Effects of process parameters on peanut skins extract and CO$_2$ diffusivity by supercritical fluid extraction

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Abstract. Peanut skins ($Arachis hypogea$) are an agricultural waste product which has received much attention because they contain high nutritional values and can be potentially utilized in difference industries. At present, only a few studies have been conducted to study the effects of parameters on the peanut skins oil extraction. Therefore, this study aimed to determine the best extraction condition in order to obtain the highest extract yield using supercritical carbon dioxide (SC-CO$_2$) with co-solvent Ethanol as compared to Soxhlet extraction method. Diffusivity of carbon dioxide in supercritical fluid extraction was determined using Crank model. The mean particle size used in this study was 425 µm. The supercritical carbon dioxide was performed at temperature (40 – 70 °C), flow rate of co-solvent ethanol (0 - 7.5% Vethanol/Vtotal), and extraction pressure (10 – 30 MPa) were used in this studies. The results showed that the percentage of oil yields and effective diffusivity increase as the pressure, rate of co-solvent, and temperature increased.

1. Introduction
Red peanut skins refer to the outer thin layer of the peanut endosperm and it may cause problems in the peanut butter industries. It can also reduce the quality of butter because the skins have astringent taste and it is the primary reason that the skins should be removed. There are 0.74 million metric tons of peanut skins being annually produced worldwide as waste from peanut butter industries[1]. It is commonly known that red peanut skins are rich in antioxidant and may contribute benefits toward the economy and human health. The extract of peanut skins contains 12% protein, 16% fat, and 72% of carbohydrate, and also rich in polyphenols [2]. The total phenolics (TPs) of defatted peanut skin was reported to be 140–150 mg/g dry skins [2]depending on the solvent used. The exploitation of peanut skins as renewable raw material for antioxidant compounds provides protection against human health and enhancement of the sustainable environment [3]. Most of these antioxidant activities on peanut skins rich in catechin and procyanidins have been associated with reduced risk of cardiovascular diseases and cancers [4].

Supercritical fluid extraction (SFE) is a green technology built to extract oil, antioxidant, and bioactive compounds. This method has been conducted by many researchers to effectively extract

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pharmaceuticals and cosmeceutical products from plants and herbs. The supercritical fluid extraction has many advantages, namely, high purity on solute content, free of organic solvent, easy to separate, SFE has high selectivity, and the solvent used CO$_2$ which is nontoxic. Generally, carbon dioxide (CO$_2$) is used as the solvent in food processing as it has low critical temperature and pressure, non-toxic, not expensive as a solvent. The key factor for using supercritical carbon dioxide extraction was the solubility of solvent as it can be manipulated by pressure and temperature [5].

Diffusivity or diffusion coefficient, $D_e$ is defined as a measure of the capability of a substance or energy to be diffused or to allow something to pass by diffusion. The higher the diffusivity of one substance with respect to another, the faster they diffuse into each other. Temperature, pressure, and particle size are the common factors affecting diffusivity in SFE. Diffusion model proposed Crank is more suitable to be used in order to determine diffusivity of carbon dioxide (CO$_2$) as it is more effective for particle size factor [6]. Although CO$_2$ supercritical extraction is advantageous, it can only extract nonpolar compound. Supercritical CO$_2$ only extract oil inside of peanut skins, but it cannot extract bioactive compound (procyanidin, catechin, epicatechin, gallocatechin, and epigallocatechin) [4]. The presence of ethanol is needed for this extraction process to encourage the extraction due to its polarity. Since ethanol is a bipolar compound based on its polarity, ethanol can increase the polarity of CO$_2$ and can also extract polar bioactive compound. The objectives of the study are to determine the best parameter in order to obtain the highest extract yield and to study the diffusivity of carbon dioxide in supercritical fluid extraction using Crank model.

2. Methodology

2.1 Chemicals
Liquid carbon dioxide (99% purity) was used in the supercritical extraction apparatus purchased from Kras Instrument, Johor Bahru, Malaysia. Technical grade of ethanol (99.86%) was obtained from Permula Sdn Bhd, Johor Bahru Malaysia.

2.2 Plant Material
Peanut skins were obtained from G-Tachfood Industries Sdn Bhd, Johor Bahru Malaysia which is the waste of peanut industries. Peanut skins were dried in an oven at 60 °C for 4 hours. The obtained dried peanut skins were blended into powder and classified into different particle sizes which are then stored in air tight plastic and placed in a freezer at -20 °C.

2.3 Supercritical Fluid Extraction
A set of laboratory scale supercritical extraction was used for this experiment. The extraction process was performed at the temperature of 40, 55, and 60 °C, with the pressure of 10, 20, and 30 MPa, the rate of co solvent 0, 5, and 7.5% (Vethanol/Vtotal), the CO$_2$ flow rate of 3.0 mL/minute, and particle size range of 425 μm. The extraction was carried out for 120 minutes. Chiller temperature was set at 6 °C while the heater on the back pressure regulator was set at 50 °C. Next, 5 ±0.005 g of peanut skins were placed into the extraction vessel. Then, liquid CO$_2$ was pumped from the CO$_2$ tank into the system continuously with a supercritical pump at a flow rate of 3 mL/min. The co-solvent ethanol 98.86% was also pumped continuously when the desired temperature was achieved. It fed into the extractor through high pressure. The extracted oil was collected by vial for every 30 minutes of the extraction process. After each extraction process, the extract obtained was sealed and stored at 4°C to prevent any possible degradation.
Table 1. Calculated Parameters for mass transfer using single sphere model for peanut skins.

| Pressure (MPa) | Temperature (°C) | Rate of co-solvent (%) | Yield (%) | $D_e \times 10^{12}$ (m²/s⁻¹) | %AARD (%) |
|---------------|------------------|------------------------|-----------|-----------------|-----------|
| 20            | 40               | 7.5                    | 13.85     | 6.250           | 4.39      |
| 30            | 40               | 7.5                    | 14.77     | 7.181           | 2.74      |
| 10            | 40               | 7.5                    | 13.42     | 5.159           | 3.84      |
| 30            | 70               | 0                      | 6.63      | 4.989           | 5.52      |
| 20            | 55               | 5                      | 14.23     | 4.731           | 2.97      |
| 30            | 70               | 5                      | 15.39     | 6.793           | 3.53      |
| 20            | 55               | 5                      | 14.17     | 4.398           | 3.48      |
| 20            | 40               | 7.5                    | 15.26     | 8.867           | 0.72      |
| 20            | 40               | 5                      | 7.49      | 3.880           | 12.85     |
| 20            | 70               | 5                      | 15.786    | 6.982           | 1.627     |
| 30            | 70               | 7.5                    | 17.55     | 7.133           | 2.76      |

2.4 Percentage of Oil Yield Measurement

Percentage of oil yield can be defined as the percentage weight of oil divided by the weight of sample at a given temperature and pressure at 180 minutes of time extraction. The equation of percentage of oil yield is:

$$\text{Percentage of Oil Yield (\%)} = \frac{W_o - W_f}{W_o}$$

Where: $W_o$ = weight of vial and weight of oil, g $W_f$ = weight of vial, g, and $W_o$ = weight of raw material, g

2.5 Mathematical Model

Single sphere model which was introduced by Crank considers the relationship between the size of particle and diffusion coefficient [7]. High diffusion coefficient indicates that good extraction phenomena have been obtained. The assumptions made are [8, 9]: Intraparticle mass transfer is the controlling and important factor in the extraction process, mass transfer resistance of the fluid is zero, solute is extracted from particulate bed composed of porous inert sphere, size of sphere is similar, entire particles in the bed are at the same stage of extraction, and components to be extracted move through the particles by process ‘similar to diffusion’.

The basic equation for the rate of solute that transports radially across an internal surface within spherical and isotropic particle takes the form of Fick’s law as:

$$Rate = -4\pi r^2 D_e \left(\frac{\partial q}{\partial r}\right)$$  \hspace{1cm} (1)

Where $q$ is solute concentration inside the particle at radius $r$ (kg solute/m³ of particle) and $D_e$ is Effective diffusivity. The equation given by Crank to solve the diffusion coefficient is [7]:

$$Y' = \frac{M_t}{M_{∞}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{∞} \frac{1}{n^2} \exp \left(\frac{D_e n^2 \pi^2 t}{R^2}\right)$$  \hspace{1cm} (2)

Where $M_t$ is the total amount of solute diffused from the sphere at time t, $M_{∞}$ is the total amount of solute, $n$ is number of iterations, $D_e$ is diffusion coefficient, R is particle radius, and t is time.
Figure 1. Extraction kinetics of peanut skins oil: comparison of experimental data and model output.

The general equation of single sphere model (SSM) is applicable for high velocity but fails to represent the extraction behavior at low velocity [10]. In this study, the good fitting and correlation have a range from $7.133 \times 10^{-12}$ to $8.867 \times 10^{-12}$ m$^2$/s. For the low velocity, the single sphere model is difficult to represent the extraction behavior due to high %AARD. Based on the result, single sphere model is mainly focused on the solute extraction inside the particles, assuming that the easily accessible oil has been removed from the galls.

Based on the literature, various approaches have been successfully performed which can be adapted to model the supercritical fluid extraction. In this study, in conjunction with SSM, some equations were used based on linear adsorption equilibrium model in order to determine the mass transfer coefficients of the extraction process.

2.6 Soxhlet Extraction

Soxhlet extraction was performed using 10 g of powdered peanut skins with particle size 425 µm and was placed in a thimble holder. Soxhlet extraction was carried out using 100 mL of solvents (n-Hexane, Ethanol, and Water). The heating power was used slightly above the boiling point of the solvent. The arrangement is such that vapors of the solvent are generated from the round-bottomed flask, get condensed into the water as a condenser, and pass through to the thimble that was contained in the sample. The condensed solvent comes into contact with the sample where the extraction occurs. When the liquid reaches the overflow level in the thimble, the liquid moves through the siphon back into the round-bottomed flask, carrying extracted solutes into the bulk liquid. The solvent was removed by rotary vacuum evaporator at the temperature above the boiling point of the solvent to avoid degradation of bioactive compound inside extract.

3. Result and discussion

3.1 Effect of pressure on the percentage of oil yield and diffusivity of extraction.
Figure 2. Effect of Pressure on the Percentage of Oil Yield.

Figure 2 shows that the percentage of oil yield using SC-CO₂ extraction with co-solvent of ethanol at different pressure of 10, 20, and 30 MPa, with constant temperature 70 °C, constant flow rate of CO₂ 3 mL/min, and 7.5% rate of co-solvent (V_{ethanol}/V_{total}). The highest extracted oil yield was 14.7% at the highest pressure of 30 MPa. Meanwhile, the lowest oil yield was 13.42% at the lowest pressure of 10 MPa. Fig. 2 shows the effect of different pressure at the highest temperature of the process (70 °C). It shows that the curve of all pressure conditions become uniform to each other. In this study, the oil extracted reached the asymptotic yield at the end of the extraction process after 120 minutes of extraction time. Asymptotic yield refers to the maximum amount of oil obtained at the maximum condition of extraction[11]. The asymptotic yield obtained was 14.7% (74.54 mg of oil per 5.0 g sample used). Furthermore, by reaching an asymptotic value, it can be assumed that the extraction was complete where the oil from the seeds was considered completely removed. The results of this study have shown that the effect of pressure is noticeable. This is because the highest pressure can obtain the high percentage of oil yield. Increasing pressure will lead to an increase of density of the solvent in the extraction process. The high density of solvent can create a big opportunity to contact and interact with oil in the inside of particle which is known as the solvating power increased[12].

Figure 3. Effect of Pressure on the Effective diffusivity.

Figure 3 shows the effective diffusivity of SC-CO₂ extraction with co-solvent ethanol at a different pressure condition (10-30 MPa), and constant temperature 70 °C, flow rate of CO₂ 3 mL/min, and rate of co-solvent 7.5% (V_{ethanol}/V_{total}). The highest effective diffusivity was obtained 7.18 × 10⁻¹² m²/s at the highest pressure 30 MPa. Meanwhile, the lowest effective diffusivity 5.159 × 10⁻¹² m²/s was at the lowest pressure of 10 MPa.

From figure 3 and table 1, the single sphere model gives a useful fit to the experimentally determined yield versus data at the high effective diffusivity those in the range (5.1-7.2) x 10⁻¹² m²/s.
The overall mean deviation is below 5%. In this condition, the effect of pressure is noticeable due to effective diffusivity. Increasing pressure enhances the solubility of extraction and also the density. The increasing of solubility and the density in solvent will increase the driving force and extraction rate of the galls [10].

3.2 Effect of Temperature On The percentage of oil yield and diffusivity of extraction

Figure 4. Effect of Pressure on the Percentage of Oil Yield.

Figure 4 shows that the percentage of oil yield by using SC-CO$_2$ extraction with co-solvent ethanol at different temperature conditions at 40, 55, and 70 °C, constant pressure 20 MPa, constant flow rate of CO$_2$ 3 mL/min, and 5% rate of co-solvent (Vethanol/Vtotal) versus time. In this study, the highest percentage extracted oil yield was 15.78% at the highest temperature of 70 °C. Meanwhile, the lowest oil yield was 7.49% at the lowest temperature of 40 °C. In a different temperature condition, the effect of temperature on the supercritical fluid extraction is dominant. This is because increasing temperature enhances the total percentage of oil yield. In this study, temperature effect has similar behaviors with a previous study that examines the extraction of *Pithecellobium Jiringan* (Jack) Prain Seeds that the increase of temperature affects the increase of oil yield [13].

Figure 5. Effect of Temperature on the Effective diffusivity.

Figure 5 illustrates the effective diffusivity of SC-CO$_2$ extraction with co-solvent ethanol in different temperature conditions (40, 55, and 70 °C). The highest effective diffusivity was obtained $6.98 \times 10^{-12}$ m$^2$/s at the highest temperature 70 °C. Meanwhile, the lowest effective diffusivity 3.88 ×
$10^{-12}$ m$^2$/s at the lowest temperature condition 40 °C. This is because the increase in temperature has resulted in the increase of the solute vapor pressure which contributed to the increase of mass transfer rate of oil into the solvent [13]. It is a different explanation with previous studies since the increase of temperature decreases the solubility and density of solvent that may affect the mass transfer of extract to solute [14].

3.3 Effect of Co-solvent Ethanol

![Figure 6](image6.png)

**Figure 6.** Effect of rate co-solvent ethanol on the Percentage of Oil Yield.

Figure 6 shows that the percentage of oil yield by using SC-CO$_2$ extraction with co-solvent ethanol at different rates of co-solvent condition 0, 5, and 7.5% ($V_{ethanol}/V_{total}$), constant pressure 30 MPa, constant temperature 70 °C, and constant flowrate of CO$_2$ 3 mL/min. The highest extracted oil yield was 15.39% at the highest rate of co-solvent ethanol. Meanwhile, without co-solvent ethanol, the lowest oil yield was 6.63%. Figure 6 shows the effect of co-solvent is not significant on the 5% and 7.5% ($V_{ethanol}/V_{total}$). This is because the percentage of oil yield is almost the same 14.77% and 15.39%. The rate of co-solvent ethanol enhances the percentage of oil yield because the polarity of the supercritical fluid increases. Therefore, supercritical CO$_2$ and ethanol can interact and make a bond with nonpolar compound and polar compound in the solute[15].

![Figure 7](image7.png)

**Figure 7.** Effect of rate co-solvent ethanol on the Effective diffusivity.
Figure 7 shows that the effective diffusivity of SC-CO$_2$ extraction with co-solvent and without co-solvent ethanol. The highest effective diffusivity was obtained $7.13 \times 10^{-12}$ m$^2$/s at the highest rate of co-solvent $7.5\%$ (V$_{\text{ethanol}}$/V$_{\text{total}}$). Meanwhile, the lowest effective diffusivity $4.98 \times 10^{-12}$ m$^2$/s at without of co-solvent ethanol condition. The increase in $D_e$ indicated the decrease in the mass transfer resistance in the fluid phase. However, extraction rate in the fast extraction period increased due to the increase in driving force and decrease in mass transfer resistance in the fluid phase [16]. Increase in the oil yield with ethanol addition into SC-CO$_2$ was reported for fungal lipid [17] and removal caffeine from green tea [18]

4. Conclusion
The extraction of peanut skins using supercritical carbon dioxide extraction and co-solvent ethanol was performed at temperatures ranging from 40 $^\circ$C to 70 $^\circ$C, rate of co-solvent ethanol ranging from 0$\%$ to 7.5$\%$, and pressures ranging from 10 MPa to 30 MPa. In this study, the results showed that percentage of total oil yield increased as the pressure increased at a constant temperature, flow rate of CO$_2$, and rate of co-solvent ethanol. Similarly, the percentage of total oil yield has also increased as the temperature increased at constant pressure, flow rate of CO$_2$, and rate of co-solvent ethanol. The maximum percentage of oil yield obtained was 15.78$\%$ mg at the highest supercritical extraction condition of pressure at 30 MPa, the temperature at 70$^\circ$C, and rate of co-solvent ethanol 5$\%$, respectively. The effective diffusivity, $D_e$ was ranging from $3.881 \times 10^{-11}$ to $9.181 \times 10^{-12}$ m$^2$/s. The value of all adjustable parameters increases with increase in pressure, temperature, and rate of co-solvent.

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