World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:10, No:5, 2016

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

Boy Arief Fachri

***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;

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

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

Boy Arief Fachri is with the Faculty of Engineering, University of Jember, Jawa Timur, Indonesia (e-mail: fachri.b.arief@gmail.com).

Open Science Index, Chemical and Molecular Engineering Vol:10, No:5, 2016 publications.waset.org/10004367.pdf

$$RT\ln\frac{f^{s}}{p}=\left[RT\ln\frac{f^{sat}}{p^{sat}}+\int_{p=p^{sat}}^{p=p}v^{s}dp-RT\ln\frac{p}{p^{sat}}\right] \tag{12}$$

$$f^{s}=p^{sat}\varphi^{sat}\exp\left(\int_{p=p^{sat}}^{p=p}\frac{v^{s}}{RT}dp\right) \tag{13}$$

with

$$\varphi^{sat}=\frac{f^{sat}}{p^{sat}} \tag{14}$$

For solute A, then (13) will be;

$$f_{A}^{s}=p_{A}^{sat}\varphi_{A}^{sat}\exp\left(\int_{p=p_{A}^{sat}}^{p=p}\frac{v_{A}^{s}}{RT}dp\right) \tag{15}$$

Fugacity on supercritical phase is;

$$f_{A}^{SCF}=\varphi_{A}y_{A}P \tag{16}$$

substitute (15) and (16) to (6), then (6) can be re-written as;

$$p_{A}^{sat}\varphi_{A}^{sat}\exp\left(\int_{p=p_{A}^{sat}}^{p=p}\frac{v_{A}^{s}}{RT}dp\right)=\varphi_{A}y_{A}P \tag{17}$$

Then,

$$y_{A}=\frac{p_{A}^{sat}\varphi_{A}^{sat}\exp\left(\int_{p=p_{A}^{sat}}^{p=p}\frac{v_{A}^{s}}{RT}dp\right)}{\varphi_{A}P} \tag{18}$$

If

$$E=\frac{\varphi_{A}^{sat}}{\varphi_{A}}\exp\left(\int_{p=p_{A}^{sat}}^{p=p}\frac{v_{A}^{s}}{RT}dp\right) \tag{19}$$

Equation (18) can be re-written as;

$$y_{A}=\frac{p_{A}^{sat}}{P}E \tag{20}$$

with $y_A$ = solubility (solut) in the phase supercritical, $p_A^{sat}$ = the saturation pressure of component (A).

Equation (20) can be used to calculate the solubility of ϒ-oryzanol in supercritical $CO_2$.

## II. METHODOLOGY

### A. Materials

Rice bran (IR 64 rice varieties with a water content of less than 10% (w/w) was supplied from Central Rice Production in Central Java, Indonesia. High purity of 99.98% Carbon dioxide ($CO_2$) was purchased from Gas Depo Industry, Indonesia.

### B. Experimental

Research procedures are such as in Fig. 1. Process parameters observed in this study are the temperature (40-60ºC), pressure (80-90 atm) and reaction time (5-30) minutes. To quantify the amount of ϒ-oryzanol, the liquid product was analysed by HPLC.

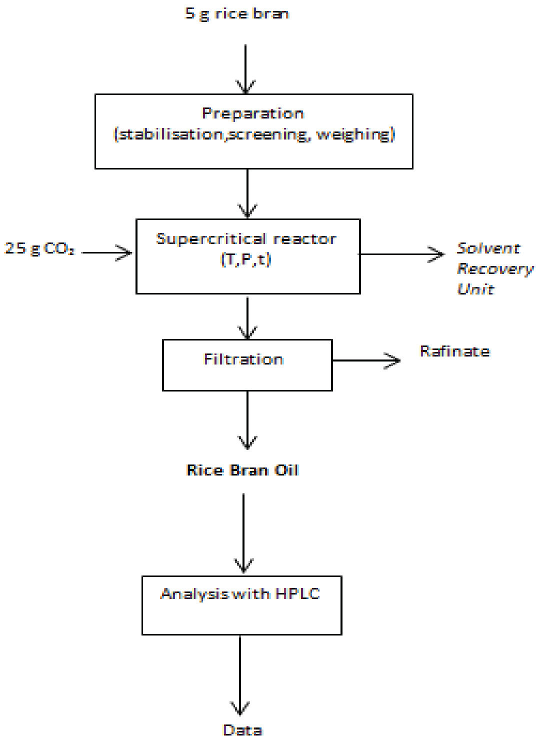

Fig. 1 Flow diagram of experimental procedures

## III. RESULTS AND DISCUSSION

Exploratory experiments to determine the solubility of ϒ-oryzanol were performed at 50ºC and 90 atm, using rice bran intake of 5 g. A typical concentration profile showed solubility is given in Fig. 2.

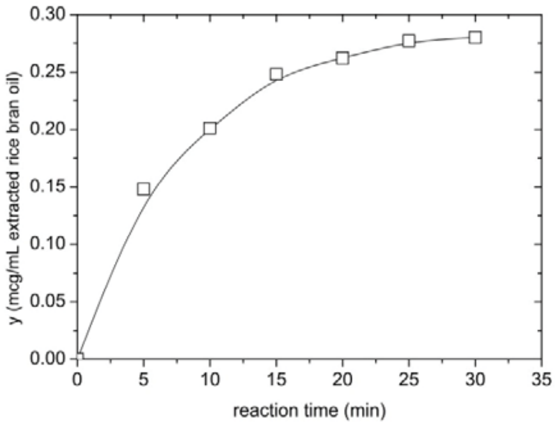

Fig. 2 The solubility of ϒ-oryzanol

To investigate the effect of process variables on the solubility of γ-Oryzanol in supercritical $CO_2$, 20 experiments were conducted in a batch reactor set up. Three independent variables, as shown in Table I, were explored and the solubility of γ-Oryzanol was taken as the dependent variables. The results are provided in Table I.

TABLE I
OVERVIEW OF EXPERIMENTS

| Run | reaction time (min) | pressure (atm) | Temperature, (°C) | y ϒ-orizanol (mcg/mL rice bran oil) |
|---|---|---|---|---|
| 1 | 15 | 85 | 40 | 0.067 |
| 2 | 30 | 90 | 60 | 0.303 |
| 3 | 15 | 90 | 50 | 0.188 |
| 4 | 15 | 85 | 60 | 0.115 |
| 5 | 30 | 90 | 40 | 0.211 |
| 6 | 15 | 85 | 50 | 0.108 |
| 7 | 5 | 80 | 40 | 0.020 |
| 8 | 5 | 90 | 60 | 0.101 |
| 9 | 15 | 85 | 50 | 0.108 |
| 10 | 30 | 80 | 40 | 0.060 |
| 11 | 15 | 80 | 50 | 0.072 |
| 12 | 15 | 85 | 50 | 0.108 |
| 13 | 5 | 90 | 40 | 0.090 |
| 14 | 15 | 85 | 50 | 0.108 |
| 15 | 30 | 80 | 60 | 0.184 |
| 16 | 5 | 85 | 50 | 0.054 |
| 17 | 15 | 85 | 50 | 0.108 |
| 18 | 30 | 85 | 50 | 0.214 |
| 19 | 15 | 85 | 50 | 0.108 |
| 20 | 5 | 80 | 60 | 0.050 |

Based on Table I, the highest solubility of ϒ-oryzanol is 0.303 mcg/mL rice bran oil (entry 2,) and was gained at reaction time of 30 min, pressure of 90 atm at 60°C. The parity plots described in Fig. 3 indicate a good agreement between the experimental and predicted data. The effect of process variable on solubility can be illustrated in Fig. 4. It is obviously drawn that pressure and temperature has profound effect. As pressure increases, the solubility increases. Higher pressure and temperature lead to higher diffusivity and density of fluid. It makes the supercritical $CO_2$ strongly pushing out the oil from the rice bran matrice.

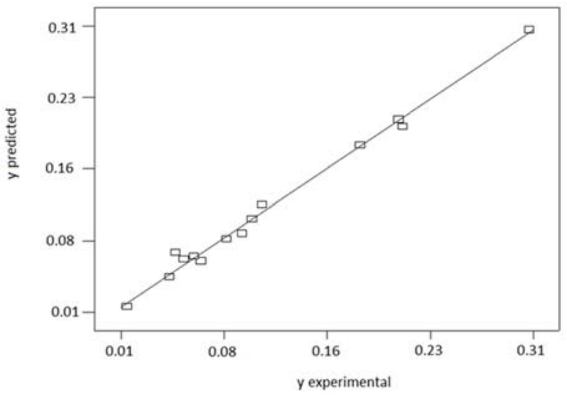

Fig. 3 Parity plot of ϒ-oryzanol

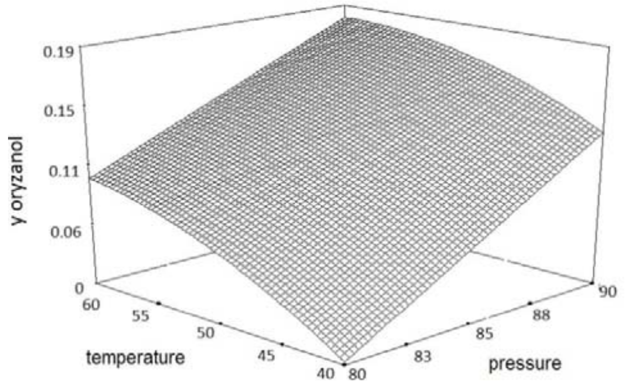

Fig. 4 Effect of temperature and pressure on solubility ϒ-oryzanol in supercritical $CO_2$

Herein this study, we also found the tocopherol content in extracted rice bran oil. This finding (in Table II) shows the relationship between reaction time, pressure and temperature to yield of tocopherol.

TABLE II
OVERVIEW ON TOCOPHEROL CONTENT

| Run | reaction time (min) | pressure (atm) | Temperature, (°C) | y ϒ-tocopherol (mcg/mL rice bran oil) |
|---|---|---|---|---|
| 1 | 15 | 85 | 40 | 0.015 |
| 2 | 30 | 90 | 60 | 0.050 |
| 3 | 15 | 85 | 60 | 0.026 |
| 4 | 30 | 90 | 40 | 0.029 |
| 5 | 15 | 85 | 50 | 0.016 |
| 6 | 5 | 80 | 40 | 0.008 |
| 7 | 5 | 90 | 60 | 0.011 |
| 8 | 15 | 85 | 50 | 0.016 |
| 9 | 30 | 80 | 40 | 0.019 |
| 10 | 15 | 80 | 50 | 0.009 |
| 11 | 15 | 85 | 50 | 0.016 |
| 12 | 5 | 90 | 40 | 0.010 |
| 13 | 15 | 85 | 50 | 0.016 |
| 14 | 30 | 80 | 60 | 0.030 |
| 15 | 5 | 85 | 50 | 0.009 |
| 16 | 15 | 85 | 50 | 0.016 |
| 17 | 30 | 85 | 50 | 0.028 |
| 18 | 15 | 85 | 50 | 0.224 |
| 19 | 5 | 80 | 60 | 0.016 |

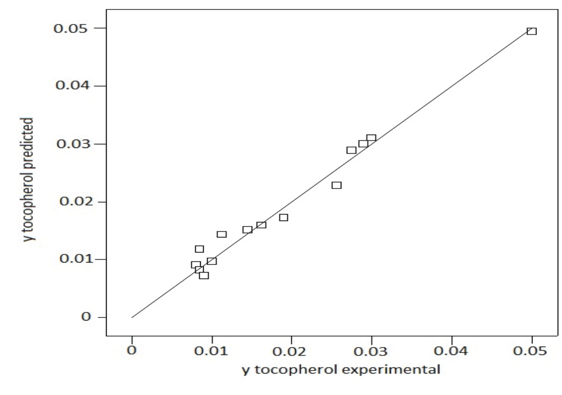

Fig. 5 Parity plot of tocopherol

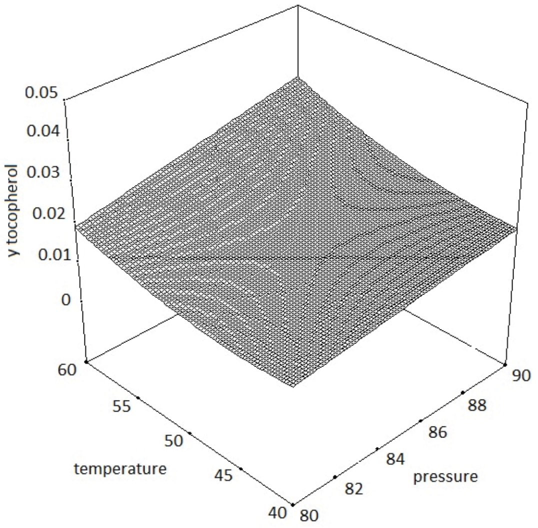

Fig. 6 Effect of temperature and pressure on solubility tocopherol in supercritical $CO_2$

Table II informs that the highest yield of tocopherol is 0.224 mcg/mL rice bran oil (entry 18) at condition of T=50oC, P=85 atm and t=15 min. Meanwhile, Fig 5 shows that experimental values fit with predicted values. The effect of temperature and pressure on yield of tocopherol is explicitly stated in Fig. 6.

## IV.CONCLUSION

An in-depth experimental study on the determination of ϒ-oryzanol solubility in supercritical was conducted in a batch supercritical reactor. The highest experimental solubility (0.303 mcg/mL RBO) was obtained at 60ºC, pressure of 90 atm, a reaction time of 30 min.

This work also concludes that (1) the solubility of ϒ-oryzanol become greater with increasing temperature and pressure; (2) the solubility data on the extraction of solid-supercritical fluid in this research can be obtained based on the concept of phase equilibrium.

## ACKNOWLEDGMENTS

Thanks to the Directorate General of Higher Education of Republic Indonesia for supporting the research in accordance with the Letter of Agreement Implementation Research Grants.

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