Journal of Cereal Science 60 (2014) 477–483

Contents lists available at ScienceDirect

Journal of Cereal Science

journal homepage: www.elsevier.com/locate/jcs

Wet-milling of buckwheat with hull and dehulled – The properties of the obtained starch fraction

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ARTICLE INFO

Article history:
Received 16 May 2014
Received in revised form
1 August 2014
Accepted 5 September 2014
Available online 12 October 2014

Keywords:
Wet-milling of buckwheat
DSC
RVA
Particle size distribution

ABSTRACT

The buckwheat with or without hull were used for the laboratory wet-milling. Starchy materials obtained was characterised by determining starch extraction efficiency, particle size distribution and microstructure. The pasting (RVA) and thermal properties (DSC) were also analysed. The starch extraction efficiency was higher for total starch isolated from buckwheat with hull compared to dehulled. The mean particle diameter of the pure starch isolated from both buckwheats was about 18 μm. The longer time of steeping of buckwheat with hull caused a decrease in temperature of gelatinization compared to the dehulled ones. Significantly higher enthalpy values for both pure starches compared to the other samples were noticed. The increasing of gelatinisation enthalpy with increasing of the steeping time and the higher protein amount was observed. The used wet-milling method did not change significantly the properties of the obtained starchy materials compared to raw material.

1. Introduction

Cultivation of buckwheat declined for many years, but recent interest in old, traditional foods and a re-evaluation of typical regional products, has led to resurgence in its cultivation. Buckwheat is a pseudocereal which has been grown for centuries in Europe and now, alongside spelt wheat, is one of the most important alternative crops, suitable for ecological growing, without the use of artificial fertilizers or pesticides. Buckwheat is generally used as human food and as animal or poultry feed. Similarly to cereal crops, buckwheat produces seed with high starch content. In addition, buckwheat proteins have a high biological value, and relatively low true digestibility. Also the content of other nutritionally important fractions, like antioxidative substances, trace elements or dietary fibre is currently under consideration (Wijngaard and Arendt, 2006). Due to the quite well-known health-promoting values of buckwheat, some countries already have special health programs. In those program, buckwheat is included in the normal diet for children and adults or some of them promote its healthy properties, like North American Buckwheat Promotion Committee in Canada (CSCA, 2001) or project named "Buckwheat Conservation And Utilisation" in Bhutan (Drukpa et al., 2010). Buckwheat dehulling process is carried out by raising the moisture content of raw whole buckwheat kernels followed by simultaneous steaming and heating. Buckwheat hull can be used in the food industry. Oomah and Mazza (1996) have reported that buckwheat hull contains 4-times more phenolic compounds compared to groats. Zielińska et al. (2013) found that buckwheat hull tea showed a lower content of total phenolic compounds and lower antioxidant capacity in comparison to green tea. Nowadays, the hull is used in the production of therapeutic mattresses and cushions, which adapt to the position of the body, quickly absorb the moisture, do not heat up and are always cool. An extremely important feature of these products, due to the presence of tannins, is inhibiting the development of harmful micro-organisms: mites, mold, bacteria and fungus. The by-products from the processing of buckwheat are characterized by a high content of carbon and hydrogen, that is why it is used as a raw material for the production of granular biofuels (Borkowska and Robaszewska, 2012).

Wet-milling is an industrial process involving physical, chemical, biochemical and mechanical operations to separate the principal components for different types of grains. This process consist basically of two steps: soaking in water solutions of alkali or acid at a given temperature, followed by mechanical separation that takes advantage of the differences in the physical properties (density and

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http://dx.doi.org/10.1016/j.jcs.2014.09.004
0733-5210/

particle size) of the fractions: starch, protein, germ, fibre and hull. During soaking, water diffuses into the grain, and softens and degrades the intercellular structure, which allows for efficient milling. Soaking being a diffusive process, its rate will depend on temperature and presence or not of chemicals (acid or alkali). Literature data provide information about the use of wet-milling process for the isolation of fractions from maize, sorghum, amaranth, wheat or buckwheat (Haros et al., 2004; Xie and Seib, 2002; Calzetta Resio et al., 2009; Sayaslan, 2004; Zheng et al., 1998). In conventional wet-milling, maize is steeped in an aqueous solution containing sulphur dioxide (0.1–0.2%), a reducing and antimicrobial agent, which solubilises and disperses the proteinaceous matrix that envelops and binds starch granules. Modification of structural characteristics, physicochemical and functional properties of starch due to steeping and milling conditions have been reported (Pérez et al., 2001). The presence of lactic acid in the steeping water makes the cell walls easier to break, and for better simulates the industrial steeping process at a laboratory level (Pérez et al., 2001). However, scarce information exists concerning the effect of steeping time and the addition of lactic acid on the starch characteristics. Shandera and Jackson (1996) studied the effect of steeping temperature and concentration of lactic acid and sulfur dioxide on the starch functionality. They found that maize kernel steeping conditions affect the physicochemical properties of the starch. In fact, Pérez et al. (2001) found that the starch from maize steeped for various time intervals presented an increase in peak temperature and a narrowing of the gelatinization range, due to the annealing produced during the steeping process. The changes in starch properties induced by steeping and milling conditions could be important because its physicochemical characteristics and functional properties determine suitability for use in different industrial processes. Moreover, the method used for wet-milling should allow for the best selection of buckwheat fractions, which will be utilized for creation of new food ingredients.

This study was undertaken to determine the recovery of each component of buckwheat with or without hull by wet-milling. The aim of this work was analysis of buckwheat starch obtained by wet-milling procedure from kernels with and without hull.

2. Material and methods

2.1. Materials

Commercial Polish common buckwheat with and without the hull were purchased from a local market (Melvit S.A., Kruki, Poland). The proximal chemical characteristics of buckwheat kernels with hull and without hull on a dry basis were: 58.5 ± 0.3% and 69.4 ± 0.3% of starch, 12.3 ± 0.1% and 15.2 ± 0.1% of protein (Nx5.7), and 3.9 ± 0.4% and 1.7 ± 0.1% of ash, respectively.

2.2. Wet-milling

An applied wet-milling procedure was chosen based on the preliminary studies (data not shown), in which different temperatures, time and pH of steeping water were evaluated (Perez et al., 2001; Zheng et al., 1998). Buckwheat with hull and dehulled were steeped in 250 mL of sufficient sodium bisulfite solution (Sigma, No 243973) to give a dioxide concentration of 0.25% in distilled water (1:9 w/v) at 28 °C for 16 h and 2 h, respectively. The pH was adjusted to 4.0 by using lactic acid (Sigma, DL-lactic acid solution, No W261114). The steeped buckwheat with or without hull were ground with a blender for 3 min with a small amount of distilled water. The water slurry was manually sieved through a set of stainless screens: 600 (buckwheat with hull), 300, 80 and 53 μm (30, 50, 200 and 270 U.S., respectively). Hull was retained in the first screen, germ and fibre fractions in the second, protein fraction in the third and fourth. Sodium hydroxide (4% w/v) was added dropwise to the starch slurry passing through 80 and 53 μm sieves and the starchy milk was mixed vigorously for 30 min at room temperature. Then slurry was centrifuged 5-times at 20,000 rpm for 20 min at 4 °C. After centrifugation, the pure starch and starch with tailings (sediment) were obtained. The steeping water and the water obtained during the centrifugation were freeze-dried. The pure starch, starch with tailings, protein, germ and fibre, and hull fractions resulting from the wet-milling process were dried for 24 h at 40–45 °C.

The yield of each fraction was calculated as a ratio of the totally dried isolated fraction to the initial amount of dried buckwheat. Extraction efficiencies were calculated by the formula proposed by Zheng et al. (1998):

$$\%\text{starch extraction efficiency} = [(\%\text{fraction yield} \times \%\text{starch content}) \times /\%\text{starch content in kernel}] \times 100.$$

The assays were realized three times.

2.3. Fractional chemical characterisation

Moisture was determined by using a moisture analyser KERN DBS 60-3 (Kern & Sohn GmbH, Balingen-Frommern, Germany). For a better characterisation of the material, protein (Nx5.7) was measured by the micro-Kjeldahl method (AOAC, 1995). The total starch content was determined by Total Starch (AA/AMG) Assay Kit (K-TSTA) (Megazyme, Irland).

2.4. Starch damage analysis and whiteness

Starch damage was measured with a SDmatic (Chopin, France) which uses the method of analysis based on the amperometric method (AACC, 1995). This method consists of measuring the amount of iodine absorbed by the starch granules in a solution at a temperature of 35 °C. The instrumental measurement of starchy sample colour was carried out with a ColorFlex (HunterLab, USA), and the results were expressed in accordance with the CIELab system with reference to illuminant D65 and a visual angle of 10°. The measurements were performed through a glass sample cup. The parameters determined were: L^* ($L^* = 0$ [black] and $L^* = 100$ [white]), a^* ($-a^*$ = greenness and $+a^*$ = redness) and b^* ($-b^*$ = blueness and $+b^*$ = yellowness). All measurements were performed in four replicates. Whiteness index (WI) was calculated as: $WI = 100 - (100 - L)^2 + a^2 + b^2)^{0.5}$ (Ghanbarzadeh et al., 2010).

2.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were made with a Perkin–Elmer DSC-7 (Norwalk, CT). Briefly, 10 mg of obtained starchy materials were directly weighed into DSC stainless steel pans (PE 0319-0218) and distilled water was added to obtain a water:starch ratio of 3:1, in order to ensure complete gelatinisation. After sealing, they were scanned at a rate of 10 °C/min from 20 to 130 °C. An empty pan was used as reference. Three replicates for each sample were run. The parameters recorded were onset temperature (To), peak temperature (Tp) and conclusion temperature (Tc) of gelatinisation. Straight lines were drawn between To and Tc and the enthalpies (ΔH) associated with starch gelatinisation were calculated as the area enclosed by the straight line and the