A Rapid and Ecofriendly Treatment Technique for Rice Bran Oil Stabilization and Extraction under Sub-critical Water Condition

O. Pourali, F. Salak Asghari, H. Yoshida

***Abstract*—The target of this research work is application of sub-critical water as an ecofriendly medium for inactivation of rice bran lipase enzyme simultaneous with the extraction of rice bran oil to obtain favorable cooking oil. Experiments were carried out at temperature ranging from 393 to 513 K with 10 and/or 20 min residence time in a batch reactor. The quality of the treated oils was assessed by measuring of their total free fatty acids concentration over storage period. Results indicated that sub-critical water could effectively inactivate enzyme and, total free fatty acids concentration remained constant in the treated oils whereas it considerably increased from 5.6% to 36.0% in a untreated samples. Meanwhile rice bran oil could be successfully extracted using sub-critical water. It was found that the extraction yield was a function of temperature and increased by temperature increasing.**

Key words: Extraction, Rice bran oil, Stabilization, Sub-critical water treatment

I. Introduction

Rice bran is one of the most abundant biomass in the world. Its production amount is about 50-60 million tons per year which is normally used as animal food [1]. It is a natural resource of minerals, proteins, carbohydrates, vitamins, and antioxidants [2]. In addition, this biomass contains 10-26% oil [3] which is used for different purposes. Rice bran oil has several unique nutritional properties; however, less than ten percent of this valuable oil is used for edible oil production [4]. The main reason is that the oil is exposed to rice bran lipase enzyme after rice milling which causes, as a catalyst, the triglyceride of oil is quickly hydrolyzed into glycerol and free fatty acids. Stabilization of rice bran and extraction of oil soon after milling process are two effective methods for lipase enzyme inactivation and prohibition of free fatty acids formation [5].

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So far extraction of rice bran oil has been performed using conventional techniques like soxhlet extraction and solid-solvent extraction. These techniques usually use organic solvents which are expensive and sometimes toxic. Green extraction techniques such as supercritical fluid and sub-critical water (sub-CW) treatment have received more attentions in recent years [6].

To date, for stabilization of rice bran oil several techniques have been studied [3], [7], [8]. Although a number of studies like microwave heating, ohmic heating, and pH lowering have been conducted for rice bran oil stabilization; however, sub-CW treatment has not been used for this purpose. In fact, it is an environmentally friendly technique with a wide range of applications, such as extraction, hydrolysis, and decomposition of organic compounds [9].

The objective of this research work was to develop sub-CW as rapid and ecofriendly treatment technique in order to inactivate lipase enzyme simultaneous with oil extraction, in a very short time.

II. Experimental

Japanese rice was utilized in this experimental study. The batch reactor used for sub-CW treatment was a stainless steel tube. In typical experiment, an accurately weighed amount of rice bran and distilled water were charged into the reactor. Argon gas was utilized to force air out of the reactor, and then it was capped tightly. It was immersed in a preheated oil or salt bath for 10 and/or 20 min. The reactor was then removed from the thermal bath and quickly quenched by soaking in a cold water bath at room temperature. Reactor content was washed into a test tube, and it was classified and isolated into three phases: hexane-soluble, water-soluble, and solid residue phases. Hexane-soluble phase was a yellowish liquid, which contained mainly rice bran oil. Its extraction yield was calculated by weight after evaporation of hexane by a rotary evaporator.

Direct solid-solvent extraction (soon after rice milling) and soxhlet extraction techniques were performed in order to compare with the sub-CW method.

The concentration of total free fatty acids in the extracted oils was evaluated according to alcoholic alkali titration method [10] which is expressed as oleic acid equivalent grams in 100 g of rice bran oil.

III. Results and discussion

A. *Stabilization of Rice Bran Oil*

Rice bran oil is unstable oil and its triglyceride is hydrolyzed into glycerol and free fatty acids during storage. In order to understand the formation rate of these undesired compounds, the concentration of free fatty acids was evaluated in the rice bran as function of storage time. Fig. 1 (right axis) shows time course of total free fatty acids concentration in the untreated samples. It reveals that total free fatty acids concentration increased by time; it rose from 5.6% to 36.0% during 12 weeks. Generally rice bran oil with total free fatty acids levels of over 10% is not economically suitable for edible oil production [11]; therefore, it can be concluded that the obtained oil from untreated rice bran after one week from the milling date is not suitable feed stock for cooking oil production.

To overcome this problem, a series of sub-CW experiments were performed at temperature ranging from 393 to 513 K with 10 and/or 20 min residence time. Fig. 1 (left axis) shows the concentration of total free fatty acids in the sub-CW treated oils as a function of storage time. This figure indicates that concentration remained constant and, no increase was observed even after 12 weeks. It also demonstrates that total free fatty acids concentration was a function of treatment temperature; the greater the sub-CW temperature, the greater was the concentration of total free fatty acids. In addition, total free fatty acids concentration was also influenced by residence time. The highest and lowest concentrations of total free fatty acids were obtained at 473 K for 20 min and 433 K for 10 min.

It has been understood that proteins could be decomposed to amino acids and organic acids under sub-CW condition [12]. Therefore, since lipase enzyme is a protein it can be decomposed under sub-CW medium. Meanwhile, the results revealed that the inactivation of lipase enzyme was an irreversible process.

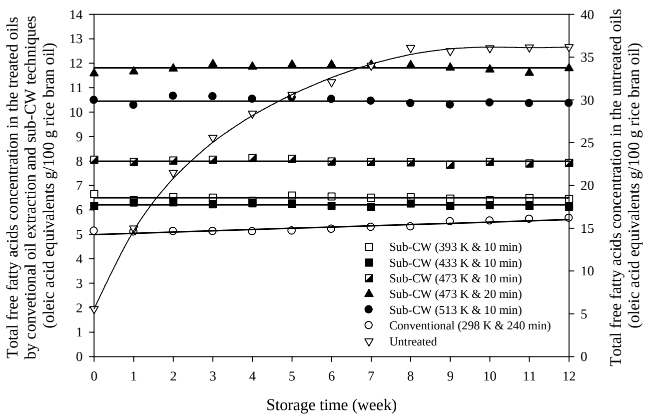

Fig 1. Total free fatty acids concentration in the treated and untreated oils during storage.

pH is another important parameter which has considerable effects on the activity of lipase enzyme [3]; decomposition of rice bran under sub-CW condition produces organic acidic compounds which decrease the pH of the treatment medium [13]; therefore, inactivation of rice bran lipase can also be due to this pH lowering.

Fig. 1 also indicates the concentration of total free fatty acids in the extracted oil by hexane, using conventional extraction method, as a function of storage time. It demonstrates that total free fatty acids amount gradually increased from 5.0% to 5.6% in the course of storage. The result reveals that lipase enzyme could not be completely inactivated by the conventional extraction technique.

B. *Extraction of Rice Bran Oil*

Extraction of rice bran oil was also investigated in this research work. Sub-CW not only could effectively inactivate lipase enzyme but also could extract oil from rice bran. Table I shows the extraction amount of rice bran oil. For comparison conventional soxhlet and solid-solvent extraction methods were also carried out in this study.

Under sub-CW treatment, the extraction yield of oil was increased from 140.6 to 248.9 (mg/g dry matter) by temperature rising from 393 to 513 K. This increase can be attributed to the decreasing of water dielectric constant with the increasing of temperature [6]. It was also found that the extraction yield was a function of residence time.

Although relatively higher oil yields were obtained by soxhlet and solid-solvent extractions; however, considering the processing time of the utilized extraction techniques and ecological point of view, it can be concluded that sub-CW is competitive and a green alternative technique compare to the conventional methods.

IV. Conclusion

In presence of lipase enzyme, the concentration of total free fatty acids in the untreated rice bran enhanced from 5.6% to 36.0% over the storage period of 12 weeks. However sub-CW as a rapid and ecofriendly treatment technique could effectively inactivate the enzyme, and as result, total free fatty acids concentration was not increased in the treated samples by time. It was also found that sub-CW could efficiently extract rice bran oil in a very short residence time.

Table I. Oil extraction yield of different techniques

Extraction technique	*Temp. (K)*	*Extraction time (min)*	*Extraction yield (mg/g dry matter)*
Sub-CW	393	10	140.6
Sub-CW	433	10	173.7
Sub-CW	473	10	195.6
Sub-CW	473	20	208.8
Sub-CW	513	10	248.9
Soxhlet	345	240	265.6
Solid-hexane	298	240	217.8

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REFERENCES

[1] R. Renuka Devi, C. Arumughan, “Phytochemical characterization of defatted rice bran and optimization of a process for their extraction and enrichment,” *Biores. Tech.,* vol. 98, 2007, pp. 3037-3043.

[2] R. M. Saunders, “Rice bran: composition and potential food uses,” *Food Rev. Int.,* vol. 1, 1985, pp. 465-495.

[3] J. V. Prabhakar, K. V. L. Venkatesh, “A simple chemical method for stabilization of rice bran,” *JAOCS,* vol. 63, 1986, pp. 644-646.

[4] S. Zullaikah, C. C. Lai, S. R. Vali, Y. H. Ju, “A two-step acid-catalyzed process for the production of biodiesel from rice bran oil,” *Biores. Tech.,* vol. 96, 2005, pp. 1889-1896.

[5] Y. H. Ju, S. R. Vali, “Rice bran oil as a potential resource for biodiesel: a review,” *J. Sci. Ind. Res.,* vol. 64, 2005, pp. 866-882.

[6] M. Herrero, A. Cifuentes, E. Ibanez, “Sub- and supercritical fluid extraction of functional ingredients from different natural sources: plants, food by-products, algae and microalgae: a review,” *Food Chem.,* vol. 98, 2006, pp. 136-148.

[7] N. Rao Lakkakula, M. Lima, T. Walker, “Rice bran stabilization and rice bran oil extraction using ohmic heating,” *Biores. Tech.,* vol. 92, 2004, pp. 157-161.

[8] J. Tao, R. Rao, J. Liuuzo, “Microwave heating for rice bran stabilization,” *J. Microw. Power Electromagn. Energy,* vol. 28, 1993, pp. 156-164.

[9] A. Kruse, E. Dinjus, “Hot compressed water as reaction medium and reactant properties and synthesis reactions,” *J. Supercrit. Fluids,* vol. 39, 2007, pp. 362-380.

[10] C. L. Hoffpauir, D. H. Petty, J. D. Guther, “Germination and free fatty acid in individual cotton seeds,” *Science,* October 1947, pp. 344-345.

[11] R. V. Enochian, R. M. Saunders, W. G. Schultz, E. C. Beagle, P. R. Crowley, “Stabilization of rice bran with extruder cookers and recovery of edible oil: a preliminary analysis of operational and financial feasibility,” *Marketing Research Report,* USDA No. 1120, 1981.

[12] H. Yoshida, M. Terashima, Y. Takahashi, “Production of organic acids and amino acids from fish meat by sub-critical water hydrolysis,” *Biotech. Prog.,* vol. 15, 1999, pp. 1090-1094.

[13] O. Pourali, F. Salak Asghari, H. Yoshida, “Sub-critical water treatment of rice bran to produce valuable materials,” *Food Chem.,* vol. 115, 2009, pp. 1-7.