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Conversion/degradation of isoflavones and color alterations during the drying of okara

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6″-*O*-Acetyldaidzin (PubChem CID: 156155)
6″-*O*-Malonyldaidzin (PubChem CID: 53442202)
Genistein (PubChem CID: 5280961)
Genistin (PubChem CID: 5281377)
6″-*O*-Acetylgenistin (PubChem CID: 22288010)
6″-*O*-Malonylgenistin (PubChem CID: 15934091)
Glycitein (PubChem CID: 5317750)
Glycitin (PubChem CID: 187808)
6″-*O*-Acetylglycitin (PubChem CID: 53398650)
Malonylglycitin (PubChem CID: 23724657)

ABSTRACT

The aim of this work was to investigate the convective drying of okara, a by-product from soymilk processing. The specific objectives were as follows: to model the drying kinetics using the Fick and Page models; and to evaluate the color and isoflavone content during drying. An oven-dryer with hot air circulation at 50, 60 and 70 °C was used. Samples were taken at each predetermined time to analyze the isoflavone profile by UHPLC and the color. The Page model fitted the drying kinetics data well. Throughout drying, there was a decrease in the color parameters (lightness and hue angle), showing sample browning. A significant reduction in the isoflavone content was observed at 70 °C, possibly due to thermal degradation. During the initial stage of drying at 50 °C, daidzin and genistin were converted to the aglycones daidzein and genistein, respectively, probably due to residual β-glucosidase activity. However, isoflavone degradation was observed during the final stages of drying at 50 °C.

1. Introduction

Approximately 10% of the world soybean production is used directly as human food. The soybean is commercialized *in natura* and as soy-derived products, such as textured soy, soymilk, *tofu*, fermented products (*miso*, *shoyo*, *tempeh*) and others (Riaz, 2006). The production of soymilk and *tofu* results in an insoluble byproduct called okara which has little market value and is usually used as animal feed. In these processes, about 1.2 kg of wet okara is

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generated from every kilogram of soybeans (Wang & Murphy, 1996). The okara has a high nutritive value due to its high quality protein, fat, carbohydrates and fiber. The proteins have high nutritive value and a superior protein efficiency ratio, indicating that okara is a potential source of low cost vegetable protein for human consumption (O'Toole, 1997). Thus currently, considerable quantities of this material are underutilized as animal feed or discarded, constituting a waste of nutrients which could have been used in human food.

Due to its high moisture content (75–80 g/100 g), okara deteriorates rapidly, and it is therefore of interest to process okara in order to extend its shelf life. Of the several methods used for conservation, drying is a process by which water is removed by vaporization or sublimation, thus reducing the degradation reaction rates. The drying rate is influenced by transfer mechanisms, such as the vapor pressures of the food and of the drying air, temperature and air velocity, moisture diffusion in the product, thickness and surface exposed for drying (Van Arsdel, 1973). Although drying is an alternative to extend the shelf life of food and to facilitate storage and transportation, the quality of dehydrated food is usually drastically reduced as compared to that of the original foodstuff. Thus, it is of interest to minimize chemical changes, such as enzymatic and non-enzymatic browning, and to maximize nutrient retention, such as that of the isoflavones, during drying.

Several drying technologies have been investigated for okara in order to evaluate the dryer performance and quality of the dried product (Itaya, Kobayashi, & Nakamiya, 2010; Wachiraphansakul & Devahastin, 2005, 2007; Grizotto & Aguirre, 2011; Li, Li, Sun, & Tatsumi, 2006; Perussello, Mariani, & Amarante, 2009; Perussello, Amarante, & Mariani, 2012). Nevertheless, little information about the influence of the process conditions on the isoflavone profile during the drying of okara has been reported. Using an air jet impingement dryer, Wang et al. (2016) evaluated the effect of air temperature, air velocity and sample loading density on the quality of dried okara, including the total isoflavone content. However, the authors did not investigate all the isoflavone forms and their changes during the process of drying.

Okara contains about 12%–40% of the raw soybean isoflavones, resulting in a concentration of 0.02–0.12 g/100 g solids (Jackson et al., 2002; Wang & Murphy, 1996). Soybean isoflavones have four different chemical forms: β-glycosides (daidzin, genistin and glycitin), acetylglucosides (6″O -acetyldaidzin, 6″O-acetylgenistin and 6″O-acetylglycitin), malonylglucosides (6″O-malonyldaidzin, 6″O-malonylgenistin and 6″O-malonylglycitin) and aglycones (daidzein, genistein and glycitein). Malonyl- and acetylglucosides can be converted into β-glycosides after heating (Chien, Hsieh, Kao, & Chen, 2005), which can be hydrolyzed to produce aglycones by the action of endogenous β-glycosidase, heat or acid/alkaline treatment (Niamnuy, Nachaisin, Laohavanich, & Devahastin, 2011). Therefore, the content and distribution of the isoflavones can be affected by the processing conditions.

Recently, several investigators have reported that soybean isoflavones may benefit human health due to their several biological activities, amongst which antioxidant properties (Lee et al., 2005) and the ability to reduce menopause (Filiberto et al., 2013) and diabetes mellitus types 1 and 2 (Park, Ju, Park, & Han., 2013). The various isoflavone forms present differences with respect to their bioavailability. The aglycone is more easily absorbed than the conjugated glycosides because its low molecular weight facilitates diffusion (Mathias, Ismail, Corvalan, & Hayes, 2006). This isoflavone form has been widely investigated, due to its ability to reduce the incidence of breast cancer (Wada et al., 2013). There is therefore a growing interest in preparing soy products with higher aglycone contents, and hence a study of the conditions that lead to lower isoflavone degradation and favor the formation of aglycones during the drying of okara, without imparing the other product characteristics, has become necessary. Moreover, the monitoring of the kinetics of the isoflavone contents during the hot air drying of okara allows one to verify the influence of processing time on such alterations. Thus, knowledge of this information is essential to obtain a dried product with a significant isoflavone content, mainly aglycones, from a low cost source (okara), which can be applied as a nutritional supplement or as an ingredient in several foods, such as meat products (Su, Yoshida, Contreras-Castillo, Quiñone, & Venturini, 2013; Grizotto, Andrade, Miyagusku, & Yamada, 2012).

Color has been used as a quality attribute of dried products. Darker okara reduces consumer acceptance, since a uniform pale yellow color is desired. Moreover, it can affect the quality of the products to which it is added, since okara can partially replace wheat flour in food production (Li, Qiao, & Lu, 2012). As a general rule, high drying temperatures and long times negatively influence food colors due to enzymatic or non-enzymatic browning.

Thus the objective of the current work was to evaluate the influence of temperature (50, 60 and 70 °C) on the drying kinetics and product characteristics such as the color and isoflavone conversions, during the oven-drying of okara.

2. Material and methods

2.1. Material

Wet okara from soymilk processing was acquired from a local soymilk processing industry and stored in a cold chamber at −22 °C. The main characteristics of the okara, obtained according to AOAC (2006), were on a wet weight basis: a moisture content of 78.1 ± 0.1 g/100 g, fiber content of 13.6 ± 1.0 g/100 g, protein content of 6.8 ± 0.2 g/100 g, fat content of 3.5 ± 0.1 g/100 g and ash content of 1.0 ± 0.1 g/100 g.

For the isoflavone determination, the standards 6″-*O*-acetylglycosides and 6″-*O*-malonylglycosides (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and β-glycosides and aglycones (Sigma–Aldrich Co., St. Louis, MO, USA) were used.

2.2. Air drying experiments

Before the drying experiments, the wet okara was molded to a flat plane geometry with a circular cross section of 6 cm in diameter and a thickness of 5 mm. Since the sample thickness was considerably smaller than its diameter (thickness:diameter ratio < 0.1), the samples were considered to behave like a semi-infinite plate during the further modeling of the experimental data, during which moisture transfer is unidirectional (Azuara-Nieto, Gutiérrez-Lopéz, & Beristain-Guevara, 2003).

The drying experiments were carried out in an oven-dryer with air circulation and renovation (TE-394/2 model, Tecnal, Piracicaba, Brazil) at air temperatures of 50, 60 and 70 °C and an air flow rate of 59 ± 1 l/min with air renovation. A thermal-hygrometer (30.5000.02 model, TFA, Reicholzheim, Germany) was used to monitor the room temperature and relative humidity of the air. For the drying experiments at 50, 60 and 70 °C, the room temperatures and relative humidities were, respectively, 20.8 ± 1.2 °C and 62 ± 2%, 22.4 ± 0.5 °C and 69 ± 2%, and 23.3 ± 1.1 °C and 69 ± 2%. During processing, samples were taken at each predetermined time in order to evaluate the okara quality with respect to its isoflavone profile and color. Moreover, okara samples were weighed at regular time intervals during drying, using a semi-analytical balance with a resolution of 0.001 g, until constant weight, in order to evaluate the drying kinetics. The sample moisture content was gravimetrically determined using an oven at 105 °C for 48 h (Kurozawa, Hubinger,