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Contributed Paper

Value Added Products from By-products of Rice Bran Oil Processing

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ABSTRACT

This study deals with the production of value-added product derived from rice bran oil processing by-products. The investigation was divided into two parts, Part I: subcritical water (SW) hydrolysis of deoiled rice bran and Part II: separation of γ-oryzanol from rice bran oil soapstock. In Part I SW hydrolysis reaction was carried out in a closed batch reactor in which the effect of temperature in the range of 200-220 °C, reaction time of 10-30 min, raw material to water weight ratio of 1:5 and 2:5, were determined on the of protein, amino acid, reducing sugars, and antioxidant activity. The results in the present study suggested that subcritical water could be used to potentially hydrolyze deoiled rice bran into more valuable products. The suitable condition for protein and amino acids production from deoiled rice bran by subcritical water hydrolysis was 1:5 at 30 min and hydrolysis temperature of 220 °C. At this condition, the protein: 130.17 mg/g rice bran, amino acid: 9.14 mg/g rice bran. In Part II, separation of γ-oryzanol from rice bran oil soapstock was conducted following the selected processes from literatures. The processes involve saponification, dehydration, leaching and crystallization. The content of γ-oryzanol was analyzed by using UV spectrophotometer. The selected processes were demonstrated as suitable means for separating γ-oryzanol from soapstock obtained locally.

Keywords: Subcritical water, rice bran oil, deoiled rice bran, soapstock, γ-oryzanol.

1. INTRODUCTION

Rice is a major agricultural product of Thailand with annual productivity of about 29 million tons due to suitable topography and climate nature [1]. Commonly, consumers prefer white rice therefore brown rice is subjected to milling process. Rice bran is an important by product of the milling process which is enriched with fibre, proteins, oil, and important antioxidants such as vitamin E and γ-oryzanol. Currently, rice bran is mostly used as animal feed (60%), while the rest (40%) is used to produce value added edible cooking oil. Although rice oil is considered nutritious oil and is becoming popular especially in USA and Europe, during rice bran oil processing, a large amount of bran nutrition was lost along with the by products. Here we are interested in two major by products of the

rice oil processing: deoiled bran and soapstock. Deoiled bran is rich in proteins and amino acid and is obtained after oil extraction. Soapstock is obtained after deacidification by alkali treatment of crude rice bran oil during the refining process. It has a significant amount of γ-oryzanol, which is an important component that shows many health benefits such as reduction of cholesterol in the blood and anti-aging effect etc. At present, the majority of both deoiled bran and soapstock is used as animal feed. The objective of this study is therefore to increase the value of these by products.

Generally, proteins and amino acid that are presented in deoiled bran can be extracted by chemical method which is alkai or acid hydrolysis, followed by acid precipitation. However, low protein yield was obtained due to degradation at extreme pH condition. Alternatively, enzymatic process has been studied but the process takes a long time and the high cost of enzymes make the process commercially uneconomical. Subcritical water or pressurized water at the temperature between boiling point (100 °C) and its critical temperature (374.15 °C) is an interesting alternative. At such condition, water polarity decreases, thus make it better solvent for extraction of several organic bioactive substances.

Separations of γ-oryzanol from rice bran oil soapstock have been investigated for many decades. In the development of these processes into commercial scale, several factors such as productivity, environmental and health concerns, process investment, and separation efficiency (purity and yield) must be considered. Furthermore, isolation procedure developed for one soapstock does not necessarily work well with another soapstock [2]. Consequently, in this study, we employed selected processes from literatures and further investigated the experimental separation of γ-oryzanol from domestic soapstock.

In this study we divided our investigation into two parts. Part I: Subcritical water hydrolysis of deoiled rice bran and Part II: Separation of γ-oryzanol from rice bran oil soapstock.

2. MATERIAL AND METHOD

Part I: Subcritical water hydrolysis of deoiled rice bran

2.1.1 Materials. Deoiled rice bran was obtained from Thai Edible Oil Co., Ltd., Ayuthaya, Thailand.

2.1.2 Subcritical water hydrolysis. The hydrolysis reaction was carried out in closed batch reactor in which the effect of temperature in the range 200-220 °C, reaction time of 10-30 min and raw material to water weight ratio of 1:5 and 2:5 on the yield of protein, amino acid and reducing sugar.

2.1.3 Analytical method

1) Analysis of protein. Protein content of soluble portion was assayed using Lowry's method [3], using bovine serum albumin (BSA) as a standard.

2) Analysis of amino acids. Amino acids content was analyzed by Ninhydrin assays using L-Glutamic acid as a standard.

3) Analysis of reducing sugar. Reducing sugars content was assayed by dinitrosalicylic colorimetric method, using D-Glucose as a standard using dinitrosalicylic reagent developed by Sumner (1921) [4].

4) $ABTS^{\cdot+}$ scavenging assay. ABTS (2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) radical cation scavenging assay was carried out following a modified method described by Re et al., 1999 [5]. For comparing the antioxidant activity of the extracts obtained at various conditions, concentration of sample producing 50% reduction of the radical absorbance (IC_{50}) was used as an index. The IC_{50} values for various extracts were found

from the plots of percent inhibition (PI) versus the corresponding concentration of the sample. The values of PI were calculated using the following equation:

$$PI\ (\%) = [1-(A_t / A_r)] \times 100$$

where A_t and A_r are absorbance of test sample and absorbance of the reference, respectively.

Part II: Separation of γ-oryzanol from rice bran oil soapstock

2.2.1 Materials Rice bran oil soapstock was obtained from Thai Edible Oil Co., Ltd., Ayuthaya, Thailand.

2.2.2 Separation of γ-oryzanol The selected processes [6, 7, 8] were applied to separate γ-oryzanol from soapstock. This process includes the following steps: saponification, dehydration, leaching, and crystallization.

2.2.3 Quantification of γ-oryzanol γ-oryzanol contents was determined by spectrophotometric method.

3. RESULTS AND DISCUSSIONS

Part 1: Subcritical water hydrolysis of deoiled rice bran

3.1.1 Protein of soluble products

The amounts of protein in the soluble products obtained by SW hydrolysis of deoiled rice bran at various conditions are shown in Figure 1. The highest protein (130.17 ± 2.48 mg/g deoiled rice bran) was obtained from the 220 °C hydrolysis for 30 min. Based on the amount in the original bran reported by NIR (15.53 %wt) this account for the protein recovery of 84%.

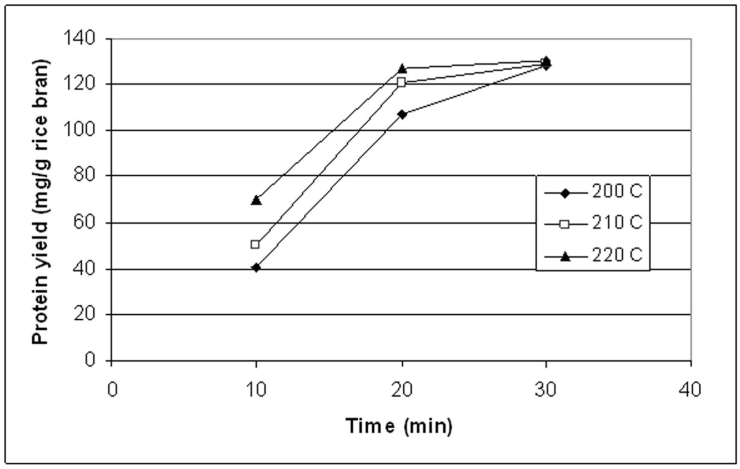

Figure 1. Protein yield after hydrolysis of deoiled rice bran at different temperature and time.

3.1.2 Amino acid of soluble product

The amino acids of soluble products obtained at various hydrolysis conditions are shown in Figure 2. The highest yield was 9.74 ± 50.08 μg/g raw rice bran, which was obtained at 220 °C for 20 min. This relatively low yield indicates that the rate of amino acids decomposition to smaller molecules of organic acids or other products was faster than the amino acid production. The temperature and reaction time do not have significant effects on the amount of total amino acids. At this condition, the result indicated that the rate of amino acid production was comparable to the rate of amino acid decomposition into smaller organic acids.

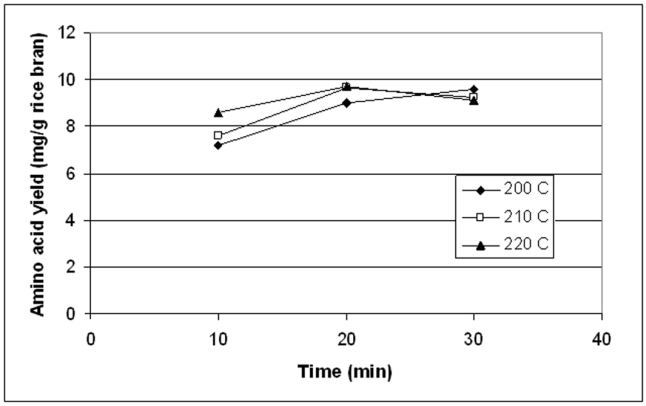

Figure 2. Amino acid yield after hydrolysis of raw materials at different temperature and time

3.1.3 Reducing sugar in soluble products

When carbohydrate reacts with hydronium and hydroxide ions, reducing sugars are produced. The reducing sugar of the soluble hydrolysis products at different temperature and time are shown in Figure 3. The reducing sugar content in the soluble products increased with increasing temperatures and times of reaction, except for the hydrolysis product obtained at 220°C and 30 min, whose reducing sugar content decreased. This result again indicated that at this condition, the rate of reducing sugar decomposition into smaller molecules of organic carbon was high, and that the decomposition of reducing sugar to other product was favored over the production of reducing sugar.

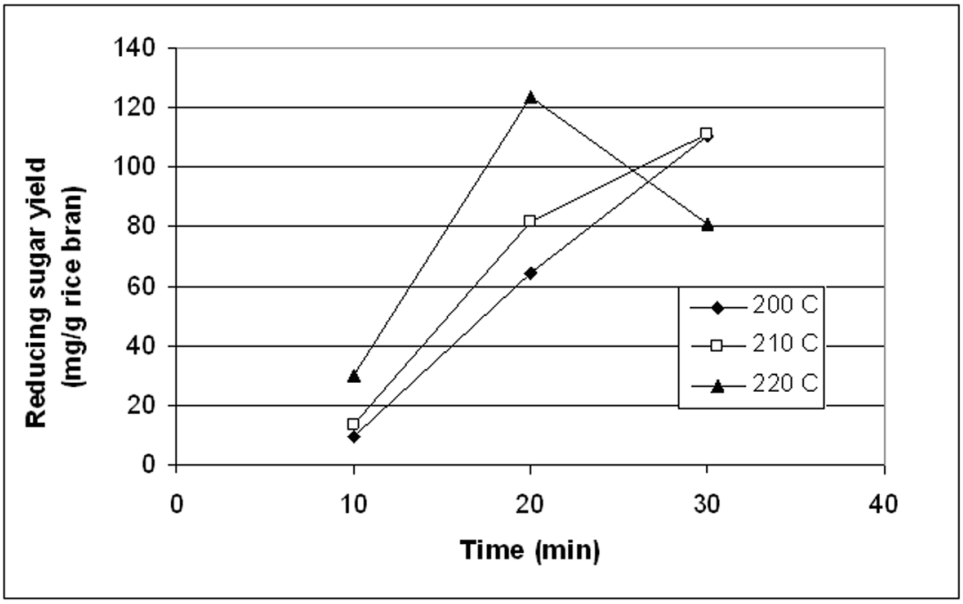

Figure 3. Reducing sugar yield after hydrolysis of raw materials at different temperature and time

3.1.4 Effect of ratio of raw material-to-water on extraction yield

The effect of the ratio of raw material-to-water on extraction yield was studied by comparing the product obtained from two different ratios of deoiled rice bran-to-water, 1:5 and 2:5 for reaction conditions at 210 °C and 30 min (Figure 4). It was found that the of protein, amino acids and reducing sugar decreased when the ratio of raw material-to-water was increased from 1:5 to 2:5. This is mainly because the high content of raw material increases the density and viscosity of the mixture, therefore caused the poor mixing of raw material and water, thus mass transfer decreased and the accessibility of water to particles of raw materials was difficult. The ratio of raw material-to-water of 1:5 was therefore more suitable.

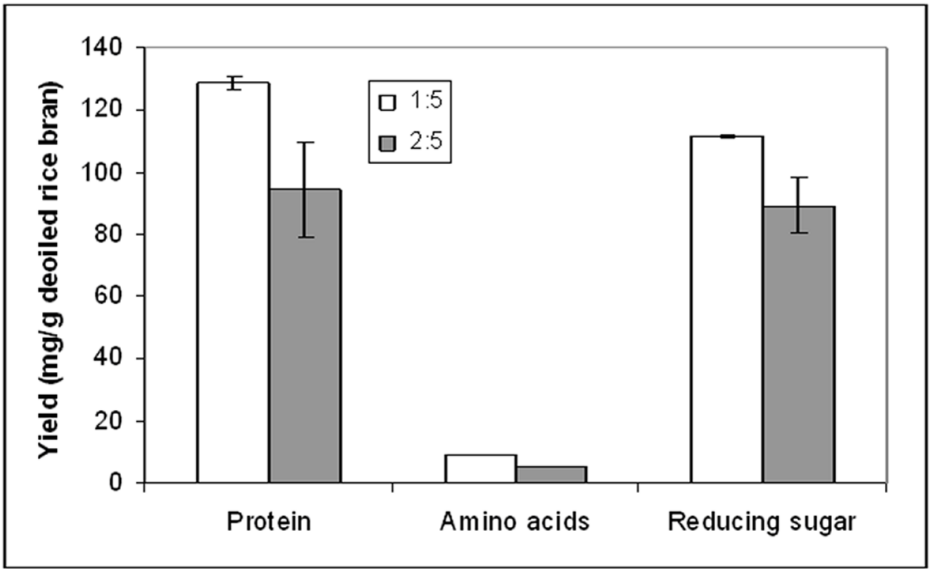

Figure 4. Effect of ratio of deoiled rice bran-to-water (1:5 and 2:5) for 210 °C and 30 min

3.1.5 Antioxidant activity

In this study, the antioxidant activity of soluble products obtained with SW was evaluated with $ABTS^{\bullet+}$ scavenging assay. Antioxidant activity was represented by (IC_{50}) index which is the concentration of sample producing 50% reduction of the radical absorbance. The antioxidant activity was measured at hydrolysis temperature of 200°C and 220 °C and hydrolysis time at 20 min and 30 min. These conditions were found to be suitable and were selected for the antioxidatant test. The results in Figure 5 indicated that with the hydrolysis time of 20 min, antioxidant activity increased as temperature increased from 200°C to 220°C. For the reaction time of 30 min, however, the antioxidant activity only increased slightly or stayed constant with the increase in temperature. The increase in water temperature not only increases the ion product which causes hydrolysis reaction but also causes the breakdown of hydrogen bonds. Hydrogen bonds of water keep the water molecules together, thus separating themselves from other organic compounds. When the H-bonds breakdown, several antioxidative organic

compounds within the rice bran and soybean samples were better able to dissolve in water, thus the soluble products exhibited higher antioxidant activity. At long exposure time with high temperature, however, some antioxidative compounds might be degraded, thus the activity might decrease [8]. It is recommended that in the future study, analysis should be carried out to identify the antioxidant compounds obtained in the soluble products.

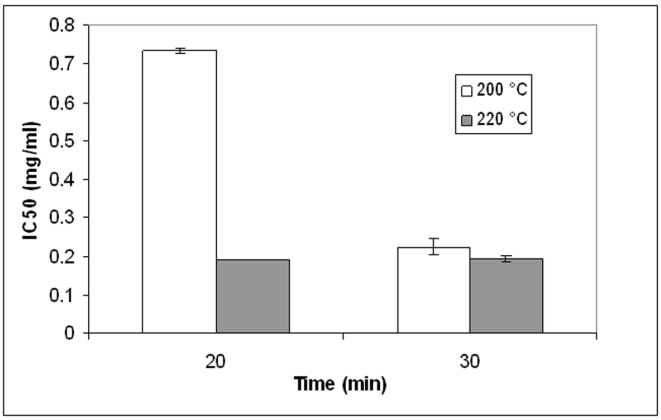

Figure 5. Antioxidant activity (IC_{50}) of the soluble products at hydrolysis times of 20 and 30 min and temperature of 200 °C and 220 °C.

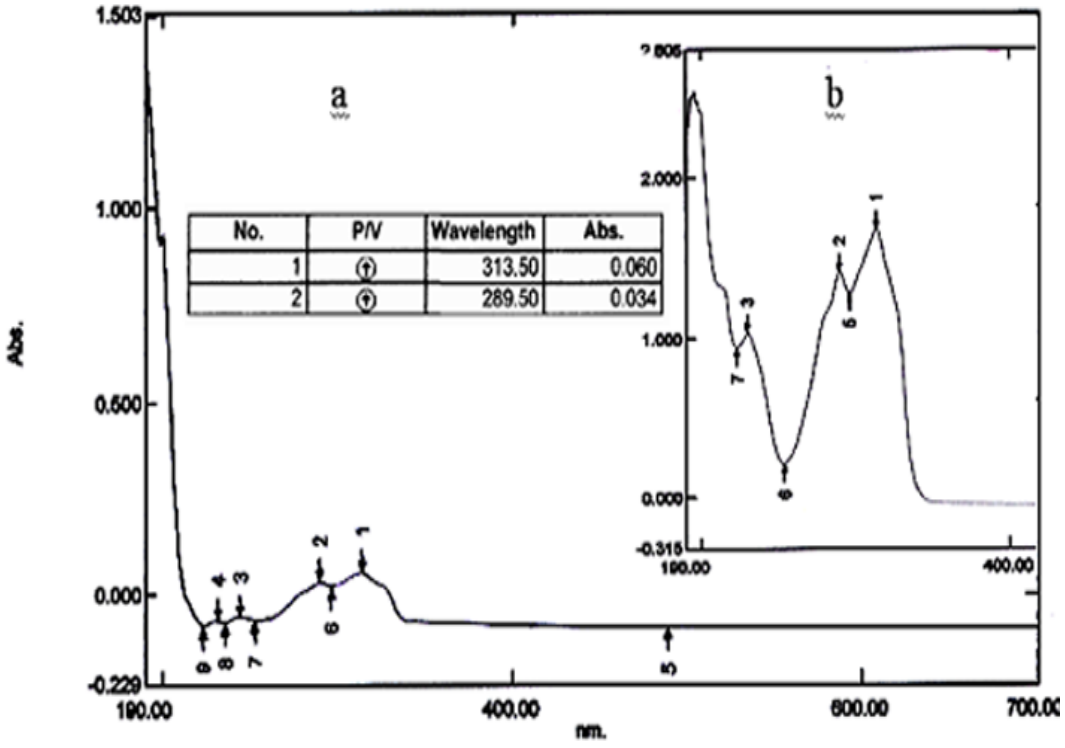

Figure 6. Spectrum peak scanning report for sample comparable to γ-oryzanol standard. (a) γ-oryzanol standard, (b) sample.

Part II: Separation of γ-oryzanol from rice bran oil soapstock by using selected processes

The separation γ-oryzanol from soapstock by selected processes was found to be appropriate for the acquired soapstock. Quantification γ-oryzanol in the sample obtained after recrystallization could be achieved by using UV spectrophotometer. It was found that spectrum peak of the sample was comparable to that of the standard with the same maximum absorption wave length as shown in Figure 6. Details on the effects of process conditions will be discussed further.

4. CONCLUSIONS

The results in the present study suggested that subcritical water could be used to potentially hydrolyze deoiled rice bran into more valuable products. The suitable condition for protein and amino acids production from deoiled rice bran by subcritical water hydrolysis was 1:5 at 30 min and hydrolysis temperature of 220 °C. At this condition, the protein: 130.17 mg/g rice bran, amino acid: 9.14 mg/g rice bran. The selected processes from literature could be applied for separation of γ-oryzanol from locally obtained soapstock.

ACKNOWLEDGEMENT

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