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Equlibrium Solubilities of Tiger nut (*Cyperus esculentus L.*) Oil in Supercritical Carbon Dioxide

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Abstract

The aim of the present work is to determine the solubility of tiger nut oil by using supercritical carbon dioxide as extracting solvent. A simple dynamic technique was used to obtain the solubility of tiger nut oil in supercritical carbon dioxide. The solubility was measured at temperatures ranging from 313.2 to 358.2 K and pressures from 7.24 to 14.68 MPa. Under extraction conditions, the measured solubilities were in the range from 6.8×10^{-2} to 1.29×10^{-1} (g of oil)/(mL of CO_2). The solubilities of this component increased with a pressure increase, whereas they decreased with temperature increase. The Chrastil equation and Adachi and Lu equation were used correlate the solubility behavior of tiger nut oil in supercritical CO_2, which revealed that both equations are in good agreement with the experimental data. Since the average absolute relative deviation (AARD%) values of the Chrastil equation range from 0.42 to 4.99 % and the AARD values of Adachi and Lu equation range from 0.16 to 1.71 %, it was shown that the Adachi and Lu models correlated better with the experimental data.

Keywords: Solubility, Supercritical carbon dioxide, Chrastil equation, Adachi and Lu equation, Correlation, Tiger nut oil

1. Introduction

Tiger nut oil has a golden colour and a nutty aroma, which makes it ideal for different uses in cosmetic applications, deep frying and bio-diesel. Its use in deep frying is quite exceptional because of its resistant to chemical decomposition at high temperature and the amount of oil absorption is lower for this oil than other frying oils [1]. The oil content of tiger nut ranges from 26 to 38 g/100 g sample. Physical and chemical characteristics of tiger nut are well documented in the literatures [2, 3]. Tiger nut oil consists of 12.70 g/100 g sample of linoleic acid (C18:2), 68.8 g/100 g sample Oleic acid (C18:1) and 15.5 g/100 g sample of palmitic acid (C16:0).

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Vegetable oil is commonly obtained by mechanical pressing and solvent extraction using organic solvents such as hexane. However, pressing gives relatively low yields, while the solvents used for extraction are often harmful to human health and the environment. Supercritical carbon dioxide is an inexpensive, non-flammable and non-toxic solvent and, for these reasons, the supercritical fluid extraction (SFE) technique using supercritical CO_2 is considered to be an attractive alternative to these conventional extraction methods [4]. SFE has been extensively used in many processes, such as in food, pharmaceutical, biochemical industries, polymer processing and environmentally friendly chemical processing [5, 6].

The extraction rate from solid materials such as seeds is often limited by the solubility of the oil in the supercritical CO_2. SFE process optimisation requires the knowledge of the solubility data, which allows the selection of the most adequate operating conditions, such as temperature, pressure, extraction time and solvent flow rate [7]. Besides, the solubility information is important for the process design as well as analytical applications. Oil solubility can be measured using either static or dynamic method, both by contacting CO_2 with the previously obtained oil directly or with the ground substrate materials [8]. In the dynamic method, the supercritical fluid flows continuously through an equilibrium vessel containing the oil being studied or with a solid material of large surface wetted with the oil. The operation conditions are chosen so that the outlet stream can be assumed to have reached the equilibrium. The dissolved or extracted oil is usually precipitated out and weighed, and the gaseous flow exiting the restrictor is measured by using a wet or dry flow metre to determine the amount of the supercritical fluid used to dissolve the oil [9]. A lot of researchers have used the dynamic method to investigate the solubility of different oils in supercritical carbon dioxide, such as sunflower oil [10], rosehip oil [11] and borage oil [12].

A few studies have been conducted on the use of SC-CO_2 to extract tiger nut oil [13]. However, to the best of our knowledge, no reports have been published on the experimental solubilities of tiger nut oil in SCFs in general, particularly in SC-CO_2. The scarcity of experimental data led to the present study, which supports the design and identification of operating conditions for SCF processes.

2. Materials and methods

2.1. Raw material and pre-treatment

Tiger nut were purchased from Katsina State, Nigeria. Carbon dioxide (purity 99.99%) was supplied by the Kras Instrument & Service (Larkin, Johor Bahru, Malaysia). All chemicals and solvents were either analytical grade or GC grade and were purchased from

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Fisher Scientific Chemical (Loughborough, UK) and Merck (Darmstadt, Germany). The nuts were ground using a conventional electric mill and sieved with a mesh to produce an average size of 0.54 mm. Samples were stored in a refrigerator at 4^{o}C for not more than 24 h prior to extractions. The moisture content was determined according to the PORIM Test Method [14]. For the PORIM test, an approximately 25 g of test sample was first heated at 10 ^{o}C/min up to 90 ^{o}C and the temperature was further increased to 103 $\pm$2 ^{o}C. Once the bubbles have ceased the sample was cooled to ambient temperature inside a desiccator. The moisture content was expressed as a percentage by mass.

2.2. Extraction of tiger nut oil using supercritical carbon dioxide.

The SFE analyses were performed using a CO_2 HPLC pump (Lab Alliance SFT-24). The CO_2 was delivered from the supply tank to a cooling jacket fitted to the CO_2 HPLC pump. For each experiment, a mixture of 1:1 (v/v) ground (15 g) tiger nut and (1 mm diameter) glass beads was placed in a 50 mL stainless steel extraction vessel (Model EV-3, Jasco Corporation, Japan). The vessel was then placed in an oven at a selected temperature. Carbon dioxide flowed through the preheated 4 m long coil, and we ensured that the desired temperature was attained before contacting the sample in the extraction vessel. A back pressure regulator (Model BP-2080, Jasco Corporation, Japan) was used to control the extraction pressure. The CO_2 flow rate was maintained at 1.05 – 2.20 mL/min, and the extraction time was measured at 30 min-intervals for an overall time of 180 min. Operating conditions such as temperature, pressure and flow rate were chosen on the basis of a preliminary study. Extractions were performed in the temperature range from 313.2 to 358.2 K and a pressure range from 7.24 to 14.68 MPa. Dynamic extractions were initiated when the system reached a predetermined pressure and temperature. A 5 mL vial was utilized as the collection vessel for the extracts. After extraction, the oil was refrigerated at −4 ◦C. A schematic of the experimental setup for the extraction is shown in Fig. 1.

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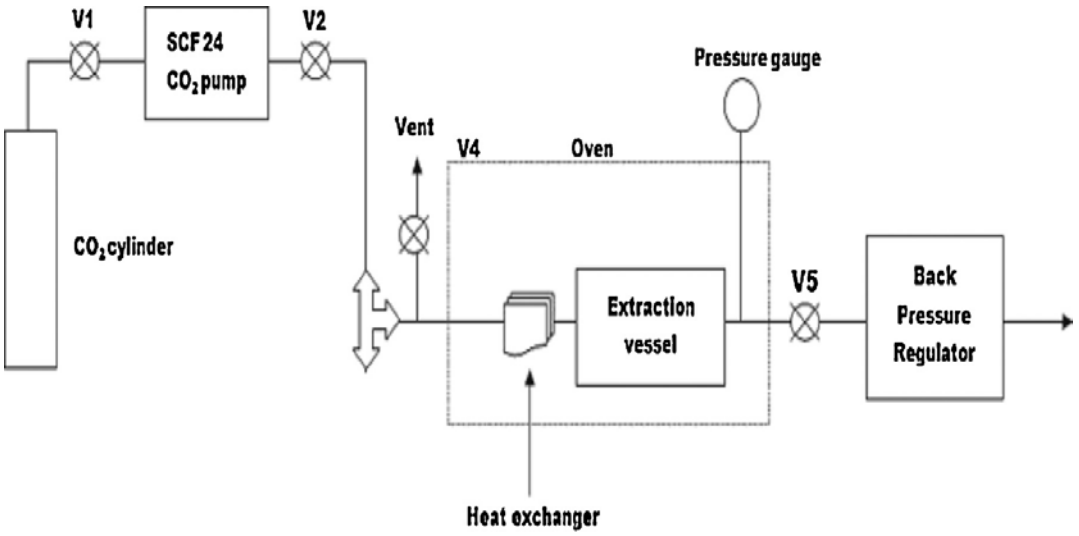

Fig. 1. Schematic of SFE using supercritical carbon dioxide.

2.3. Calculation of yield

Extraction yields were measured gravimetrically by collecting the oils precipitated at the collection vial. The oil yield (%) was determined by the following equation [15]:

$$\text{Weight} = \frac{\text{wo x 100}}{\text{ws}} \quad (1)$$

where wo is the weight of the extracted oil and ws is the weight of the tiger nut.

2.4 Solubility of tiger nut oil in SC-CO_2

Equilibrium solubilities data of tiger nut oil in supercritical CO_2 for temperatures ranges from 313.2 to 358.2 K and pressures ranges from 7.24 to 14.68 MPa were measured by plotting experimental data of mass of oil extracted against the mass of CO_2 used (overall extraction curves). The curves were developed at 2.2 mL/min of CO_2 flow rate. Therefore, the solubility (S) was the slope of the constant extraction rate period of the overall extraction curves. Chrastil and Adachi and Lu models were selected to evaluate the use of empirical model to correlate solubility data of tiger nut oil in supercritical CO_2. These models are described to be appropriate for the range of temperature and pressure from which the experimental values were obtained.

A multi linear regression was performed by using Solver in Excel 2007 program to determine the model constants. The accuracy of Chrastil models and Adachi and Lu model were quantified by analysis of average absolute relative deviation percentage (AARD). Equation 2 represents the method in calculating AARD%.

$$\text{AARD\%} = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\ln Scal - \ln \exp}{\ln S \exp}\right| X100 \quad (2)$$

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where n = is the number of data points, Sexp is the solubility obtained from experimental data and Scal is the solubility calculated using the model.

3. Correlation of experimental solubility data

In the present work, the tiger nut oil experimental solubility data were correlated using two semi-empirical density-based models, namely the Chrastil and Adachi and Lu.

3.1. Density-based correlations

3.1.1. Chrastil model

One of the first empirical models for correlating the solubilities of solids and liquids in supercritical fluids was developed by Chrastil [16]. It was derived by considering the equilibrium of the hypothesized solvato-complex with solute and solvent molecules. The model is mathematically described as follows:

$$\ln S = k \ln \rho + \frac{\alpha}{T} + \beta \quad (3)$$

In this expression, S (kgm^{-3}), is the solubility of the solid in the supercritical phase, ρ (kgm^{-3}), is the density of the pure supercritical fluid, k, is the association number, α, is a constant, defined as $\Delta H/R$ (where ΔH, is the sum of the enthalpies of vaporization and solvation of the solute, and R is the gas constant) and, β, is another constant somehow related to the molecular weights of the solute and solvent. The parameters k, α, and β, are obtained performing a multiple linear regression on the experimental solubility data.

3.1.2. Adachi and Lu

Adachi and Lu [17] have changed the association number to a second-order polynomial of the supercritical fluid density, therefore, they proposed another equation as shown in eq. (4):

$$\ln S = (e_0 + e_1.\rho + e_2.\rho^2) \ln \rho + \frac{a}{T} + b \quad (4)$$

The association number is the exponent of the density (referred to as k in the original Chrastil equation) and shows the dependence of the solubility on density. In the Adachi–Lu version of the model, k is a function of the density as seen in Eq. (5):

$$k = e_0 + e_1\rho + e_2\rho^2 \quad (5)$$

4. Results and discussion

The experimental solubility of tiger nut oil was measured using a gravimetric method which was verified by measuring the solubility of palm kernel oil [18]. The obtained solubility data are listed in Table 1 in terms of (g of oil)/(mL of CO_2).

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Table 1: Measured solubilities of tiger nut oil in SC-CO_2 at selected pressures and temperatures.

T/K	P(MPa)	ρ of CO_2 (g/mL)	y (CO_2)	S (g/mL)
313.2	7.38	0.224	0.955	0.068
	8.24	0.331	0.954	0.096
	9.30	0.512	0.953	0.174
	10.20	0.636	0.952	0.207
	11.62	0.714	0.950	0.235
	12.52	0.740	0.948	0.253
	13.75	0.767	0.946	0.280
328.2	7.30	0.174	0.956	0.052
	8.22	0.214	0.955	0.065
	9.08	0.261	0.954	0.080
	10.24	0.351	0.953	0.109
	11.24	0.435	0.952	0.142
	12.08	0.508	0.951	0.169
	13.24	0.586	0.949	0.200
343.2	7.26	0.151	0.956	0.044
	8.58	0.192	0.955	0.058
	9.52	0.227	0.955	0.070
	10.38	0.264	0.954	0.082
	11.68	0.328	0.953	0.105
	13.39	0.422	0.951	0.141
	14.18	0.463	0.950	0.159
358.2	7.24	0.136	0.957	0.039
	8.30	0.163	0.956	0.048
	9.36	0.192	0.956	0.057
	10.82	0.238	0.954	0.073
	12.36	0.293	0.953	0.093
	13.48	0.336	0.952	0.109
	14.68	0.384	0.950	0.129

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The resulting solubilities for tiger nut oil ranged between 6.8×10^{-2} and 1.29×10^{-1}(g of oil)/(mL of CO_2) as shown in Table 1. Solubility increased as the pressure increased. This trend is related to higher density of supercritical carbon dioxide at higher pressures. Higher density and pressure lead to higher salvation power of SC-CO_2 and as such, more tiger nut oil is dissolved in SC-CO_2, whereas solubilities decreased with temperature increase. The experimental results measured in this study revealed that at 313.2 K the solubility of the tiger nut oil increases from approximately 0.068 to 0.280 g/mL CO_2 for pressures ranging from 7.38 to 13.75 MPa; at 328.2 K the solubility increases from approximately 0.052 to 0.200 g/mL CO_2 for pressures ranging from 7.30 to 13.24 MPa; at 343.2 K the solubility increases from approximately 0.044 g/mL to 0.159 g/mL CO_2 for pressures ranging from 7.26 to 14.18 MPa; at 358.2 K the solubility increases from approximately 0.039 to 0.129 g/mL CO_2 for pressures ranging from 7.24 to 14.68 MPa. The solubilities of tiger oil nut in SC-CO_2 showed that the solubilities of this solute highly relied on the density of CO_2.

Table 2: Fitting Constants Obtained for Chrastil Model

T/K	k	α	β	AARD%
313.2	1.1176	−473.0629	0.4832	2.23
328.2	1.1094	−495.7320	0.4835	0.42
343.2	1.1312	−682.7308	0.4835	2.59
358.2	1.1417	−530.7713	0.5726	4.99

Table 3: Fitting Constants Obtained for Adachi and Lu Model

T/K	e_0	e_1	e_2	a	b	AARD%
313.2	1.397	−0.656	2.739	−408.813	0.688	1.71
328.2	1.205	0.366	0.794	−442.008	0.647	0.18
343.2	1.199	0.631	0.254	−455.196	0.668	0.16
358.2	1.102	0.521	−0.884	−523.583	0.533	0.19

The optimum fitting parameters for the correlations were obtained using a least squares method and curve-fitting approach. The fitted parameters are listed in Table 2 for each correlation; they enabled us to correlate tiger nut oil solubilities in the pressure range from 7.24 to 14.68 MPa and the temperature range from 313.2 to 358.2 K. The fits contained an acceptable level of engineering error. The parameter of (α) in Table 2 shows the influence of temperature changes within the extraction vessel. It was also reported that high absolute values of the parameter (α) are related to high temperature effects [19]. In contrast, low values of k indicate that most of the oil was extracted with SC-CO_2, while the parameter β indicates that the solute was extracted. In addition it was reported that the values k and β can

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be assumed to be independent of temperature [20]. Correlating solubility data with the density-based correlations of Chrastil (1982) revealed that the correlations produced the solubility data with an AARD% of 0.42 to 4.99%.

The Adachi and Lu equations are given in Table 3, with an AARD% values range from 0.16 to 1.71 %. As shown in this Table, indicating that all of the two selected empirical equations can very well correlate the experimental data. When the Chrastil equation is compared with Adachi and Lu equation, it is revealed that the Adachi and Lu equation obtained the better correlation for the experimental data with an overall AARD of 2.24 %. These equations provide a simple and reliable way to correlate the solubility of tiger nut oil component in SC-CO_2, so that relevant factors such as the critical or thermophysical properties of the oil are not estimated.

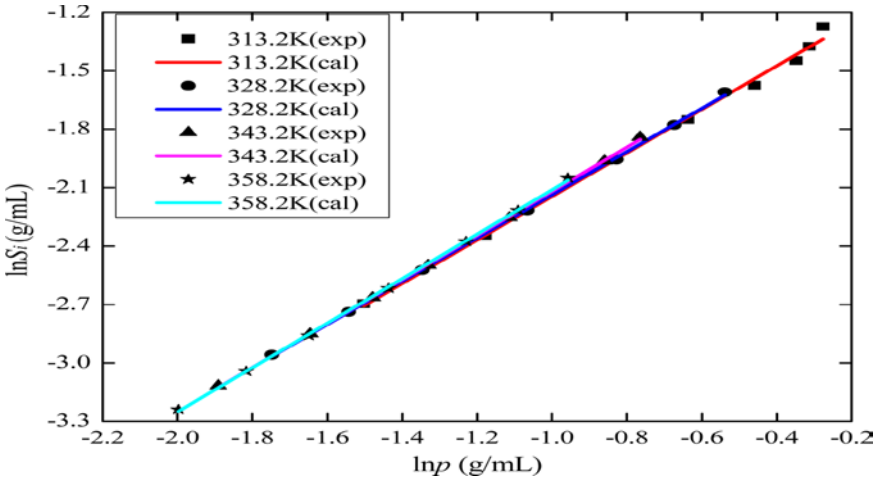

Fig. 2. Experimental solubilities (points) of tiger nut oil correlated by the Chrastil model (straight lines).

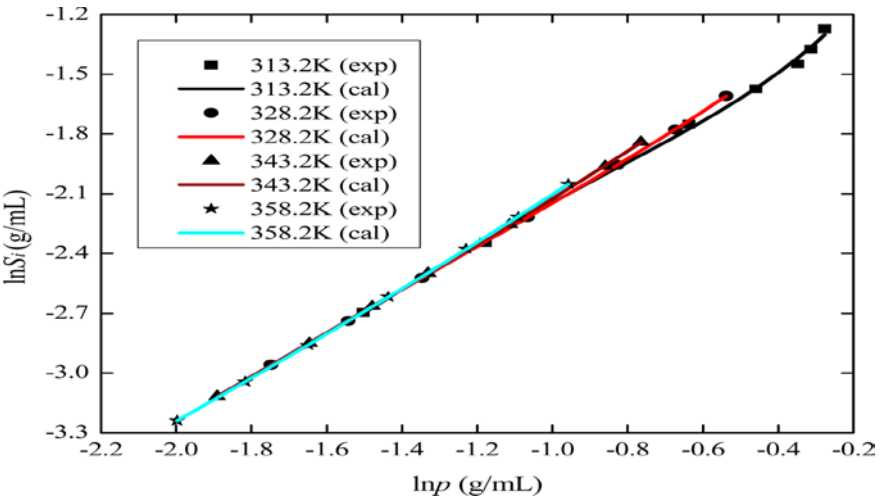

Fig. 3. Experimental solubilities (points) of tiger nut oil correlated by the Adachi and Lu model (straight lines).

Figs. 2 and 3 shows the calculated solubility curves of tiger nut oil using the Chrastil model and Adachi and Lu model with the experimentally measured data. It can be observed that the experimental results were satisfactorily simulated as the two functions. The solubility curves of the two density-based equations provide good representation of the measured values.

5. Conclusions

The solubility of tiger nut oil in supercritical carbon dioxide was measured under pressures of 7.24 to 14.68 MPa and temperatures of 313.2 K, 328.2 K, 343.2 K, and 358.2 K. Under the experimental conditions, the solubility increased with increasing pressure at the constant temperature, however, the solubility decreased with increasing temperature at the constant pressure.

The equilibrium solubilities data were analyzed with the two density based equations (Chrastil model and Adachi and Lu model). When the two models are compared, it was found that the Adachi and Lu model gave the better correlation. It could be concluded that the tiger nut oil can be extracted by supercritical CO_2, and can dissolve about 0.280 g/mL CO_2 under 313.2 K and 13.75 MPa.

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