Review

Sub-critical water treatment of rice bran to produce valuable materials

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ABSTRACT

The target of this study is application of sub-critical water as a green solvent for hydrolysis of rice bran and extraction of its oil in order to obtain value-added materials. Experiments were carried out at temperatures ranging from 100 to 360 °C with 5 min residence time in a batch reactor. Four phases were isolated after reaction: hexane-soluble, acetone-soluble, water-soluble, and solid residue phases. Rice bran oil was successfully and efficiently obtained by sub-critical water extraction. Significant increases of total organic carbon (TOC) and total nitrogen (TN) in the water phase were also observed, because polysaccharides and proteins (generally bio-macro polymers) in rice bran were hydrolysed by sub-critical water. The highest yields of TOC and TN were 140 and 13 mg/g dry matter, respectively. As a result, varieties of compounds, such as amino acids, organic acids, and water-soluble saccharides, were identified in the water phase. In particular, significant amounts of water-soluble sugars (maximum yield of total sugars was nearly 190 mg/g dry matter) proved that sub-critical water was a promising medium for dissolution of biomass in water. Acetone-soluble contents were attributed to tar, carbonized biomass, and in general, water- and hexane-insoluble compounds. Solid residue consisted of mainly un-reacted rice bran and insoluble inorganic compounds.

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Contents

1. Introduction

Sub-critical water (hereafter called sub-CW) treatment is an environmentally friendly technique with a wide range of applications, such as extraction, hydrolysis, and wet oxidation of organic compounds (Holliday, Jong, & Kolis, 1998; Kruse & Dinjus 2007). Sub-CW is defined as hot water at temperatures ranging between 100 and 374 °C under high pressure to maintain water in the liquid state. Dielectric constant, which can be changed by temperature, is the most important factor when using water as an extraction solvent; it decreases from 80 (at room temperature) to 27 (at 250 °C) which is almost equal to that of ethanol at ambient temperature (Galkin & Lunin, 2005; Herrero, Cifuentes, & Ibanez, 2006). Thus, sub-CW can be used for extraction of organic compounds instead of using organic solvents which are environmentally unacceptable. On the other hand, sub-CW has been widely used for hydrolysis of organic compounds. Recently growing attention has led to extensive research activities using sub-CW for hydrolysis and conversion of biomass and carbohydrates to useful compounds (Bicker, Endres, Ott, & Vogel, 2005; Kruse & Gawlik, 2003; Salak Asghari & Yoshida, 2006; Salak Asghari & Yoshida, 2007; Sasaki et al., 1998; Tavakoli & Yoshida, 2006; Yoshida, Terashima, & Takahashi, 1999).

A most useful biomass is rice. Nearly 610 million tons of rice are produced each year in the world (Sereewatthanawut et al., 2008). Rice bran is a by-product of the rice milling process which is nearly 8% of milled rice (Danielski, Zetzl, Hense, & Brunner, 2005). The production amount of rice bran is about 50–60 million tons per year, which is normally used as animal feed (Renuka Devi & Arumughan, 2007). Japan produces about 0.9 million tons of rice bran (Tanaka et al., 2006) which is used for different purposes. In Japan, approximately 34.0% of the rice bran is used to extract its oil which, depending on its quality, can be used for cooking or industrial applications. Other utilizations of rice bran are: 30.0%, 28.5%, 5.0%, 2.0%, and 0.5%, as waste and unknown, animal food, mushroom production, pickle preservation, and fertilization, respectively.

Rice bran should be a natural resource of oil, proteins, fibres, vitamins, and antioxidants. In addition, it is a good resource of minerals, such as silica, iron, calcium, and zinc (Luh, 1980). There are many methods for treatment and extraction of its useful compounds, such as Soxhlet extraction, direct solid–liquid extraction and, more recently, supercritical CO_2 and sub-CW treatments (Hu, Wells, Shin, & Godber, 1996; Mamidipally & Liu, 2004; Xu & Godber, 2000). Mostly, organic solvents, such as methanol, ethanol, ethyl acetate, hexane, acetone, and isopropanol (Chen & Bergman, 2005; Proctor & Bowen, 1996; Proctor, Jackson, Scott, & Clark, 1994) have been used for rice bran treatment.

The above-mentioned conventional methods have disadvantages; e.g. they are time-consuming, are of low selectivity, give low extraction yield and utilise large amounts of expensive and/or toxic organic solvents (Wang & Weller, 2006). Moreover, some of organic solvents create problems of explosion, pollution, and fire escape. These disadvantages of organic solvents can be overcome by using sub-CW as a so-called green solvent.

Recently, increasing attention has been paid to sub-CW treatment of rice bran as a cheap and abundant biomass. For instance, defatted rice bran has been treated in sub-CW in order to study the extraction of phenolic and other antioxidant compounds at 50–250 °C for a 5 min residence time (Wiboonsirikul et al., 2007b). Wiboonsirikul, Hata, Tsuno, Kimura, and Adachi (2007a) have studied the production of functional substances from defatted black rice bran by sub-CW treatment. Protein, carbohydrates, and radical-scavenging activity of the products were investigated in detail. Sereewatthanawut et al. (2008) have investigated defatted rice bran under sub-CW; highest yields of protein and amino acids were obtained after 30 min of reaction at 200 °C.

There are only a few available reports on sub-CW treatment of rice bran. To the best of our knowledge, there is no previous report on the study of rice bran over the whole temperature range of sub-CW. In this study, our objective was to develop and evaluate sub-CW in order to better understand its temperature effects (from 100 to 360 °C) on rice bran.

2. Materials and methods

2.1. Materials

A Japonica-type rice (*Oryza sativa* L. japonica) was used in this experimental study. Sodium carbonate, sodium hydrogen carbonate, and phenol were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). EDTA and Bis-Tris were bought from Dojindo, (Japan); n-caprilic acid was purchased from Tokyo Chemical Industry Co. Ltd. (Japan). Mercaptoethanol and brij-35 (Polyoxyethyleneglycol dodecyl ether) were obtained from Pierce (USA). Potassium hydrogen phthalate, sulphuric acid, and sodium hypochlorite were purchased from Chameleon Reagent (Osaka, Japan). All other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. (Japan).

2.2. Procedure

The batch reactor used for sub-CW treatment was a stainless steel tube (SUS316, i.d. 16.5 mm × 150.4 mm) with a Swagelok fitting (ready-made, from Swagelok AG). In a typical experiment, an accurately weighed amount (about 3.0 g) of rice bran (comminuted and sieved through a 590 μm-mesh sieve) and about 18 ml 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. It was immersed in a preheated oil bath (Thomas Kagaku Co. Ltd., Celsius M type) with temperatures ranging from 100 to 180 °C or in a preheated salt bath (Thomas Kagaku Co. Ltd., Celsius 600H) in the temperature range 200–360 °C for 5 min. In this work, the reaction time (i.e. 5 min) mentioned above includes the heat-up time. The salt bath mixing speed and reactor shaking rate have great effects on the rate of heating-up. The combined effects of both reactor shaking and salt bath mixing speed can significantly increase heating-up rate to a steady state condition in a very short time (e.g. 25 s) (Abdelmoez & Yoshida, 2006). 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, taking particular care to prevent loss of any of the liquid. The reaction pressure was estimated from a steam table. The details were explained elsewhere (Yoshida et al., 1999).

2.3. Separation of produced phases after sub-CW treatment

After sub-CW treatment, contents in the reactor were classified and isolated into four phases: hexane-soluble (HS), water-soluble (WS), acetone-soluble (AS), and solid residue phases. The separation procedure was as follows: Hexane (5 ml) was gently added to the test tube and allowed to stand for 5 min at 25 °C, then centrifuged at 2500 g for 10 min and supernatant was separated. This procedure was repeated eight times. Then, aqueous phase and solid residue were separated by filtration. Hexane (5 ml) was added to the remaining rice bran solid residue and this mixture was shaken for 5 min. After centrifugation, the supernatant was separated and added to the obtained HS phase from the water-soluble phase.
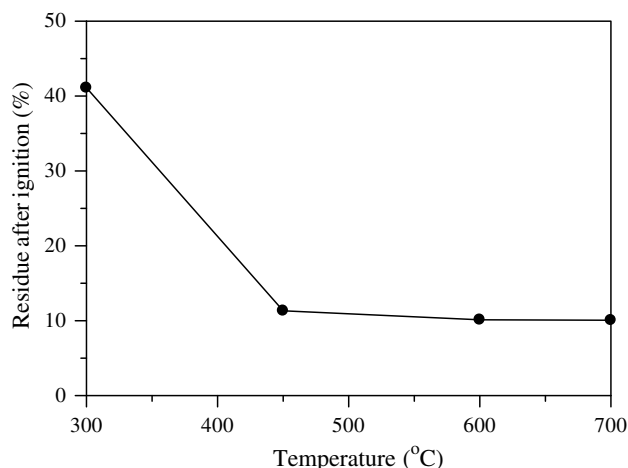
Fig. 1. Effect of ignition temperature on residue of rice bran (ignition period 6 h).

This procedure was repeated four times. HS amount was calculated by weight after evaporation of hexane. Solid residue was also washed with 10 ml of acetone, several times. AS amount was calculated by weight after evaporation of the solvent. Finally, remaining solid residue was placed in an oven at 60 °C to dry to constant weight. The solubility, solid residue and rice bran conversion yields are calculated as follows:

$$\text{Solubility yield} = \frac{W_s}{W_i} \tag{1}$$

$$\text{Solid residue yield} = \frac{W_{sr}}{W_i} \tag{2}$$

$$\text{Rice bran conversion yield} = 1 - \text{Solid residue yeild} \tag{3}$$

in which W_s, W_{sr}, and W_i are weights of soluble materials (into hexane, acetone, or water), solid residue, and initial dry sample, respectively.

2.4. Analysis

Concentrations of organic acids were determined by HPLC, using a pump (Shimadzu LC-10AD VP, Shimadzu Co., Japan) with two ion-exclusion chromatography columns (Shim-pack SCR-102H, 8 mm × 300 mm, Shimadzu Co., Japan) in series and their detection effected using post-column pH-buffered electroconductivity detection (Shimadzu CDD-6A, Shimadzu Co., Japan). The mobile phase was 5.5 mM p-toluensulfonic acid solution at a flow rate of 0.8 ml/min. Mixtures of 5.5 mM p-toluensulfonic, 20 mM Bis-Tris, and 100 μM EDTA were used as post-column reagents, all at flow rates of 0.8 ml/min. The column (Shimadzu CTO-10AC VP, Shimadzu Co., Japan) temperature was kept at 45 °C.

Amino acids concentration was determined by an HPLC system (Shimadzu LC-10AT VP, AM1NO-NA column) using a fluorescence detector (Shimadzu RF-10A XL, Shimadzu Co., Japan). The temperature of the column (Shimadzu CTO-10A VP, Shimadzu Co., Japan) was 60 °C.

Two size-exclusion chromatography columns in series (Shodex-sugar KS-804 and KS-801, 8 mm × 300 mm, Shodex Co., Japan) in an HPLC system, in conjunction with a pump (Jasco PU-2080plus, Jasco Crop., Japan) coupled to a refractive index detector (Jasco RI-2031plus, Jasco Crop., Japan), were used for quantitative analysis of the products, which could not be detected using a UV detector. This HPLC system was operated at an oven (Jasco CO-2065plus, Jasco Crop., Japan) temperature of 32 °C using mili-Q water at 0.4 ml/min flow rate as a mobile phase.

TOC and TN were measured by a TOC/TN analyzer (Shimadzu TOC-V CPH/CPN, Shimadzu Co., Japan). A double-beam UV–visible spectrophotometer (Shimadzu UV-1600, Shimadzu Co., Japan) was used for all spectrophotometric measurements. A CHNS analyzer (Perkin–Elmer, model 2400) was used to calculate the carbon, hydrogen, nitrogen, and sulphur contents of the solid samples.

3. Results and discussion

3.1. Specifications of rice bran

Rice bran contains organic and mineral compounds. The contents and composition of rice bran depend on the internal (species) and external (soil, climate) conditions. The organic part of the rice bran was identified as 44.9% of carbon, 7.2% of hydrogen, 3.3% of nitrogen, and 1.2% of sulphur. Phosphorus, potassium, iron, magnesium, calcium, silica, and zinc have already been reported as main inorganic compounds (Luh, 1980). Water content was 8.8%. Fig. 1 shows the effect of ignition temperature on the residue of the rice bran after 6 h of ignition. The loss of the sample weight increased up to 90% at temperatures higher than 600 °C. Obviously the lost and remaining amounts were attributed to organic and non-volatile inorganic compounds, respectively.

Fig. 2 shows photos of products after sub-CW reaction for 5 min. Generally, rice bran is a water-insoluble biomass. However, after sub-CW treatment, at low temperatures (i.e. 100–160 °C) a slurry phase was obtained. It was viscous and its colour was almost not changed. However, at moderate temperatures (i.e. 160–280 °C), it was slightly viscous and reddish to brown in colour. At high temperatures (i.e. 280–360 °C), it was a very viscous slurry with dark brown to black colour.

3.2. Isolated phases from rice bran slurry after sub-CW treatment

Fig. 3 demonstrates the effects of reaction temperature on HS, AS phases and solid residue of rice bran after sub-CW treatment for 5 min. The amounts of HS and AS increased with increasing temperature and solid residue amount decreased consequently. HS phase was a yellowish viscous liquid, which was mainly rice bran oil (Liu & Mamidipall, 2005) with maximum yield of 27% (see Fig. 3). On the other hand, any other extractive compounds, which may be soluble in hexane, can also be extracted into this phase. The extracted oil has a variety of applications. For instance, depending
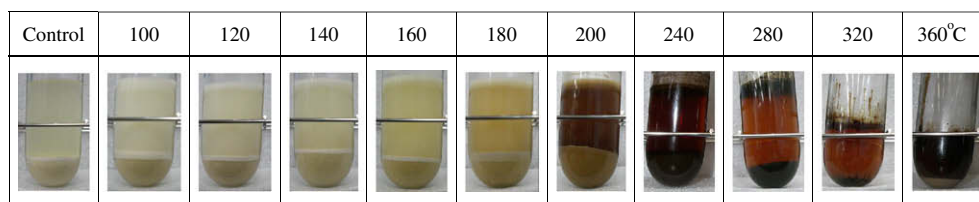

Control	100	120	140	160	180	200	240	280	320	360 °C

Fig. 2. Typical photographs of sub-CW treatment of rice bran as function of temperature for 5 min reaction time.
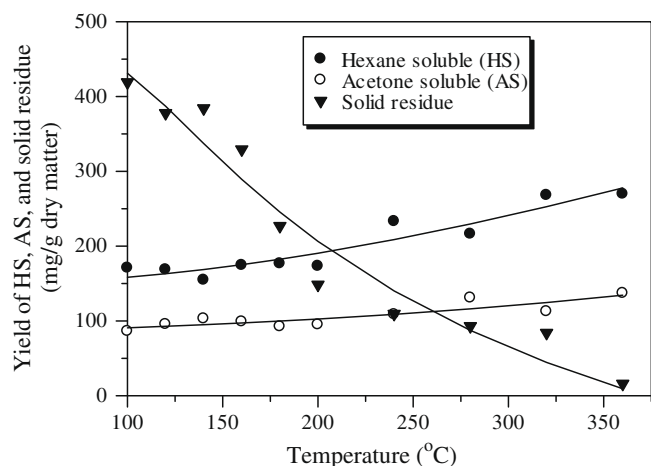
Fig. 3. Effect of temperature on amounts of hexane-soluble (HS), acetone-soluble (AS), and solid residue obtained by sub-CW treatment of rice bran at the reaction time of 5 min.

on its quality, it can be used as an edible oil or as feedstock of biodiesel (Zullaikah, Lai, Vali, & Ju, 2005). The AS phase is ascribed to tar, carbonized sample, and any other compounds that can dissolve neither in water nor in hexane. Most of the solid residue contains un-reacted rice bran and mineral compounds. The aqueous phase, as will discuss later, contains mainly hydrolysed products of proteins, cellulose, and hemicellulose parts of rice bran (Sasaki et al., 1998; Sereewatthanawut et al., 2008; Wiboonsirikul et al., 2007a; Wiboonsirikul et al., 2007b). In this research work, we mainly focus on the WS compositions.

3.3. Water-soluble (WS) phase

3.3.1. General

As the most important measures of decomposition of rice bran by the sub-CW hydrolysis reaction, TOC, and TN were investigated. Fig. 4 shows the effect of sub-CW temperature on TOC and TN yields at a reaction time of 5 min. As both curves showed peaks, the soluble products were produced by hydrolysis reactions in sub-CW. TOC showed a peak at around 232 °C, and then this decreased with increasing temperature, owing to a weak hydrolysis reaction, pyrolysis, and gasification of the organic compounds.

The shape of the TN profile is similar to the TOC curve (see Fig. 4). This profile showed a peak at 280 °C, which decreased
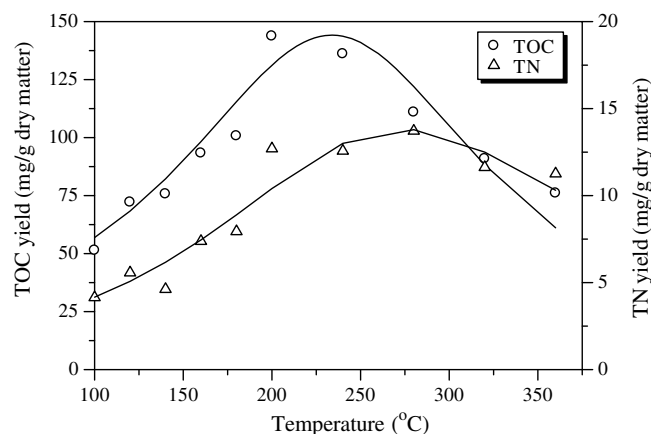
somewhat by increasing temperature due to final degradation of N-containing organic compounds to gaseous by-products such as NH_3. Generally, TN contents in the aqueous phase are a function of N-containing soluble proteins, peptides, and particularly of the amino acids and ammonia. The small amounts of the produced gases were not quantified in this research work.

3.3.2. Amino acids

Protein in the rice bran was decomposed in sub-CW and converted to water-soluble amino acids. Up to eight essential amino acids (histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, and valine) and six non- and/or conditionally essential amino acids (glutamic acid, alanine, tyrosine, serine, glycine, and asparatic acid) were found in the WS phase. Figs. 5a and 5b show the effect of reaction temperature on amino acid yields at the reaction time of 5 min. In general, peaks appeared around 127 °C. Lysine and glutamic acid had the highest yield among the identified essential and nonessential amino acids, respectively. Due to decomposition of amino acids to low molecular weight carboxylic acids and gaseous products (Lamoolphak et al., 2006), amino acids were not identified at temperatures higher than 227 °C. Yield and temperature differences between amino acid and TN peaks confirmed that other N-containing compounds were produced in the aqueous phase by decomposition of rice bran under sub-CW conditions. These compounds were not analyzed in this research work.
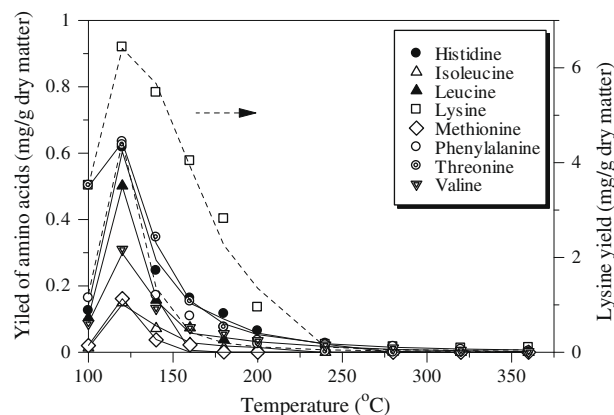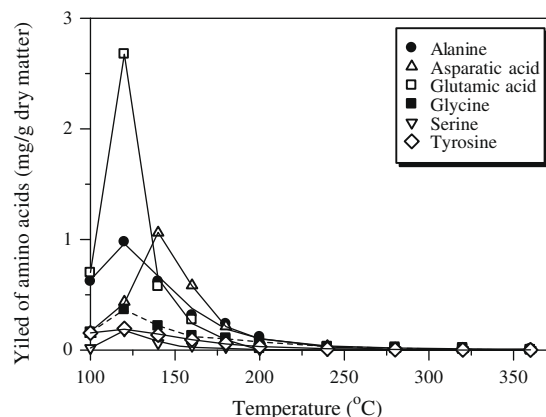

Fig. 5a. Yield of essential amino acids after sub-CW treatment of rice bran (identified in the aqueous phase) versus temperature at 5 min residence time.

Fig. 4. Effect of sub-CW temperature on TOC and TN yields at the reaction time of 5 min.

Fig. 5b. Yield of nonessential amino acids after sub-CW treatment of rice bran (identified in the aqueous phase) versus temperature at 5 min residence time.
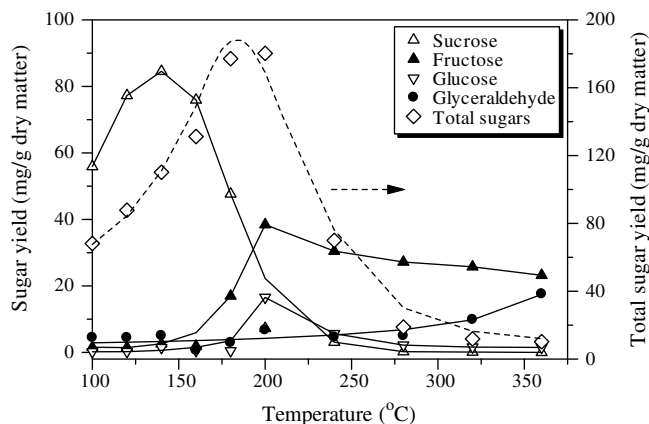
Fig. 6. Effect of sub-CW temperature on sugar production yields in aqueous phase at the residence time of 5 min.

Fig. 8. Effect of reaction temperature on the element composition of solid residue at 5 min residence time.

3.3.3. Saccharides (total soluble sugars)

As rice bran is a rich source of polysaccharides, sub-CW hydrolysed them to significant amounts of water-soluble sugars. Fig. 6 shows the production yields of several quantified soluble sugars (sucrose, fructose, glucose, and glyceraldehyde) as a function of temperature at the reaction time of 5 min. Sucrose showed a peak at 140 °C, and decomposed to fructose and glucose (Haghighat Khajavi, Kimura, Oomori, Matsuno, & Adachi, 2005) at higher temperatures. In fact, it must give equimolar amounts of fructose and glucose from hydrolysis of sucrose; on the other hand, fructose is less stable than glucose at the sub-CW condition (Salak Asghari & Yoshida, 2006). Since production yield of fructose was higher than that of glucose (see Fig. 6), it seems that another pathway must also exist for production of fructose (besides that obtained from hydrolysis of sucrose) (Salak Asghari & Yoshida, 2006). The yield of glyceraldehyde increased almost linearly by increasing temperature.

Furthermore, total sugars of the aqueous phase (including mixtures of poly-, oligo-, di-, and mono-saccharides) were quantified by a photometric method (Hodge & Hofreiter, 1962) and results are shown in the same Figure. About 20% of total sugars in the aqueous phase is a very promising amount of rice bran hydrolysis by sub-CW. This amount decreased steeply from 200 to 360 °C.

3.3.4. Organic acids

Organic acids can be produced by decomposition of biomass, carbohydrates, and amino acids (Lamoolphak et al., 2006; Salak
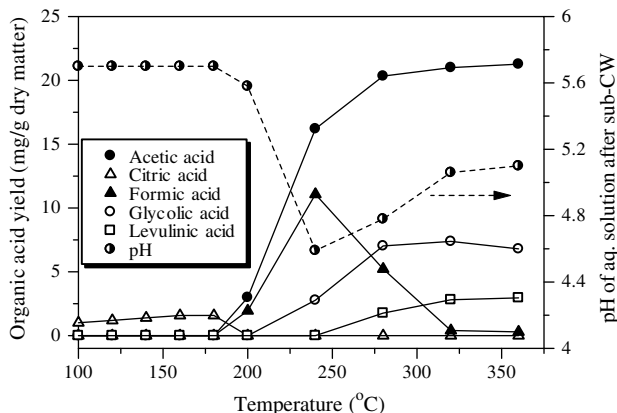
Asghari & Yoshida, 2006). In this work, five WS organic acids were identified from decomposition of the rice bran. Fig. 7 shows that acetic, formic, glycolic, and levulinic acids were produced at temperatures above 190 °C. Acetic acid increased up to 280 °C and then levelled off to a constant yield. Formic acid showed a peak at 240 °C and decreased to zero at temperatures above 320 °C. Glycolic and levulinic acid yields continuously rose with increasing temperature; however, glycolic acid showed a small amount of degradation at higher temperatures (i.e. 350 °C). Citric acid was only identified at temperatures lower than 200 °C. Due to the formation of WS organic acids, pH in the aqueous phase was changed, by increasing sub-CW temperature, to acidic values. The minimum pH was 4.6 at around 240 °C. Then it was again increased to 5.1 at 320 °C. This increment may be attributed to the decomposition of organic acids to other compounds, especially gaseous products and may also be due to buffering of the solution. Production of organic acids and, consequently, decreasing of the pH, led to the conclusion that autocatalysis may occur during sub-CW treatment of rice bran.

3.4. Solid residue phase

In order to realise the changes in composition of solid residue by sub-CW treatment, CHNS (carbon, hydrogen, nitrogen, and sulphur) amounts in solid residue were evaluated. Fig. 8 shows the effect of temperature on the ratios of H/C, N/C, and S/C in the solid

Fig. 7. Organic acid yields of aqueous phase and its pH as a function of sub-CW temperature at 5 min residence time.
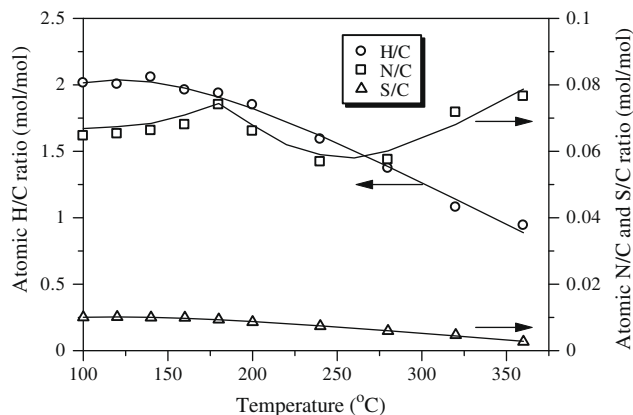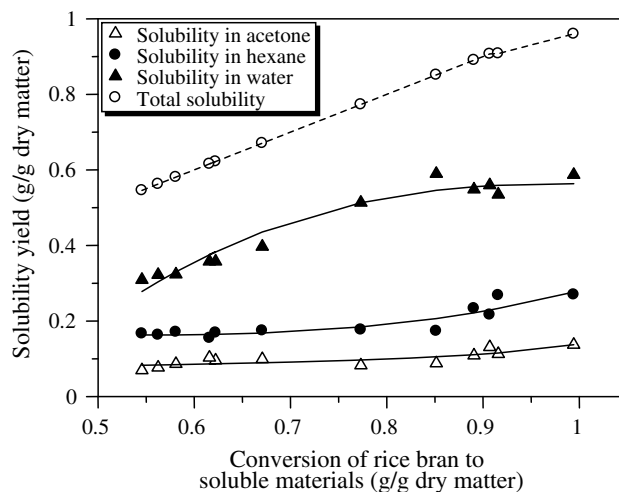

Fig. 9. Solubility yields versus rice bran conversion caused by sub-CW treatment.

residue for 5 min of reaction time. The H/C was decreased by increasing sub-CW temperature, particularly at higher temperatures, due to pyrolysis reactions. N/C ratio showed a minimum at 240 °C and, the S/C ratio was gradually decreased by sub-CW temperature increase.

3.5. Hexane, acetone, and water solubilities by rice bran conversion

Part of the rice bran was dissolved in the three phases (HS, AS, and WS) by treating it under sub-CW conditions. Solid residue was the phase which was not dissolved in the above phases. Obviously the amounts of solid residue and dissolved materials depended on rice bran conversion. The solubilities of rice bran in hexane, acetone, and water phases, as functions of rice bran conversion by sub-CW were calculated by Eqs. (1)–(3) and the results are shown in Fig. 9. The greater the rice bran conversion, the greater were the amounts of HS, AS, and WS produced. Clearly, rice bran conversion and solubility yields depended on sub-CW reaction temperature (see Fig. 3). Fig. 9 also reveals that HS yield was always higher than that of AS, and WS yield was greater than those of HS and AS. This Figure shows that WS, HS, and AS solubilities were non-linear functions of rice bran conversion whilst total solubility was a linear function of rice bran conversion.

4. Conclusions

Sub-CW processing, as a green and environmentally friendly technique, has been successfully applied for rice bran treatment and production of valuable materials. The extraction of rice bran oil was found to be a feasible process. Rice bran oil was successfully extracted with higher yields than those obtained by conventional methods. It was apparent that sub-CW temperature influenced oil production. The higher the sub-CW temperature, the greater was the amount of oil obtained. Maximum extracted rice bran oil, as HS phase, was nearly 27% of the initial dry matter. In addition, temperature had considerable effects on the yield of the obtained tar and solid residue.

Another interesting finding was that of rice bran liquefaction by sub-CW reaction and hydrolysis in a short residence time (5 min). The experimental TOC and TN confirmed that protein and cellulosic parts were hydrolysed and efficiently converted into water-soluble compounds. TOC and TN yield curves showed peaks at around 232 and 280 °C, respectively. Sub-CW converted cellulosic parts of rice bran into water-soluble di- and mono-saccharides. Maximum total yield of sugars produced by the hydrolysis reaction was nearly 20% of initial dry matter. This is a very suitable feedstock for bioethanol production and or other industrial and food applications. The protein part of rice bran was hydrolysed to a variety of essential and nonessential amino acids. Totally, more than 14 amino acids were identified in the aqueous phase. Among the obtained amino acids, the most plentiful yields were those of lysine, glutamic acid, alanine, and asparatic acid. Besides amino acids, five organic acids, in considerable amounts, were produced from decomposition of rice bran. Acids may autocatalyze further solubility of rice bran under sub-CW conditions. It was found that amino acid and organic acid yields were functions of sub-CW temperature. The optimum production temperature for most of the amino acids was 127 °C and, at temperatures higher than 227 °C no amino acid was detected whilst organic acids production began at temperatures higher than 190 °C.

Acknowledgements

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