# Solubility examination of palm kernel oil in supercritical $CO_2$ and its correlation with solvent density based model

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***Abstract***

Application of supercritical carbon dioxide (SC-$CO_2$) to vegetable oil extraction became an attractive technique due to its high solubility, short extraction time and simple purification. The method is considered as earth friendly technology due to the absence of chemical usage. Solubility of solute-SC-$CO_2$ is an important data for application of the SC-$CO_2$ extraction. In this work, the equilibrium solubility of the PKO in SC-$CO_2$ has been examined using extraction curve analysis. The examinations were performed at temperature and pressure ranges of 323.15 K to 353.15 K and 20.7 to 34.5 MPa respectively. It was obtained that the experimental solubility were from 0.0160 to 0.0503 g oil/g $CO_2$ depend on the extraction condition. The solubility experimental data was well correlated with a solvent density based model with absolute percent deviation of 0.96.

***Keywords****:* Carbon dioxide, Extraction, model, Palm kernel cake, Palm kernel oil, Solubility, Supercritical

## 1. Introduction

Supercritical $CO_2$ has been explored to be utilized as solvent for extraction of many natural product [1-11]. Using SC-$CO_2$ solvent allows extraction processes to operate near ambient temperature. Furthermore, SC-$CO_2$ is non-toxic, can be used in food-grade form for food processing. The process is considered as environmental friendly process since it does not use a chemical solvent but utilized $CO_2$ emission as a solvent extraction. Apart from that, the conventional processing method of vegetables oil involved many operation processes i.e. refining degumming, deodorization and bleaching after screw pressing. By using SC-$CO_2$ extraction, the oil can be fractionated and refined by adjusting the density as a function of pressure and temperature of the $CO_2$. This operation will eliminate processing such as degumming, bleaching and deodorization.

For developing extraction or other processes using SC-$CO_2$, the knowledge of solubility is essential. The design of supercritical fluid process requires the solubilities of each component in the supercritical fluid[12]. Many of the solubility/phase equilibrium measurements have been made to meet the need for fundamental data for process design purposes as well as analytical application. The data are important in determining the optimal operating condition, the solvent to feed ratio, and the selectivity of the extracted solute in engineering-scale supercritical fluid extraction. The experimental data may also be used to develope solubility correlation model.

One of the method for determining of solut solubility in SC-$CO_2$ is dynamic method [13, 14]. In the method, the supercritical fluid is continually swept through the cell using a set of equipment that can ensure the equilibrium condition between supercritical $CO_2$ and the solute. Therefore the measurement involved the formation of a saturated solution by passing the supercritical fluid over the solute in an extraction cell, decreasing the pressure to precipitate the solid or liquid solute, and analysis of the resulting solution is usually accomplished using a gravimetric method. In this research, a solubility of PKO in SC-$CO_2$ was examined using the dynamic method. The solubility data was fiitted with a solubility model which is based on solvent density.

## 2. Materials and Methods

### *2.1. Materials*

Sample palm kernel cake (PKC) was collected from palm kernel oil (PKO) industry. The sample impurities was removed using sieved. The sample was also clasified according to the particle size by sieving. Sample with partikel size 40-80 mesh was used in this experiment. Oil content and moisture content were determined before it were used for extraction. The oil content analysis was performed by soxhlet extraction, resulted 14.25±0.5% oil content

(dry basis). Moisture content of the sample needs to be determined for material balance calculation. Carbon dioxide gas with purity of 99.95% was used as rechieved.

### *2.2. Solubility examination*

Solubility measurement according to dynamic method can be carried out through a "like extraction process" method. The principles of SC-$CO_2$ extraction apparatus are shown in the Figure 1. In the extraction process, firstly, the $CO_2$ was liquefied in the cooler and then its pressure is elevated using the pump to above its critical pressure according to the required condition. Then, the pressurized $CO_2$ is flown to a high pressure vessel. The vessel was heated in a jacket heater, and the temperature is adjusted at above the critical temperature according to the required condition. The $CO_2$, which is in a supercritical condition, then flows to the sample inside the vessel and form a mixture/solution with the analyte in the sample matrices. The mixture then flows to the expansion valve. Due to the depressurization, the analyte will be separated from the $CO_2$ and it was collected in a trap. The mass of $CO_2$ that used in the extraction is measured using a gas meter.

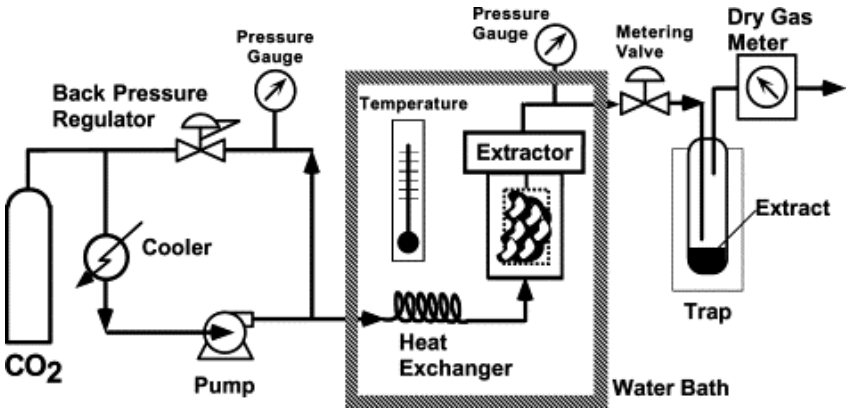


**Figure 1.** The principle of SC-$CO_2$ extraction apparatus [15]

A set of supercritical fluid extraction apparatus with 30 mL high pressure vessel (SFT-100, Supercritical Fluid Technologies, Inc) was utilized for the experiments. Approximately 30 g of the palm kernel cake sample were loaded into the extraction cell. The solvent $CO_2$ was saturated with the PKO by flowing it through a PKC sample bed with 0.5-0.6 $cm^3$/min flow rate. The solubility's were measured at temperatures from 313.15 to 353.15 K and at pressures from 20.7 to 34.5 MPa. Mass of the extracted oil was obtained gravimetrically at certain time interval of the extraction. The weight of extracted oil at a certain interval time of extraction was measured. Experimental data were plotted as total carbon dioxide used versus grams of extracted oil. Solubility values at each temperature and pressure are equilibrium concentrations that are indicated by linear portion of the extraction curve. A linear regression was performed at the constant extraction rate (CER) for each condition. The solubility at each pressure and temperature was obtained from the slope of the fitted line on the experimental data.

## 3. Results and Discussion

### *3.1. Experimental Solubility*

In the solubility examination the supercritical $CO_2$ is allowed to flow through the solute in the cell. The flow rate of the $CO_2$ must be very low to ensure the saturation of $CO_2$ with solute. Mass of the extracted solute versus the total mass of supercritical $CO_2$ used to dissolve the solute are plotted. In the extraction process, the extraction curves can be described by a three-step process [16]. The first linear portion is denoted by constant extraction rate (CER) period and is characterized by the convective mass transfer between the solid material surface and the fluid phase. In this period, the amount of free-oil in the plant oil bearing cell was sufficient to allow for solvent saturation. The second part of the extraction curve represents the falling rate period. At this step both convection and diffusion in the solid must be considered. For the third step or the diffusion-controlled rate period the diffusion in the solid controls the rate of mass transfer. The CER period indicates an equilibrium condition of the system is achieved. The extract concentration at the exit of the extractor represents the solubility of the solute. Therefore, the slope of the CER is the measured solubility at the temperature and pressure of the solute in SC-$CO_2$ at the correspondence operation condition [13, 14, 17-19].

Solubility examination data is presented at Figure 2. At the Figure 2, It can be observed that at pressures between 24.3 and 34.5 MPa the oil solubility increases with temperature. However, increasing temperature from 313.15 to 353.15 K at lower pressure (below about 24 MPa), lowers the solubility. The trend created a solubility cross-over zone in the region of the experiment. The cross-over zone obviously could be observed by plotting the solubility against pressure (Fig. 2). The cross-over zone occurred at the pressure of about 24 MPa. At the cross-over zone, the solubility of the oil is almost independent of temperature. However, the solubility can slightly increase or decrease with temperature depending on the pressure condition within the zone.

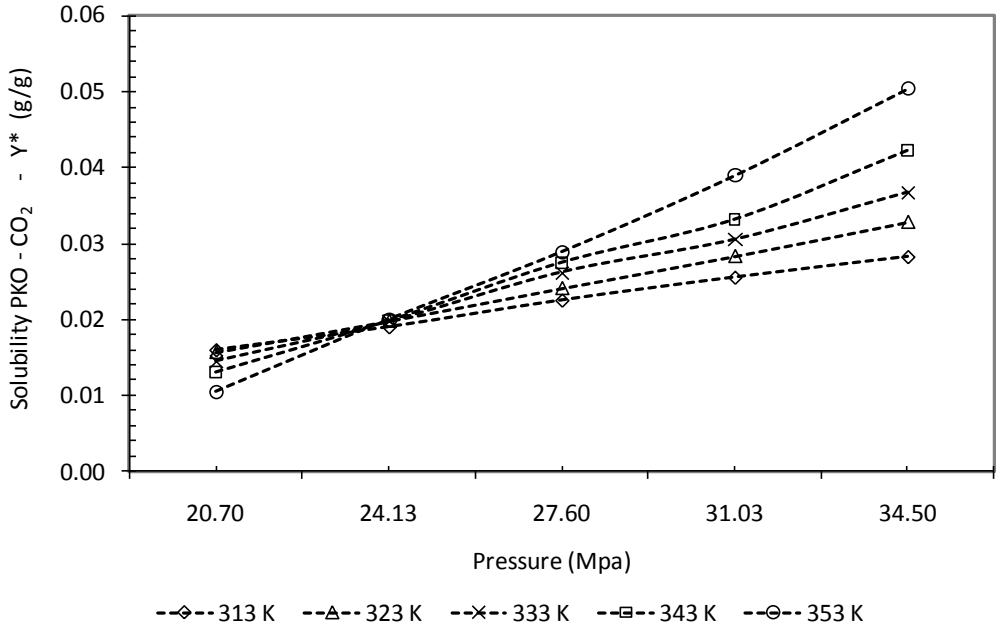


**Figure 2**. Plotting pressure-solubility of PKO - SC-$CO_2$ . It shows cross-over region where PKO solubility decreases with increasing temperature at the pressure of below cross-over zone and where solubility PKO increases with increasing temperature at the pressure of above cross-over zone.

The solubility cross-over phenomenon often happen in the phase of supercritical and have been noticed by previous researchers observed effect of temperature on the solute solubility in SC-$CO_2$. For example, Asghari-Khiavi et al. (2004) [20] reported that cross-over zones of medroxyprogesterone and cyproterone acetate to be about 22 and above 30 MPA respectively. Vatanara et al. (2005) [21] also reported that beclomethasone diproprionate and budesonide showed the zones at 24.3 MPa. Furthermore, Setianto et al. (2009) [6] calculated phase behavior of of CNSL and $CO_2$ system using Peng-Robinson EOS. It was reported that the cross-over zone appeared at pressures between 12 to 20 Mpa. The inverse effect on solubility occurred possibly due to the combined effect of solvent solvating power and solute vapor pressure that are affected by temperature. In the isobaric experiment set, effect of increasing temperatures increases the solute vapor pressure and decreases of the solvent solvating power. These two competing factors letting the cross-over zone occurs in the SC-$CO_2$-solute systems. The zone varies depend on typical of the solutes.

*3.2. Solubility Modeling*

The solubility of a solute in supercritical fluid is probably the most important thermophysical property that must be determined and modeled in order to design effective supercritical fluid processes. The pressure and temperature, therefore the density of the supercritical fluid, dependence of solubility must be understood. This will allow the engineer to specify the operating conditions of unit operations such as extractors, separators, transfer line, valves and process controllers.

In this section, the measured solubility experimental data was modeled using solvent density based model proposed by Chrastil (1982) [22]. The Chrastil model (Equation 1) related the solubility directly to the density of the gas solvent ($CO_2$).

The Chrastil model is given by :

$$Y^* = \rho^k \exp\left(\frac{a}{T} + b\right) \quad (1)$$

where,

$Y^*$ = solute solubility in solvent [g/g].
$\rho$ = $CO_2$ density [g/cm$^3$].
$k$ = association number
$a$, $b$ = constants
$T$ = temperature [K]

The correlation considers the system as complex solution of solutes under SC-$CO_2$ condition. 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.

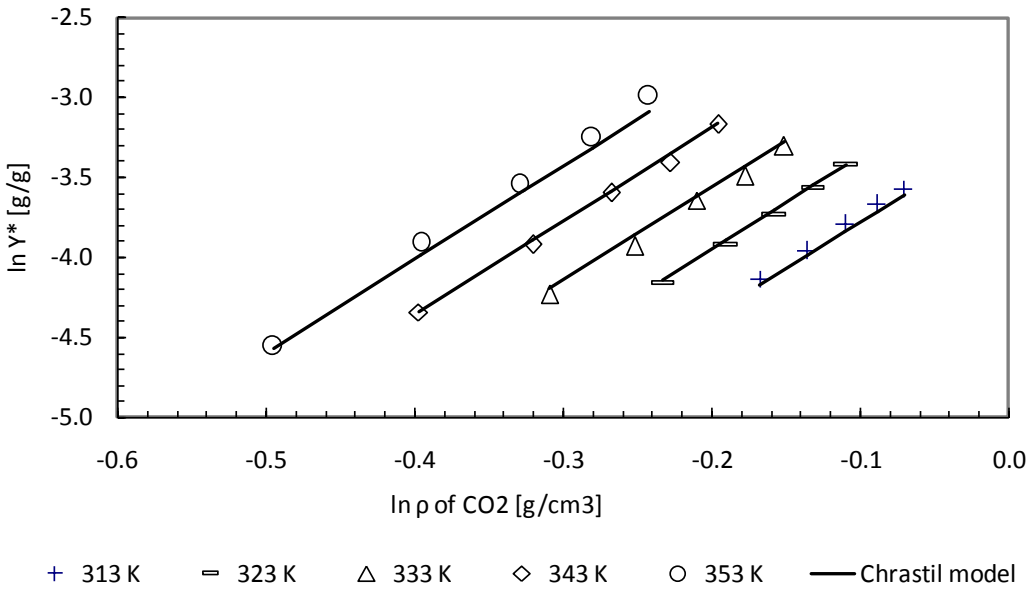


**Figure 3**. Correlation of PKO solubility in SC-$CO_2$ experimental data with Chrastil model.

The parameters were determined by searching the minimum error of the fitting. Average absolute percent deviation $(AAPD)$ was used as an objective function (OF) (Equation 2).

$$AAPD = \frac{100}{n} \sum_{i=1}^{n} abs. \frac{\left[\ln Y^*_{calc.} - \ln Y^*_{\exp.}\right]}{\ln Y^*_{\exp.}} \quad (2)$$

where,

$Y^*_{calc.}$ = calculated solubility using the model
$Y^*_{\exp.}$ = experimental solubility data
$n$ = number of data point

Figure 3 shows the fitting results of the experimental solubility data to the Chrastil model. Within the range of experimental conditions, the model gave good correlation of the data. Estimated fitting parameters for the model ( $k$, $a$, and $b$ ) and the $AAPD$ are given in Table 1.

**Table 1.** Parameters of the Chrastil model for palm kernel oil solubility in supercritical $CO_2$

| No. | Parameter | Value |
|---|---|---|
| 1. | $k$ | 5.583 |
| 2. | $a$ | -4213.001 |
| 3. | $b$ | 10.258 |
| 4. | AAPD | 0.96 |

## 4. Conclusions

Solubility of the PKO in supercritical carbon dioxide has been examined using dynamic method and has been well-correlated using empirical density based model. The oil-$CO_2$ system showed a cross-over phenomenological.

**Acknowledgement**

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