



## Production of phenolic compounds from rice bran biomass under subcritical water conditions

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### ABSTRACT

This study investigated the application of subcritical water as green and environmentally friendly treatment medium for hydrolysis and decomposition of rice bran in order to obtain phenolic compounds as well as other valuable materials. Experiments were performed in a batch stainless steel reactor at different temperatures ranging from 100 to 360 °C at the residence time of 10 min. The effect of residence time was also studied up to 30 min at 220 °C. After subcritical water treatment, it was evaluated for their individual concentrations of phenolic compounds, total phenolic content, antioxidant activity, total soluble sugars, pH, and electrical conductivity as well as remained solid (solid residue). Eleven phenolic compounds were identified from decomposition of rice bran: caffeic, ferulic, gallic, gentisic, p-coumaric, p-hydroxybenzoic, protocatechuic, sinapic, syringic, vanillic acids and vanillin. Results indicated that total phenolic content and antioxidant activity increased with temperature. They also sharply increased with residence time up to 15 min.

Also at an optimum condition, significant amounts of soluble sugars in aqueous solution (approximately 215 glucose equivalents mg/g dry matter) were identified which demonstrated that subcritical water also is a promising treatment medium for hydrolysis of this biomass into water soluble sugars using a short residence time.

Changing the pH of the solution due to the hydrolysis of rice bran into phenolic compounds with acidic function and also production of other organic compounds, suggested that autocatalysis may occurred during subcritical water treatment.

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### 1. Introduction

Rice is one of the most important cereals in the world which is the main staple food in many countries, especially Asian countries like Japan. Global production of paddy in 2007 was estimated to be 638 million tons [1]. After harvesting of paddy, dehusking, and milling processes are performed to separate different parts of paddy; i.e. white rice, bran, and hull or husk [2]. During the milling process, rice bran is produced as major by-product which is a brown layer present between rice and the outer husk of the paddy [3], and its weight ratio to milled rice is about 8% [4]. Annually about 50–60 million tons of rice bran is produced in the world [5]; in Japan, it is about 900 thousand tons [6]. This abundant biomass contains oil,

proteins, carbohydrates, and dietary minerals [7,8]. Also, it is well known to be rich in various kinds of phenolic compounds [9].

On the other hand, there has been a considerable increasing demand for natural phenolic compounds in recent years [10]. Natural phenolic compounds are not uniformly distributed in plants: some of them linked with cell walls, while others exist without any chemical bonds within the plant cell vacuoles [11]. Phenolic compounds are important due to their antioxidant activities. They possess aromatic structure along with hydroxyl substituents which enable them to protect human tissues from damages caused by oxygen or free radicals [12], and consequently reduce the risk of different diseases, and offer beneficial effects against cancers, cardiovascular disease, diabetes, and Alzheimer's disease [13]. For instance, ferulic acid (3-(4-hydroxy-3-methoxyphenyl)prop-2-enoic acid) is one of the major phenolic compounds that owing to its high antioxidant properties, has applications in food industries as well as in the health and cosmetic markets [14].

Rice bran as a natural source of phenolic compounds is currently underutilized and a large quantity of rice bran remains unused as agricultural waste or use as animal feed and boiler fuel [15,16]. In

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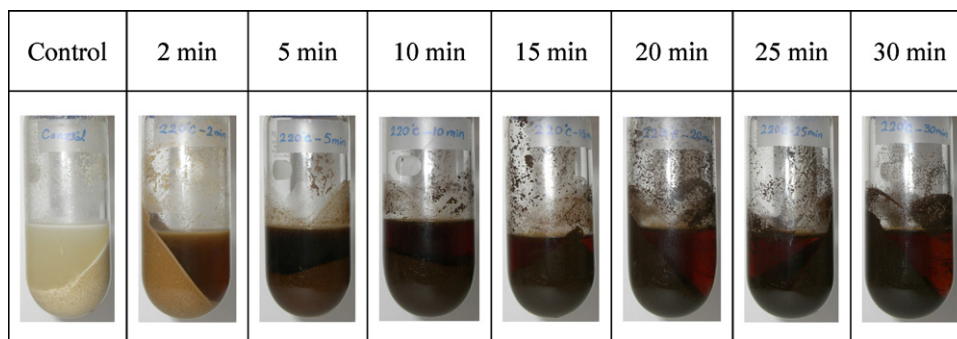


Fig. 1. Typical photographs of subcritical water treatment of rice bran as function of residence time at 220 °C.

Japan, nearly 30% of the produced rice bran goes to waste [17].

So far, numerous attempts have been conducted for recovery and extraction of phenolic compounds from rice bran using conventional techniques. For this purpose, application of organic solvents such as methanol, ethanol, propanol, acetone, ethyl acetate, dimethylformamide and/or their combinations have been reported [18]. For example, Renuka and Arumugan [5] have studied the extraction of phenolic compounds from rice bran by using organic solvents and utilization of soxhlet technique. Chotimarkorn et al. [19] and Iqbal et al. [9] extracted phenolic compounds with methanol from various kinds of rice bran by application of direct solvent–solid extraction method. Taniguchi et al. [20] have patented a method for hydrolyzing of waste materials of rice bran oil production industries at 100 °C and pH of 10 at residence time from 8 to 10 h, the produced ferulic acid which was extracted by hexane solvent.

Conventional extraction methods 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 sometimes toxic organic solvents [21]. Furthermore, the phenolic compounds in the rice bran are extensively bounded to carbohydrate and lignin in the cell wall, and their solubility in common organic solvent is low, unless rice bran is treated at high temperature and/or under acidic and basic conditions [22]. Therefore, utilization of supercritical carbon dioxide and particularly subcritical water methods (which later one provides both temperature and acidic condition for hydrolysis reactions) has been reported recently to eliminate or reduce the above limitations [23].

Generally, subcritical water has been extensively utilized in various fields of green engineering and material cycling [24–32]. In fact, its applications are due to the easy manipulation of its dielectric constant, and variable concentration of hydrogen and hydroxide ions with temperature. For instance, its dielectric constant decreases from 80 (at room temperature) to 27 (at 250 °C) almost equaling that of ethanol at ambient temperature [33]. The increase/decrease in hydrogen and hydroxide ions in subcritical water [34] along with the decreasing of its dielectric constant, make it very suitable medium for the extraction and hydrolysis of natural matrices.

So far there have been several academic reports on the applications of supercritical fluid and subcritical water for treatment of rice bran. King and Dunford [35,36] have reported an efficiently method for extraction of the valuable phytosterol-enriched products from rice bran oil under supercritical fluid conditions. Wiboonsirikul et al. [22,37] have produced phenolic compounds from defatted rice bran using subcritical water at 50–250 °C and 20–260 °C for 5 min, and also at 200 and 260 °C for 5–120 min; they investigated total phenolic content (TPC) yield and antioxidant activity of the aqueous extract. In another report [34], antioxidant activity, and total soluble sugars yield were evaluated after subcritical water treat-

ment of the defatted rice bran at the limited temperature range of 180–280 °C for 5 min.

To the best of our knowledge, there is no comprehensive report on the study of rice bran hydrolysis into phenolic compounds over the whole temperature range of subcritical water. The objective of this research work was to investigate the possibility of phenolic compounds production by decomposition of rice bran under subcritical water conditions as a green and environmentally friendly treatment technique. The influences of whole subcritical water temperature and residence time as main experimental parameters were studied in detail.

## 2. Materials and methods

### 2.1. Materials

Japonica-type rice (*Oryza sativa*) was used in this study. Gallic acid (3,4,5-trihydroxybenzoic acid) was purchased from Tokyo Chemical Industry Co. Ltd. (Japan). Sodium bicarbonate (sodium hydrogen carbonate) and phenol (hydroxybenzene) were obtained from Nacalai Tesque, Inc. (Japan). Folin-Ciocalteu phenol reagent, gentisic acid (2,5-dihydroxybenzoic acid), p-coumaric acid (3-(4-hydroxyphenyl)-2-propenoic acid), sinapic acid (3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoic acid), syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid), vanillic acid (4-hydroxy-3-methoxybenzoic acid), and vitamin C (2-oxo-L-threo-hexono-1,4-lactone-2,3-enediol) were obtained from Sigma-Aldrich, Inc. (USA). All other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. (Japan).

### 2.2. Procedure

The rice sample containing bran was milled by a milling machine (Satake SKM-5B, Satake Corporation, Japan). The obtained bran was sieved with a 590- $\mu\text{m}$ -mesh sieve, and then the sieved bran was immediately treated by subcritical water.

Defatted rice bran was obtained by soxhlation of milled rice bran. It was placed into a soxhlet thimble, and extraction of rice bran oil was conducted using hexane over a period of 240 min.

A batch reactor used for subcritical water treatment was a stainless steel tube (SUS316, i.d. 16.5 mm  $\times$  150.4 mm) with a Swagelok fitting (ready-made, from Swagelok). In a typical experiment, an accurately weighed amount of rice bran and/or defatted rice bran (about 3.0 g) and about 18.0 cm<sup>3</sup> of distilled water were charged into the reactor. Argon gas was used to force air out of the reactor before the reaction, and it was capped tightly. The reactor was immersed in a preheated oil bath (Thomas Kagaku Co. Ltd., Celsius M type) with temperatures ranging from 100 to 180 °C for 10 min or in a preheated salt bath (Thomas Kagaku Co. Ltd., Celsius 600H) over the temperature range 180–360 °C for 10 min, and at 220 °C

for 2–30 min. The reactor was then removed from the thermal bath and quickly quenched by soaking in a cold water bath at room temperature. The reaction pressure was estimated from a steam table [24].

After subcritical water treatment, reactor contents were transferred in a 50 cm<sup>3</sup> test tube, taking particular care to prevent loss of any of the liquid and/or remained solid. Fig. 1 shows photographs of rice bran after subcritical water treatment at 220 °C.

The contents were isolated and classified into three phases: aqueous solution, ethanolic solution, and remained solid (solid residue). Phase isolation procedure was as follows: each tube was centrifuged at 1500 × g for 10 min, and then aqueous solution and remained solid were separated with taking out and transferring of supernatant (aqueous solution) to a volumetric flask by Pasteur pipette. The supernatant was made up to the final volume of 20 cm<sup>3</sup> with Milli-Q water, and transferred to the new test tube, and then its pH, conductivity, and total soluble sugars were measured according to Section 2.3. Then 9 cm<sup>3</sup> of ethanol (95%) was added to the above remained solid to dissolve the obtained phenolic compounds which are insoluble in water at room temperature [11,38]. It was shaken for 1 min, and then centrifuged at 1500 × g for 5 min. The supernatant (ethanol soluble phase) was isolated by Pasteur pipette and added to the aqueous solution (this mixture hereafter called ethanolic solution). Mixing of this 9 cm<sup>3</sup> of ethanol and the aqueous solution allowed phenolic compounds to be soluble even in higher amounts at room temperature while wax, hemicelluloses and other undesired materials were precipitated [38]. This procedure was repeated three times to extract ethanol soluble compounds completely. The precipitate was separated from the ethanolic solution by centrifuging at 2000 × g for 5 min. Supernatant was taken out and made up to the final volume of 50 cm<sup>3</sup> with ethanol (95%), and filtered with a 0.2 μm filter. The filtrated ethanolic solution was analyzed by UV–visible and HPLC according to Section 2.3. The remaining solid was placed in an oven at 60 °C to dry to constant weight.

### 2.3. Analysis

Total soluble sugars of aqueous solution was analyzed by a photometric method [39]. Briefly, 0.4 cm<sup>3</sup> of aqueous solution or standard was mixed with 0.4 cm<sup>3</sup> aqueous phenol solution (5%, w/v), and this mixture was vigorously shaken at ambient temperature for 5 min. Then, 2 cm<sup>3</sup> of sulfuric acid (98%) was added to the mixture. The mixture was vigorously shaken and kept at ambient temperature for 10 min to complete the reaction. Finally, this mixture was shaken again, and its total soluble sugars concentration was evaluated by a UV–visible spectrophotometer (Shimadzu UV-160, Shimadzu Co., Japan) at 490 nm. Glucose (6-(hydroxymethyl)oxane-2,3,4,5-tetrol) was used as the standard, and total soluble sugars concentration in the obtained results was expressed as “glucose equivalents mg/g dry matter”.

The pH of all aqueous solutions was measured using a glass pH electrode attached to a Horiba pH meter F-52 (Horiba Co., Japan). Also the conductivity of the aqueous solution was determined by a glass conductivity electrode attached to a Horiba conductivity meter DS-51 (Horiba Co., Japan).

TPC of ethanolic solution was determined using Folin–Ciocalteu phenol reagent [40]. Briefly, 1 cm<sup>3</sup> of ethanolic solution or standard was mixed with 1 cm<sup>3</sup> Folin–Ciocalteu reagent (previously diluted 10-fold with distilled water), and this mixture was vigorously shaken and allowed to stand at ambient temperature for 5 min. Then, 1 cm<sup>3</sup> of sodium hydrogen carbonate (60 g/l) solution was added to the mixture. This mixture was vigorously shaken, covered with aluminum foil, and kept in the dark at ambient temperature for 90 min to complete the reaction. Finally, this mixture was shaken again, and its TPC concentration was evaluated by a

**Table 1**

Composition of mobile phases with gradient elution program in a HPLC analysis of phenolic compounds.

Time (min)	% of mobile phase A: 1.0% acetic acid solution	% of mobile phase B: methanol
0	100	0
5	100	0
110	0	100
140	0	100
142	100	0
150	100	0

UV–visible spectrophotometer at 725 nm. Ferulic acid was used as the standard, and TPC concentration in the obtained results was expressed as “ferulic acid equivalents mg/g dry matter”.

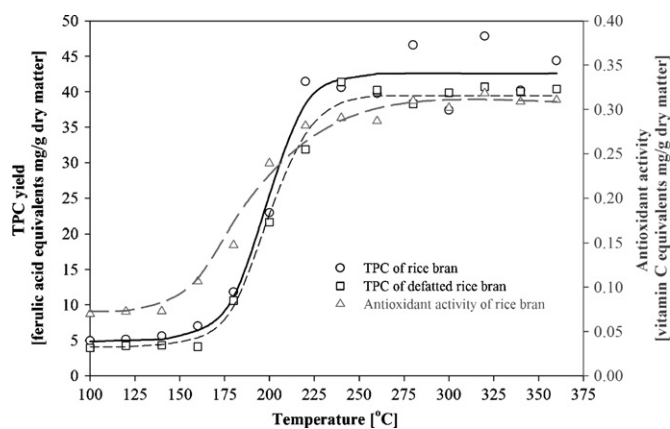
Antioxidant activity of ethanolic solution was assayed according to the modified methods of McCue and Shetty [41] and Wiboonsirikul et al. [22,37]. For this propose, 1 cm<sup>3</sup> of the prepared 1,1-diphenyl-2-picrylhydrazyl (diphenyl-(2,4,6-trinitrophenyl)iminoazanium) solution (0.5 mM 1,1-diphenyl-2-picrylhydrazyl in 95% ethanol) was added to 3 cm<sup>3</sup> of ethanolic solution or standard, and then was well shaken and covered with aluminum foil, and then placed in the dark at ambient temperature for 30 min to complete the reaction. After 30 min, the antioxidant activity was determined by a UV–visible spectrophotometer at 517 nm. Vitamin C was used as the standard, and antioxidant activity was expressed as “vitamin C equivalents mg/g dry matter”.

A CSPAK narrow-bore column C18 (2.0 mm × 150 mm) from Chromato Science Co. Ltd. (Japan) in a HPLC using two Varian ProStar210 (Varian Inc., USA) solvent-delivery modules coupled with PDA (photodiode array) detector (Varian PDA 330 Detector, Varian Inc., USA) was used for quantitative analysis of products (in ethanolic solution). PDA collected data between 250 nm and 330 nm and absorbance was monitored at 270 nm. Column temperature was kept at 25 °C. Gradient elution program at 0.2 cm<sup>3</sup>/min flow rate was used as mentioned in Table 1.

## 3. Results and discussion

### 3.1. TPC yield and antioxidant activity of ethanolic solution

In order to realize the application of subcritical water for production of phenolic compounds from rice bran and/or defatted rice bran, a series of experiments were performed over a temperature range of 100–360 °C at residence time of 10 min. Fig. 2 shows the effect of reaction temperature on the yield of TPC obtained both



**Fig. 2.** Effect of subcritical water temperature on TPC yield and antioxidant activity at residence time of 10 min.

from rice bran and defatted rice bran. Based on previous reports, there are two possibilities for formation of TPC: from decomposition of bounds between lignin, cellulose, and hemicellulose [22,37], and/or production from oil part of the rice bran [20,35,36].

For rice bran, TPC yield sharply increased from 5 to 42 mg/g dry matter (ferulic acid equivalents) when temperature increased from 150 to 220 °C. This increase was attributed to higher bound cleavage rate of lignin/phenolic–carbohydrate complexes of rice bran, and also to the more solubility and consequently extraction of TPC in water with relating lower polarity of subcritical water. Fig. 2 also demonstrates that TPC yield remained constant at temperatures higher than 220 °C. This may be caused by extracting all TPC from the rice bran in this temperature range.

As mentioned before, a series of experiments were used to evaluate the share of rice bran oil on the TPC production. Therefore, the defatted rice bran was utilized under subcritical water conditions at the same conditions as rice bran. Results showed that the TPC curve of rice bran and defatted rice bran were extremely similar. Therefore, it concluded that majority of phenolic compounds were produced from decomposition of lignin/phenolics–carbohydrate complex part of rice bran and not from its oil.

Generally, phenolic compounds have antioxidant activity; however, it was probable that besides phenolic compounds, other nonphenolic compounds with antioxidant activity were also produced and/or extracted from rice bran in subcritical water medium. Therefore, antioxidant activity as a criterion of total produced antioxidants was also investigated. Fig. 2 shows the antioxidant activity of ethanolic solution versus subcritical water temperature. Results indicate that the shape of this profile is quite similar to the TPC yield profile; hence, it can be concluded that most of the produced antioxidants under subcritical water conditions corresponded to the phenolic compounds.

Fig. 3 shows the influence of residence time on the yield of TPC and antioxidant activity at 220 °C. Obviously, the production of phenolic compounds was also a function of residence time [18]. Both TPC yield and antioxidant activity showed peak at around 15 min, and then decreased somewhat by increasing residence time. After 15 min, produced TPC may be decomposed by subcritical water. Fig. 3 also demonstrates that the shape of antioxidant activity is similar to TPC curve which suggested again that antioxidant activity corresponded mainly to the produced phenolic compounds.

Results indicate that subcritical water technique could successfully hydrolyze rice bran to obtain phenolic compounds. It has been reported that phenolic compounds exist in the insoluble-bound forms with lignin and carbohydrates (hemicellulose and cellulose) in rice bran cell wall (see Fig. 4) [37]; lignin, cellulose, and hemicellulose contents in commercial rice bran ranged from 7.7 to 13.1%, 9.6 to 12.8%, and 8.7 to 11.4%, respectively [8]. We understand that, the existing bonds (ester and/or ether bonds) between these materials can be effectively hydrolyzed by subcritical water

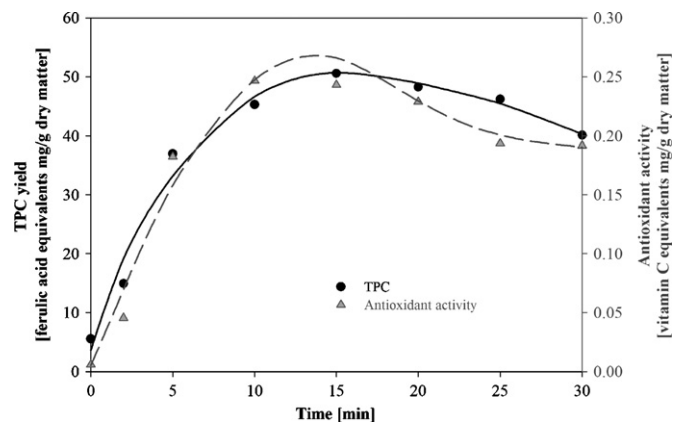


Fig. 3. Effect of residence time on TPC yield and antioxidant activity at subcritical water temperature of 220 °C.

and consequently phenolic compounds, lignin, and carbohydrate are released. In addition, the liberated lignin and carbohydrate parts can be decomposed to the other smaller components by subcritical water hydrolysis reactions (i.e. phenolic compounds and soluble sugars, respectively) [17,42,43] in subcritical water medium.

### 3.2. Identified phenolic compounds in ethanolic solution

Some of phenolic compounds obtained from decomposition of rice bran under subcritical water conditions were identified and quantified in this study. Up to 11 phenolic compounds were identified from decomposition of rice bran: caffeic ((E)-3-(3,4-dihydroxyphenyl)-2-propenoic acid), ferulic, gallic, gentisic, p-coumaric, p-hydroxybenzoic (4-hydroxybenzoic acid), protocatechuic (3,4-dihydroxybenzoic acid), sinapic, syringic, vanillic acids, and vanillin (4-hydroxy-3-methoxybenzaldehyde). The phenolic compounds (except gentisic and sinapic acids) were quantified in this research work. Fig. 5 shows the effect of temperature on the production yields of individual phenolic compounds at residence time of 10 min. Protocatechuic and vanillic acids showed the highest yields among the others. They were considered as major products of rice bran. Protocatechuic and vanillic acid showed maximum production at temperatures of 230 and 295 °C, respectively. Due to the decomposition reactions [44,45], their yield decreased at high temperatures (see Fig. 5). Vanillin and p-coumaric acid showed peaks in the lower temperature region while the other ones generally showed at temperatures higher than 245 °C. The mass balance difference between TPC yield and sum of concentration of individual phenolic compounds confirmed the presence of still other unknown phenolic compounds from the decomposition of rice bran

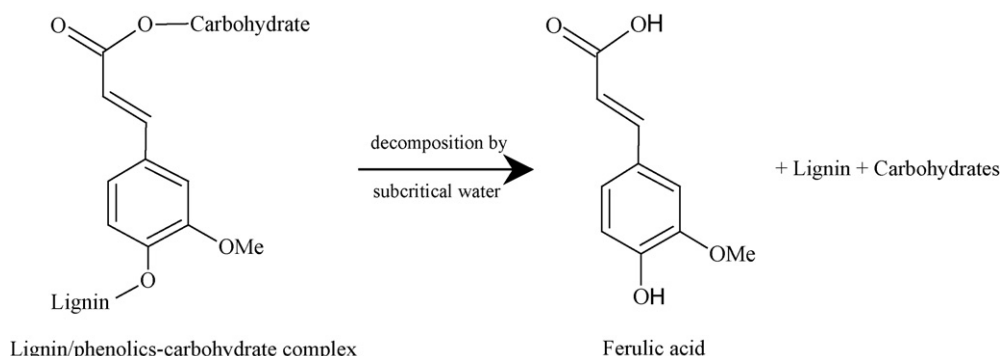
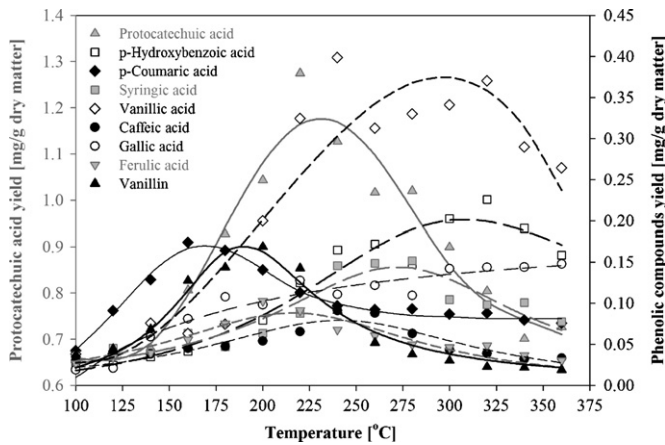


Fig. 4. Proposed hydrothermal degradation of a typical lignin/phenolics–carbohydrate complex under subcritical water conditions [36].



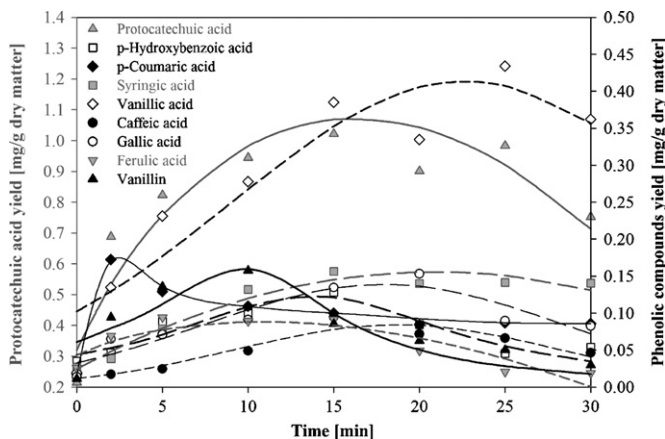
**Fig. 5.** Effect of subcritical water temperature on the production yield of identified phenolic compounds at residence time of 10 min.

in subcritical water medium which could not be identified in this study.

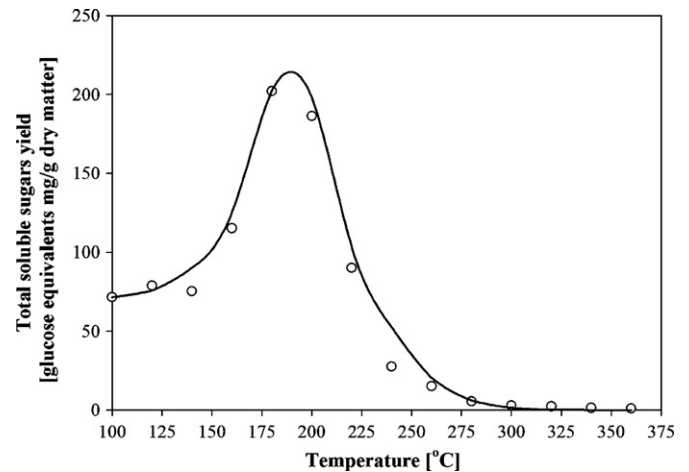
The time dependence of production of identified phenolic compounds at 220 °C is shown in Fig. 6. In general, most of the peaks appeared within the range of 10–20 min. Protocatechuic and vanillic acids showed peaks in 15 and 23 min, respectively. It was understood that longer residence times as well as higher temperatures had destructive effects on the phenolic compounds yield; further decomposition reactions may occur under subcritical water conditions.

### 3.3. Decomposition of carbohydrate part of the rice bran

Subcritical water treatment of lignin/phenolics–carbohydrate complexes of rice bran results not only the production of phenolic compounds but also may hydrolysis of carbohydrates and also lignin. Carbohydrates can be depolymerized into smaller sugars depending on the subcritical water conditions [42]. Fig. 7 shows the influence of subcritical water temperature on the yield of total produced sugars in the aqueous solution. It demonstrates that total soluble sugars yield increased with temperature increasing to reach a peak at 190 °C, and then decreased drastically to zero at temperatures above 300 °C. The results proved that water insoluble carbohydrate part of rice bran could be effectively hydrolyzed into water soluble oligomers and monomers by subcritical water treatment. In addition, the decreasing yield at high temperatures could be interpreted as a sign of the conversion of soluble sugars into



**Fig. 6.** Effect of residence time on the production yield of identified phenolic compounds at subcritical water temperature of 220 °C.



**Fig. 7.** Effect of subcritical water temperature on the yield of total soluble sugars at residence time of 10 min.

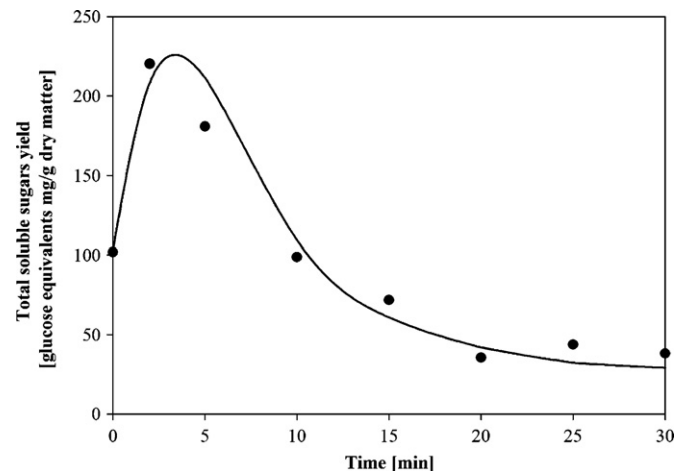
other constituents, mainly to HMF (5-hydroxymethyl-2-furfural) and soluble polymers [28,34].

The effect of residence time on the yield of total produced sugars at temperature of 220 °C is shown in Fig. 8. The yield profile showed a peak at 3 min, and then it decreased steeply with residence time.

It was observed that the color of aqueous solution after reaction became darker by increasing the temperature and residence time (see Fig. 1). This phenomenon might be due to the formation of HMF and soluble polymers from decomposition of the produced soluble sugars (from carbohydrate part of rice bran) in subcritical water medium [28]. It is also attributed to the formation of undesired materials undergoing the Millard browning reaction [46].

### 3.4. pH and conductivity of the aqueous solution

Fig. 9 shows that the pH of aqueous solution measured after subcritical water reaction. It decreased as temperature increased and reached a minimum. The minimum pH was 4.4 at around 220 °C and gradually increased with temperature to a constant value about 5.0 at temperatures above 340 °C. Obviously, pH decreases indicates that aqueous solution contains acidic materials, such as phenolic compounds [47]. We have shown that other compounds with acidic function such as organic acids and amino acids were produced by decomposition of rice bran [17,28] also changes the pH of aqueous solution.



**Fig. 8.** Effect of residence time on the yield of total soluble sugars at subcritical water temperature of 220 °C.

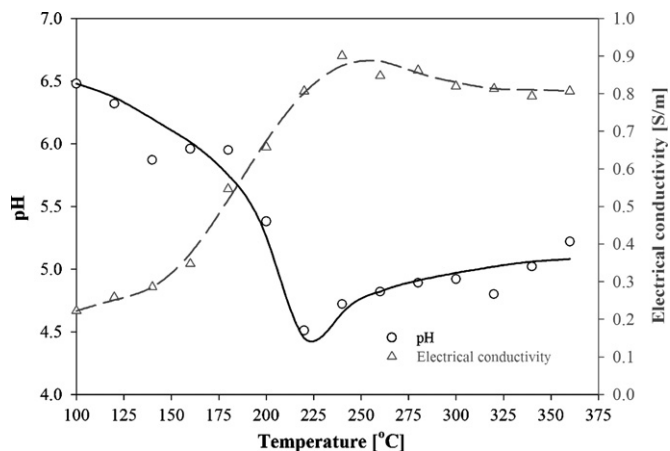


Fig. 9. Effect of subcritical water temperature on the pH and electrical conductivity of the aqueous solution at residence time of 10 min.

In fact, pH has destructive effect on the existing (ester and/or ether) bonds of lignin/phenolics–carbohydrates complex of biomass [48]; therefore, production of acidic materials and consequently a decrease in pH led to conclusion that autocatalysis may occur during subcritical water treatment of rice bran. The increase in the pH at temperatures above 220 °C may be attributed to the decomposition of the acidic compounds to the other substances.

Fig. 9 also shows the electrical conductivity of aqueous solution, measured after subcritical water reaction, as a function of subcritical water temperature. Electrical conductivity of aqueous solution is majority a function of ions amount within the solution [49]. It steadily rose by temperature up to 240 °C. This increase may be attributed to the pH lowering, dissolution of rice bran minerals, and production of other ions and organic acids over the treatment process. Change in the electrical conductivity as well as pH shows the promising results for decomposition of rice bran in water. Fig. 9 demonstrates that the conductivity decreased somewhat when temperature increased above 240 °C.

Fig. 10 shows the effect of residence time on pH and electrical conductivity of aqueous solution measured after subcritical water reaction. The pH of aqueous solution decreased sharply up to 15 min by residence time and then leveled off. Fig. 10 also proved that the electrical conductivity of solution was influenced by residence time. It continuously rose with residence time prolonging.

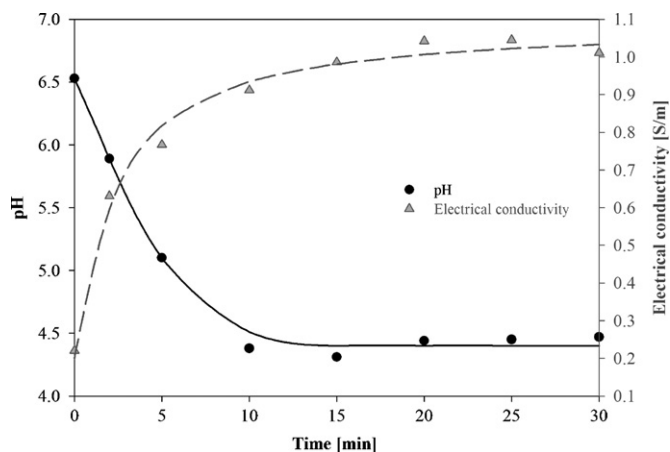


Fig. 10. Effect of residence time on the pH and electrical conductivity of the aqueous solution at subcritical water temperature of 220 °C.

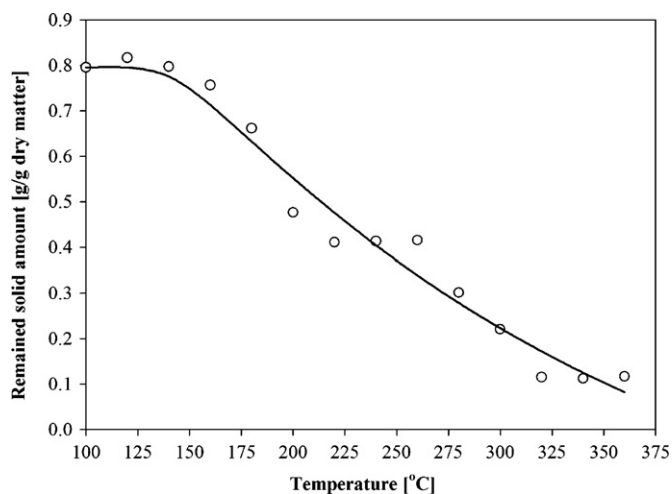


Fig. 11. Effect of subcritical water temperature on remained solid amount at residence time of 10 min.

### 3.5. Remained solid after treatment of rice bran

The amount of remained solid after subcritical water treatment was also evaluated. This residue mainly consisted of un-reacted rice bran, carbonized rice bran, hydrolyzed but still insoluble parts of rice bran as well as inorganic compounds. Their amount after treatment in temperature range of 100–360 °C for 10 min is shown in Fig. 11. The amount of remained solid slightly decreased from 100 to 140 °C, and then sharply decreased to a minimum of 8% at 360 °C. This sharp decrease proved that subcritical water could effectively decompose insoluble macromolecules of rice bran into smaller soluble compounds in a short residence time. The composition of remained solid was not investigated in this research work.

Fig. 12 shows the effect of residence time on the amount of remained solid at 220 °C. It decreased drastically by residence time increasing and then stayed constant (about 40%) in the residence times longer than 15 min.

There was a considerable difference between the final minimum amounts of remained solid obtained from temperature and time effect studies (8% and 40%, respectively) which proves clearly that subcritical temperature is more effective than residence time on the dissolution and decomposition of rice bran (see Figs. 11 and 12).

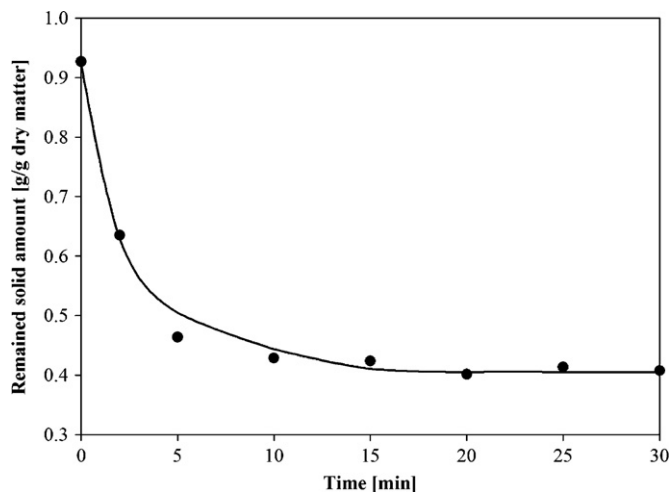


Fig. 12. Effect of residence time on remained solid amount at subcritical water temperature of 220 °C.

#### 4. Conclusions

Decomposition and conversion of rice bran into valuable chemical compounds were successfully conducted using sub-critical water. Degradation of the lignin/phenolics–carbohydrates complexes of rice bran were achieved (up to 92% of rice bran) in the water without using organic solvent, acid, base, and/or enzyme. Decomposition of rice bran and defatted rice bran have resulted almost the same amount of phenolic compounds; it was understood that phenolic compounds were mainly produced from decomposition of bounds between lignin, carbohydrate, and phenolic compounds, and not from rice bran oil. Some of phenolic compounds were identified and quantified in this study. Protocatechuic and vanillic acids were the major ones among identified phenolic compounds.

Subcritical water temperature and residence time were two studied parameters which influenced the decomposition of rice bran and production of phenolic compounds. It was found that phenolic compounds could be selectively produced by temperature variations. From residence time point of view, production of phenolic compounds could be efficiently achieved in a very short time which was much less than those reported in conventional methods that increases economic feasibility of this method.

Finally, production of phenolic compounds and sugars from decomposition of rice bran using subcritical water as green, simple, and non-flammable medium can be scaled up to the industrial level to treat underutilized rice bran before discarding which may be practical and cost-effective.

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