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Adding value to onion (*Allium cepa* L.) waste by subcritical water treatment

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ABSTRACT

In this study, the treatment of brown type onion (*Allium cepa* L.) waste was investigated under subcritical water conditions. Experiments were carried out in a wide temperature range from 373 to 593 K, at a residence time of 5 min. Several phases were segregated after the reaction, including the aqueous phase, solid residue, and hexane and acetone soluble phases. In the aqueous phase, significantly increased amounts of total organic carbon and total nitrogen were identified from the decomposition of mainly the carbohydrate and protein parts of the onion. In addition, very promising amounts of water-soluble sugars were also quantified in the aqueous phase (65% of the dry matter for onion bulbs and 7% for skins). For the remaining solid phases obtained at different temperatures, higher heating values (HHVs) were calculated and compared, based on the ultimate analysis. Generally, the remaining solids showed increased amounts of carbon content, which led to increased HHVs and energy densities of the solids. Acetone and hexane soluble fractions were also evaluated. Very small amounts of hexane and acetone soluble compounds were obtained. Furthermore, two valuable products – fructooligosaccharides and quercetin – were successfully obtained from onion bulbs and skins, respectively.

1. Introduction

Annually, more than 450,000 tons of onion waste (residues and surpluses) are produced each year in the European Union and about 144,000 tons in Japan [1], due to technical difficulties, such as storage, transportation and nonstandard sizes, and economic reasons (mainly when supply exceeds demand). Utilization of such a huge waste is one of an important global challenge.

In fact, the nutritional composition of onions is very complex. About 80% of the dry matter of onion bulbs consists of nonstructural 1carbohydrates [2]. The predominant carbohydrates are glucose, fructose, sucrose, and low-molecular weight fructooligosaccharides (FOS) [2,3].

Over the past decade, due to the great interest of consumers in diet foods, several companies have been trying to obtain permission to use FOS as food ingredients in the U.S. and Europe [4], where they are not yet being marketed. The approval of FOS in Japan prompted the establishment of an acceptable daily intake of about 0.8 g/kg of body weight/day [5].

The skin part of onions has also attracted attention as a good source of flavones, antioxidants and radical scavenging compounds. Quercetin is one of the abundant flavonol-type flavonoids found commonly in several fruits and vegetables, including onions [6]. Onions ranked highest in quercetin content in a survey of 28 vegetables and 9 fruits [7].

Due to their strong aroma, onion waste is not suitable for fodder; and, due to the rapid growth of phytopathogens, it is not suitable for landfill disposal [8]. Moreover, as a result of a high percentage of moisture, their removal by combustion is rather expensive. Onion waste is, therefore, an environmental problem. The onion processing industry is being forced to develop innovative methods to solve this problem. These may not only provide a solution to the environmental problem of disposal, but may also obtain bio-based products and bioenergy from the waste. Subcritical water, as a green technique for the treatment of variety of biomass waste, has received increased attention in recent years [9–14]. This technique has been widely used for the treatment of a variety of vegetables and fruits as well as food waste [15–17]. J. King and his co-workers have done extensive researches on extraction of variety of flavonoids from natural products. For example, they have recently reported extraction of quercetin and its dihydrate (as model compounds) using a flow type subcritical water apparatus. From their solubility values under subcritical water, the thermodynamic properties of the solution of quercetin and its dihydrate estimated [18]. In another report, Turner et al. [19] studied the extraction of quercetin species from onion waste under subcritical water conditions as well.

To the best of our knowledge, there is no previous report on the study of onion treatment for the whole temperature range of subcritical water. The principal objective of this investigation was, therefore, the application of the subcritical water technique for the hydrolysis, decomposition and extraction of onion waste, in order to obtain value-added materials.

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2. Experimental

2.1. Onion samples

Onions grown in the Sumoto city of the Hyogo Prefecture (Japan) were harvested and stored at 278 K until use. The average moisture contents of the onion bulbs and skins were 90.4 and 12.3%, respectively. The residue on ignition under air atmosphere at 873 K for 6 h was 0.5 and 7.5% for onion bulbs and skins, respectively.

2.2. Chemicals

Sodium carbonate, sodium hydrogen carbonate and phenol were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Ethylenediaminetetraacetic acid (EDTA) and Bis-Tris were obtained from Dojindo (Japan), and n-caprilic acid was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Mercaptoethanol and brij were obtained from Pierce Biotechnology, Inc. (USA); and, potassium hydrogen phthalate, sulfuric acid and sodium hypochlorite were purchased from Chameleon Reagent (Osaka, Japan). FOS (fructooligosaccharides) was obtained from Meiji Seika Kaisha, Ltd. (Japan), and quercetin was purchased from Sigma-Aldrich. All other reagents and solvents were obtained from Wako Pure Chemical Industries, Ltd. (Japan).

2.3. Procedure

The batch reactors used for the subcritical water treatment were stainless steel tubes (SUS 316, diameter of 7.5 mm and length of 150.4 mm for the bulb samples, and diameter of 16.5 mm and length of 150.4 mm for the skin samples) and a Swagelok fitting (ready-made, from Swagelok AG). For sampling, onions were randomly selected and hand peeled. Skin parts were dried and crushed to obtain a powder with an average grain size of less than 1 × 1 mm. Onion bulbs were cut into small pieces, approximately sized 5 × 5 mm, before use.

In a typical experiment of onion bulbs, an accurately weighted amount (about 2.5 g) of onion bulbs and about 2.7 g of distilled water were charged into the reactor. For onion skins, an accurately weighted amount (about 2.0 g) and about 20 g of distilled water were charged into the reactor.

Argon gas was used to force air out of the reactor, which was then capped tightly. It was immersed for 5 min in a preheated oil bath (Thomas Kagaku Co., Ltd., Model Celsius M type) for temperatures ranging from 373 to 453 K or a preheated salt bath (Thomas Kagaku Co., Ltd., Model Celsius 600H) for the temperature range of 473 to 593 K. The reaction time included the heat-up time, which was approximately 120 s at lower temperatures and declined sharply with increasing reaction temperatures to 10 s at 643 K [20].

The reactor was then removed from the thermal bath and quickly quenched by soaking in a bath of room temperature water. The reactor content was placed in a test tube, taking particular care to prevent loss of any of the liquid.

For comparison, a series of experiments were carried out utilizing Soxhlet extraction of quercetin from onion skins. In a typical experiment for Soxhlet extraction, the weight of a blank thimble filter (22 × 90 mm) (Advantec, Japan) and a blank round bottom extraction flask were weighed before and after placing approximately 2 g of sample into thimble. 350 mL of methanol (99.9%) is poured into the round bottom extraction flask, weighed and placed on the heating mantle. After this, the thimble containing the sample was placed into the extraction chamber. Lastly, the condenser was placed on top of the extraction flask and all these parts were fixed vertically. The extraction was carried out for 9 h. The process was repeated three times and an average extraction was taken.

2.4. Segregation of produced phases after subcritical water treatment

After subcritical water treatment, samples were classified into several phases: aqueous, solid, hexane soluble (HS), acetone soluble (AS) and methanol soluble (MS, only for skin) phases. In the separation procedure of the phases, 5 mL of hexane was added to the test tube and gently shaken for 5 min at 298 K and then centrifuged at 2500 *g* for 10 min; and, the supernatant liquid was separated. This procedure was repeated eight times. The HS amount was calculated by weight after the evaporation of hexane.

The aqueous phase and solid residue were then separated by filtration. The solid residue was washed with 10 mL of acetone several times. The AS amount was calculated by weight after evaporation of the solvent. Finally, the remaining solid residue was placed into an oven at 333 K to dry it to a constant weight.

Methanol was used as a suitable solvent for removing the extracted amount of quercetin from the onion skins.

2.5. Analysis

Concentrations of organic acids were determined by a 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 a post-column pH-buffered electroconductivity detection system (Shimadzu CDD-6A, Shimadzu Co., Japan). The mobile phase was 5.5 mM of a p-toluensulfonic acid solution at a flow rate of 0.8 mL/min. Mixtures of 5.5 mM of p-toluensulfonic, 20 mM of Bis-Tris and 100 μM of EDTA were used as post-column reagents, all at a flow rate of 0.8 mL/min. The column (Shimadzu CTO-10AC VP, Shimadzu Co., Japan) temperature was kept at 318 K.

The concentrations of amino acids were determined by a high-performance liquid chromatography (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 333 K.

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 the quantitative analysis of the products that could not be detected using a ultraviolet (UV) detector. This HPLC system was operated at an oven (Jasco CO-2065plus, Jasco Crop., Japan) temperature of 305 K, using Milli-Q water as a mobile phase at a flow rate of 0.4 mL/min.

The amount of total soluble sugars in the aqueous phase was determined by a photometric method (phenol-sulfuric acid assay), using D-glucose as a standard curve [21]. Phenol reagent, 5% (v/v) (0.4 mL) was added to appropriately diluted aqueous solutions (0.4 mL). Samples were then mixed with 2 mL of concentrated sulfuric acid using a bottle top dispenser. The solutions were mixed immediately by shaking and allowed to cool to room temperature. After 10 min, the absorbance at 490 nm was determined using a double-beam spectrophotometer (UV-1700 Pharmas Pec- Shimadzu).

Total organic carbon (TOC) and total nitrogen (TN) were measured with 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 spectrophotometric measurements of the total sugar [21]. A CHNS elemental analyzer (Perkin-Elmer, model 2400) was used to calculate the carbon, hydrogen, nitrogen and sulfur contents of the solid samples.

The methanol soluble (MS) phase was analyzed by a Shimadzu HPLC column C18 (VP-ODS), 150 L × 2.0, in an HPLC system using two Varian ProStar 210 solvent delivery modules coupled with a photodiode array (PDA) detector (Varian PDA 330 Detector) for the identification and quantitative analysis of products. The absorbance of the