

International Journal of Food Engineering

Volume 8, Issue 1

2012

Article 18

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Recommended Citation:

Sandi, Délcio; Araújo, Júlio M.A.; Montes-Montes, Everaldo J.; Coimbra, Jane S.R.; and Ferreira, Sandra R.S. (2012) "Modeling Oil Extraction from Green and Roasted Coffee by Means of Supercritical CO₂," *International Journal of Food Engineering*: Vol. 8: Iss. 1, Article 18.

DOI: 10.1515/1556-3758.2058

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Modeling Oil Extraction from Green and Roasted Coffee by Means of Supercritical CO₂

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Abstract

Green and roasted coffee oil was extracted using supercritical CO₂ at temperatures of (333, 343, 353 and 363) K and pressures from (235 to 380) bar, providing a CO₂ densities range from (680 to 880) kg.m⁻³. The mathematical models of Del Valle-Aguilera and Chrastil were applied to predict the oil solubility. The Del Valle-Aguilera led to elevated deviations between the predicted solubility values and those observed experimentally. The Chrastil model provided better results, with better fitting being observed. With this procedure, the mean percentage deviation was 0.16 and 0.19, respectively, for green and roasted coffee oil, showing a good correlation between the observed and predicted values.

KEYWORDS: supercritical fluid extraction, coffee oil, solubility modeling, cafestol, kahweol

Author Notes: * Corresponding author: jaraujo@ufv.br (Júlio M. A. Araújo). Acknowledgement The authors are thankful to Prof. Eduardo B. de Oliveira for their scientific contribution. The authors also wish to acknowledge CNPq, FAPEMIG and CAPES for their financial support. The present work is part of the doctorate thesis of D. Sandi, supported by CNPq, FAPEMIG and the Federal University of Viçosa.

Introduction

Green coffee oil has been used by cosmetic industries due to its emollient and sunblock properties provided by its fatty acid profile (A and E Connock, 1999; Alvarez and Rodrigues, 2000; Groiller and Plessis, 1988; Pelle, 1999). Biological properties such as anticarcinogenic (Lam et al., 1982; Scharf et al., 2001) and anti-inflammatory (Bertholet, 1987; Bertholet, 1988) are also attributed to coffee oil, mainly due to its high concentration in diterpenes cafestol and kahweol, exclusively present in this oil, which have made its use potentially attractive to pharmaceutical and food industries. Roasted coffee oil has also been widely used as a flavor source in foods and cosmetics (Brimmer, 1996).

Various models for solubility dependence on pressure and temperature have been reported in the literature related to supercritical CO₂ (SC-CO₂) extraction (Sovová et al., 2001; Chrastil, 1982; Del Valle and Aguilera, 1988; Stahl et al., 1980). Oil solubility was measured by static and dynamic methods, both included the direct interaction of CO₂ with liquid oil and its contact with ground vegetable materials, as presented by Danielski et al. (2007).

The extraction of green and roasted coffee oil using supercritical carbon dioxide was performed in our laboratory and presented yields similar to those obtained by hexane extraction and considerably higher than those obtained by mechanical pressing (Araújo and Sandi, 2007).

Chrastil (1982) developed an empirical model for predicting solubility of several compounds in SC-CO₂ (eq. 1), including fatty acids, triglycerides, water and cholesterol, based on the assumption that the solubility of a solute in the SC-CO₂ system is closely related to its density and extraction temperature:

$$C = d^k \exp(a / T + b) \quad (1)$$

Where, C (kg.m⁻³) is the solute solubility, d (kg.m⁻³) is the density of the pure CO₂, T (K) is the absolute temperature and k and b are the model constants.

Later, del Valle and Aguilera (1988) developed a comprehensive equation based on the Chrastil model (1982), in order to determine vegetable oil solubility (eq. 2) based on solubility data obtained from soybean, sunflower seed, cottonseed and corn oils (Friedrich, 1984; Stahl et al., 1980). The equation was validated for temperatures ranging from 293 K to 353 K, pressures from 150 atm to 888 atm and solubility values up to 100 kg.m⁻³.

$$C = d^{10.724} \exp(-18708 / T + 40.361 + 2186840 / T^2) \pm 2.7 \quad (2)$$

In this equation, d is the oil density (kg.dm⁻³), and C and T are expressed as in the Chrastil equation.

The objective of this work was to predict the solubility of green and roasted coffee oils in SC-CO₂ and compare them to those experimentally obtained using this technique, applying the models developed by Chrastil (1982) and Del Valle and Aguilera (1988). Operational temperature, carbon dioxide density, moisture content, granulometry and CO₂ flow rate were optimized for coffee oil extraction.

Materials and Methods

Sample preparation

Commercial green and roasted coffee beans (*Coffea arabica*) were tested for oil extraction by supercritical extraction. The coffee beans were ground in a bench coffee grinder and sieved to obtain particles with diameters ranging from 0.297 to 0.350 mm.

Supercritical fluid extraction

Extractions were conducted in a 4x4 factorial experiment, with three repetitions, according to variable levels defined in Table 1. Green and roasted coffee oils were obtained using a supercritical extraction instrument HP7680A equipped with an ODS collector. The oil was eluted from the collector with hexane and collected in 2 mL glass vials.

Table 1: Temperatures and CO₂ densities used for extraction

Temperature (K)	Density (kg.m ⁻³)	Pressure (bar)
333	770	235
	810	275
	840	314
	880	380
343	740	253
	770	280
	810	327
	840	371
353	710	268
	740	294
	770	327
	810	379
363	680	280
	710	316
	740	337
	770	373

Two hundred milligrams of green coffee beans containing 11.4 % oil or roasted coffee beans containing 15.5 % oil, with a reduced diameter (0.297 mm to 0.350 mm) were utilized for the CO₂-SC. Thus, approximately 0.02 g of oil was in contact with the solvent CO₂. Supercritical carbon dioxide flow was maintained constant at 1.5 mL.min⁻¹ (1.2 g/min) and the static and dynamic extraction times were 5 min and 20 min, respectively. During extraction, the restrictor temperature was maintained at 343 K, the collector temperature at 308 K, and to remove oil from the collector, both temperatures were maintained at 331 K.

The amount of oil extracted was gravimetrically determined after hexane evaporation with nitrogen at 320 K, for approximately 5 min, until all solvent was removed.

Mathematical Modeling

The constants a, b, and k of the Chrastil model (eq. 1) were obtained by linear regression (Sigma Plot 2001 Program, 7.0 version) following its linearization (eq. 3 and 4):

$$y = \beta_0 + \beta_1 / T + \beta_2 \ln d \quad (3)$$

$$y = \beta_0 + \beta_1 X_{11} + \beta_2 X_{12} \quad (4)$$

Where, $y = \ln C$; $\beta_0 = b$; $\beta_1 = a$; $\beta_2 = k$; $X_{11} = 1 / T$; $X_{12} = \ln d$

Results and Discussion

The difference between the experimental oil solubility (C_{exp}) and the predicted values (C), expressed as percentage deviation (eq. 5). The behavior of the models was evaluated by comparing experimental and modeled solubility data by means of the mean percentage deviation (eq. 6) and the root mean square percentage deviation (eq. 7)

$$\Delta(\%) = (c_{calc} - c_{exp}) / c_{exp} \quad (5)$$

$$MD(\%) = 100 \left(\frac{1}{k} \right) \sum_{i=1}^k (S_{calc,i} - S_{exp_i}) / S_{exp_i} \quad (6)$$

$$RMSD(\%) = 100 \left\{ \frac{1}{k} \sum_{i=1}^k [(S_{calc,i} - S_{exp_i}) / S_{exp_i}]^2 \right\}^{0,5} \quad (7)$$

Where, k is the number of the experimental data.

The solubility data obtained experimentally were first compared to the results determined according to the Del Valle-Aguilera equation, which presented a very poor performance in representing the coffee oil solubility data, with high deviation. Solubility values provided by the Del Valle-Aguilera model were much higher than the experimental data, and two reasons can explain this behavior.

First, the Del Valle-Aguilera model was derived using experimental data for the solubility of pure oil from literature, rather than the raw material. Second, these experimental data were determined from the extraction of soybean, sunflower, cotton and corn oils, which compositions are different from that of coffee oils. The major fatty acids are palmitic (38.7 %) and linoleic (35.9 %) and a slightly higher solubility than that predicted by the correlation would be expected due to high content of palmitic acid.

Coffee oil has a high unsaponifiable content (about 12%) compared to that normally found in other plant oil. Cafestol and kahweol represent the major part of the unsaponifiable lipid fraction in coffee beans (Al Kanhal, 1977). They are mainly present as esters of fatty acid, but small amounts of free alcohol can also be found. The Robusta coffee is almost devoid of kahweol but contain a third diterpene 16-O-methylcafestol, which is absent in the Arabic coffee beans.

The variation found between the experimental and the calculated values when using the Del Valle & Aguilera equation was very high. Therefore, the Chrastil equation was used to predict the coffee oil solubility. Initially, it was used for the data containing the results for both kinds of oils, from the green and the roasted coffee beans. The values of the equation constants were determined and the regression fitted by minimizing the RMSD values (eq. 8). Table 2 shows the variance analysis of the fitted model.

$$C = d^{8.0736} e^{(-3702.49/T - 44.0125)} \pm 0.169 \quad (R^2 = 0.855) \quad (8)$$

Table 2: Variance analysis of the fitted regression for both coffee oil solubility data, according to the Chrastil model

	GL	SQ	QM	F	P
Regression	2	4.89	2.44	85.39	<0.0001
Residue	29	0.83	0.03		
Total	31	5.72	0.18		
Variable	Estimated Parameter	Standard Deviation	t for H ₀ : parameter = 0	Prob. > t	
Intercept	-44.01	3.34	-13.18	0.0001	
1/T	-3702.49	456.71	-8.17	0.0001	
ln d	8.07	0.62	12.98	0.0001	

Table 3: Solubility values obtained experimentally (C_{exp}) and calculated according to the Chrastil Model

T	P	D	C_{exp}	$C_{Chrastil}$	Δ (%) Eq. 8
(K)	(bar)	(kg.m ⁻³)	(kg.m ⁻³)	(kg.m ⁻³)	
Green coffee oil					
333	235	770	0.21 ± 0.01	0.21	0
	275	810	0.35 ± 0.03	0.31	11.8
	314	840	0.42 ± 0.03	0.41	2.9
	380	880	0.55 ± 0.01	0.59	-6.1
343	253	740	0.21 ± 0.00	0.21	0
	280	770	0.28 ± 0.02	0.28	0
	327	810	0.41 ± 0.02	0.41	0
	371	840	0.50 ± 0.04	0.54	-8.6
353	268	710	0.20 ± 0.00	0.20	0
	294	740	0.25 ± 0.01	0.27	-6.0
	327	770	0.40 ± 0.03	0.37	9.1
	379	810	0.52 ± 0.04	0.54	-3.0
363	280	680	0.17 ± 0.00	0.18	-7.4
	306	710	0.25 ± 0.01	0.25	0
	337	740	0.36 ± 0.00	0.35	3.6
	373	770	0.51 ± 0.02	0.47	8.6
MD (%)					0.16
RMSD (%)					0.40
Roasted coffee oil					
333	235	770	0.25 ± 0.02	0.25	0
	275	810	0.43 ± 0.03	0.38	11.0
	314	840	0.50 ± 0.03	0.52	-3.7
	380	880	0.72 ± 0.09	0.78	-7.0
343	253	740	0.24 ± 0.03	0.26	-6.4
	280	770	0.37 ± 0.02	0.36	3.5
	327	810	0.55 ± 0.03	0.55	0
	371	840	0.76 ± 0.02	0.76	0
353	268	710	0.24 ± 0.01	0.25	-7.0
	294	740	0.39 ± 0.02	0.36	8.5
	327	770	0.57 ± 0.06	0.51	12.7
	379	810	0.77 ± 0.03	0.78	-2.1
363	280	680	0.24 ± 0.01	0.24	0
	30	710	0.35 ± 0.02	0.35	0
	337	740	0.54 ± 0.03	0.50	6.7
	373	770	0.65 ± 0.03	0.71	-8.2
MD (%)					0.19
RMSD (%)					0.44

It can be observed in Table 3, that the experimental solubility values (C_{exp}) for roasted coffee oil solubility in SC-CO₂ are higher than those found for the green coffee oil. This fact and the low R² value observed from eq. 8 lead to the adjustment of the Chrastil model using the green and roasted coffee oil data banks separately. Two regression models were thus adjusted, one for the green coffee oil (eq. 9) and the other for the roasted coffee oil (eq. 10).

$$C = d^{7.63863} e^{(-3217.19/T-42.6617)} \pm 0.0638 \quad (R^2 = 0.977) \quad (9)$$

$$C = d^{8.50865} e^{(-4187.79/T-45.3632)} \pm 0.0696 \quad (R^2 = 0.977) \quad (10)$$

Table 4 shows the variance analysis of the fitted models. The results indicate that a better adjustment of the oil solubility was obtained by means of Chrastil model by using the experimental data of green and roasted coffee oil separately. This result was verified based on the higher determination coefficient and F parameter values, obtained for regressions 9 and 10 compared to regression 8, and also due to their respective lower standard deviations. All equation constant values were also considered significant (0.1 % by the t test).

Table 4: Variance analysis of the fitted regression and constants obtained for the separated coffee oil solubility data, according to the Chrastil model

Green coffee oil					
	GL	SQ	QM	F	Prob. > F
Regression	2	2.24	1.12	274.22	0.0001
Residue	13	0.054	0.01		
Total	15	2.29	0.15		
Variable	Estimated Parameter	Standard Deviation	t for H ₀ : parameter = 0	Prob. > t	
Intercept	-42.66	1.78	-23.94	0.0001	
1/T	-3217.19	243.71	-13.20	0.0001	
ln d	7.64	0.33	23.02	0.0001	
Roasted coffee oil					
	GL	SQ	QM	F	Prob. > F
Regression	2	2.69	1.34	277.59	0.0001
Residue	13	0.06	0.01		
Total	15	2.75	0.18		
Variable	Estimated Parameter	Standard Deviation	t for H ₀ : parameter = 0	Prob. > t	
Intercept	-45.36	1.94	-23.36	0.0001	
1/T	-4187.79	265.54	-15.77	0.0001	
ln d	8.51	0.37	23.53	0.0001	

Besides the evaluation of the determination coefficient, the standard deviations and the significance of the equation constants, a Durbin-Watson statistical test was applied. Regression procedures found an association between independent and dependent variables that, when plotted on a Cartesian coordinated system, produce a straight, plane or curved line. This, also commonly known as curve fitting, assumes that the residuals are independent of each other as verified by the Durbin-Watson test. Therefore, the Durbin-Watson statistic (DW) is a measure of correlation between the residuals. A DW value of 2 implies that they are not correlated, however, as this value differs from 2, the greater the likelihood that the residuals are correlated.

The DW value obtained for the green and roasted coffee oil data together was 0.38 and for the adjustment obtained using the green coffee oil data and the roasted coffee oil data individually were 1.98 and 2.02, respectively. This values showed that fitting the model using the data for each type of oil separately was much more efficient. Table 3 presents the observed solubility values ($C_{exp.}$) and those predicted by the Chrastil model, as well as the variation between them. The mean percentage deviations were 0.16 and 0.19 for the green and roasted coffee oils, respectively, showing a good agreement between data even though a few deviation values were greater than 10%.

Figure 1 shows the behavior of the coffee oil extraction in SC-CO₂ as a function of the density and temperature for the both observed and predicted oil solubility data. It can be observed that from a single isotherm, its inclination is more pronounced for the roasted coffee oil (Figure 1 b) as density increases.

This indicates that oil solubility in the CO₂ becomes higher for roasted coffee oil than for the green coffee oil, at comparable condition of solvent density, which also explains the better fitting of the model.

The predictions of the maximum oil solubility in CO₂, furnished by model, were 0.59 kg.m⁻³ at 333 K and a CO₂ density of 880 kg.m⁻³ for green coffee and 0.78 kg.m⁻³, at 353 K and 810 kg.m⁻³ for roasted coffee.

Conclusions

Two models were tested for the prediction of coffee oil solubilities in SC-CO₂. The Del Valle & Aguilera and Chrastil models were fitted using three different data sets containing solubility values of green coffee oil, roasted coffee oil and both green and roasted coffee oil. The Chrastil model provided better predictions when compared to the Del Valle & Aguilera equation. Agreement between observed and predict oil solubility values was better for the adjusted Chrastil model using the individual data sets for which predicted errors, expressed as mean deviations, were less than 0.2%.

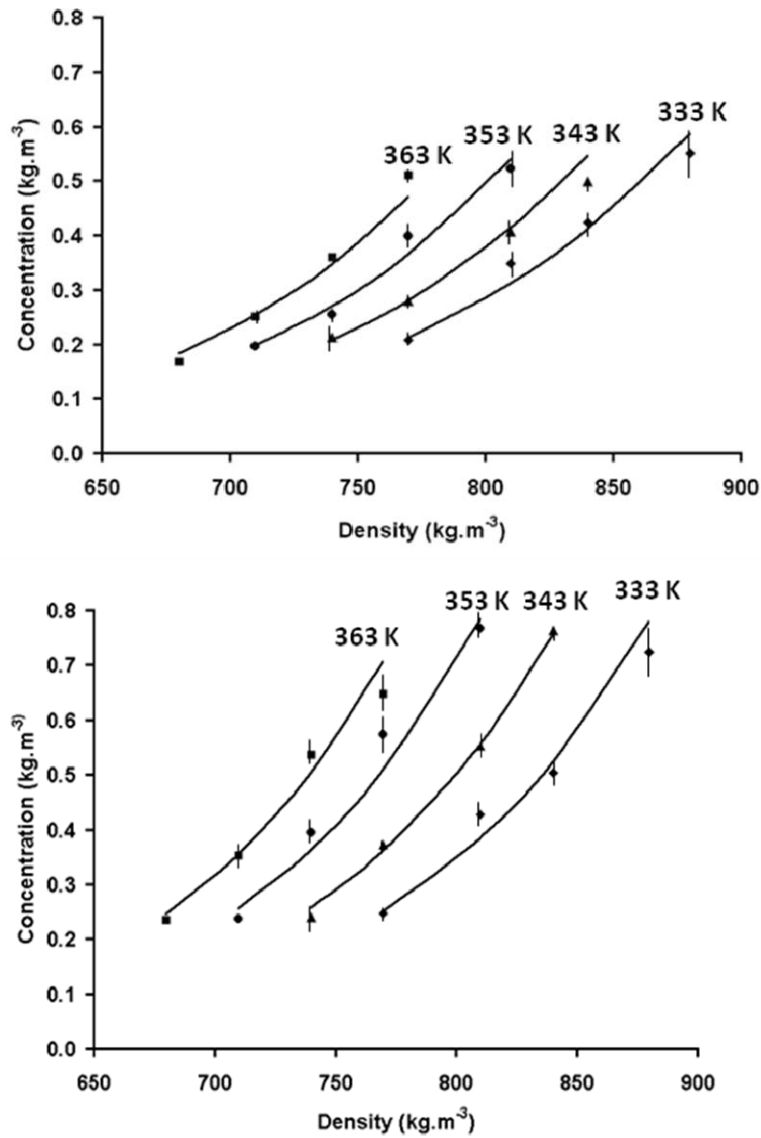


Figure 1. Solubility of green (a) and roasted (b) coffee oils in the SC-CO₂ (dots = experimental data; lines = fitted).

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