initial period of the SFE, where there is a linear dependence of the amount of

oil extracted with the mass of the supercritical fluid. The second part of the model applies to the SFE at longer extraction times, where the unsteady state predominates, and mass transfer is limited by diffusion.

Using the convention of BRUNNER (1984) and HONG et al (1990), the amount of oil extracted per unit time during the constant rate period may be expressed as:

$$m = k_g A_s \Delta C_m \qquad (1)$$
and
$$A_s = 6 (1 - \Psi) V_t/d \qquad (2)$$

where k_g is the external mass transfer coefficient (m/s), A_s is the specific mass transfer area (m²), Ψ is the void volume fraction, V_t is the total volume in the bed (m³), d is the particle diameter (m), and ΔC_m is the concentration difference between the oil at the mass transfer interface and in the bulk phase in g/m³.

The required external mass transfer coefficient, k_g, is computed using the following correlation:

$$Sh\{1 + 1.5(1 - \Psi)\} = m \, Re^{1/2}Sc^{1/3} \qquad (3)$$

where Sh = Sherwood number = $k_g d/D_g$
   Re= Reynolds number = $\rho u d/\mu$
   Sc = Schmidt number = $\mu/\rho D_g$
   D_g = Binary diffusion coefficient
   (m²/s)

The required Sherwood, Reynolds and Schmidt numbers were computed for the experimental data points and are presented in Table 1 for various pressures, temperatures and fluid velocities, u. Utilizing the computed values for Re, Sh, and Sc and estimates for V_t, Ψ, and d (see Table 1), the mass transfer coefficient, k_g, can be determined using eq. 3. Density (ρ) values for SC-CO_2 were obtained from KENNEDY (1954), while the relevent fluid viscosities (μ) utilized were taken from VUKALOVICH and ALTUNIN (1968). The binary diffusion coefficient

Table 1 - Mass transfer coefficients for the constant rate period of extraction.

Temp.	Pres.	u(m/s)	Re	Sc	Sh	K_g(m/s)
40	20	0.00148	0.507930	103.00230	0.013749	3.89E-07
40	30	0.00138	0.504045	96.78308	0.012554	3.55E-07
40	50	0.00126	0.489964	90.90668	0.011773	3.33E-07
40	70	0.00119	0.475426	88.48162	0.011552	3.27E-07
50	20	0.00159	0.587914	95.60331	0.011219	3.17E-07
50	30	0.00143	0.575896	87.77710	0.013151	3.72E-07
50	50	0.00130	0.563522	81.54964	0.011476	3.25E-07
50	70	0.00122	0.544743	79.16947	0.011234	3.18E-07
60	20	0.00712	0.685789	88.65987	0.017044	4.28E-07
60	30	0.00151	0.677723	78.76158	0.014687	4.15E-07
60	50	0.00133	0.649383	72.40026	0.011815	3.34E-07
60	70	0.00125	0.630234	70.11289	0.011879	3.36E-07
40	20	7.4E-05	0.025397	103.00230	0.006796	1.92E-07
40	20	0.00148	0.507930	103.00230	0.014037	3.97E-07
40	20	0.00222	0.761896	103.00230	0.021429	6.06E-07
40	30	0.00069	0.252022	96.78308	0.006426	1.82E-07
40	30	0.00138	0.504045	96.78308	0.015414	4.36E-07
40	30	0.00206	0.752415	96.78308	0.023701	6.70E-07
50	25	0.00149	0.582746	90.50629	0.014226	4.02E-07
50	40	0.00135	0.569766	83.75813	0.012632	3.57E-07
50	60	0.00125	0.551331	80.14702	0.013036	3.09E-07
60	50	0.00067	0.337303	70.21734	0.006202	1.75E-07
60	50	0.00133	0.669571	70.21734	0.011049	3.13E-07
60	50	0.00200	1.006874	70.21734	0.025569	7.23E-07
60	70	0.00062	0.312596	70.11289	0.006637	1.88E-07
60	70	0.00125	0.630234	70.11289	0.011534	3.26E-07
60	70	0.00188	0.947871	70.11289	0.020885	5.91E-07

The following parameters were used for calculation of mass transfer coefficients: $\Psi = 0.04$, d (particle diameter = 0.0002828 m, $D_g = 8.0 \times 10^{-9}$ m^2/s, $V_t = 7.31 \times 10^{-5}$ m^3, Temp. (°C), Pres. (MPa)

was estimated to be 8.0E-9 m^2/s, based on an average of values given by HONG (1990) for soybean oil in CO_2. Such an approximation is reasonable since the composition of EPO is similar to that of soybean oil, a triglyceride-based seed oil.

Implicit in the derivation of eq. 1 is that concentration of extracted oil at the mass transfer interface is constant. By anology with HONG et al.(1990), ΔC_m was assumed to be 95% of the equilibrium value. The experimental values for Re, Sc and Sh were plotted (Fig. 1), and linear regression used to determine the con-

stant m in eq. 3. HONG et al. (1990) reported a value for m equal to 0.035; in this study, m was found to be 0.2548. As noted in Fig. 1, the calculated values are somewhat scattered, yielding a regression coefficient of only 0.59. Despite this correlation, the computed mass transfer coefficients were found to be more then adequate to model the steady state sector of the extraction curves for EPO in SC-CO_2.

Inspection of the computed values for k_g in Table 1 indicate that external mass transfer coefficient increases with increasing fluid velocity. The values of k_g

Table 2 - Diffusivities for diffusion controlled region.

u(m/s)	Temp. (°C)	Pres. (MPa)	D_s (m²/s)
0.00126	40	50	3.04E-12
0.00119	40	70	3.60E-12
0.01300	50	50	2.88E-12
0.00122	50	70	3.68E-12
0.00133	60	50	4.64E-12
0.00125	60	70	4.96E-12
0.00067	60	50	4.16E-12
0.00133	60	50	4.64E-12
0.00200	60	50	7.28E-12
0.00062	60	70	7.60E-12
0.00125	60	70	4.96E-12
0.00188	60	70	6.88E-12
0.00135	50	40	1.60E-12
0.00135	50	60	8.00E-12

computed for the EPO extractions are an order of magnitude higher than those reported for soybean oil at the same particle diameter. This can be attributed to the higher flow rates utilized in this study.

For the unsteady state mass transfer sector, we have used the diffusion equation given by HONG et al (1990), where:

$$m(t)/m_o = A \exp(-Kt) \qquad (4)$$

and
$$K = F_o/t$$
$$F_o = D_s t/d^2$$

Here, m(t) is the amount of oil that remains in the seeds at time t, m_o is the initial amount of oil in the seed bed at time zero, F_o is the Fourier number that results from a series solution to the original differential equation, and D_s is the diffusivity in the solid phase. The parameters A and K can be determined by linear regression of the experimental data in the diffusion-controlled sector. The computed diffusivities are approximately the same for all of the experimental runs, and do not exhibit the sensitivity to temperature noted by HONG et al. (1990).
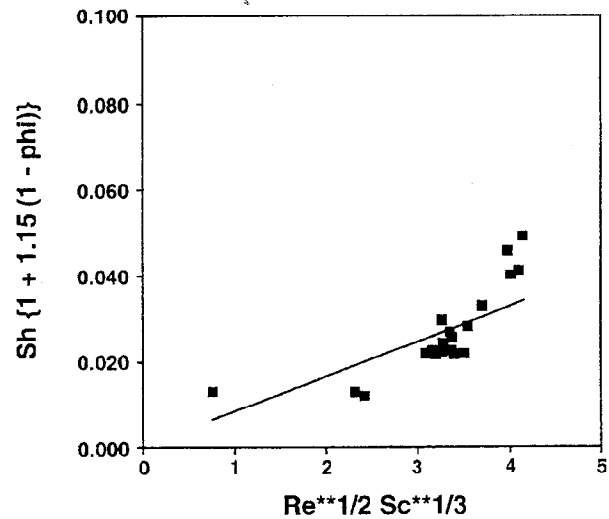

Fig. 1 - Dimensionless number correlation for obtaining mass transfer coefficient for constant rate sector of extraction curve.

RESULTS AND CONCLUSIONS

The rate of extraction of EPO from the respective seeds using SC-CO$_2$ can best be understood by examining its dependence on several processing variables. In Fig. 2, the weight fraction of oil removed from the seeds per total mass of oil collected and CO$_2$ used is plotted as a func-

tion of the mass of CO_2 passed through the seed bed for four different extraction pressures at 50°C. It is apparent from the differential extraction yields in Fig. 2, that a CO_2 pressure of 20 MPa will require a considerable larger mass of CO_2 to complete the extraction. Increasing the extraction pressure diminishes the total CO_2 mass requirements for extraction, and as shown for practical purposes, only 0.5 kg of CO_2 is needed to remove most of the EPO from the seed bed. The results shown in Fig. 2 are a direct consequence of the influence of the CO_2 density on EPO solubility in the fluid phase.

As shown in Fig. 3, the oil solubility increases with temperature in °K for each of the fitted lines representing approximating a constant fluid density, similar to the trends recorded by FATTORI et al. (1988). The data trend in Fig. 3 clearly shows that fluid density is the controlling variable with respect to oil solubility and that by selecting different pressures and temperatures, the processor can enhance or diminish oil solubility in the SC-CO_2 phase.

It has previously been shown (FAVATI et al., 1991a,b) that the flow rate depen-

dence of seed oil extraction can be expressed as a function of the mass of extract(oil)/mass of extracted seed as a function of extraction time. Such plots clearly indicate the quantity of extract that one can expect as a function of extraction time and the advantages attendant with using higher CO_2 flow rates. The dependence of extraction yield for a given mass of substrate can be normalized by dividing by the mass of seeds in the extraction vessel, i.e., to eliminate the time dependence of oil yield by plotting mass of extract/mass of seeds versus mass of CO_2 used/mass of seed after EGGERS (1989a). This is shown in Fig. 4 for the extraction of EPO at 20 MPa and 313°K for three different CO_2 flow rates (9, 18, 27 g/min). The superimposition of each curve is consistent with previous results noted at 70 MPa and 333°K (FAVATI et al., 1991a,b). Fig. 4 also indicates that the EPO yield is not appreciably effected by the quoted three-fold difference in flow rate, the m_{ex}/m_{seeds} being equal to 16.9 at approximately m_{CO2}/m_{seeds} equal to 53.

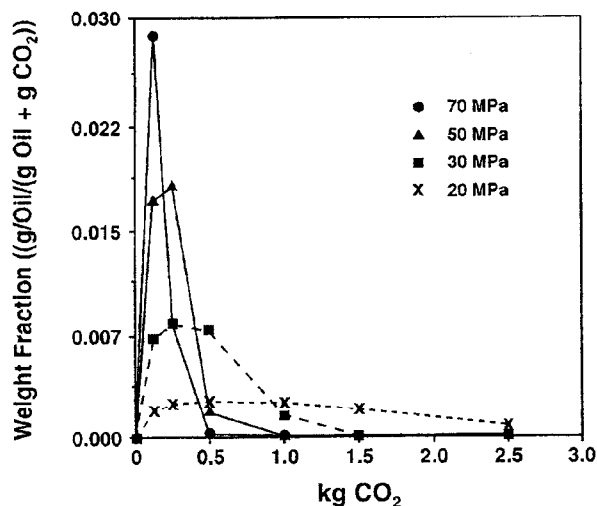It is interesting to use the above approach to contrast the difference in extraction efficiency of EPO conducted on

Fig. 2 - Weight fraction of extracted oil vs. kg SC-CO_2 for the SC-CO_2 extraction of EPO at 50°C as a function of pressure.
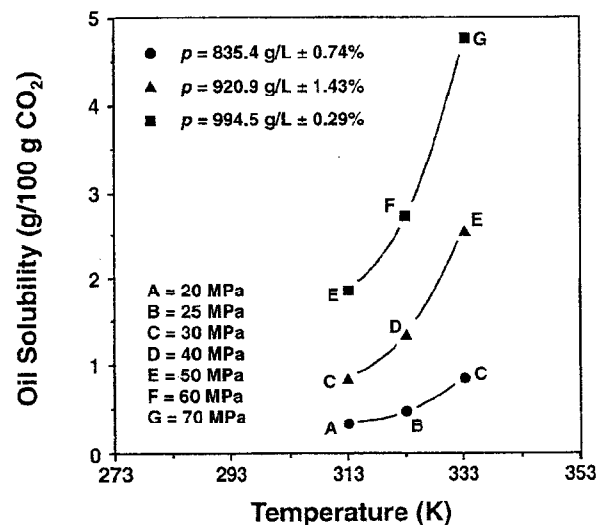
Fig. 3 - Weight fraction of extracted oil vs. extraction temperature as a function of SC-CO_2 density.

an experimental extractor versus studies performed on systems defined as a "pilot plant" or production plant (EGGERS and SIEVERS, 1989b). This comparison has been made by EGGERS and SIEVERS (1989a,b) and CLAVIER et al. (1995) and we have used the former's data on EPO extraction for comparison purposes. Figure 5 shows our extraction results at

Fig. 4 - EPO extraction yields at 20MPa and 313°K. Effect of using different CO_2 mass flow rates.

30 MPa and 40°C (circles) with those found by EGGERS and SIEVERS (1989a) for pilot and production scale plant runs. The plots of $m_{ex}/\dot{m}_{seeds}$ versus m_{CO2}/m_{seeds} show that there is good agreement between production plant run conducted under the same extraction conditions and our data, up to a m_{CO2}/m_{seeds} of approximately 30. The data for EGGERS pilot plant run tends to be somewhat lower than our experimental values over most of the encompassed range of m_{CO2}/m_{seeds} values. We have no rationale for this disagreement, however it is encouraging to note that overall, the results from experimental, pilot, and production plant runs are similar in magnitude, thereby allowing extrapolation of experimental data as a guide for optimizing plant scaleup. However, EGGERS and SIEVERS (1989 b) have cautioned against scaling up at constant specific mass flows (m_{CO2}/m_{seeds}) to rationalize the differences they have observed in going from pilot to production plant operation.

To compare the calculated extraction rate curves, derived from the theory and calculations discussed in the Materials and Methods section with experimental
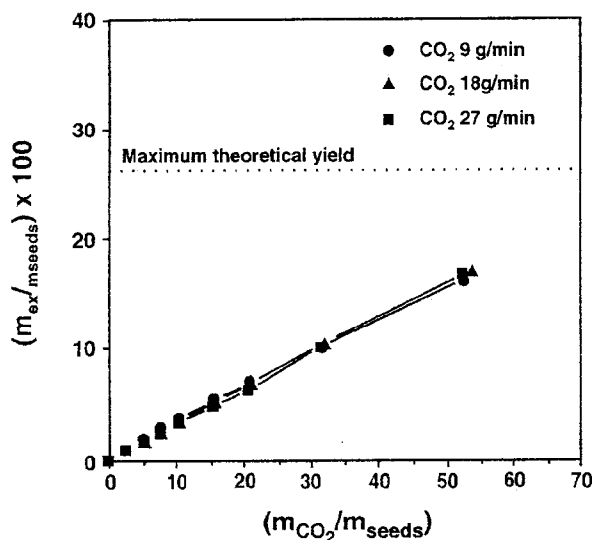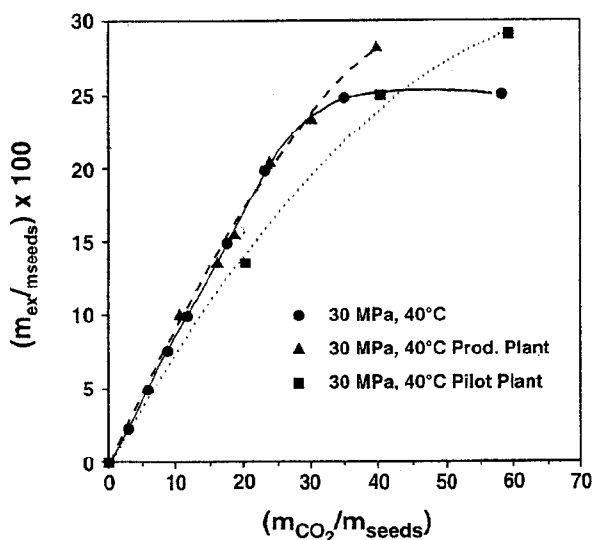

Fig. 5 - Comparison of extraction rate curves for the SC-CO_2 processing of EPO on a laboratory, and production and pilot plant. (Data from EGGERS and SIEVERS, 1989a).
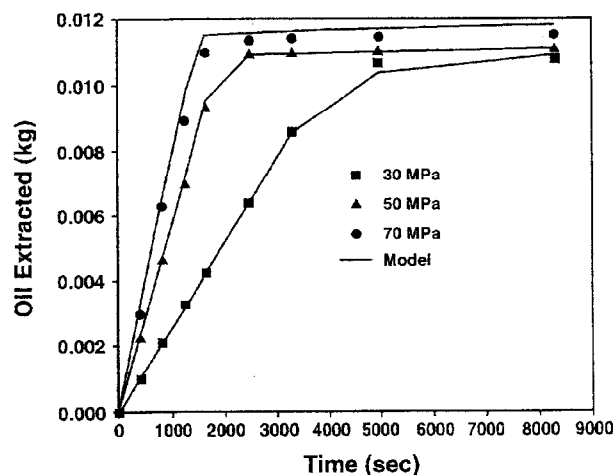

Fig. 6 - Extraction rate curves for EPO at 40°C as a function of extraction pressure - Experimental data vs. predicted extraction curve.

data, we plotted the mass of oil extracted versus time for extractions at several temperatures and CO_2 flow rates. As shown in Fig. 6, the incremental experimental data points have been plotted for three different pressures and the extraction curve calculated from theory superimposed for each set of data corresponding to the different extraction pressures. As indicated in Fig. 6, the agreement between experiment and theory is quite encouraging at all three extraction pressures.

To further test the agreement between theory and our experimental results, we have plotted mass of EPO recovered versus time at both 50° and 60°C for three different extraction pressures as shown in Figs. 7 and 8. Once again, the agreement between the experimental data points, regardless of pressure, and the curve from the extraction model is excellent, lending credence to the concepts and calculations incorporated for describing both the mass transfer and diffusion-controlled sectors of the extraction rate curves. Only in the 30 MPa case in Fig. 7 does there appear to be a small disagreement between theory and experiment, most likely due to experi-

mental error. Results for extractions at 20 MPa were not plotted since at this low extraction pressure the curves are linear and are of limited interest in terms of confirming the agreement between the employed model and experimental data.

Similarly, plots were also constructed for the three different flow rates utilized in extracting the EPO for several combinations of extraction pressure and temperature (Figs. 9-11). For the SFE conducted at a CO_2 flow of 9g/min, the agreement between theory and the experimental data is excellent as shown in Fig. 9. Excellent agreement between the extraction data and model curve is also obtained for the extractions conducted at a flow rate of 18g/min of CO_2 as noted in Fig. 10. For the final case examined, extraction of EPO using a CO_2 flow of 27 g/min, there appears to be an error in the derived experimental data in the diffusion-controlled regime of the extraction conducted at 50 MPa and 60°C, since the calculated extraction curve from the model parallels the results found in the previous figures (i.e., the diffusion controlled sector of the extraction curve for 50 MPa is below that calculated for 70 MPa). Again, the data and model curve
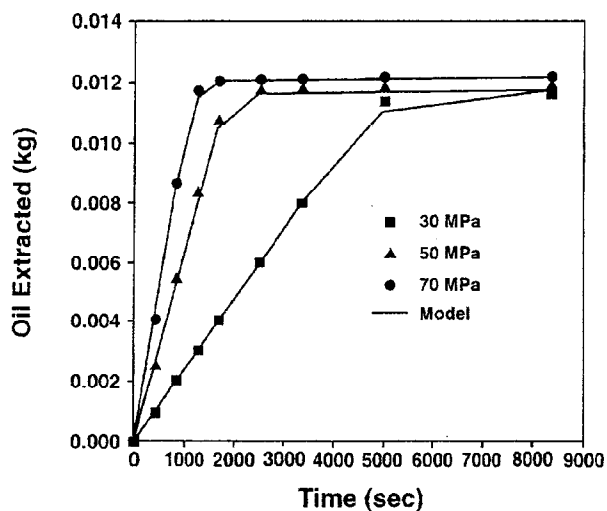

Fig. 7 - Extraction rate curves for EPO at 50°C as a function of extraction pressure - Experimental data vs. predicted extraction curve.
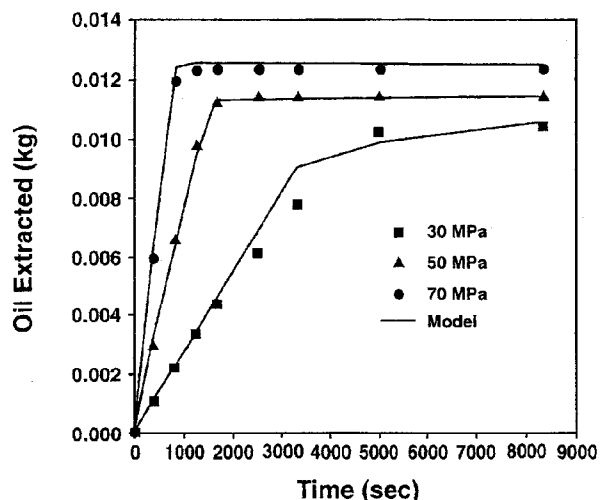
Fig. 8 - Extraction rate curves for EPO at 60°C as a function of extraction pressure - Experimental data vs. predicted extraction curve.

are in good agreement for the extraction conducted at 70 MPa and 60°C, suggesting that the data determined at 50 MPa and 60°C are too high. This appears to be a good example of how theory can be used to diagnose errors in experimentally-derived data.

In conclusion we feel that the results presented in this study and their interpretation in terms of theory and the parameters that control the SFE of EPO adequately describe the extraction kinetics and its dependance on mass transfer and kinetic factors, such as diffusion. We have verified that CO_2 density plays a predominat role in controlling EPO solubility in SC-CO_2, and that for the range covered by our experimental data, a three-fold increase in CO_2 flow rate does not substantially reduce the EPO concentration solubility or mass recovered in the steady state region of extraction.

Our laboratory extraction results are in general agreement with extraction trends determined under the same pressure and temperature conditions on a pilot or production plant noted by other investigators. However subtle differences do exist as one transcends from the steady state to non-steady state regime of extraction, hence the caution advocated by POLETTO and REVERCHON (1995) should be heeded with respect to scaleup of the extraction. Utilization of the binary mass transfer model of HONG et al. (1990) has been found to produce excellent agreement with our experimentally-derived extraction curves at different pressures, temperatures and flow rates.
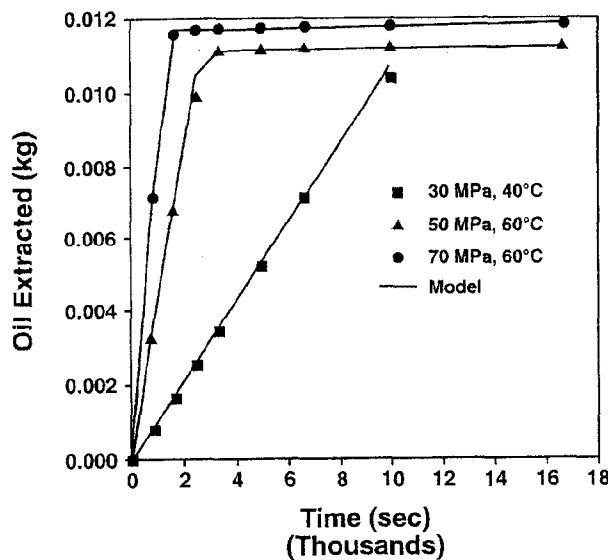

Fig. 9 - Extraction rate curves for EPO at 9 g/min CO_2 flow for various pressures and temperatures - Experimental data vs. predicted extraction curve.
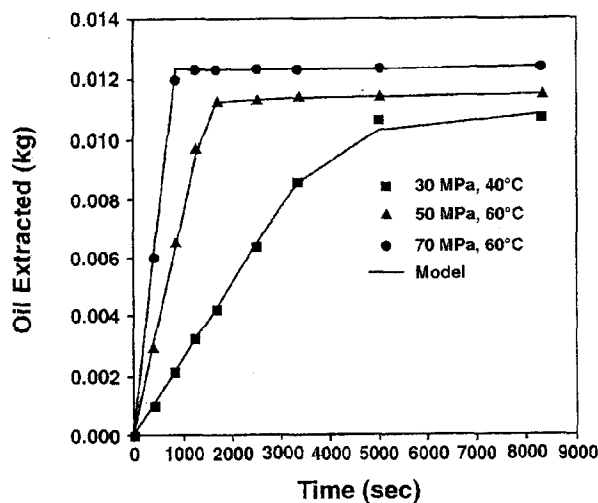

Fig. 10 - Extraction rate curves for EPO at 18 g/min CO_2 flow for various pressures and temperatures - Experimental data vs. predicted extraction curve.
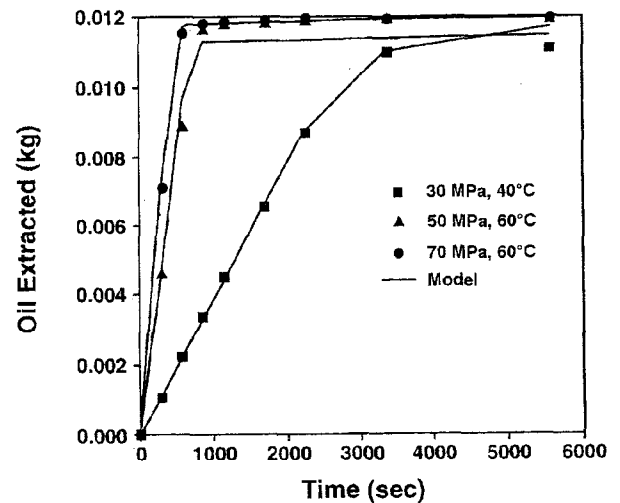

Fig. 11 - Extraction rate curves for EPO at 27 g/min CO_2 flow for various pressures and temperatures - Experimental data vs. predicted extraction curve.

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the products to the exclusion of others that may also be suitable.

REFERENCES

Andrich, G., Zinnai, A., Balzini, S., Silvestri, S., Fiorentini, R., and Galoppini, C. 1994. Thermal oxidative stability of evening primrose oil extracted with supercritical carbon dioxide and hexane. Ital. J. Food Sci. 6:217.

AOCS. 1989. "Official Methods and Recommended Practices", 4th ed. American Oil Chemists' Society, Champaign, IL, USA.

Bartle, K.D., Clifford, A.A., Hawthorne, S.B., Lagenfeld, J.J., Miller, D.J. and Robinson, R. 1990. A model for dynamic extraction using a supercritical fluid. J. Supercrit. Fluids 3:143.

Bartolomeo, G., Bertucco, A. and Guarise, G.B. 1990. Mass transfer in a semibatch supercritical fluid extraction contractor for liquid mixtures. Chem. Eng. Comm. 95:57.

Brunner, G. 1984. Mass transfer from solid material in gas extraction. Ber. Bunsenges. Phys. Chem. 88:887.

Clavier, J.Y., Majewski, W. and Perrut, M. 1995. Extrapolation from pilot plant to industrial scale SFE: A case study. In "I Fluidi Supercritici e le Loro Applicazioni". I. Kikic and P. Alessi (Eds.). p. 107. Proceedings of the 3rd Italian Congress on Supercritical Fluids, Grignano, Italia, 3-6 Settembre.

Coelho, L.A.F., Stuart, G.R., Oliveira, J.V. and D'Avila, S.G. 1995. Extraction of Brazilian basil oil using carbon dioxide at high pressures: Experimental data and process modeling. In "I Fluidi Supercritici e le Loro Applicazioni". I. Kikic and P. Alessi (Eds.). P. 115. Proceedings of the 3rd Italian Congress on Supercritical Fluids, Grigano, Italia, 3-6 Settembre.

Cygnarowicz-Provost, M., O'Brien, D.J., Boswell, R.T. and Kurantz, M.J. 1995. Supercritical-fluid extraction of fungal lipids: Effect of cosolvent on mass transfer rates and process design and economics. J. Supercrit. Fluids 8:51.

Cynarowicz-Provost, M. 1996. Design and economic analysis of supercritical fluid extraction processes. Ch. 7. In "Supercritical Fluid Technology in Oil and Lipid Chemistry". J.W. King and G.R. List (Eds.), p. 155. American Oil Chemists' Society Press, Champaign, IL, USA.

Eggers, R., Sievers, U. and Stein. W. 1985. High pressure extraction of oilseed. J. Am. Oil Chem. Soc. 62:1222.

Eggers, R. and Sievers, U. 1989a. Processing of oilseed with supercritical carbon dioxide. J. Chem. Eng. Japan 22:641.

Eggers, R. and Sievers, U. 1989b. Current state of extraction of natural materials with supercritical fluids and developmental trends. Ch. 30. In "Supercritical Fluid Science and Technology". K.P. Johnston and J.M.L. Penninger (Eds.), p. 478. American Chemical Society, Washington, DC.

Fantozzi, P. Montanari, L., DeStefano, A. and Sensidoni, A. 1993. Gamma-linolenic acid in human nutrition. Sources, extraction processes, possible uses. In "I Fluidi Supercriti e le Loro Applicazioni". E. Reverchon and A. Schiraldi (Eds.), p. 123. Proceedings of the 2nd Italian Congress on Supercritical Fluids, Ravello, Italia, 20-22 Giugno 1993.

Fattori, M., Bulley, N.R. and Meisen, A. 1988. Carbon dioxide extraction of canola seed: Oil solubility and effect of seed treatment. J. Am. Oil Chem. Soc. 65:968.

Favati, F. King, J.W. and Mazzanti, M. 1991a. Extraction dynamics and optimization for the supercritical fluid extraction of evening primrose oil. p. 2. Proceedings of the 2nd International Symposium on Supercritical Fluids, Boston, MA, USA. May 20-22.

Favati, F. King, J.W. and Mazzanti, M. 1991b. Supercritical carbon dioxide extraction of evening primrose oil. J. Am. Oil Chem. Soc. 68:422.

Favati, F. and Florentini, R. 1993. Supercritical CO_2 extraction of sunflower oil. In "I Fluidi Supercritici e le Loro Applicazioni". E. Reverchon and A. Schiraldi (Eds.). p. 93. Proceedings of the 2nd Italian Congress on Supercritical Fluids, Ravello, Italia, 20-22 Giugno.

Friedrich, J.P., List, G.R. and Heakin, A.J. 1982. Petroleum-free extraction of oil from soybeans with supercritical CO_2. J. Am. Oil Chem. Soc. 59:288.

Goodrum, J.W., Kilgo, M.K. and Santerre, C.R. 1996. Oilseed solubility and extraction modeling. Ch. 5. In "Supercritical Fluid Technology in Oil and Lipid Chemistry". J.W. King and G.R. List (Ed.s), p. 101. American Oil Chemists' Society Press, Chamapign, Il, USA.

Goto, M., Smith, J.M. and McCoy, B.J. 1990. Kinetics and mass transfer for supercritical fluid extraction of wood. Ind. Eng. Chem. Res. 29:282.

Goto, M., Roy, B.C. and Hirose, T. 1996. Shrinking-core leaching model for supercritical fluid extraction. J. Supercrit. Fluids 9:128.

Hong, I.K., Rho, S.W., Lee, K.S., Lee, W.H. and Yoo, K.P. 1990. Modeling of soybean oil bed extraction with supercritical carbon dioxide. Korean J. Chem. Eng. 7:40.

Huang, Y.-S. and Mills, D.E (Eds.) 1996. "γ-Linolenic Acid" American Oil Chemists' Society Press, Champaign, IL, USA.

Kennedy, G.C. 1954. Pressure-volume-temperature relations in CO_2 at elevated temperatures and pressures. Am. J. Sci. 252: 225.

King, J.W. and List, G.R. (Eds.). 1996. "Supercritical Fluid Technology in Oil and Lipid Chemistry". American Oil Chemists' Society Press. Champaign, IL, USA.

King, M.B. Kassim, K. and Bott, T.R. 1983. Mass transfer into near-critical extractants. Fluid Phase Equil. 10:249.

Lahiere, R.J. and Fair, J.R. 1987. Mass-transfer efficiencies of column contractors in supercritical extraction service. Ind. Eng. Chem. Res. 26:2086.

Lee, B.-C., Kim, J.D., Hwang, K.-Y. and Lee, Y.Y. 1994. Extraction of oil from the evening primrose seed with supercritical carbon dioxide. Ch. 13. In "Supercritical Fluid Processing of Food and Biomaterials". S.S.H. Rizvi (Ed.), p. 168. Blackie Academic & Professional, London.

Lim, G.B., Holder, G.D. and Shah, Y.T. 1990. Mass transfer in gas-solid systems at supercritical conditions. J. Supercrit. Fluids 3:186.

Mendes, R.L. , Fernandes, H.L., Cygnarowicz-Provost, M., Reis, E.C., Cabral, J.M.S., Novais, J.M. and Palavra, A.F. 1996. Modelisation de l'extraction supercritique de lipides d'algues. In "Proceedings of the 3rd Colloqium on Supercritical Fluids - Applications to Natural Products." P. Pellerin and M. Perrut (Eds.). p. 141. Grasse, France, January 29-30.

Poletto, M. and Reverchon, E. 1995. Mathematical modelling of supercritical extraction from vegetable matter: A sensitivity analysis. In "I Fluidi Supercritici e le Loro Applicazioni". I. Kiic and P. Alessi (Eds.). p. 173. Proceedings of the 3rd Italian Congress on Supercritical Fluids, Grignano, Italia, 3-6 Settembre.

Poletto, M. and Reverchon, E. 1996. Comparison of models for the supercritical fluid extraction of seed and essential oils in relation to the mass-transfer rate. Ind. Eng. Chem. Res. 35:3680.

Reverchon, E. 1992. Fractional separation of SCF extracts from majoram leaves: Mass transfer and optimization. J. Supercrit. Fluids 5:256.

Reverchon, E. and Osseo, L.S. 1993. Supercritical CO_2 extraction: Model evaluation of the processing time. In "I Fluidi Supercritici e le Loro Applicazioni". E. Reverchon and A. Schiraldi (Eds.). p. 69. Proceedings of the 2nd Italian Congress on Supercritical Fluids, Ravello, Italia, 20-22 Giugno.

Rizvi, S.S.H., Benando, A.L., Zollweg, J.A. and Daniels, J.A. 1986. Supercritical fluid extraction: Fundamental principles and modeling methods. Food Tech 40(6):55.

Sakaki, K. Yokochi, T., Suzuki, O. and Hakuta, T. 1990. Supercritical fluid extraction of fungal oil using CO_2, N_2O, CHF_3 and SF_6. J. Am. Oil Chem. Soc. 67:553.

Snyder, J.M., Friedrich, J.P. and Christianson, D.D. 1984. Effect of moisture and particle size on extractability of oils from seeds with supercritical CO_2. J. Am. Oil Chem. Soc. 61:1851.

Stahl, E., Schutz, E. and Mangold, H.K. 1980. Extraction of seed oils with liquid and supercritical carbon dioxide. J. Agric. Food Chem. 28:1153.

Stahl, E., Quirin, K.-W. And Gerard, D. 1983. Solubilities of soybean oil, jojoba oil, and curticular wax in dense carbon dioxide. Fett Seifen Anstrichmittel 85:458.

Sovova, H. 1994. Rate of vegetable oil extraction with supercritical CO_2. I. Modeling of extraction curves. Chem. Eng. Sci. 49:409.

Stastova, J., Jez, J., Bartlova, M. and Sovova, H. 1996. Rate of the vegetable oil extraction with supercritical CO_2 - III. Extraction from sea buckthorn. Chem. Eng. Sci. 51:4347.

Vukalovich, M.P. and Altunin, V.V. 1968. "Thermophysical Properties of Carbon Dioxide", Collets, London.

Yoo, K.P. and Hong, I.K. 1996. Modeling of the supercritical fluid extraction of oilseeds. Ch. 6. In "Supercritical Fluid Technology in Oil and Lipid Chemistry". J.W. King and G.R. List (Eds.), p. 132. American Oil Chemists' Society Press, Champaign, IL, USA.

Zehnder, B. and Trepp, C. 1993. Mass-transfer coefficients and equilibrium solubilities for fluid-supercritical-solvent systems by online near-IR spectroscopy. J. Supercrit. Fluids 6:131.