Industrial Crops and Products 86 (2016) 273–278

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Water sorption behaviour of by-products from the rice industry

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ARTICLE INFO

Article history:
Received 9 January 2016
Received in revised form 22 March 2016
Accepted 3 April 2016
Available online 7 April 2016

Keywords:
Rice flour
Starch
Adsorption
Desorption
Isotherms
Sorption heat

ABSTRACT

The adsorption and desorption isotherms of rice flour made from by-products from the rice industry and isolated starch were determined at different temperatures (25, 35, 45 and 55 °C) using a static gravimetric method. Several saturated salt solutions were selected to generate different water activities over a range of 0.09–0.91. The obtained isotherms for all systems were of Type II following the BET classification. The observed hysteresis cycles were of Type H3 for all tested systems according IUPAC classification. GAB ($R^2 > 0.993$, $E_{RMS} < 3.9\%$) and Chung-Pfost ($R^2 > 0.992$, $E_{RMS} < 3.9\%$) models nicely fitted all experimental isotherms. The net isosteric sorption heat, calculated by means of Clausius–Clapeyron equation, decreased when moisture content increased. The maximum values of net isosteric sorption heat (kilojoules per mole) were approximately 51 and 58 for rice flour and 34 and 42 for rice starch, for adsorption and desorption processes, respectively, in the range of temperature from 25 °C to 55 °C.

1. Introduction

Rice flour is the most common cereal grain flour for the production of gluten-free products due to its bland taste, white colour, digestibility, lightness and hypoallergenic properties. In addition, other attributes such as the low content of protein, sodium and fat as well as the presence of easily digested carbohydrates make rice the flour preferred for patients suffering from food allergies (Moreira et al., 2012; Torres et al., 2014). The main by-products in rice milling are rice hull, rice germ and bran layers, and broken rice. Most rice varieties are composed of roughly 20% rice hull or husk, 11% bran layers, and 69% starchy endosperm, referred to the total milled rice (Gujral and Rosell, 2004). In this context, this study was motivated by the interest on the knowledge of the moisture sorption behaviour of the rice flour made of by-products and isolated starch, which could be valuable information on its drying behaviour and storage quality, as a strategy to add value to the rice processing industry.

Understanding of the sorption properties is essential in regard to stability and acceptability of starchy materials, drying process modelling, design and optimization of drying equipment, calculation of moisture changes which may occur during storage, and for selecting appropriate packing materials (Fasina, 2006; Oyelade et al., 2008). The sorption characteristics can be influenced by temperature or water activity (*i.e.* ratio between vapour pressure of water in the foodstuff and vapour pressure of pure water at the same temperature). The water activity is one of the main control variables in food preservation technology (McMinn and Magee, 2003). The quality of the product on storage is largely depended on the water activity of the product which in turn depends on the moisture content and temperature of storage. In the drying process, equilibrium moisture content represents the moisture content of the product which is approached at the completion of the process. It determines the minimum moisture content to which foodstuff (*i.e.* flours) can be dried under a given set of drying conditions (Koloor et al., 2006).

The relationship between total moisture content and water activity of food at constant temperature, it is known as moisture sorption isotherm. Moisture sorption isotherms can be constructed either by adsorption (*i.e.* starting from $a_w \approx 0$) or desorption (*i.e.* starting from $a_w \approx 1$) processes. The phenomenon of hysteresis is produced when equilibrium moisture content at a given water activity do not present the same value in both the processes (Bell and Labuza, 2000). Hysteresis cycles can be classified into four types, H1–H4, following the IUPAC classification (Sing et al., 1985). Namely, Type H1 is a fairly narrow cycle with very steep and nearly parallel adsorption and desorption branches. Contrarily, Type H2 cycle is broad with a long and almost flat plateau and a steep desorption branch. Types H3 and H4 do not terminate in a plateau at high water activity and the limiting desorption boundary curve is consequently more difficult to establish. The characteristic features of above types of cycle are associated with certain well defined pore

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http://dx.doi.org/10.1016/j.indcrop.2016.04.014
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structures as explained in detail elsewhere (see as *e.g.* Moreira et al., 2010).

Therefore, the main aim of this work was to determine the water adsorption and desorption isotherms of rice flour and isolated rice starch over a range of temperatures and water activities commonly experienced for starchy materials. Parallel objectives included the presentation of the effect of temperature on sorption isotherms, the hysteresis cycles, the fitting of the water sorption isotherms using two widely recommended isotherm models and the assessment of the net isosteric sorption heats at different moisture levels for rice flour and isolated starch.

2. Materials and methods

2.1. Raw materials

Rice processing by-products (*i.e.* rice bran and broken rice grains) were kindly provided by a local manufacturer (Portugal). Rice samples were milled in a stainless steel grinder, subsequently rice flour particle size was determined by previous sieving of the material as reported elsewhere (*e.g.* Moreira et al., 2012). Distribution of particle size for this flour was of 200–80 μm (29.8%) and < 80 μm (71.2%).

Rice starch was isolated using a representative portion of rice flour (200 g), following the protocol previously reported for other gluten-free flour (Moreira et al., 2011). Briefly, rice flour was mixed with 400 mL of distilled water (ratio 1:2). The mixture was filtered and separated into residue and filtrate. The residue was mixed again with water in the same ratio and re-filtered. The second filtrate was added to the first one and allowed to settle over 24 h. Settled solids were separated from the supernatant and washed several times with distilled water using a vacuum system, until a clear wash and white starch were obtained. The resulting starch was dried in a vacuum oven at 50 °C. Average particle size of the obtained starch was less than 80 μm. Moisture content in dry basis (d.b.) was 12.9% for rice starch and 12.6% for rice flour (AOAC, 1995).

2.2. Experimental sorption isotherms

The equilibrium moisture content, X (kg water/kg d.b.), for adsorption and desorption of rice flour and isolated starch at several temperatures (25, 35, 45 and 55 °C) and over a wide water activity, a_W (–), range (from 0.09 up to 0.91) were experimentally determined following gravimetric static procedure based on the device proposed by Evans and Critchfield (1933). The different relative humidities of the atmospheres were created using several saturated salt (KOH, LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, NH_4NO_3, NaCl, KCl and $BaCl_2$) solutions prepared following previous recommendations (Greenspan, 1977). The changes of water activity of the salt solutions due to change in temperature were estimated using the relations reported by Labuza et al. (1985). Triplicate samples (approximately, 0.5 g) were stored on Petri dishes inside jars in a constant relative humidity atmosphere and were periodically weighed until to reach constant weight (±0.0004 g) in an analytical balance (accuracy ± 0.0001 g) during approximately two months. At water activity (>0.6), small amounts of crystalline thymol were placed in the jars in order to avoid the microbial degradation. After reaching equilibrium, the moisture content of each sample was determined by drying in a vacuum oven at 70 °C and 15 kPa (AOAC, 1995).

Note here that it was necessary, before introducing samples of rice flour and rice starch into saturated salts solutions, to increase the moisture content by means of a saturated water system up to 0.5 kg(kg.d.b.)$^{-1}$ (desorption isotherms) and decrease the moisture content by means of a drying up to 0.03 kg(kg.d.b.)$^{-1}$ (adsorption isotherms) in order to confirm the type of process (adsorption or desorption). For both the cases the operation temperature was of 40 °C in both the processes and the process finished when constant weight was reached.

2.3. Sorption isotherms models

The Guggenheim-Anderson-de Boer (GAB) model (Van den Berg and Bruin, 1981) was used in this work to describe the relationship between equilibrium moisture content and water activity at each temperature in the full range of water activity:

$$X = \frac{X_M C K a_W}{[(1 - K a_W)(1 - K a_W + C K a_W)]} \quad (1)$$

where X_M is the moisture content of the monolayer, *C* is related to sorption heat of the first layer and *K* is related to the heat of sorption of the multilayer. These parameters have physical relevance and they depend on the temperature and characteristics the product and can be calculated by Arrhenius equations (Kim and Bhowmik, 1994):

$$X_M = X_{MO} \exp\left(H/RT\right) \quad (2)$$

$$C = C_O \exp\left[\left(h_M - h_N\right)/RT\right] \quad (3)$$

$$K = K_O \exp\left[\left(h_L - h_N\right)/RT\right] \quad (4)$$

where *R* is the ideal gas constant (8.314 J (mol K)$^{-1}$), *T* represents the absolute temperature (K), *H* is the heat of GAB model (kJ mol^{-1}), h_L is the heat of condensation of water vapour. The heat of condensation is a function of the temperature and a linear relationship (R^2 = 0.997) can be established between 25 and 55 °C Weast (1982):

$$h_L = 45.04 - 0.0438T \quad (5)$$

h_M-h_N and h_L-h_N show strength of the bounding between water molecules in the respective layers. Particularly, h_M-h_N is the difference between monolayer and multilayer sorption enthalpy, and h_L-h_N represents the difference between the condensation heat of water and the multilayer sorption heat.

The Chung-Pfost model (Chung and Pfost, 1967), recommended as a standard to describe the equilibrium moisture content-water activity data of cereals in ASAE Data D245.4 (Chen and Morey, 1989), was also used in this study to express the experimental sorption isotherms for the hysteresis cycle for rice flour and isolated rice starch in the full range of water activity.

$$X = A + B\ln(-\ln a_w) \quad (6)$$

The parameters (X_M, C, K, A and B) of both used models (GAB and Chung-Pfost) were estimated by non-linear regression procedure employing Table Curve software (Jandel Scientific).

2.4. Net isosteric heat of sorption

The net isosteric sorption heat, h_e, is defined by the difference between total isosteric sorption heat and condensation heat. Estimation of the net isosteric heat of sorption at constant moisture contents can be made from the slope of the Clausius-Clapeyron equation:

$$\ln\left(\frac{a_{W2}}{a_{W1}}\right) = \frac{h_e}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (7)$$

Water activity values (a_{w2} and a_{w1}) were calculated using GAB model at each moisture content and temperature tested.