KINETIC PARAMETERS FOR SFE OF PEACH ALMOND OIL

N. Mezzomo[1], J. Martínez[1], and S. R. S. Ferreira[1]*.

[1] *Departamento de Engenharia Química e Engenharia de Alimentos. Universidade Federal de Santa Catarina. CP 476, Trindade, 88040-900 Florianópolis, SC, Brazil*
sandra@enq.ufsc.br

ABSTRACT

The recovery of extracts from vegetal sources is an activity of great interest, since there are compounds in plants that have high potential applications in many industry[1]. Supercritical fluid extraction (SFE) is one of the most promising techniques to obtain highly aggregated value products. The analysis of the mass transfer mechanisms allows the definition of process variables. Mathematical modeling allows calculation of kinetic parameters from experimental data in order to predict larger scale processes[4]. The aim of this work is to evaluate the influence of particle diameter (d_p), pressure (P) and solvent flow rate (Q_{CO2}) on kinetic aspects of SFE of peach almond oil. The peach kernels were supplied by a local company, separated manually, milled and dried. After mechanical separation, d_p was selected at two levels: d_p1 (16 to 48 Mesh) and d_p2 (6 Mesh). The SFE assays were carried out with 12g of grounded particles at 40°C, 150bar and 250bar, 3.3 g/min and 10.0 g/min of Q_{CO2}, according the procedure and equipment described by Michielin[6]. The global yield (X_0) was calculated by the ratio between the extract and feed mass. The time (t_{CER}) and mass extraction rate (M_{CER}) of CER (constant extraction rate) period were calculated by the software SAS. The modeling of the extraction curves was performed by the software Mass Transfer[7] using the models: logistic[8], diffusion[9], simple single plate model (SSP)[10] and empirical[11]. The reduction of the d_p lead to higher oil mass extracted and lower t_{CER} and M_{CER}. The increase in Q_{CO2} provided higher mass transfer rate. The increase in pressure enhances the M_{CER}; with higher concentrations of solute on the solvent phase, shorter CER period and higher X_0 is obtained, due to increased in solvent density. The logistic model provided the best fit to experimental SFE curves obtained at 150bar, while for the empirical model the best adjustment was at 250bar. The diffusion and SSP models, in general, had better fit in the high d_p, Q_{CO2} and P.

INTRODUCTION

The supercritical fluid extraction (SFE) is based on the contact between a solid raw material and a pressurized solvent, which removes soluble compounds from the solid phase. After the extraction, the solute is separated from the solvent through pressure reduction. The recovery of extracts from vegetal sources is an activity of great interest, since there are compounds in plants that have high potential applications in cosmetic, food and pharmaceutical industry [1].

The study of a SFE curve and the knowledge of the effects caused by operational variables allow the definition of the extractor volume and solvent flow rate (Q_{CO2}). SFE can be related to the process time, by the evaluation of the extraction curve. According to the literature, the extraction curves are clearly divided into three sections [2; 3]:

1. Constant extraction rate (CER): the external surface of the particles is covered with solute (easily accessible solute) – the mass transfer resistance is in the solvent phase.
2. Falling Extraction Rate (FER): failures in the external surface oil layer appear. The easily accessible solute is completely depleted at the extractor's entrance – the diffusion mechanism starts.
3. Diffusion-controlled: mass transfer occurs only by the diffusion in the bed and inside the solid substratum particles.

The mathematical modeling of experimental data of SFE has the objective to determine parameters for process design, such as equipment dimensions, solvent flow rate and particle size, in order to make the estimation of the viability of SFE processes in industrial scale, through the simulation of overall extraction curves (OECs) [4]. There are a lot of mathematical models on the literature for the oil extraction with pressurized CO_2. A model has to be a mathematical instrument and also have to reflect the physical behavior of the solid structure and experimental observations [5].

The objective of this work is to evaluate the influence of particle diameter (d_p), pressure (P) and solvent flow rate (Q_{CO2}) on kinetic aspects of SFE of peach almond oil.

MATERIAL AND METHODS

Raw Material

Peach kernels were supplied by Conservas Oderich S/A, a local company from Rio Grande do Sul/Brazil. They were washed and separated manually in almond and kernel. The almonds were milled in a domestic miller (LiqFaz, Wallita, São Paulo/SP, Brazil) and dried in oven (E.L. 003, Odontobrás, Ribeirão Preto/SP, Brazil) at 30°C for 25 hours. The almonds were characterized by their size trough mechanical analysis. The particle size separation was conduce in a sieves agitating (Bertel Indústria Metalúrgica Ltda., Caieiras/SP, Brazil) and the particles of size 16 to 48 Mesh were defined as level 1 (d_p1) and 6 Mesh as level 2 (d_p2).

Kinetic experiments of Supercritical Fluid Extraction (SFE)

The SFE kinetic experiments from peach almond was performed at a temperature of 40 °C, pressure of 150 bar and 250 bar, and Q_{CO2} of 3.3 g/min and 10.0 g/min, with 12 g of grounded particles according to equipment and procedure described by Michielin et al. [6].

Parameter determination

The global yield (X_0) was calculated by the ratio between extract and feed mass. The time (t_{CER}) and mass extraction rate (M_{CER}) of CER (constant extraction rate) period were calculated by the software SAS.

The model parameters determination was realized with a software (Mass Transfer), development by Correia et al. [7], applying the logistic model of Martínez et al. [8], diffusion model of Crank [9], simple single plate model (SSP) of Gaspar et al. [10] and empirical model of Esquível et al. [11]. The parameters determined were: D – diffusion coefficient of diffusion model [9]; b and t_m – adjustables parameters of logistic model [8]; D_m – diffusivity of SSP model [10]; b_1 – adjustable parameter of empirical model [11]. The model equations and parameters are summarized in Campos et al. [12].

RESULTS AND DISCUSSION

The average size of almond particles used on the SFE for level 1 (d_p1) was 882 μm and for the level 2 (d_p2) was 3360 μm. The peach almond mass used in all the extractions was of 12.02 ± 0.02 g, occupying a volume of 13.4 ± 0.5 cm^3.

Table 1 presents kinetic parameters of the curves, while the SFE curves for the different particle diameters, operational pressure and solvent flow rate are presented in figure 1.

Evaluating the effect of the particle size at constant Q_{CO2} and at 150 bar of pressure, it can be observed from table 1 that the time of CER period (t_{CER}) was 43 to 203 % lower, which resulted in higher times of FER and diffusional periods, for the curves with higher d_p. In the same figure, observing the final oil mass extracted with d_p of 3360 μm and 10.0 g/min of Q_{CO2}, is verified that in the same flow rate but with d_p of 882 μm, it can reach the same mass in 150 min, that is, in 33.3 % of the necessary time in the curve with higher d_p. In the same way, to reach the final oil mass extracted in the curve with d_p of 3360 μm and Q_{CO2} of 3.3 g/min, with d_p of 882 μm it is needed a 2,6 times lower time (230 min).

Table 1 Time (t_{CER}), extraction rate (M_{CER}) and solvent phase solute mass ratio (Y_{CER}) on the constant extraction period, solvent specific mass (ρ) and global yield (X_0) for the SFE curves in function of the operational pressure, particle size and solvent flow rate evaluated.

P (bar)/d_p (μm)/Q_{CO2} (g/min)	t_{CER} (min)	M_{CER} (g/min)	Y_{CER} (g/g)	ρ (kg/m^3)	X_0 (%)
250/882/10.0	27.2	0.0568	5.68 x 10^{-3}	880	19.51
250/3360/10.0	38.9	0.0369	3.69 x 10^{-3}	880	18.21
150/882/10.0	122.8	0.0136	1.36 x 10^{-3}	781	17.72
150/3360/10.0	65.3	0.0165	1.65 x 10^{-3}	781	14.15
150/882/3.3	186.7	0.0077	2.31 x 10^{-3}	781	16.10
250/882/3.3	16.2	0.0932	27.99 x 10^{-3}	880	18.86
250/3360/3.3	26.1	0.0491	14.74 x 10^{-3}	880	16.72
150/3360/3.3	91.8	0.0095	2.85 x 10^{-3}	781	12.65

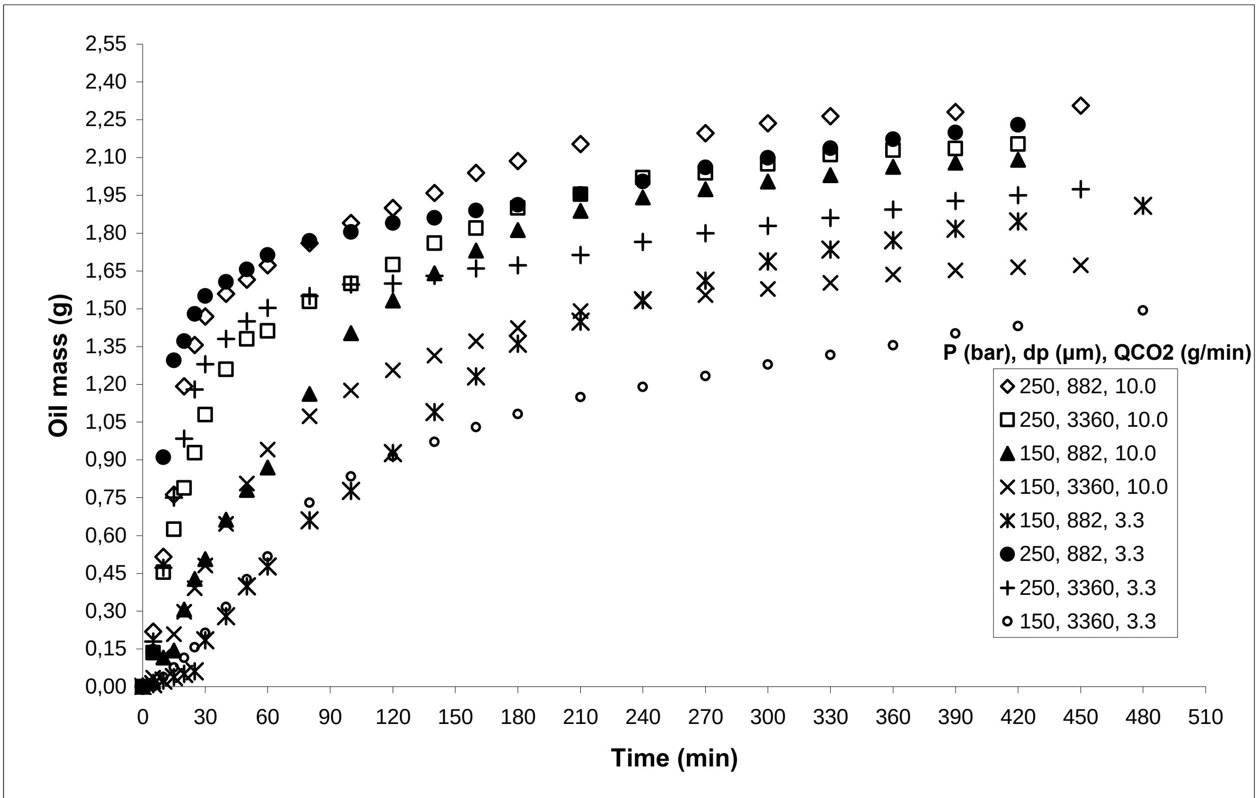

Figure 1 SFE curves from peach almond evaluating particle size, operational pressure and solvent flow rate effects

However, it can be visualized that the effect of d_p is more visible in the FER and diffusional periods, and practically not perceived in CER period. This can indicate that the d_p variation has more influence on the mass transfer mechanism of diffusion and less in the convection of solute in the solvent in the SFE. The diffusion occurs mainly inside of the particle, that is, of most internal part for the surface of the particle. Reducing the particle size, the internal diffusion resistance of the particles is also reduced.

The solvent phase solute mass ratio, Y_{CER}, is determined by the SFE curve slope on the linear part that represents the CER period. According to table 1, higher values of Y_{CER} (27.99 x 10^{-3} g oil/g CO_2) were achieved with higher CO_2 specific mass (880 kg/m^3), where the number of soluble compounds number is higher, because of the increase of the supercritical solvent solubilization power.

The results presented in table 1 indicate that the extraction rate is higher if the oil is available on the particle surfaces, and that is comparatively lower when it is incorporated inside the almond particles. The reduction of the peach almond particle size is necessary with the intention of diminish the extraction time. On the other hand, producing small particles can increase the milling costs significantly and also form compact extraction beds, with the formation of preferential paths for supercritical solvent, reducing the extraction efficiency [13].

The pressure effect in extraction curves is also described in figure 1. It can be observed that the oil mass extracted is higher at the highest pressure (250 bar). The increase in the pressure caused a higher inclination on the first part of the curve, which corresponds to CER period, leading to higher Y_{CER} and X_0, and lower t_{CER}. With pressure increase there is an increase on X_0 because of the increase of the soluble compound concentration in the highest pressure condition. This is reflected in the extraction rate of each curve represented by M_{CER}. However, when evaluating only X_0, we could not say if this is caused by the increase of the easy or difficult access solute concentration. Thus, when visualizing the inclination of the CER and diffusional periods on the curves presented in figure 1, it can be observed that the pressure increase, in same d_p and Q_{CO2}, provides a higher CER extraction rate and equal FER and diffusional extraction rates. As CER period is characterized by the extraction of easily accessible solute, and the diffusional period for the extraction compounds inside the vegetal matrix (difficult access solute), it can be said that the increase of the operational pressure provides an increase of the easily accessible solute concentration and, therefore, of X_0.

Table 2 presents the parameters and the medium square error for the mass transfer models applied to SFE modeling from peach almond oil.

Table 2 Parameters and medium square error (MSE) of mass transfer models applied to SFE curves from peach almond at different solvent flow rates (Q_{CO2}), particle sizes (d_p) and pressures (P).

P (bar)/d_p (μm)/ Q_{CO2} (g/min)		250/882/ 10.0	250/3360/ 10.0	150/882/ 10.0	150/3360/ 10.0	150/882/ 3.3	250/882/ 3.3	250/3360/ 3.3	150/3360/ 3.3
Diffusion	D (m^2/min)	9.60×10^{-10}	1.01×10^{-8}	4.27×10^{-10}	6.96×10^{-9}	2.46×10^{-10}	1.25×10^{-9}	1.37×10^{-8}	4.17×10^{-9}
	MSE	0.0192	0.0092	0.0551	0.0210	0.7256	0.0363	0.0192	0.0264
Logistic	b (min^{-1})	0.0255	0.0174	0.0114	0.0119	0.0108	0.0374	0.0281	0.0074
	t_m (min)	-1711	-2522	-15	-280	56	-1171	-1554	-347
	MSE	0.0306	0.0180	0.0016	0.0019	0.0020	0.0557	0.0303	0.0024
SSP	D_m (m^2/min)	1.00×10^{-10}	7.06×10^{-11}	4.38×10^{-11}	4.88×10^{-11}	2.62×10^{-11}	1.38×10^{-10}	1.03×10^{-10}	3.00×10^{-11}
	EMQ	0.0230	0.0091	0.0332	0.0121	0.0497	0.0463	0.0248	0.0169
Empirical	b_1 (min)	22.01	30.55	56.90	48.23	100.65	16.21	21.62	82.91
	MSE	0.0101	0.0078	0.0440	0.0167	0.0485	0.0157	0.0067	0.0157

The MSE presented in table 2 shows that the logistic model was the best adjusted model to SFE curves at 150 bar, while the empirical model of Esquível et al. [11] had better adjustments in curves at 250 bar.

The adjustable parameter t_m corresponds to the time where the extraction rate reaches its maximum. However, except for the curve at 150 bar, 882 μm and 3.3 g/min (t_m = 56 min - table 2), all other modeled curves presented negative value of t_m, which no physical meaning. This result indicates that the extraction rate is decreasing because its maximum value was reached at the initial instant of the extraction [1].

For the adjustment of the empiric model is necessary the knowledge of X_0 and the raw material mass. This model represented well the experimental data of all SFE curves from peach almond, because of the hyperbolic form of its curve. The thermodynamic and kinetics effects are represented only by one adjustable parameter (b_1), therefore it is not possible to verify the influence of the different mechanisms in the description of the extraction curve. As this model is empirical, it only can be used to predict SFE kinetic curves for the experimental range where the parameter b_1 was estimated [14].

The Diffusion and SSP models, which consider mass transfer as an analogy to heat transfer where the extraction process is controlled by diffusion, had presented better adjustments in higher d_p, Q_{CO2} and P. These models only consider the different mass transfer mechanisms through one adjustable parameter of each model: D and D_m, respectively, that do not permit to determine the predominant mechanism verification in the peach almond oil extraction. By observing the medium square error, it can be identified that the Diffusion and SSP models had adjusted better to experimental data when a higher solvent flow rate was used, in contrast with the logistic and empirical models, that had presented better or equal adjustment with 3.3 g/min.

When evaluating the d_p effect in the models, it can be noticed that the Diffusion, SSP and empirical models had presented better adjustments with higher d_p. As the extraction rate increases with the solvent flow rate and with reduction of d_p, this means that the mass transfer resistance is mainly external. In this way, it was expected that the diffusional models were better for low flow rates and high particle size (lower extraction rates). Probably the inversion of the flow rate influence occurred because of the contour condition used in the resolution of these two models, which considers the solute concentration in the surface of the solid particle is zero in any extraction time. That is, the mass transfer is higher in the particle surface than on the inside of it, with no existing resistance in the fluid phase.

The modeling of SFE experimental curves from peach almond is important for the project optimization, such as the extractor volume definition and also for the prediction of the extraction behavior throughout the process, as the total extraction time for a specific operation. Moreover, the extraction curves modeling supplies information regarding the studied system and how the extraction will behave depending on the predominant mass transfer phenomenon in the peach almond oil/supercritical CO_2 system (convective and diffusive phenomena).

CONCLUSION

The reduction of d_p provided higher oil mass extracted and lower t_{CER} and M_{CER}, while the increase in Q_{CO2} provided higher mass transfer rates. The increase in pressure enhances the M_{CER}, with higher concentrations of solute on the solvent phase. Shorter CER period and higher X_0 are obtained, due to high solvent density, which increases the easily accessible solute concentration.

The logistic model provided the best fit to experimental SFE curves obtained at 150bar, while for the empirical model the best adjustment was at 250bar. The diffusion and SSP models, in general, had better fit in the high d_p, Q_{CO2} and P.

The selection of good mathematical models witch described the experimental curves well is useful on the scale-up studies of the system and, therefore, predict industrial scales.

REFERENCES

[1] MARTÍNEZ, J.; ROSA, P. T. V; MENUT, C.; LEYDET, A.; BRAT, P.; PALLET, D.; MEIRELES, M. A. A. *Journal of Agricultural and Food Chemistry*. **2004**, 52, 6578-6584

[2] SOVOVÁ, H. *Chemical Engineering Science.* **1994**, 49, 409-414.

[3] FERREIRA, S. R. S.; MEIRELES, M. A. A. *Journal of Food Engineering*. **2002**, 54, 263-269.

[4] MARTÍNEZ, J.; MONTEIRO, A. R.; ROSA, P. T. V.; MARQUES, M. O. M.; MEIRELES, M. A. A. *Industrial Engineering of Chemistry Research.* **2003**, 42, 1057-1063

[5] MARTÍNEZ, J.; ROSA, P. T. V.; MEIRELES, M. A. A. *The Open Chemical Engineering Journal*. **2007**, 1, 1-7.

[6] MICHIELIN, E. M. Z.; BRESCIANI, L. F. V.; DANIELSKI, L.; YUNES, R.; FERREIRA, S. R. S. *Journal of Supercritical Fluids*. **2005**, 33, 131–138.

[7] CORREIA, J.; MICHIELIN, E.M.Z.; FERREIRA, S.R.S. *Relatório de iniciação científica (PIBIC-CNPQ)*. 2005.

[8] MARTÍNEZ, J.; MONTEIRO, A. R.; ROSA, P. T.; MARQUES, M. O. M.; MEIRELES, M. A. A. *Industrial Engineering of Chemical Research.* **2003**, 42, 1057-1063.
[9] CRANK, J. *Clarendon Press.* **1975**, 85 p.
[10] GASPAR, F.; LU, T.; SANTOS, B.; AL-DURIN, B. *Journal of Supercritical Fluids.* **2003**, 25, 247-260.
[11] ESQUÍVEL, M. M.; BERNARDO-GIL, M. G.; KING, M. B. *Journal of Supercritical Fluids*. **1999**, 16, 43-58.
[12] CAMPOS, L. M. A. S.; MICHIELIN, E. M. Z.; DANIELSKI, L.; FERREIRA, S. R. S. *Journal of Supercritical Fluids*, **2005**, 34, 163-170.
[13] ÖZKAL, S.G.; YENER, M.E.; BAYINDIRLI, L. *Journal of Supercritical Fluids*. **2005**, 35, 119–127.
[14] QUISPE-CONDORI, S.; SANCHEZ, D.; FOGLIO, M. A.; ROSA, P. T. V.; ZETZL, C.; BRUNNER, G. *Journal of Supercritical Fluids*. **2005**, 36, 40-48.