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SORPTION CHARACTERISTICS OF BUCKWHEAT GRAIN

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Abstract

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Moisture equilibrium data (adsorption and desorption) of buckwheat grain were determined using the static gravimetric method of saturated salt solutions at three temperatures 10, 25 and 40°C. The range of water activities for each temperature was between 0.11 and 0.85. Equilibrium moisture content decreased with increase in storage temperature at constant water activity. A suitable model was selected to describe the water sorption isotherms. The monolayer moisture content of the grain was estimated and the optimal storage water activity was proposed.

Key words: buckwheat, sorption, isotherms, monolayer moisture, modeling, water activity

Introduction

With recent consumer interest in functional food, buckwheat grain (*Fagopyrum esculentum* Moench) is increasingly being used as an ingredient and a functional modifier in many foods (Li and Zhang, 2001; Otles and Cagindi, 2006; Radovic et al., 1996; Wijngaard and Arendt, 2006).

Sorption properties of foods (equilibrium moisture content and monolayer moisture) are essential for the design and optimization of many processes such as drying, packaging and storage (Al-Muhtaseb et al., 2002). The water activity of the grains as a hygroscopic material exerts a strong influence on its quality and technological properties (Abdullah et al., 2000). Mazza (1993) investigated the influence of storage, relative humidity, and temperature on lipid, and protein content, color and flavor characteristics of buckwheat and developed recommendations for long-term storage of buckwheat at a low temperature at a water activity below 0.45.

Tagawa et al. (1993) obtained the sorption isotherms of buckwheat without reading the hysteresis effect. Koloor Tabatabaee et al. (2006) and Mazza (1993) built the sorption isotherms using solely five experimental points, as between them only one is at water activity under 0.5.

A number of models have been suggested in the literature for the dependence between the equilibrium moisture content (EMC) and the water activity (a_W) (Van der Berg and Bruin, 1981). The modified Chung-Pfost, modified Henderson, modified Halsey, modified Oswin and Guggenheim-Anderson-de Boer (GAB) equations which incorporate the temperature effect have been adopted as standard equations by the American Association of Agricultural and Biological Engineers for the description of sorption isotherms (ASABE, 2007).

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The monolayer moisture content value and the corresponding water activity (a_{Wm}) are important parameters in food storage and deterioration. The higher values of a_W led to the faster reaction rate because of the greater solubility and increased mobility. If a product is susceptible to oxidation of unsaturated lipids, the rate of shelf life loss increases as a_W decreases below a_{Wm} (Bell and Labuza, 2000).

The objectives of this work are: 1. to obtain experimental equilibrium sorption isotherms of buckwheat grain at 10, 25, and 40°C; 2. to find out the suitable model describing the isotherms; 3. to calculate the monolayer moisture content.

Materials and Methods

Material

Buckwheat grain variety "Dialog" produced in Bulgaria was used in this study. AOAC standard procedures (AOAC, 1990) were used for the determination of the proximate chemical composition (on wet basis): moisture – 14.9 %, crude fat – 3.5 %, protein – 13.5 %, carbohydrate – 64.6 %, fiber -3.5%.

Procedure

The EMC of buckwheat grain was determined at 10, 25, and 40 °C. The static gravimetric method was applied (Bell and Labuza, 2000; Wolf et al., 1985). For the adsorption process, grain was dehydrated in a dessicator with P_2O_5 at a room temperature for 20 days prior to the beginning of the experiment. The desorption isotherms were determined on samples hydrated in a glass jar over distilled water at a room temperature to moisture content approximately 23 % dry basis (d.b.). Samples of 1 ±0.02 g were weighed in weighing bottles. The weighing bottles were then put in hygrostats with eight saturated salt solutions (LiCl, $MgCl_2$, CH_3COOK, K_2CO_3, $Mg(NO_3)_2$, NaBr, NaCl, KCl), used to obtain constant water activities environments (Greenspan, 1977). All used salts were of reagent grade. At high water activities (a_W > 0.70) crystalline thymol was placed in the hygrostats to prevent the microbial spoilage of the grain (Bell and Labuza, 2000). The hygrostats were kept in thermostats at 10, 25, and 40 +/- 0.2°C. Samples were weighed in balance, sensitivity +/- 0.0001 g every three days. Equilibrium was reached when three consecutive weight measurements showed a difference of less than 0.001 g. The moisture content of each sample was determined by the oven method by means of triplicate measurements.

Analysis of data

The description of the sorption isotherms was verified according to the following five models proposed in ASABE Standard D245.6 (ASABE, 2007):

Modified Chung-Pfost $$a_W = \exp\left[\frac{-A}{t+B}\exp(-CM)\right] \quad (1)$$

Modified Halsey $$a_W = \exp\left[\frac{-\exp(A+Bt)}{M^C}\right] \quad (2)$$

Modified Oswin $$M = (A+Bt)\left(\frac{a_W}{1-a_W}\right)^C \quad (3)$$

Modified Henderson $$1-a_W = \exp[(-A(t+B)M^C] \quad (4)$$

GAB $$M = \frac{AB'C'a_W}{(1-B'a_W)(1-B'a_W+B'C'a_W)} \quad (5)$$

$$B' = B\exp\left(\frac{h_1}{RT}\right) \quad (6)$$

$$C' = C\exp\left(\frac{h_2}{RT}\right), \quad (7)$$

where M is the moisture content (% d.b.), a_W is the water activity (fraction), A, B, C, h_1 and h_2 are coefficients; t is the temperature (°C), T is the temperature (K); R is the universal gas constant ($J.mol^{-1}.K^{-1}$).

A nonlinear, least squares regression program was used to fit the five models to the experimental data (all replications). The suitability of the equations was evaluated and compared using the mean relative error (%), standard error of moisture and randomness of residuals (Chen and Morey, 1989):

where M_i and Mi are experimentally observed and predicted by the model values of the EMC, respectively, N is the number of data points, and d_f is the degree of freedom (number of data points minus number of constants in the model).

Mean relative error $P = \frac{100}{N} \sum \left| \frac{M_i - \hat{M}_i}{M_i} \right|$ (8)

Standard error of moisture $SEM = \sqrt{\frac{\sum \left(M_i - \hat{M}_i\right)^2}{df}}$ (9)

Residual $e = M_i - \hat{M}_i$, (10)

The monolayer moisture contents (M_e) for each temperature were calculated using the Brunauer-Emmett-Teller (BET) equation with the experimental data for water activities up to 0.45 (Bell and Labuza, 2000; Brunauer et al., 1938):

BET $M = \frac{M_e C a_W}{(1 - a_W)(1 - a_W + C a_W)}$ (11)

Results and Discussion

The obtained adsorption and desorption isotherms at 25°C are presented in Figure 1. The hysteresis effect is statistical insignificant in the most experimental points. Similar hysteresis lack is observed for the isotherms at 10°C and 40°C, which confirms the results obtained from Tagawa et al. (1993).

The unified (adsorption and desorption) mean values of EMC at the respective water activities and temperatures are presented in Figure 2. The sorption isotherms have an S-shape profile. The EMC values decreased with an increase in the temperature at constant a_W. Similar trends for many foods have been reported in the literature Al-Muhtaseb et al. (2002). The comparison with the published data for buckwheat grown in Asia (Tagawa et al., 1993) and in America (Mazza, 1993; Koloor Tabatabaee et al., 2006) shows that the buckwheat grown in Europe is with higher sorption capacity independently of the similar chemical composition.

The coefficients of the models, *P* and *SEM* values are presented in Table 1. The *P* and *SEM* values obtained by the Modified Chung-Pfost model were lower. The comparison between measured and predicted values with this model of EMC in Figure 2, confirm the goodness of fit. Figure 3 shows randomly distribution of the residuals of Modified Chung-Pfost model. Similar results were obtained in the literature for another grain – medium rough rice (Basunia and Abe, 2001) and amaranth (Pagano and Mascheroni, 2005).

The values of BET monolayer obtained with the standard procedure are present in figure 4. The val-

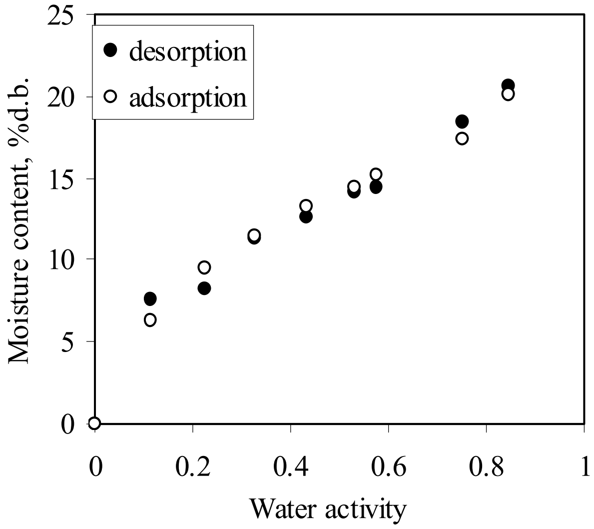

Fig. 1. Equilibrium sorption isotherms of buckwheat grain (adsorption and desorption) at 25°C

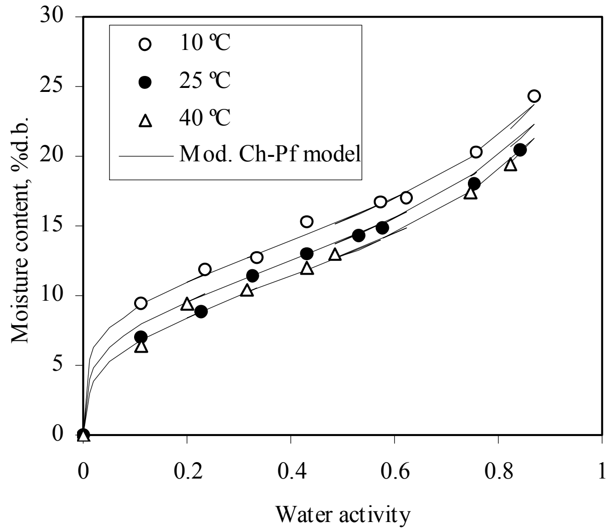

Fig. 2. Equilibrium sorption isotherms (measured and predicted with Chung-Pfost model) at several temperatures

Table 1
Coefficients (*A*, *B*, *C*, h_1, h_2), mean relative error (*P*, %) and standard error of moisture (*SEM*) of the models

Model	*A*	*B*	*C*	*h* 1	*h* 2	*P*	*SEM*
Mod. Chung-Pfost	638.7255	38.86128	0.190578			3.58	0.58
Mod. Oswin	15.91225	-0.08017	0.254796			5.44	0.88
Mod. Halsey	7.718706	-0.01722	2.94587			6.37	0.93
Mod. Henderson	0.000211	18.69474	1.72488			19.34	2.75
GAB	11.34283	0.059308	18.39309	5555973	657157	4.75	0.78

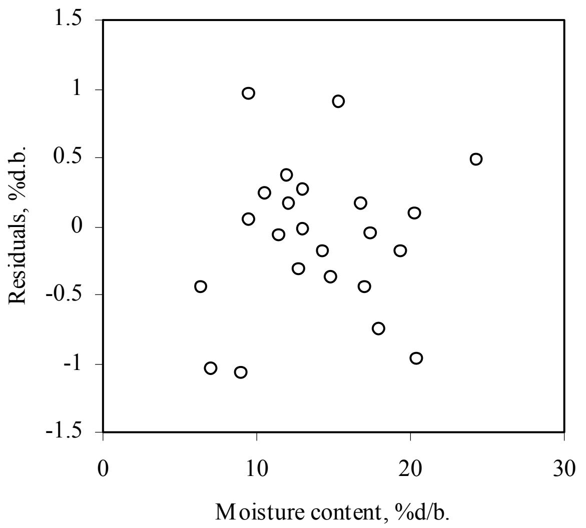

Fig. 3. Distribution of residuals for the Modified Chung-Pfost model

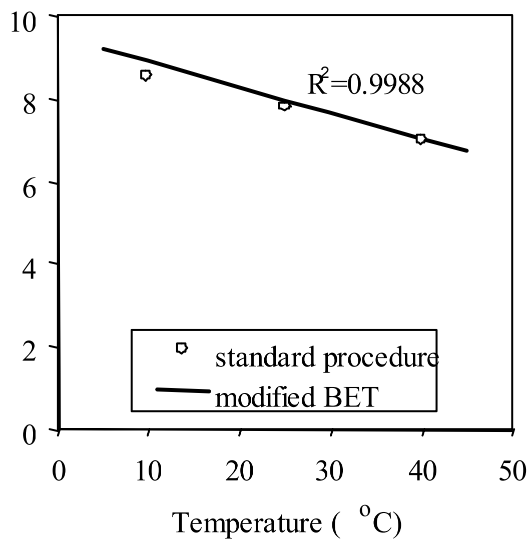

Fig. 4. Effect of temperature on the monolayer moisture content

ues decreased with an increase in temperature. Menkov et al. (1999) established a linear dependence between monolayer moisture content and temperature for a large number of biological products and proposed a three-parameter modification of BET equation incorporating the temperature effect. The parameters of modified BET equation were obtained with a program for nonlinear regression with all experimental data for $a_W < 0.45$:

Figure 4 compare the BET monolayer moisture obtained with the standard procedure and modified BET equation and shows a good agreement.

The water activity value (a_{Wm}) corresponding to the monolayer moisture content was calculated from equation (12) by substituting $M = M_e$ (Iglesias and Chirife, 1976) as:

We recommend this value (a_{Wm} = 0117) for buckwheat as optimal for grain storage. The value of a_{Wm}

Modified BET

$$M = \frac{(A - Bt)Ca_W}{(1 - a_W)(1 - a_W + Ca_W)} =$$

$$\frac{(9.4989 - 0.06133t)56.8793a_W}{(1 - a_W)(1 - a_W + 56.8793a_W)} \qquad (12)$$

Monolayer moisture

$$M_e = A - Bt = 9.4989 - 0.06133t \qquad (13)$$

is inversely proportional to the value of model constant *C* and is independent of temperature in the diapason from 10°C to 40°C.

$$a_{Wm} = \frac{\sqrt{C} - 1}{C - 1} = \frac{\sqrt{56.8793} - 1}{56.8793 - 1} = 0.117 \qquad (14)$$

Conclusions

The sorption capacity and monolayer moisture content of buckwheat grain decreased with an increase in temperature at constant water activity. The modified Chung-Pfost and GAB models are suitable for describing the relationship between the equilibrium moisture content, the water activity, and the temperature for the buckwheat grain. The modified BET model is suitable for calculating of monolayer moisture for several temperatures and water activity corresponding to the monolayer moisture.

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