Application of Subcritical Water Treatment for Production of Phenolic Compounds from Rice Bran Biomass

F. Salak, O. Pourali, H. Yoshida

***Abstract*—This study deals with the production of phenolic compounds from decomposition of rice bran biomass under subcritical water condition. Experiments were performed in a batch stainless steel vessel over a wide temperature ranging from 373 to 633 K for 10 min. The main identified and quantified phenolic compounds were caffeic acid, ferulic acid, gallic acid, p-coumaric acid, p-hydroxybenzoic acid, protocatechuic acid, syringic acid, vanillic acid and, vanillin. In addition, the antioxidant activity of aqueous solution were also evaluated. Both phenolic compounds and antioxidants showed increasing with temperature rising, and leveled off at the temperatures higher than 493 and 553 K, respectively. It was also realized that due to acidic properties of produced compounds, autocatalysis may occur during subcritical water treatment of rice bran.**

Key words: Antioxidants, Phenolic compounds, Rice bran biomass, Subcritical water treatment

I. Introduction

Rice is the main staple food in Asian countries like Japan. During rice milling process, rice bran is produced as major by-product. Its production rate only in Japan is about 900 thousand tons per year [1]. This abundant biomass is a natural resource of oil, proteins, carbohydrates and, dietary minerals [2]. Also, it has been discovered that rice bran may contain even 100 different antioxidants like phenolic compounds [3]. The health-promoting properties of phenolic compounds of rice bran reduce the risk of different diseases, and offer beneficial effects against cancers, cardiovascular disease, diabetes, and Alzheimer's disease [4]. Although rice bran has great nutrition and pharmaceutical benefits; however, is currently underutilized and a large quantity of rice bran (nearly 30% of the produced rice bran) goes to waste in Japan [5]. It is worth and necessary to extract and recover these valuable materials before discarding this precursor. So far, this purpose has been achieved by utilization of conventional extraction methods using several organic solvents [6]. Conventional methods usually have several drawbacks; e.g. they are time-consuming, are of low selectivity, give low extraction yield, and use large amount of expensive, explosive, and/or sometimes toxic organic solvents [7]. To overcome to these drawbacks, alternative methods like supercritical fluid and subcritical water treatment can be used. Subcritical water as green treatment method has wide applications in various fields of green engineering and material cycling [8]-[10]; however, very few research works have been conducted for phenolic compounds production from rice bran using subcritical water.

The objective of this study was to investigate the feasibility of decomposition and hydrolysis of rice bran and consequently production of phenolic compounds under subcritical water condition in a short residence time.

Submission date: July 17, 2009. *International Conference on Chemical Engineering (ICCE'09)*

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II. Experimental

Japanese rice bran was utilized in this experimental study. The batch reactor used for subcritical 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 with temperature ranging from 373 to 633 K. After desire residence time, 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 two phases: water-soluble and solid residue phases. The pH of water-soluble phase was measured using a glass pH electrode. After centrifuging, these two phases were separated with taking out of supernatant (water-soluble phase) to a volumetric flask by Pasteur pipette. Solid residue was washed by ethanol and, the obtained mixture was shaken for 1 min and then centrifuged. The obtained ethanol phase was transferred by Pasteur pipette and added to the collected water-soluble phase. This solution was mixed and made up to 50 cm^3 with ethanol and, filtered with a 0.2 μm filter.

Total phenolic compounds (TPC) and antioxidants was assayed by UV-visible (Shimadzu UV-160, Shimadzu Co., Japan) [11]-[12]. Individual concentration of phenolic compounds was determined by an HPLC system (Varian

ISBN:978-988-17012-6-8

ProStar210, CSPAK narrow-bore column C18) using PDA (photodiode array) detector (Varian PDA 330 Detector, Varian Inc., U.S.A.). PDA collected data between 250 nm and 330 nm and absorbance was monitored at 270 nm. Column temperature was kept at 298 K. Gradient elution program (methanol and 1% acetic acid) at 0.2 cm^3/min flow rate was used.

III. Results and discussion

A. Identification of Phenolic Compounds

In order to understand the possibility of production of phenolic compounds from decomposition of rice bran under subcritical water condition, a series of experiments were performed over a broad temperature range of 373 to 633 K in the residence time of 10 min. Phenolic compounds were individually identified and qualified in the treated samples. Up to eleven phenolic compounds were identified, and nine of them (caffeic acid, ferulic acid, gallic acid, p-coumaric acid, p-hydroxybenzoic acid, protocatechuic acid, syringic acid, vanillic acid and, vanillin) were quantified in this research work. Fig. 1 shows the effect of temperature on the production yields of individual phenolic compounds at the residence time of 10 min. Protocatechuic acid had the highest yield among the quantified phenolic compounds at 503 K. p-Coumaric acid and vanillin were mainly produced at low temperatures and, showed degradation at temperatures higher than 438 and 463 K, respectively; however, syringic, vanillic and, p-hydroxybenzoic acid yields continuously rose with increasing temperature to reach the plateaus at 543, 568 and, 583 K, respectively. Gallic acid increased up to 613 K and then leveled off to a constant yield. Ferulic and caffeic acids showed peaks at 488 and 518 K, respectively, which decreased by rising temperature.

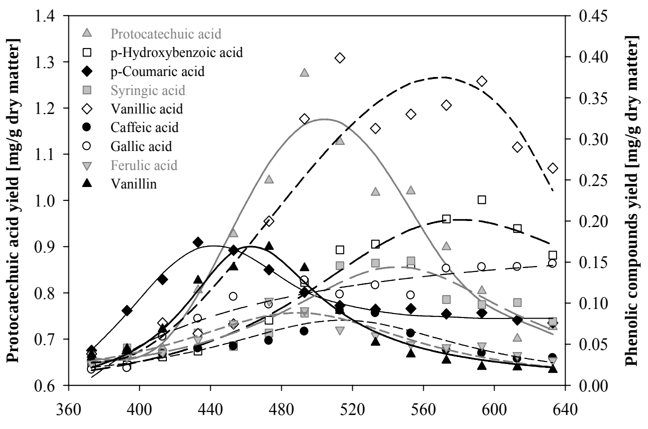

Fig 1. Influence of treatment temperature on production yield of phenolic compounds at residence time of 10 min.

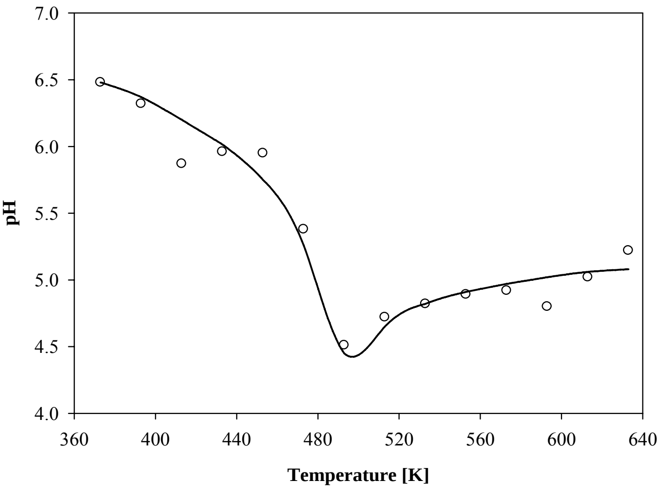

Fig 2. Effect of treatment temperature on the pH of aqueous solution of treated rice bran; residence time 10 min.

Due to acidic properties of these materials [13], the pH of aqueous solution was changed. Fig. 2 shows the pH of aqueous solutions of treated rice bran as a function of temperature. The minimum pH was 4.4 at around 493 K, and after that it gradually rose by temperature and leveled off at temperatures above 613 K. This increase may be attributed to the decomposition of acidic compounds to the other substances, especially gaseous products. The production of acidic compounds can autocatalyze the decomposition and hydrolysis reactions of the rice bran samples.

B. TPC and Antioxidant Activity of Treated Rice Bran

Since several phenolic compounds (other than identified compounds) may exist in the aqueous phase, therefore, the TPC as well as antioxidant activity of the aqueous solutions were also investigated. Fig. 3 (left axis) shows the effect of treatment temperature on the yield of TPC. The TPC yield slightly increased by subcritical temperature rising from 373 to 433 K, afterward sharply increased from 6.5 to 42 (ferulic acid equivalents mg/g dry matter) at temperature range of 433 to 493 K. TPC yield remained constant at temperatures greater than 493 K. Obviously, TPC amounts were higher than the sum of the concentration of individual phenolic compounds.

Fig. 3 (right axis) also shows the antioxidant activity of products versus subcritical water temperature. The shape of the antioxidant activity profile is quite similar to the curve of TPC yield. It can be concluded that the antioxidant activity of the aqueous solutions has direct relation with the concentration of phenolic compounds.

Results demonstrate that subcritical water can effectively hydrolyze and decompose the macromolecules of the rice bran biomass. Rice bran decomposition caused that the existing bonds between phenolic compounds with other materials were cleaved and consequently monomers of phenolic and other antioxidants could be released.

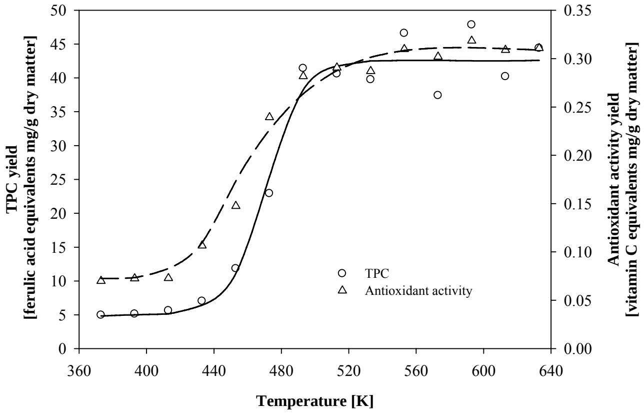

Fig 3. Yields of TPC and antioxidant activity after subcritical treatment of rice bran versus temperature at 10 min residence time.

IV. Conclusion

Subcritical water as green and ecofriendly treatment method was successfully applied for rice bran samples. Phenolic compounds and antioxidants were investigated as main products. Results indicated that temperature influenced the production yield of these compounds; optimum conditions were obtained at relatively higher temperatures.

As a main result, several phenolic compounds were obtained and identified in aqueous phase. The production of these compounds was found to be a feasible process.

Acknowledgment

The authors would like to thank the support of a part of this work provided by the ministry of Education, Culture, Sports, Science and Technology of Japan in the form of 21st Century COE program (E19, Science and Engineering for Water Assisted Evolution of Valuable Resources and Energy from Organic Wastes).

References

[1] T. Tanaka, M. Hoshina, S. Tanabe, K. Sakai, S. Ohtsubo, M. Taniguchi, “Production of D-lactic acid from defatted rice bran by simultaneous sacchrification and fermentation,” *Biores. Technol.,* vol. 97, 2006, pp. 211-217.

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

[3] S. Iqbal, M. I. Bhanger, F. Anwar, “Antioxidant properties and components of some commercially available varieties of rice bran in Pakistan,“ *Food Chem.,* vol. 93, 2005, pp. 265-272.

[4] Z. Zhao, M. H. Moghadasian, “Chemistry, natural sources, dietary intake and pharmacokinetic properties of ferulic acid: A review,” *Food Chem.,* vol. 109, 2008, pp. 691-702.

[5] 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.

[6] M. Naczk, F. Shahidi, “Phenolics in cereals, fruits and vegetables: Occurrence, extraction and analysis: A review,” *J. Pharm. Biomed. Anal.,* vol. 41, 2006, pp. 1523-1542.

[7] L. Wang, C. L. Weller, “Recent advances in extraction of nutraceuticals from plants,” *Trends in Food Sci. Technol.,* vol. 17, 2006, pp. 300-312.

[8] A. A. Galkin, V. V. Lunin, “Subcritical and supercritical water: a universal medium for chemical reactions,” *Russian Chem. Rev.,* vol. 74, 2005, pp. 21-35.

[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] F. Salak Asghari, H. Yoshida, “Kinetics of the decomposition of fructose catalyzed by hydrochloric acid in subcritical water: Formation of 5-hydroxymethylfurfural, levulinic, and formic acids,” *Ind. Eng. Chem. Res.,* vol. 46, 2007, pp. 7703-7710.

[11] A. Abdul-Hamid, R. R. Raja Sulaiman, A. Osman, N. Saari, “Preliminary study of the chemical composition of rice milling fractions stabilized by microwave heating,” *J. Food Comp. and Anal.,* vol. 20, 2007, pp. 627-637.

[12] J. Wiboonsirikul, Y. Kimura, M. Kadota, H. Morita, T. Tsuno, S. Adachi, “Properties of extracts from defatted rice bran by its subcritical water treatment,” *J. Agri. Food Chem.,* vol. 55, 2007, pp. 8759-8765.

[13] W. Vermerris, R. Nicholson, “Phenolic compounds biochemistry,” Springer, USA, 2007, pp. 38-40.