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Lauric Acid Rich Oil Supercritical Extraction and Methodology to Predict Solubility

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Abstract The seeds of *Elaeis guineensis* were submitted to extraction with supercritical carbon dioxide (CO_2) in a fixed bed. The extraction experiments were carried out in a supercritical extraction pilot plant at pressures between 15 and 25 MPa and temperatures of 318 and 323 K. The extracts were analyzed by gas chromatography to evaluate the fatty acid composition profile. The extraction results show that the maximum extraction yield was achieved at 25 MPa and 323 K. The Peng-Robinson equation of state was used to predict the solubility of the vegetable oil (extract) in carbon dioxide. The van der Waals mixing rule with two binary interaction parameters was used. The influence of the system initial composition on solubility was studied. For this purpose, the gas-liquid equilibrium was predicted for a multicomponent mixture of fatty acids and carbon dioxide. The oil (extract) was assumed to be formed by the mixture of fatty acids. The gas-liquid equilibrium predicted was compared with the palm kernel/CO_2 experimental data. The results shown that the Peng-Robinson equation was able to predict the solubility of vegetable oil in supercritical carbon dioxide from 6 to 35 MPa, when compared to experimental data. It was observed by the predicted results that palm kernel oil showed the solubility isotherms intersect in the vicinity 25 MPa at temperatures of 313 to 353 K; the palm kernel oil initial composition influenced on the calculated solubility.

Keywords Supercritical Extraction, Palm Kernel, Solubility

1. Introduction

The seeds of *Elaeis guineensis*, a palm that produces one of the world's most important vegetable oils have great economic importance in North region of Brazil. It contains about 47-50 [wt.%] of an oil whose chemical composition and physical properties are quite different from palm oil, but rather similar to coconut oil. Palm kernel oil is a rich source of low chain saturated fatty acids, particularly lauric acid (about 53%), an important raw material for the food, cosmetic and pharmaceutical industries [1-3].

Numerous applications of supercritical technology for extraction, purification/fractionation of vegetable oils and related compounds from different raw materials have been reported in important reviews published in the literature [4-9]. At supercritical conditions the solvent, for instance carbon dioxide, shown high density values and usually are called as dense gas. Carbon dioxide was the solvent most used considering its near-ambient critical temperature, relatively low critical pressure and others properties such as its nontoxicity, nonflammability, and low cost. Supercritical carbon dioxide can be used as antisolvent to micronize drugs, encapsulates drugs in polymeric structures and fractionate bioactive natural products from liquid feeds [10-17].

For supercritical technology process design a wide variety of process parameters has to be considered and one of the most important is the solubility of the target compound (or mixture of compounds) in the supercritical solvent at the operating conditions (temperature, pressure, density).

Solubility can be determined by the static or dynamic method [18]. The solubility by the dynamic method is obtained using the data for the overall extraction curve (OEC) experiments choosing the solvent flow rate that must ensure the solvent leaves the fixed bed saturated with the solute. For a wide variety of natural products there are published values of solubility [19-23].

The solubility of Malaysian palm kernel oil was calculated based on the OEC at temperatures between 313.2

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and 353.2 K and pressures from 20.7 to 48.3 MPa, with the values ranging from 0.04 to 0.20 g-oil/g-CO_2. At pressures below 27.6 MPa the solubility of palm kernel oil in carbon dioxide decreased with the increase of the temperature. At pressures higher 34.5 MPa the solubility increased with temperature, as an effect of the decreases density of the carbon dioxide [24, 25].

Cubic equations of state (EOS) models are useful tools for the correlation of experimental data and prediction of solubility. Peng-Robinson EOS with the van der Waals mixing rule with two binary interaction parameters has shown to give good results for the description of gas-liquid equilibrium of lipid-related compounds with CO_2 [26-29].

Bharath et al [30] measured the mutual equilibrium solubility of the pseudo-binary system palm kernel oil/ carbon dioxide at a wide range of temperatures from 313.15 to 353.15 K and pressures from 6.28 to 34.55 MPa and to our knowledge until now, the correlation using EOS considering this system as a pseudo-binary or multicomponent were not described in the literature.

Hong et al. [29] measured the phase equilibrium of the system palm kernel oil/ carbon dioxide at temperatures from 333.2 to 373.2 K and pressures from 8.5 to 35 MPa. The authors correlated the phase equilibrium data with Peng–Robinson Equation of State (PR-EOS) using Wong–Sandler mixing rule, considering the system as a pseudo-binary i.e., the palm kernel oil as a pseudo pure compound. The authors suggested that the thermodynamic model is capable of describing the gas-liquid equilibrium data with deviation between of 6.9–8.7%.

In this work the seeds of *Elaeis guineensis* were submitted to extraction with supercritical carbon dioxide in a fixed bed. The extraction experiments were carried out in a supercritical extraction pilot plant at pressures between 15 and 25 MPa and temperatures of 318 and 323 K. The extracted oil was analyzed by gas chromatography **to evaluate the fatty acid composition profile.** The Peng-Robinson equation of state with van der Waals mixing rules with two binary interaction parameters was used to predict the solubility of palm kernel oil in carbon dioxide. The methodology proposed is based on assumption that palm kernel oil can be considered as a mixture of fatty acids. The influence of different initial composition of palm kernel oil on predicted solubility was studied.

2. Materials and Methods

Dentauá S/A (Pará, Brazil) delivered the Palm (*Elaeis guineensis*) kernels. Carbon dioxide 99.99 [wt.%] pure was provided by White Martins S/A. The kernels were dried in an oven with air circulation (Fabbe, Model 179, São Paulo, Brazil) at 323 K for 24 hours. Afterwards, it was grounded with a comminuting mill (Tecnal, Model OB136, São Paulo, Brazil). The dried material was packed in plastic bags and kept in a freezer at 268 K.

2.1. Supercritical Extraction

The experiments were carried out in a supercritical extraction unit available at the Federal University of Pará (Pará, Brazil). A schematic diagram of the extraction unit is shown in Figure 1. It consists of an extractor (Metalwerksatt, TUHH) with 2000 cm³ (E), a diaphragm-type compressor (Andreas Hofer, Model MKZ 120-50, Mülheim, Germany,), two separators with 1000 cm³ (S1 and S2) (Metalwerksatt, TUHH), a thermostatic bath (Haake Mess-Technik GmbH, Model N3, Karlsruhe, Germany), a carbon dioxide reservoir, a gas flow meter, and a control unit that displays the temperature and pressure inside the extractor and separator. Carbon dioxide was delivered using V6 e V18 at the required pressure by the membrane compressor (Andreas Hofer, Model MKZ 120-50, Mülheim, Germany) and passed through a porous plate in order to assure a homogeneous flow of carbon dioxide along the fixed bed of 8.0 cm height and 6.0 cm internal diameter, placed inside the extractor. The supercritical carbon dioxide/solute mixture passed through VCP, V2 and V3 and then was expanded in the separator S1 containing Raschig rings made of glass of 1"/4 (0.635 cm). The fixed bed of Raschig rings was placed inside the separator in order to retain more efficiently the condensates. The samples were collected every 10 minutes using V13. The expanded carbon dioxide using V4 passed through a gas flow meter and was recycled to the extractor using V5. The pressure was measured by a Bourdon-type gauge (0-40 MPa, ± 0.5 MPa; Model DIN.S, Wika, Germany) and the temperature was monitored by a thermocouple (NiCr/Ni). All the extraction experiments were carried out in duplicate and with a fixed mass of palm kernel (180 g). All samples collected were accumulated to be submitted to chromatography analysis.

2.2. Chemical Analysis

In order to determine the chemical composition of the extracts with respect to fatty acids methyl esters, the samples were esterified. The procedure consists basically on the saponification of the extracts with a solution of sodium hydroxide 0.5 N in methanol, followed by esterification using a solution of ammonium chloride, sulfuric acid and sodium hydroxide in the proportion of 1: 1.5: 30 (vol./vol.).

The chemical composition of the esterified samples was analyzed using a GC (Perkin Elmer, Model Sigma 3B, USA) equipped with FID detector and a stainless steel column (4 m × 0.30 cm, Silar, USA) packed with Cromosorb W. The carrier gas was nitrogen (25 ml/min.) and 1µL of the sample was injected. The detector and injector temperatures were regulated at 498 K. The peak areas were computed with an integrator (Perkin Elmer, Model LCI-100, USA) coupled to the GC. The chemical identification of fatty acids methyl esters has been performed by comparing the retention time of all relevant peaks with those obtained by splitting a standard mixture of pure fatty acid methyl esters (Nu-check-prep, Inc., USA).

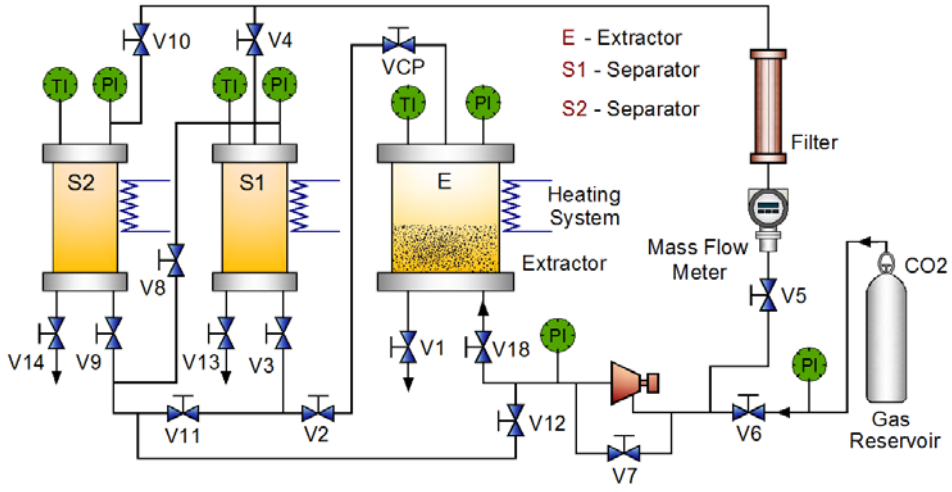

Figure 1. Flowsheet of the experimental apparatus

2.3. Palm Kernel Oil Solubility in Carbon Dioxide

The palm kernel oil solubility in supercritical carbon dioxide (mass fraction in gaseous phase) was calculated using the Peng-Robinson equation of state, with the van der Waals mixing rules with two binary interaction parameters.

The computation of multicomponent mixture solubility in carbon dioxide using an equation of state requires information concerning the thermosphysical properties (critical temperature Tc, critical pressure Pc, and the acentric factor ω) of all of the pure components constituting the multicomponent system, the composition and the binary interaction parameters between the pure components and carbon dioxide. In this work, the palm kernel oil composition was represented by a mixture of fatty acids.

The equation of Peng-Robinson is given as follows:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \quad (1)$$

The van der Waals mixing rules (vdW) with the combining rules for two binary interaction parameters (quadratic mixing rule) are given by the following equations:

$$a_m = \sum\sum x_i x_j a_{ij} \quad (2)$$

$$b_m = \sum\sum x_i x_j b_{ij} \quad (3)$$

$$a_{ij} = \sqrt{a_{ii} a_{jj}}\left(1 - k_{ij}\right) \quad (4)$$

$$b_{ij} = \frac{\left(b_{ii} + b_{jj}\right)}{2}\left(1 - l_{ij}\right) \quad (5)$$

where k_{ij} and l_{ij} are the binary interaction parameters, obtained by adjusting vapor-liquid equilibrium data and x_i, y_i are the phase equilibrium molar fraction of the liquid and gaseous phase respectively.

The binary interaction parameters were fitted to the literature phase equilibrium data by minimizing an objective function, using the program EDEflash [31]. The program uses a P-T flash algorithm and the modified Simplex method of Nelder and Mead [32].

The gaseous phase molar fraction of the multicomponent gas-liquid equilibrium calculated with the Peng-Robinson EOS with van der Waals mixing rules, for the system palm kernel oil/supercritical carbon dioxide, was converted in solubility for the various compositions in fatty acid in agreement with the following equation:

$$sol\left(g_{oil}/g_{CO_2}\right) = \frac{\sum_i M_i . z_i}{M_{CO_2} . z_{CO_2}} \quad (6)$$

z_i - molar fraction of the gaseous phase

3. Results and Discussions

The operating conditions and process parameters of the supercritical extraction of palm kernel oil from the seeds of *Elaeis guineensis* with CO_2 are in Table 1. The fixed bed characteristics were: true density of 1.00 g/ml as measured by the sand picnometry technique [33], apparent density of 0.79 g/ml; average particle diameter of 0.306 mm calculated as suggested by the ASAES-319.2 method [34]; porosity of 0.21, and volume of 226.19 cm³.

Table 1 shows that the yields were directly influenced by pressure and temperature, thus, the carbon dioxide density. The maximum extraction yield was achieved at 25 MPa and 323 K (highest CO_2 density) corresponding to 42% with minimum extraction time.

In others experimental studies described in the literature, the Malaysian palm kernel oil extracted using supercritical carbon dioxide at temperatures of 313.2 and 353.2 K and pressures from 20.7 to 48.3 MPa, showed that at pressures 20.7 and 27.6 MPa, an isobaric increase in temperature resulted in slight decrease the yield of the oil, from 18 to 17% and 34 to 33% respectively, as an effect of the decreases density of the carbon dioxide [35].

All the extraction using supercritical CO_2 as solvent showed yields lower than solvent Soxhlet extraction corresponding to 50% obtained by Chen et al. [2] and Zaidul

et al. [35].

Table 1. Process parameters and operating condition for the extraction of palm kernel oil with supercritical CO_2

P [MPa]	T [K]	Density (kg/m^3)	m_{CO2} (g/min)	Time [min]	Yield* (%)
15	318	743.17	18	170	33
20	323	785.16	18.5	90	37
25	323	834.89	16.66	60	42

*mass of extracted oil/mass of dried solid matrix

Table 2 shows the compositions in terms of total amount of fatty acids for the extraction of palm kernel oil with supercritical CO_2, under different operating conditions, obtained in this work and the composition of the palm kernel oil, extracted by pressing out mechanically by Bharath et al. [30], but the yield was not informed by the authors. The total amount of fatty acids in palm kernel oil extracted with CO_2 ranged from 0.74 to 53%. The main saturated fatty acids for all extraction conditions was lauric acid with a concentration ranging from 51 to 53% followed by myristic acid (~20%). The extracted palm kernel oil obtained at 15 MPa showed the highest lauric acid concentration, while at 25 MPa showed the lowest concentration. The same behavior was obtained by Zaidul et al. [35] that at lower pressure (20.7 MPa) obtained the highest lauric acid concentration (53%) while at 48.3 MPa obtained the lowest lauric acid concentration (48%) at 313.2 K.

Table 2. Palm kernel oil composition in fatty acids (% molar)

Fatty acid	Bharath et al. [30]	Extracted with CO_2 (323.15 K)		
		15 MPa	20 MPa	25 MPa
Caprylic acid (C8:0)	--	4.09	3.28	2.36
Capric acid (C10:0)	2.93	4.33	3.98	3.58
Lauric acid (C12:0)	60.92	53.10	52.20	51.00
Myristic acid (C14:0)	15.54	19.80	20.07	20.10
Palmitic acid (C16:0)	6.49	9.44	10.12	10.93
Stearic acid (C18:0)	1.08	3.40	3.57	4.51
Oleic acid (C18:1)	11.56	5.10	5.90	6.55
Linoleic acid (C18:2)	1.48	0.74	0.88	0.97

The composition of solvent Soxhlet extraction of palm kernel oil obtained by Pantzaris and Ahmad [3] was: 0.3% (caproic acid), 4.2% (caprylic acid), 3.7% (capric acid), 48.7% (lauric acid), 15.6% (myristic acid), 7.5% (palmitic acid), 1.8% (stearic acid), 14.8% (oleic acid) and 2.6% (linoleic acid) and the composition obtained by Zaidul et al. [35] was 4% (caprylic acid), 3.7% (capric acid), 48% (lauric acid), 15.4% (myristic acid), 7.5% (palmitic acid), 2% (stearic acid), 15.1% (oleic acid) and 2.7% (linoleic acid). The highest composition in lauric acid 60.92% was obtained when extracted by pressing out mechanically by Bharath et al. [30], followed by myristic acid 15.54%, but caprylic acid was not detected.

The Peng Robinson equation of state with the van der Waals mixing rules and the combining rules for two binary interaction parameters was selected to predict the mutual equilibrium solubility of the multicomponent system palm kernel oil/CO_2. The oil was assumed to be constituted by a mixture of fatty acids. To compare with the predicted results, the gas-liquid equilibrium experimental data and the palm kernel oil composition in fatty acid from Bharath et al. [30] were used (Table 2).

The binaries interaction parameters showed in the Table 3 was used to compute the multicomponent mutual equilibrium solubility. These parameters were calculated previously and described in details by Araújo and Meireles [31]. For binaries that equilibrium data do not exists, the binary interaction parameters were considered equal to zero, as well the parameters for the binaries systems like fatty acid *i*/fatty acid *j*.

Table 3. Binary interaction parameters used in this work

Systems: CO_2 +	Ka_{ij}	Kb_{ij}
Lauric acid	0.091733	0.061768
Myristic acid	0.104786	0.021304
Palmitic acid	0.532311	0.128817
Stearic acid	0.177818	0.030238
Oleic acid	0.122491	0.092045
Linoleic acid	0.087522	0.085821

The values for the boiling points, critical properties and acentric factors of the palm kernel oil fatty acids composition described in the Table 4 are the results of the evaluation of the physical properties predictive methods accomplished by Araújo and Meireles [31].

Table 4. Physical Properties of Pure Components

Fatty acid	CAS Number	M (g/gmol)	Tb (K)	Tc (K)	Pc (MPa)	ω
Caprylic	124-07-2	144.21	512.01	694	2.70	0.7178
Capric	334-48-5	172.27	541.92	726	2.10	0.7342
Lauric	143-07-7	200.32	571.40	742.68	1.86	0.8689
Myristic	544-63-8	228.38	599.00	762.11	1.64	0.9432
Palmitic	57-10-3	256.43	622.30	780.38	1.47	1.0104
Stearic	57-11-4	284.48	648.10	796.65	1.32	1.0861
Oleic	112-80-1	282.47	625.46	796.34	1.24	0.9245
Linoleic	60-33-3	280.45	624.10c	796.03	1.24	0.7767

Figure 2 compares the experimental data of gas-liquid equilibrium of the palm kernel/CO_2 system at 353 K measured by Bharath et al. [30], expressed in CO_2 weight fraction, with the values predicted by the Peng-Robinson equation with the van der Waals mixing rules for two binary

interaction parameters. The absolute medium deviations between the experimental data and the predicted CO_2 weight fraction were $\Delta x=0.0974$ and $\Delta y=0.0030$. As showed in Figure 2, the methodology proposed for the calculation of gas-liquid phase equilibrium of vegetable oil in supercritical CO_2, based on the vegetable oil fatty acid composition, described with success the behavior for the palm kernel oil. Similar results were observed for the isotherms 313, 323 and 333 K.

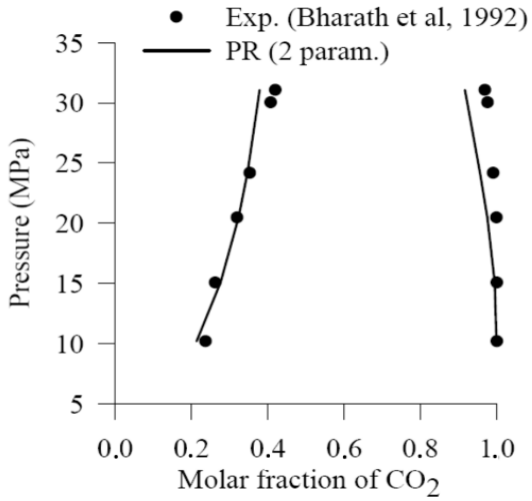

Figure 2. P-x-y diagram for the system palm kernel oil/supercritical CO_2 at 353 K

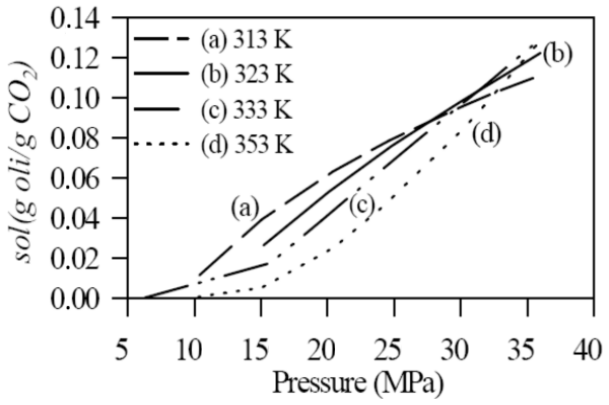

Figure 3. Solubility isotherms of the palm kernel oil in carbon dioxide

Using the same method, the Bharath et al. [30] palm kernel oil composition in fatty acids was employed to simulate solubility isotherms of the palm kernel oil in carbon dioxide. Figure 3 presents the predicted solubility isotherms in the range of 313 to 353 K. The values obtained ranging from 0.01 to 0.13 g-oil/g-CO_2 showed that at pressures below 25 MPa an isobaric increase in temperature decreases the solubility of the oil as an effect of the decrease in density of the carbon dioxide as shown in Table 5. Even so, with the increase of the pressure, remarkably above 30 MPa, the behavior of the solubility with pressure and temperature changed, and the isotherms interception point represents a measure of the effect of the temperature in the solubility where at higher pressures solubility of the palm kernel oil increases with temperature. The increase in palm kernel oil compounds vapor pressures which accompany the increases of the temperature also contributes to the increase in solubility.

The same behavior occurred when the palm kernel oil solubility in carbon dioxide was calculated [24, 25] and when were analyzed the experimental and predicted equilibrium solubility of soybean oil and jojoba oil in carbon dioxide measured by Quirin [36] and Stahl et al. [37-38], respectively. The values of the solubility of palm kernel oil at 20.7 and 27.6 MPa decreased with the increase in the temperature from 313.2 and 353.2 K, even so, at pressures higher than 34 MPa it increases with the increase of temperature, and at 48.3 MPa the solubility increased from 0.07 to 0.2 g-oil/g-CO_2 when the temperatures increased [24, 25]. It was observed that soybean oil showed the solubility isotherms intersect in the vicinity of 30 MPa at temperatures between 298 to 353 K and jojoba oil in the vicinity of 20 MPa at temperatures between 293 to 353 K [36-38].

Table 5. Carbon dioxide density from the database NIST Chemistry Web Book (2014)

Density (kg/m^3)	P (MPa)	T (K)
221.93	10	353
290.81	10	333
386.77	10	323
594.85	20	353
631.74	10	313
686.98	25	353
724.63	20	333
746.24	30	353
785.16	20	323
823.66	40	353
830.33	30	333
834.89	25	323
840.61	20	313
871.03	30	323
880.15	25	313
890.64	40	333
910.47	30	313
923.81	40	323
956.56	40	313

The different compositions of palm kernel oil extracted with supercritical CO_2 in this work (Table 2) were used to evaluate the influence of initial composition on prediction of the equilibrium solubility using the rigorous procedure for calculation of phase equilibrium using the Peng-Robinson EOS.

Figure 4 compares the predicted solubility of palm kernel

oil in supercritical CO_2 based on the different compositions in fatty acids. In spite of the small differences in fatty acids content obtained at the different pressures, the initial compositions resulted in different solubility values, mainly at pressures from 20 to 30 MPa. These results demonstrate the influence of the initial composition in the multicomponent phase equilibrium calculations at high pressures.

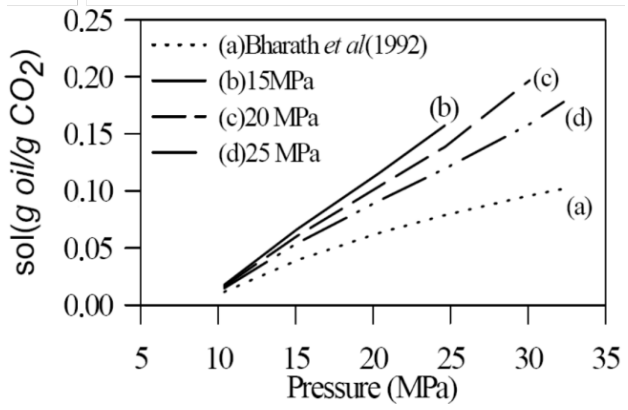

Figure 4. Palm Kernel oil predicted solubility in CO_2 at 313 K. using different initial composition

4. Conclusions

Supercritical carbon dioxide extraction of kernel oil from *Elaeis guineensis* was measured in a recirculation apparatus at pressures between 15 and 25 MPa and temperatures of 318 and 323 K. The maximum extraction yield was achieved at 25 MPa and 323 K, at the highest CO_2 density, corresponding to 42% with minimum extraction time. The extracted oil submitted to a chromatography analysis showed that the main saturated fatty acids in all extraction conditions was lauric acid with a concentration of 53.10% at 15 MPa followed by myristic acid with 20.10% at 25MPa.

The rigorous thermodynamic procedure for phase equilibrium modeling using the Peng-Robinson EOS with the van der Waals mixing rule with two binary interaction parameters has shown to be capable of predicting gas-liquid equilibrium of the multicomponent system palm kernel oil/carbon dioxide, for the investigated isotherms between 313 and 353 K at pressures in the range of 6 and 30 MPa, considering the oil as a mixture of fatty acids. It was observed that the palm kernel oil initial composition influenced on the calculated solubility.

Regarding to vegetable oils, their compositions are a complex mixture of triglycerides, therefore, the methodology proposed here can be used as an estimating of the highest solubility region using a fatty acid composition model contributing to lower the number of experimental data required in process design.

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