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Solubility of virgin coconut oil in supercritical carbon dioxide

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ABSTRACT

The dynamic method was utilized to investigate the solubility of virgin coconut oil (VCO) in SC-CO_2 at temperatures and pressures ranging from 313 K to 353 K and 20.7 MPa to 34.5 MPa, respectively. The highest solubility, 0.0408 g/g, was obtained at 353 K and 34.5 MPa, which were the highest temperature and pressure levels used in the study. VCO solubility increases with temperature at pressures between 31.0 and 34.5 MPa, while at pressures between 20.7 and 24.1 MPa, VCO solubility decreases with an increase in temperature. At pressures between 27.5 and 30.5 MPa, a solubility cross-over region was observed. VCO solubility data was correlated with the Chrastil and del Valle-Aguilera models. Within the range of experimental conditions, the solubility data showed a good correlation to both models, with an average absolute percent deviation (AAPD) value of 0.93 and 0.39 for the Chrastil and del Valle-Aguilera model, respectively.

1. Introduction

Coconut oil is obtained from the fruit of the coconut palm (*Cocos nucifera L.*). There are two types of coconut oil that can be extracted from the coconut fruit – coconut or copra oil and virgin coconut oil (VCO). What differentiates the two types of oil is the source from which the oil is obtained, which in turn affects the characteristics of the oil. Copra oil is obtained from copra, or dried coconut flesh, while VCO is obtained from fresh coconut flesh. Due to the refining process, copra oil lacks any discernible taste and fragrance. VCO, which is extracted from fresh coconut flesh without the application of heat or chemical processes, has the fragrance and taste of coconut and also possesses superior antioxidant activity compared to copra oil (Nevin and Rajamohan, 2005).

The extraction of VCO involves the separation of oil from coconut milk. Coconut milk can be obtained by either pressing of fresh coconut flesh without additional water or grating the coconut flesh followed by extraction of the water–oil emulsion with water. The oil can be separated from the emulsion by means of fermentation, enzymatic extraction, refrigeration or mechanical centrifuge (Marina et al., 2009). Separation of the oil from the water–oil emulsion can also be accomplished by breaking the emulsion and creating an oil–oil emulsion, in which pure coconut oil must be added to the coconut milk to extract the oil from the emulsion, followed by separation of the oil from the water and protein via decantation. The process requires 24–48 h, yielding about 40% of the oil available in the coconut (Sukartin and Sitanggang, 2005).

In terms of fatty acid constituents, VCO is a natural source of medium chain triglycerides (MCTs), with approximately 60% of the total oil content being comprised of C8 to C12 fatty acid constituents. MCTs have been reported to be beneficial for the human health and are mainly utilized as a nutritional supplement for patients suffering from malabsorption caused by intestinal resection and also as a component of infant feeding formulation (Nandi et al., 2005). It is also reported that MCTs have beneficial effects on weight control and glucose as well as lipid metabolism (Marten et al., 2006).

Supercritical fluids are substances which have been heated and pressurized at temperatures and pressures exceeding that of their critical values. Within the supercritical region of a fluid, the phase state resembles that of a dense gas with properties that are intermediate to those of a gas and liquid. A substance in a supercritical state possesses a density of a liquid and a viscosity near that of normal gases, while its diffusivity is about two orders of magnitude higher than that of typical liquids (Brunner, 2005). In their supercritical states, water and carbon dioxide can be used as solvents for many different extractions and reactions (Arai and Adschiri, 1999). Carbon dioxide (CO_2) in particular has been extensively applied in supercritical fluid technology due to its moderate critical

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temperature (31.1 °C) and critical pressure (7.38 MPa), which makes supercritical carbon dioxide (SC-CO_2) an ideal solvent for thermally labile substances (McHugh and Krukonis, 1994). Furthermore, the non-toxic nature of SC-CO_2 makes it an environmentally-friendly solvent which can be used for food processing (Prausnitz et al., 1999). Separation of extracts from SC-CO_2 is relatively simple as it is done by reducing the pressure of the flowing mixture through an expansion valve.

Brannolte et al. (1983) studied the extraction of coconut oil from copra utilizing SC-CO_2 at temperatures ranging from 40 to 60 °C and pressures ranging from 30 to 90 MPa. They found that extraction at higher temperatures and pressures could reduce the amount of CO_2 consumed and extraction time required. For example at a pressure of 90 MPa and 60 °C, the oil could be extracted with 10% of the amount of CO_2 needed at 30 MPa and 40 °C. Celestino et al. (2006) analyzed oil content of copra extracted using SC-CO_2 extraction and found that about 100% of coconut oil could be extracted from the copra within 1 h at 120 °C and 51.7 MPa.

The literature on the solubility of vegetable oils in SC-CO_2 was reviewed by del Valle et al. (2012), which reported on the solubility on the solubility of coconut oil in a comparative study with other vegetable oils at a temperature and pressure of 40 °C and 30 MPa. The solubility of triglycerides in vegetable oils is roughly the same in SC-CO_2, and is not dependent upon the substrate (de Filippi, 1982). Solubility of triglycerides in SC-CO_2 is dependent upon carbon number (CN) of the fatty acid constituents, and not upon the number of double bonds within the triglyceride molecule (Catchpole and Grey, 2001; de Filippi, 1982; Guçlu-Ustunda and Temelli, 2000). Most vegetable oils are composed of triacylglycerols, with their fatty acids containing 18 carbon atoms which are stearic ($C_{18:0}$), oleic ($C_{18:1}$), linoleic ($C_{18:2}$) and α- and γ-linolenic ($C_{18:3}$) acids, and which therefore result in their CN amounting to roughly 54. Coconut oil, however, is an exception because it is rich in medium chain fatty acids containing ⩽16 carbon atoms, thus making it more soluble in SC-CO_2 compared to other vegetable oils.

Chrastil (1982) utilized chemical equilibrium and entropy considerations to develop a linear log–log relationship between solute solubility and density of a supercritical fluid, which is given in the equation below;

$$\log(c_{sat}) = \log(c^{\circ}_{sat}) + (k-1)\log\left(\frac{\rho}{\rho^{\circ}}\right) - \frac{\Delta H}{2.303R}\left(\frac{1}{T} - \frac{1}{T^{\circ}}\right) \quad (1)$$

where

c°_{sat} = solubility of the solute at reference conditions of absolute temperature (T°) and supercritical fluid density (ρ°),
k = association number which gives the amount of solvent molecules that form a solvato complex together with a single solute molecule,
ΔH = total heat required to synthesize the solvato complex,
R = universal gas constant.

To improve the fitting capabilities of Eq. (1), Adachi and Lu (1983) suggested that the association number (k) is dependent upon the solvent density, as given in Eq. (2):

$$(k-1) = (k^{\circ}-1) + \alpha\left(\frac{\rho-\rho^{\circ}}{\rho^{\circ}}\right) + \beta\left(\frac{\rho-\rho^{\circ}}{\rho^{\circ}}\right)^2 \quad (2)$$

where

k = association number at ρ°.

By using Eq. (3) to model the heat requirement for synthesizing the solvato complex as a function of absolute temperature, del Valle and Aguilera (1988) accounted for eventual variations in the heat of vaporization of the solute. Eq. (3) is given below:

$$\frac{\Delta H}{2.303R} = \frac{\Delta H^{\circ}}{2.303R}\left[1 + \gamma\left(\frac{1}{T} - \frac{1}{T^{\circ}}\right)\right] \quad (3)$$

where

ΔH° = total heat required to synthesize the solvato complex at T°,
α, β, γ = empirical model parameters.

In a comparative study of density-based models for the solubility of low-volatility solutes in SC-CO2, Sparks et al. (2008) applied the two corrections simultaneously after noting that $\beta \approx 0$ in Eq. (3). Sovová et al. (2001) used both Eqs. (1) and (2) to correlate their solubility data for purified fractions of blackcurrant seed oil in SC-CO_2 at 40–60 °C and 12–28 MPa, as well as literature data for rapeseed oil at 40–100 °C and 10–85 MPa. Using Eqs. (1) and (3), del Valle and Aguilera (1988) correlated literature data on the solubilities of corn germ, cotton seed, soybean, and sunflower seed oils in high-pressure CO_2 at 20–80 °C and 15.2–89.2 MPa. del Valle et al. (2012) have also correlated the solubility of vegetable oils in SC-CO_2 using the general model as given by Sparks et al. (2008).

The solubility of a solute in supercritical fluid is probably the most important thermo-physical property that must be determined and modeled in order to design effective supercritical fluid processes. The dependence of the solute solubility upon the temperature, pressure and density of the supercritical fluid must be understood to enable the specification of operating conditions of unit operations such as extractors, separators, transfer lines, valves and process controllers (Bruno, 1991). Therefore, this study was carried out with the objective of investigating the solubility of VCO in SC-CO_2 via application of the dynamic method. Furthermore, correlation of the obtained data with the Chrastil and del Valle-Aguilera models were also investigated.

2. Materials and methods

2.1. Materials

Locally grown coconut bought from a market in Penang was used in the study. The coconut was grated and sun-dried to reduce the moisture content from 50% to about 3%. This was done to avoid clogging the capillary restrictor. The samples then were ground and sieved to obtain samples with particle size ranging from 0.5 to 1.0 mm, which were used for the experiments. Carbon dioxide gas with purity of 99.95% was purchased from Malaysian Oxygen (MOX), P. Pinang, Malaysia.

2.2. Supercritical carbon dioxide extraction and solubility measurements

Experiments were performed with an extraction apparatus that consisted of a SC-CO_2 extractor (ISCO, Inc., Lincoln, NE. U.S.A., model SFX 220), a carbon dioxide cylinder, a chiller (B/L-730, YIH DER, Taipei) for CO_2 liquefaction and a high pressure syringe pump (ISCO, Inc., Lincoln, NE, U.S.A., model 100 DX) with a maximum operating pressure of 69 MPa. The volume of the extraction vessel was 2.5 mL. The extractor was equipped with a heated capillary restrictor (ISCO, Inc., Lincoln, NE, U.S.A.) that had an outer diameter of 50 μm and a maximum operating temperature of 150 °C. The temperature and pressure were controlled with software (ISCO, Inc., Lincoln, NE, U.S.A., model SFX 200) that was integrated with the extractor system.

The solubility of VCO in SC-CO_2 was determined by the application of a dynamic method. Solubility measurements were carried out at temperatures ranging from 313 K to 353 K and at pressures ranging from 20.7 MPa to 34.5 MPa. Approximately 2.0 g of the coconut sample were placed into the extraction cell, which was