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Using Phase Equilibrium Theory to Calculate Solubility of γ-Oryzanol in Supercritical CO_2

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***Abstract*—**Even its content is rich in antioxidants ϒ-oryzanol, rice bran is not used properly as functional food. This research aims to (1) extract ϒ-oryzanol; (2) determine the solubility of ϒ-oryzanol in supercritical CO_2 based on phase equilibrium theory; and (3) study the effect of process variables on solubility. Extraction experiments were carried out for rice bran (5 g) at various extraction pressures, temperatures and reaction times. The flowrate of supercritical fluid through the extraction vessel was 25 g/min. The extracts were collected and analysed with high-pressure liquid chromatography (HPLC). The conclusion based on the experiments are as: (1) The highest experimental solubility was 0.303 mcg/mL RBO at T= 60°C, P= 90 atm, t= 30 min; (2) Solubility of ϒ-oryzanol was influenced by pressure and temperature. As the pressure and temperature increase, the solubility increases; (3) The solubility data of supercritical extraction can be successfully determined using phase equilibrium theory. Meanwhile, tocopherol was found and slightly investigated in this work.

***Keywords*—**Rice bran, solubility, supercritical CO_2, ϒ-orizanol.

I. INTRODUCTION

RICE is one of the important agricultural crops in Indonesia. One of by-products from the process of milling rice is rice bran [1]. The utilisation of rice bran is not optimal i.e. for animal livestock, ash and fuel reboiler, and sometimes casually discarded [1]. The rice bran is rich in nutrients so it may be useful as high quality health food supplement. [2], [3].

Rice bran oil can be produced by extraction [4]. Rice bran oil contains anti-oxidants i.e. tocopherol, tocotrienol and γ-orizanol. Among them, γ-orizanol is reported as a powerful antioxidant that plays an important role in the metabolism of fat in the body, and is believed to prevent the coronary heart diseases and cancer [3].

The considered method to extract oil for food is the supercritical CO_2 extraction [5]. Mostly, parameters observed in the supercritical extraction are temperature and pressure [6].

The equation of state (EOS) is widely used to determine the solubility of solid in supercritical fluid. The solubility is predicted as a function of temperature and pressure. One of the EOS models that most commonly used to study the behavior of equilibrium is the Peng-Robinson (PR-EOS) model [7], [8].

A. Peng-Robinson Model

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{1}$$

with

$$b = 0{,}07780\frac{RT_c}{P_c} \tag{2}$$

$$a(T) = a(T_c)\,\alpha(T) \tag{3}$$

$$\alpha(T) = \left[1+\beta(1-\sqrt{T/T_c})\right]^2 \tag{4}$$

$$a(T_c) = 0{,}45724\frac{(RT_c)^2}{P_c} \tag{5}$$

where R is the gas constant, T_c is the critical temperature and Pc is pressure.

The solubility of pure solid, such as A, in supercritical fluid can be determined by using the equilibrium theory. Terms of the conditional in equilibrium between pure solid and supercritical fluid (SCF) in extraction process is expressed by

$$f_A^S = f_A^{SCF} \tag{6}$$

with f_A^S = fugacity of component (A) in a solid phase, f_A^{SCF} = fugacity of component (A) in a supercritical phase.

For pure components:

$$\ln\left(\frac{f}{p}\right) = \frac{1}{RT}\int_{p=0}^{p=p}\left(v-\frac{RT}{p}\right)dp \tag{7}$$

Thus, it can be expressed in the form of

$$\ln\left(\frac{f}{p}\right) = \frac{1}{RT}\left[\int_{v=v}^{v=\infty}\left(p-\frac{RT}{v}\right)dv - RT\ln z + RT(z-1)\right] \tag{8}$$

with

$$z = \frac{pv}{RT} \tag{9}$$

To calculate fugacity of pure solid, (7) can be arranged in the form of;

$$\ln\frac{f^s}{p} = \frac{1}{RT}\left[\int_{p=0}^{p=p^{sat}}\left(v-\frac{RT}{p}\right)dp + \int_{p=p^{sat}}^{p=p}\left(v^s-\frac{RT}{p}\right)dp\right] \tag{10}$$

$$\ln\frac{f^s}{p} = \frac{1}{RT}\left[RT\ln\frac{f^{sat}}{p^{sat}} + \int_{p=p^{sat}}^{p=p}v^s dp - RT\ln\frac{p}{p^{sat}}\right] \tag{11}$$

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