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-CO2 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 or by 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 (CO2) in particular has been extensively applied in supercritical fluid technology due to its moderate critical
temperature (31.1 °C) and critical pressure (7.38 MPa), which makes supercritical carbon dioxide (SC-CO₂) an ideal solvent for thermally labile substances (McHugh and Krukonis, 1994). Furthermore, the non-toxic nature of SC-CO₂ makes it an environmentally-friendly solvent which can be used for food processing (Prausnitz et al., 1999). Separation of extracts from SC-CO₂ 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-CO₂ 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 CO₂ consumed and extraction time required. For example, extraction at higher temperatures and pressures could reduce the amount of CO₂ consumed and extraction time required. For example, extraction of CO₂ at higher temperatures and pressures could reduce the amount of CO₂ consumed and extraction time required. For example, extraction of CO₂ at higher temperatures and pressures could reduce the amount of CO₂ consumed and extraction time required.

Celestino et al. (2006) analyzed oil content of copra extracted using SC-CO₂ 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-CO₂ was reviewed by del Valle et al. (2012), which reported 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-CO₂, and is not dependent upon the substrate (de Filippi, 1982). Solubility of triglycerides in SC-CO₂ 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-Ustundaga and Temelli, 2000). Most vegetable oils are composed of triacylglycerols, with their fatty acids containing 18 carbon atoms which are stearic (C₁₈:0), oleic (C₁₈:1), linoleic (C₁₈:2) and α- and γ-linolenic (C₁₈:3) 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-CO₂ compared to other vegetable oils.

Chratsil (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:

\[
\log(c_{sat}) = \log(c'_{sat}) + (k - 1) \log\left(\frac{\rho}{\rho^*}\right) - \frac{\Delta H}{2.303R} \left(\frac{1}{T} - \frac{1}{T^*}\right)
\]

where

- \(c_{sat}\) = solubility of the solute at reference conditions of absolute temperature \(T^*\) and supercritical fluid density \(\rho^*\).
- \(k\) = association number which gives the amount of solvent molecules that form a solvato complex together with a single solute molecule,
- \(\Delta H\) = 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):

\[
(k - 1) = (k^* - 1) + \alpha \left(\frac{\rho - \rho^*}{\rho^*}\right) + \beta \left(\frac{\rho - \rho^*}{\rho^*}\right)^2
\]

where

- \(k^*\) = association number at \(\rho^*\).

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:

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

where

- \(\Delta H^*\) = total heat required to synthesize the solvato complex at \(T^*\),
- \(\alpha, \beta, \gamma\) = 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 \(\beta = 0\) in Eq. (3). Sovova et al. (2001) used both Eqs. (1) and (2) to correlate their solubility data for purified fractions of blackcurrant seed oil in SC-CO₂ 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 CO₂ 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-CO₂ 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-CO₂ via application of the dynamic method. Furthermore, correlation of the obtained data with the Chratsil and del Valle-Aguilera models was 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-CO₂ extractor (ISCO, Inc., Lincoln, NE, U.S.A., model SFX 220), a carbon dioxide cylinder, a chiller (B/L-730, YIH DER, Taipei) for CO₂ 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-CO₂ 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
then loaded into the extractor unit. The temperature was then allowed to equilibrate to the set level, after which pressurization was started and the SC-CO₂ flowed through the extraction cell from the bottom to the top of the vessel. As the SC-CO₂ flowed through the coconut sample bed, it became saturated with VCO. Flow of the VCO-SC-CO₂ mixture through an expansion valve and heated capillary restrictor then released the VCO from the CO₂, allowing the VCO to be collected in a vial. The extracted VCO was weighed using an analytical balance at certain time intervals according to the experimental design. The volume of CO₂ consumption was measured under each extraction condition using a flow meter integrated in the SC-CO₂ extractor and displayed at the extractor controller monitor. The mass of CO₂ was calculated from the SC-CO₂ density at each condition. Solubility of the extracted VCO was determined through analysis of the extraction curves.

3. Results and discussion

3.1. Solubility determination

For the extractions carried out in this study, each extraction curve possesses a linear portion which is the part of the extraction process referred to as the constant extraction rate (CER). The solubility value for each extraction temperature and pressure may be derived from the CER, which gives the equilibrium concentration of the VCO in SC-CO₂. Linear regression was performed at the CER for each extraction condition. The solubility value at each extraction pressure and temperature was obtained from the slope of the fitted line of the experimental data according to methods reported in the literature (Favati et al., 1991; Sovova, 1994; Ferreira et al., 1999; de França and Meireles, 2000; Sovová et al., 2001; Sovová, 2005).

Experiments conducted at 313 K and 34.5 MPa showed that VCO concentration in SC-CO₂ at CER was independent of the flow rate for flow rate values ranging from 0.1 to 0.7 mL/min, indicating that full saturation of VCO in SC-CO₂ had been achieved, as shown in Fig. 1. The full saturation of SC-CO₂ for various flow rates is considered as evidence for the achievement of equilibrium concentration levels under the corresponding pressure and temperature conditions (Sovová et al., 2001). A temperature and pressure level of 313 K and 34.5 MPa were chosen to determine the flow rate values at which saturation values become independent of the flow rate because within this study, at such conditions, SC-CO₂ reaches its highest density, which is 0.932 g/cm³. Thus, when such flow rates are applied in other experiments for investigation of VCO solubility in SC-CO₂, the saturation of VCO in SC-CO₂ is assured, regardless of the other conditions being applied. Therefore, all solubility measurements which were subsequently carried out in this study were performed at SC-CO₂ flow rates of 0.5 mL/min.

The curve analysis for the determination of VCO solubility in SC-CO₂ at a temperature and pressure of 313 K and 34.5 MPa is given in Fig. 2. From the graph, it can be observed that in the initial part of the extraction process, the extraction curve demonstrates a linear correlation between the amount of SC-CO₂ consumed and the mass of VCO extracted. It is within this linear part of the extraction curve wherein CER takes place and the SC-CO₂ is considered to be saturated, or in equilibrium condition, with VCO (Favati et al., 1991; Sovova, 1994; Ferreira et al., 1999; de França and Meireles, 2000; Sovová et al., 2001; Sovová, 2005; Danielski et al., 2007). The extractions were performed in triplicate, with the average solubility totaling 0.0309 g/g. The highest solubility value was obtained at temperature and pressure of 353 K and 34.5 MPa, as is shown in Fig. 3. From the graph, the average CER or solubility obtained as the average of three measurements was 0.0408 g/g.

When VCO solubility at different pressures is plotted versus temperature, as shown in Fig. 4, it can be observed that the solubility of VCO increases with increasing temperature at pressures between 31.0 and 34.5 MPa. However, the inverse effect is observed for lower pressures between 20.7 and 24.1 MPa, where the solubility of VCO decreases with increasing temperature. At a pressure of 27.6 MPa, the solubility of VCO in SC-CO₂ showed a trend of only slight decrease and increase at different temperatures. At a pressure region of 27.5–30.5 MPa, a solubility cross-over region was observed, as shown in Fig. 5. At the solubility cross-over region, the solubility of VCO in SC-CO₂ is almost independent of temperature, although the solubility can still fluctuate by slightly increasing or decreasing due to variation within the pressure in the cross-over region. In Fig. 5, it can be observed that the solubility of VCO in SC-CO₂ is virtually independent of temperature at a pressure of about 29.5 MPa.

The solvating power of SC-CO₂ is proportional to its density. Therefore, an increase in temperature will result in a decrease in SC-CO₂ density, which in turn lowers its solvating power. Temperature also has a positive effect on the vapor pressure of a solute, with higher temperatures resulting in higher solute vapor pressure, which in turn facilitates the transfer of the solute from the sample matrix into the SC-CO₂. At pressures above the cross-over region, the SC-CO₂ density will not be much affected by an increase in temperature, while the solute vapor pressure will play a dominating role, resulting in a net increase of solute solubility. At pressures below the cross-over region, SC-CO₂ density is much more sensitive to increase in temperature, which results in a large decrease of SC-CO₂ density and, despite the increase in solute vapor pressure, in a net decrease of solute solubility. Within the cross-over region itself, the effects of a decrease in SC-CO₂ density
and an increase in solute vapor pressure, which occur with temperature increase, result in a balance of the two competing forces.

Previous studies investigating the effects of temperature on solute solubility in SC-CO₂ have reported upon the solubility cross-over phenomenon. Cross-over solubilities of some esters were reported by Ismadji and Bhatia (2003) where the regions were at pressures ranging from 12 to 14 MPa, 10 to 16 MPa and 12 to 18 MPa for ethyl propionate, ethyl butyrate and ethyl isovalerate, respectively. Solubility cross-over regions of medroxyprogesterone and cyproterone acetate were reported about 22 MPa and above 30 MPa, respectively (Asghari-Khiavi et al., 2004).

Vatanara et al. (2005) reported that beclomethasone dipropionate and budesonide had the same cross-over region at 24.3 MPa. Khimeche et al. (2007) observed that the solubility cross-over pressures for 4,4-diaminodiphenylmethane (DADPM) and 1,5-naphthalediamine (1,5 NDA) were around 15.2 and 14.5 MPa respectively. The solubility cross-over region observed in the VCO-SC-CO₂ system in this study tends to be slightly higher than those reported for studies involving other compounds. However, it was generally in agreement with the phenomenon reported in the literature.

3.2. Solubility modelling

The obtained experimental solubility data was modeled using a solvent density based model proposed by Chrastil (1982). In the Chrastil model, the solubility of the solute is directly related to the density of the solvent gas, which in the case of this study is SC-CO₂. The Chrastil model is given by the following equation:

\[
Y^* = \rho^{-1} \exp(a + \frac{b}{T})
\]

where

- \(Y^*\) = solute solubility in solvent (g/g),
- \(\rho\) = SC-CO₂ density (g/cm³),
- \(k = 1\) = association number,
- \(a, b\) = constants,
- \(T\) = temperature (K).

In the correlation given by the model, the system is considered as a complex solution of solutes under supercritical conditions. The equation is based on the fact that in an isothermal condition, plotting the natural logarithm of solute solubility in the solvent (ln \(Y^*\)) against natural logarithm of solvent density (ln \(\rho\)) yields a straight line with slope \(k\), which is an association constant related to the total number of molecules in the complex mixture.

The parameter values of \(k, a\) and \(b\) were determined by searching the minimum error of the fitting of the experimental data to the Chrastil model equation. Average absolute percent deviation (AAPD) was used as an objective function (OF), the equation of which is given below (Eq. (5)):

\[
AAPD = \frac{100}{n} \sum_{i=1}^{n} \frac{| \ln Y_{\text{calc},i} - \ln Y_{\text{exp},i} |}{\ln Y_{\text{exp},i}}
\]

where

- \(Y_{\text{calc}}\) = calculated solubility using the model,
- \(Y_{\text{exp}}\) = experimental solubility data,
- \(n\) = number of data points.

An improved form of the Chrastil equation was proposed by del Valle and Aguilera (1988), which is given below (Eq. (6)):

\[
\ln Y^* = k \ln \rho + \frac{a}{T} + \frac{c}{T^2} + b
\]

where

- \(c\) = constant introduced in the del Valle-Aguilera model.

Experimental data in this study were also fitted to the del Valle-Aguilera model using Eq. (6), which were in turn used to obtain the objectives function from Eq. (4). Estimated fitting parameters for both models \((k, a, b\) and \(c\)) and the AAPD are given in Table 1. Fig. 6 shows the fitting results of the experimental solubility data to the Chrastil and del Valle-Aguilera model. Within the range of experimental conditions, both models gave good correlation of the data.
Table 1 Parameters of the Chrastil and del Valle-Aguilera model for VCO solubility.

<table>
<thead>
<tr>
<th>Model</th>
<th>k</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>AAPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrastil</td>
<td>7.532</td>
<td>-3702.806</td>
<td>8.805</td>
<td>-</td>
<td>0.93</td>
</tr>
<tr>
<td>del Valle-Aguilera</td>
<td>6.319</td>
<td>-13078.107</td>
<td>22.677</td>
<td>1575755.759</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Fig. 6. Correlation of data of VCO solubility in SC-CO₂ with Chrastil and del Valle-Aguilera models.

4. Conclusion

Solubility of VCO in SC-CO₂ utilizing the dynamic method was greatest at the highest temperature and pressure utilized. At lower pressures, an increase in temperature reduces VCO solubility in SC-CO₂. However, beyond the cross-over point, an increase in temperature positively influences VCO solubility. The CER and solubility of VCO in SC-CO₂ are independent of the solvent flow rate, but increase with temperature. Using the density-based models of Chrastil and del Valle-Aguilera, it was found that the VCO solubility data correlated well to both models within the range of experimental conditions.

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References


