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Supercritical Fluid Extraction from Mango (*Mangifera indica* L.) Leaves: Experiments and Modeling

Wilson J. Dos Santos[a], Edson A. Silva[b], Osvaldir P. Taranto*[a]

[a]School of Chemical Engineering, University of Campinas (UNICAMP), 13083-862, Campinas, SP, Brazil
[b]Department of Chemical Engineering, West Parana State University (UNIOESTE), 85903-00, Toledo, PR, Brazil
val@feq.unicamp.br

Recent studies reported that mango (*Mangifera indica* L.) leaves are an important source of phytochemicals, which have beneficial effects on human health. However, the traditional methods to obtain extracts have the main disadvantage of using toxic solvents (*e.g.* methanol and acetone). Thus, there is a great interest in developing new processes based on the use of green solvents such as supercritical fluid extraction (SFE), a technology with the potential to obtain high quality yields, which increases the product added value. In this paper, supercritical CO_2 extraction of mango leaves was investigated at temperatures of 313-333 K and pressures 15-25 MPa. The yield of the extract obtained was 1,20% at optimal conditions. Regarding the kinetics of supercritical fluid extraction, the Sovová's model was selected and sucessfully applied to the description of the extraction curves. The adjustable parameters of the model were determined using a local and a global optimization algorithm: Simplex and Simulated Annealing, respectively. As expected, the lowest deviation between experimental and correlated data was obtained by the global optimization technique.

1. Introduction

The mango (*Mangifera indica* L.) belongs to the family *Anarcadiaceae* and is one of the most important fruit species due to its phytochemical composition, which are mainly phenolic compounds. The literature reports that these compounds can be obtained from various parts of the plant such as seeds, kernel and steam bark (Ajila et al., 2007, Dorta et al., 2012).
Recently, a study on leaves extracts from *M. indica* L. using water and ethanol demonstrated potentially useful antioxidant activity which was attributed to its high content of phenolic compounds (Ling et al, 2009). However, these traditional extractions with liquid solvents has some drawbacks, such as long extraction time and large consumption of solvents requiring concentration steps that can result in a loss or degradation of active components. Thus, the supercritical fluid extraction (SFE) is an interesting alternative due to several advantages including the use of a green solvent (supercritical carbon dioxide), fast and more selective process with a low degradation of chemical compounds (Straccia et al., 2012).
Pereira and Meireles (2007) obtained a mango leaves extract with antioxidant activity and phenolic compounds using supercritical CO_2. However, before an industrial application of the SFE can be achieved, it is very important to apply a kinetic model that allows the prediction of large-scale extraction curves using model parameters fitted with small-scale experiments (Casas et al., 2009).
Many authors have used different approaches to fit mathematical models to the experimental SFE data. The Simplex algorithm (Nelder and Mead, 1965) to minimize an objective function is one of the most popular technique for fitting the parameters of the kinetic models (Zhou et al., 2004, Corso et al., 2010, Pederssetti et al., 2011, Rebolleda et al., 2012). However, this method can be trapped in local minima and a global optimization algorithm can be the solution to overcome this weakness. The Simulated Anneling algorithm (Goffe et al., 1994) is an alternative that has been applied with sucess in other areas of chemical engineering (Dolan et al., 1989, Floquet et al., 1994, Papadopoulos and Linke, 2004) and it was not found reports of its use in the estimation of model extraction parameters.

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Therefore, the objectives of this work were to obtain the kinetic curves from mango leaves extraction using supercritical CO_2 to apply the Simulated Annealing algorithm on the estimation of Sovová's model parameters and compare it to the common conventional algorithm, Simplex. In addition, the influence of pressure and temperature of supercritical CO_2 on global yield was studied.

2. Sovová's model

In literature, the model of Sovová (1994) is one of the most applied mathematical model of supercritical extraction in fixed bed. This model adopts a simplification on the mass balance to obtain an analytical solution and assumes that the solute extractible content can be divided into accessible solutes (from the broken solid particles) and hardly accessible solutes (from intact solid particles). Furthermore, the Sovová's model also defines three periods to the SFE process. The first period is the easy extraction of accessible solute from superficial structures, followed by a decrease in the accessible solute and then extraction of the hardly accessible solute. The equations are given below:

$$m(t) = Q_{CO_2} Y_r [1 - \exp(-Z)]t \ , \quad \text{if } t \le t_{CER} \tag{1}$$

$$m(t) = Q_{CO_2} Y_r [t - t_{CER} \exp(Z_w(t) - Z)] \ , \quad \text{if } t_{CER} < t < t_{FER} \tag{2}$$

$$m(t) = m_i \left[X_0 - \frac{Y_r}{W} \ln \left\{ 1 + \left[\exp\left(\frac{WX_0}{Y_r} \right) - 1 \right] \exp\left[\frac{WQ_{CO_2}}{m_i} (t_{CER} - t) \right] \left(\frac{X_p}{X_0} \right) \right\} \right], \quad \text{if } t \ge t_{FER} \tag{3}$$

where m(t) represents the extract mass calculated with the model (g), Q_{CO2} is the solvent mass flow rate (g/min), Y_r is the extract solubility in the solvent (g/g), t is the extraction time (min), t_{CER} is the end if the first extraction period (min), t_{FER} is the end of the second extraction period (min), Z is the model parameter related to convection in the fluid phase, W is the model parameter related to the diffusion in solid phase, X_p is the mass of easily accessible solute relative to mass of non-extractable material (g/g), X_k is the mass of hardly accessible solute relative to mass of non-extractable material (g/g), X_0 is the initial mass of extractable material relative to mass of non-extractable material (g/g) and Z_w is a parameter of the second extraction period.

The parameters Z_w, X_p and t_{FER} can be calculated by:

$$Z_w(t) = \frac{ZY_r}{WX_0} \ln \left\{ \left(X_0 \exp\left[\frac{WQ_{CO_2}(t - t_{CER})}{m_i} \right] - X_k \right) \Big/ (X_0 - X_k) \right\} \tag{4}$$

$$t_{FER} = t_{CER} + \frac{m_i}{WQ_{CO_2}} \ln \left[\frac{X_k + X_p \exp[WX_0 / Y_r]}{X_o} \right] \tag{5}$$

$$Z = \frac{X_p m_i}{t_{CER} Y_r Q_{CO_2}} \text{ and } X_k = X_0 - X_p \tag{6}$$

Where m_i is the mass of non-extractable material (g). Thus, the parameters Q_{CO2}, Y_r, m_i, X_0 are the input data whereas t_{CER}, t_{FER} ,X_k, X_p, W and Z are the model parameters.

3. Material and methods

3.1 Raw material characterization

Mangifera indica L. (Philippine 'Carabao' var.) leaves were collect at experimental plantations of Instituto Agronômico de Campinas (Campinas, São Paulo, Brazil) in September 2012. The leaves were dried at ambient conditions in the shade with free air circulation for a period of 7 days and subsequently grounded using a commercial blender (Philco, PH5000CL model). Then, the leaves were storage in hermetically sealed bags in a refrigerator (Consul, CVU20 model) at ca. –18 °C.

The particle size distribution was determined using a mechanical agitator (Bertel, 302 model). The leaves trapped between 28 and 32 mesh sieve (Tyler series) were chosen for the extractions. Real particle density was determined by helium gas pycnometry (Micromeritics, Accu Pyr 1330 model). The apparent bed density was calculated using the mass of feed and the volume of extractor cell. Bed porosity (ε) was calculated by Equation 7.

$$\varepsilon = 1 - \rho_{BED} / \rho_R \tag{7}$$

where ρ_{BED} is the apparent density of the bed and ρ_R is the real density of the sample.

3.2 Supercritical extraction

The experiments were performed in a laboratory scale unit, which basically consists of: a solvent reservoir (CO_2, Linde with 99.99% of purity), a syringe pump (ISCO, Model 500D), an extractor with an internal volume of approximately 53.4 mL (diameter of the bed is 2 cm, and height of the bed is 17 cm) and two thermostatic baths. The first thermostatic bath (Julabo, FP-50 model) is used to cool the solvent prior to entering in the syringe pump and the second one (Marconi, MA-184 model) to maintain the extractor at the desired temperature. In each experiment the extractor was loaded with approximately 15 g of powdered sample. First the system was pressurized (at intervals of approximately 20 bar) until the desired pressure. After column temperature and pressure were stabilized, the system was kept in contact with the mango leaves for at least 15 min to allow the system stabilization. Then, the CO_2 was pumped into the bed of mango leaves powder at ca. 3 mL/min. The volumetric flow rate of the solvent was regulated using the expansion valve at the outlet of the extractor. The temperature at the extractor outlet is maintained at 105 °C by the temorregulador (Tholz, MSC-04E model) to allow the separation between the extract and the solvent due to the depressurization. The extract is collected via an amber glass container and weighed every 10-20 min until constant weight.

3.3 Experimental design

A factorial experimental design with two factors, two levels and a central point was employed to organize the experiments and data collection. Temperature and pressure were used as independent variables, while dependent variable was the extraction yield (mass of oil extracted/mass of dried leaves). The CO_2 extraction experiments were conducted in temperatures from 313 to 333 K and pressures from 15 to 25 MPa. The experimental data were analyzed by Statistica™, version 7 software (Statsoft). The test of statistical significance, p-value, was determined accordingly to the pure error criteria at 95 % confidence level.

3.4 Mathematical modeling

We developed a software in Fortran using the Simulated Annealing (Goffe et al., 1994) and the Simplex algorithm (Nelder and Mead, 1965) to fit the parameters t_{CER}, X_p, W of Sovová's model by minimizing the errors between experimental extract mass (m_{exp}) and the extracted mass calculated with the model (m). The errors were quantified by objective function sum of squares, SS:

$$SS = \sum_{i=1}^{n} \left(m(t_i) - m_{\exp}(t_i) \right)^2 \tag{8}$$

The parameters t_{FER}, X_k and Z were calculated by Equations 5 and 6. The initial mass of extract available in the solid (X_0) is supposed to be equal the asymptotical value of the total mass of oil extracted relative to mass of non-extractable material. The apparent solubility (Y_r) was calculated from the linear part of the extraction curve (extracted oil mass/mass of used solvent).

In both algorithms the fitted parameters were subject to: $X_p < X_0$, $t_{CER} < 110$ and $W < 10$. These limitations were employed to avoid the algorithms of going beyond the likely region of a solution. X_0 is the highest possible value of X_p (Equation 6), 110 min was the final experimental point of the kinetic data, while W was set lower than 10 to prevents the fitting of an unphysical parameter. The relative tolerance was set to 1.0×10^{-6} in both optimization algorithms.

4. Results and discussion

4.1 Extraction yield

Table 1 presents the experimental conditions for the extraction of mango leaves extract using carbon dioxide as solvent. The extraction yield was calculated as the mass of the extract obtained by the mass of raw material fed into the extractor. The results observed in this work are in agreement with the data available in the literature. For example, Fernández-Ponce et al. (2012) reported a highest global yield of 1.22 % for the extraction of mango leaves at 40 MPa and 328 K. This value is very similar to the global yield obtained in our work (1.20 %) in different conditions.

Table 1: Experimental conditions and extraction yield results for the mango leaves extraction CO_2.

Run	1	2	3	4	5
Temperature (K)	313	313	333	333	323
Pressure (MPa)	15	25	15	25	20
Extraction yield (%)	0.69	1.20	0.59	1.10	1.16 ± 0.03[a]

[a] Average value of three replicates runs ± standard deviation.

The estimated effects and interaction between the range of variables studied and the analysis of variance are shown in Table 2. The curvature had a statistical significance influence in the results, thus indicating that all variables, even if their main and interaction effects were not significant (i.e., variable temperature and the interaction temperature/pressure), had to be included in the subsequent experiments and a quadratic model has to be used. However, the comparison of runs 1 and 2 at 313 K and runs 3 and 4 at 333 K suggests that the increase in pressure at fixed temperature promotes the enhancement in the extraction yield. This behavior can be explained by the increase in density with pressure resulting in a higher solvating power of CO_2 (Carvalho Jr. et al., 2005). The effect of temperature is more complex due to the opposing factors of solute vapor pressure and solvent density. Solute vapor pressure increases with increasing temperature resulting in increased solubility while solvent density of CO_2 decreases resulting in decreased solubility and solvating power (Fernández-Ronco et al., 2010). At 15 MPa (runs 1 and 3) increasing the temperature from 313 K to 333 K decreased the global yield from 0,69 % to 0,59 % and at 25 MPa (runs 2 and 3), the same increase also decreased the global yield from 1,20 % to 1,10 %. These results indicate that the solvent density effect is more pronounced than solute vapor pressure effect.

Table 2: Estimated effects and analysis of variance for the mango leaves extraction CO_2.

Variable	Temperature	Pressure	Temperature/Pressure	Curvature
Effect	-0.102	0.509	-0.004	0.521
p-value	0.0681	0.0030	0.8897	0.0067

4.2 Mathematic modeling

Mass transfer kinetic experiments were carried out at all experimental conditions showed in Table 3. We decided to test the effectiveness of the Simulated Annealing method against a well-known optimization algorithm, the Simplex method, using two different starting values in the estimation of Sovova's parameters. The fitted parameters and the respective statistical indicator (SS) are listed in Table 4.

Table 3: Experimental conditions of the runs.

Run	T (K)	P (MPa)	ε	ρ_r (g/cm³)	$\rho_{solvent}$[b] (g/cm³)	X_0 (g/g)	Y_r (g/g)	Q_{CO2} (g/min)	m_i (g)
1	313	15	0.811	1.4813	0.748	0.00694	0.000891	2.244	14.862
2	313	25	0.812	1.4813	0.886	0.01217	0.002041	2.658	14.694
3	333	15	0.813	1.4813	0.562	0.00595	0.000867	1.686	14.687
4	333	25	0.811	1.4813	0.775	0.01109	0.001505	2.325	14.796
5[a]	323	20	0.813	1.4813	0.764	0.01172	0.001532	2.292	14.593

[a] Average value of three replicates runs.
[b] Solvent density was calculated by the equation proposed by Stryjek and Vera (1986).

Table 4: Fitted parameters of Sovová's model.

Starting values	Run	Simulated Annealing					Simplex				
		X_p	t_{CER}	W	SS	NFE[a]	X_p	t_{CER}	W	SS	NFE[a]
Test 1 X_p = 0.0001 t_{CER} = 20 W = 0.1	1	0.00225	0.128	0.494	0.00006	624001	0.00685	20.001	0.111	0.00021	26
	2	0.00583	0.005	0.322	0.00016	588001	0.01178	20.014	0.112	0.00153	26
	3	0.00544	14.396	2.443	0.00995	552001	0.00595	20.005	0.106	0.00997	51
	4	0.01010	0.262	0.370	0.00014	564001	0.01109	20.001	0.109	0.00095	48
	5	0.00346	0.079	0.329	0.00007	594001	0.01057	20.007	0.112	0.00043	27
Test 2 X_p = 0.001 t_{CER} = 50 W = 5	1	0.00225	0.128	0.494	0.00006	624001	0.00694	50.003	4.998	0.00268	48
	2	0.00583	0.005	0.322	0.00016	588001	0.01218	50.008	5.004	0.01253	54
	3	0.00544	14.396	2.443	0.00995	552001	0.00595	50.007	5.003	0.01135	48
	4	0.01010	0.262	0.370	0.00014	564001	0.01109	49.995	5.010	0.01042	51
	5	0.00346	0.079	0.329	0.00007	594001	0.01171	50.017	5.010	0.00499	167

[a] Number of function evaluations.

As can be observed in Table 4, Simplex converged to different solutions when the starting values were changed (Tests 1 and 2). In general, the final values of the objective function SS are significantly higher

than those obtained by Simulated Annealing and two fitted parameters (t_{CER} and W) are always close to the initial estimate. Thus, we can conclude that the Simplex algorithm stopped in local minima.
Martínez and Martínez (2008) reported the same local minimum problem with Simplex and developed a global optimization technique using three algorithms in series which solved this problem. However, in this paper, only the use of Simulated Annealing did not fail in finding the global solution in all cases independent of the initial estimate. This occurs because Simulated Annealing explores the function entire surface, escape from local minimum and find a global optimum by moving both uphill and downhill (Goffe et al., 1994). This process substantially increased the number of functions evaluations, and consequently the response time. According to Table 4, the Simplex method typically converges after about 55 function evaluations (NFE), while Simulated Annealing technique requires ca. 10700 times more.
In some cases, e.g. Test 1, Simplex can converge to a good solution which can be considered satisfactory depending on the situation. However, there is no reason for using a local minimization algorithm if a global optimization is available in terms of computer resources. Figure 1 show the comparison between experimental and fitted kinetic curves of Sovová's model obtained by Simplex and Simulated Annealing (SA) for the Test 1.

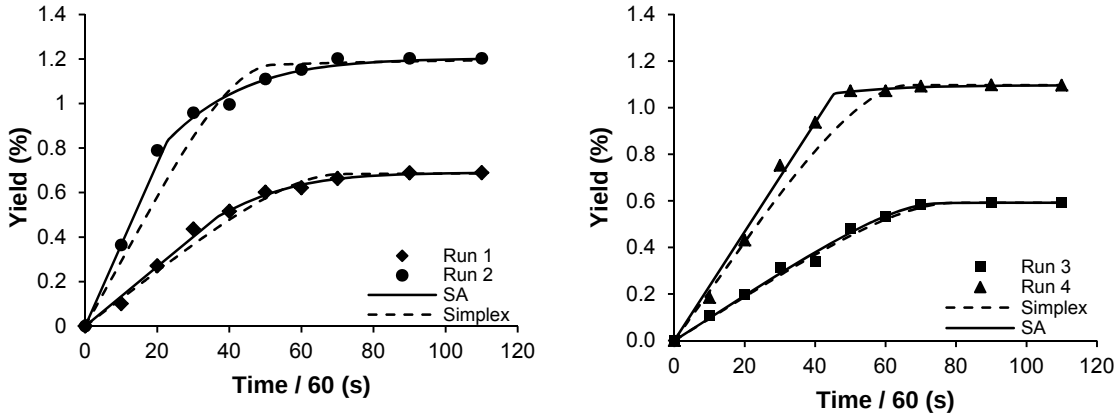

Figure 1: Comparison between experimental and fitted kinetic curves using Simplex and Simulated Annealing in the estimation of Sovová's parameters.

As can be deduced from the Figure 1, CO_2 extracts of mango leaves were completely obtained and showed a fast kinetics compared with others kinetic extraction curves in literature (Fernández-Ronco et al., 2010, Moura et al., 2012). The curves exhibit two different periods: the constant extraction rate (CER) period and the falling extraction rate (FER) period. First, the supercritical CO_2 extracts the solute available on the superficial structures, followed by a decrease in the rate where the mass transfer is controlled by internal diffusion. For example, At 313 K and 25 MPa (Run 2) the CER period ended in ca. 22 min where almost 70% of the extract was obtained, while at 333 K and 25 MPa (Run 4) the CER period extract almost 100% of the total solute available in ca. 45 min. Therefore, in order to reduce the costs of the process, the process optimization should be focus on this region.

5. Conclusion

In this paper, it was determined the global yield of extracts from *Mangifera indica* L. leaves and two different optimization algorithm were applied to fit the kinetic parameters of Sovová's model. The highest global yield was observed for SFE extraction at lower temperature and higher pressure (313 K and 25 MPa). The statistical analysis showed that the curvature was significant, thus the response (global yield) could not be described by a linear model.
The model proposed by Sovová was successfully applied to correlate the experimental data. The mathematic modelling performed on two very different starting values showed that the Simulated Annealing is most reliable compared to the classical Simplex method, because it does not depend on initial guesses and gives preference to global optima. Thus, the Simulated Annealing technique is especially suitable for fitting the parameters of Sovova's model, despite its considerable extra time requirement.

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