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# Extraction of rice bran oil by supercritical carbon dioxide and solubility consideration

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ABSTRACT

Among vegetable oils, rice bran oil has been considered to be one of the most valuable and healthy oil because it contains many nutraceutical components. In this work, extraction of oil and γ-oryzanol from crushed rice bran using supercritical carbon dioxide at various $CO_2$ flow rate (1–9 ml/min), temperatures (40–80 °C) and pressures (20–40 MPa) was investigated. The experimental extraction behavior was explained using two simple models of thermodynamic model and simple kinetic model. In addition, solubility data of rice bran oil in $SCCO_2$ showed a good agreement with the values of the correlation of Chrastil model. The effect of extraction temperature and pressure on the γ-oryzanol recovery was studied.



## 1. Introduction

Some frequent diseases in developed societies such as obesity or cardiovascular disease have been associated with an increase in blood cholesterol, triacylglycerol, and lipoproteins because of excessive consumption of animal products. This leads to high consumer demand in healthier foods and make big efforts in the development of novel products with improved functional properties and nutritional value for healthy food industries. A diet rich in food of plant origin can significantly retard the development of cardiovascular disease. Vegetable oils, such as rice bran oil, soy bean oil, olive oil and perilla seed oil, play an important role in making the healthy foods.

Among vegetable oils, rice bran oil has been considered to be one of the most valuable and healthy oil because it contains many nutrition including protein, vitamin B complex, vitamin E (α-tocopherol and tocotrienol), vitamin K and γ-oryzanol. γ-Oryzanol is important component peculiar to rice bran oil since it has been suggested to show biological and physiological abilities such as serum cholesterol lowering, anti-oxidation, anti-carcinogenic and to attenuate allergic inflammation [1–3]. Therefore, many researchers have studied on separation of oil and high value substances from rice bran.

The various separation methods for rice bran oil and its active compounds such as cold press extraction, Soxhlet extraction, ultrasonic extraction, and microwave extraction have been studied [4,5]. However, there are some concerns including low yield obtained, toxicity of organic solvent used and degradation of active compounds during the processes. Alternatively, supercritical fluids extraction, especially supercritical carbon dioxide ($SCCO_2$), is attracting as the alternative method for oil and sensitive substances because it is non-toxic solvent, recyclable, cheap, relatively inert, non-flammable and easily separated from the extracts. Hence, vegetable oils extraction such as sesame seed oil, soy bean oil, and rice bran oil by using $SCCO_2$ have been reported by some research groups [6–9].

Extraction of oil from crushed seeds by $SCCO_2$ has been claimed to be divided in two stages [10–15]. In the first stage, "free oil" is extracted initially from the surface of seed particles at constant rate that is partially determined by external mass transfer mechanisms. A plot of cumulative yield (g oil/g oil-free substrate) produces a straight line with a slope that corresponds to the apparent solubility of the oil in $SCCO_2$. In the second stage, when free oil is depleted from the particles, the extraction rate is determined by internal mass transfer mechanisms of "tied oil", and the

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aforementioned plot approaches an oil yield value asymptotically. Several studies have focused on explaining mechanisms of vegetable oils extraction from crushed seeds in $SCCO_2$ using the diffusion-based "hot-ball" model and simple two-site kinetic models have been used to describe the supercritical extraction process [10,11,16–28]. Nevertheless, only few studies have explained the oil release mechanism for rice bran.

In this work, extraction of oil and γ-oryzanol from crushed rice bran using $SCCO_2$ was investigated. The effect of extraction temperature and pressure on the γ-oryzanol recovery was studied. In addition, two simple models of thermodynamic model using distribution coefficient, $K_D$, and simple kinetic model using rate constant, $k$ were employed to describe the data in order to make advances in further clarification of the $SCCO_2$ extraction behavior.

## 2. Material and methods

### 2.1. Material and chemicals

Rice bran samples were supplied by Aichi Federation of Economic Organizations JA. Standard oryzanol (consisting of ~23% cycloartenol ferulate, ~51% cyclobranol ferulate, ~15% campesterol ferulate, ~10% beta-sitosterol ferulate), hexane, methanol, acetonitrile, and isopropanol used for HPLC analysis were purchased from Wako Pure Chemical Industries, Ltd., Japan. $CO_2$ (99.9%) was obtained from Sogokariya Co., Japan.

### 2.2. $SCCO_2$ extraction

Extraction was carried out using an experimental apparatus shown in Fig. 1. The apparatus included a high pressure pump for $CO_2$ (Jasco PU-2086 Plus 100 MPa, Japan), a heating chamber (EYELA WFO-400 Japan), a 10 mL extraction vessel (Thar Tech, Inc., USA), back-pressure regulator (Jasco BP-2080, Japan), collection vials, and a wet gas meter (Sinagawa Co., Japan). In order to determine the effect of temperature and pressure on the yield of extracted components, the oil was extracted from rice bran at temperatures of 40, 60 and 80 °C, pressures of 20, 30, and 40 MPa, and $CO_2$ flow rate of 1, 3, 6 and 9 mL/min. In each experiment, approximately 4.5 g of rice bran sample was loaded into the extraction vessel, and filled with glass beads at the bottom and top of the cell. The cell was placed in the heating chamber to maintain the operating temperature.

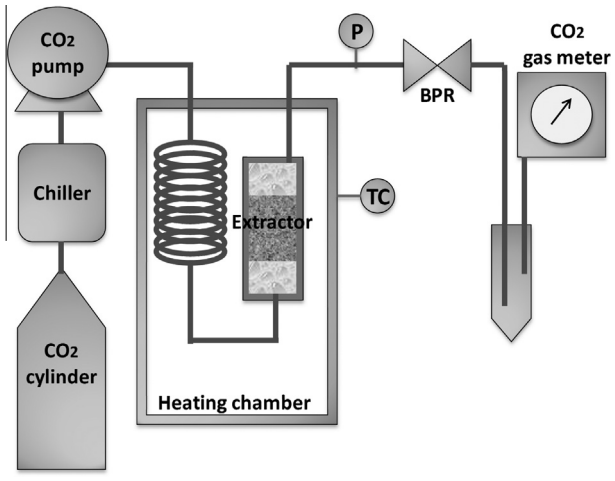


**Fig. 1.** Schematic flow diagram of the $SCCO_2$ extraction apparatus.

### 2.3. Soxhlet extraction

A sample of 9 g of rice bran was extracted with 200 mL of n-hexane as a solvent in a Soxhlet apparatus for 7 h. Subsequently, the solvent was removed by rotary vacuum evaporator (Shanghai Eyela Co., Ltd.) and the remaining extract was dried to constant weight [29,30].

### 2.4. Data analysis

In this work, two simple models of thermodynamic and kinetic desorption model were used to describe rice bran oil extraction behavior. Thermodynamic model is a model based on a single distribution coefficient defined as $K_D$ = (concentration of analyte in the matrix) ÷ (concentration of analyte in the extraction fluid) at equilibrium. For this model, it is assumed that the kinetics of the initial desorption step and subsequent fluid–matrix partitioning are rapid, and thus do not significantly affect the extraction rate. Essentially, the mass of analyte in each unit mass of extraction fluid and the mass of analyte remaining in the matrix at that period in the extraction time is calculated for the entire extraction time based on the $K_D$ value determined for each compound. Therefore, if the $K_D$ model applies to a certain extraction, the shape of an extraction curve would be defined by:

$$\frac{S_b}{S_0} = \left(1 - \frac{S_a}{S_0}\right) \div \left(\frac{K_D m}{(V_b - V_a)\rho} + 1\right) + \frac{S_a}{S_0} \quad (1)$$

where $S_a$ is the cumulative mass of the analyte extracted after volume $V_a$ (ml), and $S_b$ is the cumulative mass of the analyte extracted after volume $V_b$ (where the data point $V_b$, $S_b$ is the next sequential data point after $V_a$, $S_a$). $S_0$ is the initial total mass of analyte in the matrix. $S_b/S_0$ and $S_a/S_0$ are the cumulative fractions of the analyte extracted by the extraction fluid of the volume $V_b$ and $V_a$, respectively. $K_D$ is the distribution coefficient, $\rho$ is the density of extraction fluid at given conditions (g/ml), and m is the mass of the extracted sample (g). The Microsoft excel Solver regression routine was used to fit extraction data to Eq. (1). The fitting parameter was $K_D$. It is noted that the $K_D$ model does not include extraction time, but only relies on the volume of extractant fluid used. Therefore, doubling the extraction fluid flow-rate should double the extraction rate vs time if the extraction is described by thermodynamic partitioning (and if all the other extraction parameters remain constant) [16,17,19,20].

Kinetic models typically require two steps to define an extraction curve. In order to simplify model equation, the following simplification of material balance equation, Eq. (2) was made.

$$\frac{S_r}{S_0} = 1 - e^{-kt} \quad (2)$$

where $t$ is time (min), $S_r$ is the mass of the analyte removed by the extraction fluid after time $t$, $S_0$ is the total initial mass of analyte in the matrix. $S_r/S_0$ is the fraction of the analyte extracted after the time t, and k is released fraction ($min^{-1}$). The Microsoft excel Solver regression routine was used to fit the release data to Eq. (2). The fitting parameter was k as previously described. While it is possible that a single-site kinetic model and a $K_D$ model could yield similar fits to extraction curve data. The dependence of the $K_D$ model on extraction fluid volume (not time) and the dependence of kinetic models on extraction time (not volume of fluid) yields a simple method to determine the major factor controlling a particular extraction [16–18,22,27,28].

### 2.5. HPLC analysis

γ-Oryzanol in the extracts was quantified using HPLC according to method of Jesus et al. [8] The analysis system was composed of