DETERMINATION OF MOISTURE ADSORPTION ISOTHERMS OF RICE FLOUR USING A DYNAMIC VAPOR SORPTION TECHNIQUE

Aleida J. Sandoval, José A. Barreiro and Alejandro J. Müller

SUMMARY

Moisture adsorption isotherms for rice flour were determined in a temperature range of 5 to 45°C using a dynamic vapor sorption technique. A water activity range from 0 to 0.945 was studied. Typical type-II isotherms were obtained. The equilibrium moisture content (EMC) decreased with increasing temperature over the whole water activity range studied. The EMC did not exhibit isotherm cross-over with temperature as previously reported for rice flour using thymol as an antimicrobial agent. The adsorption data obtained was fitted to various isotherm models. It was found that EMC data was better described by the modified GAB model. Moisture sorption data obtained in this study can be considered more reliable and accurate than those previously reported for this product using static gravimetric techniques since no antimicrobial agents were used during experimentation.

Introduction

Dynamic vapor sorption (DVS) techniques are currently used to determine the sorption characteristics of food products. When compared with the static gravimetric technique (SGT), extensively used as a classical method in the existing scientific literature, DVS techniques have shown many advantages, including shorter equilibration time. As a consequence, no antimicrobial agents are needed at elevated water activities to prevent microbial growth and sample deterioration during experimentation. The use of antimicrobial agents could alter isotherm performance and the reliability of the results obtained (Yu *et al*., 2008; Sandoval *et al*., 2011). Among others, DVS techniques have the advantage of allowing determination of adsorption rates under constant or varying hydration conditions with the same sample, and further calculation of apparent water diffusion coefficients, as illustrated by Román-Gutiérrez *et al*. (2003).

A large number of moisture sorption isotherm models have been proposed in the literature for different food products. They include those derived theoretically and based on thermodynamic considerations such as the BET (Brunauer, Emmett and Teller; Brunauer *et al*., 1938) and the GAB (Guggenheim-Anderson-De Boer; Van den Berg and Bruin, 1981) models; and additional semi-empirical and empirical models (Peleg, 1993; Viollaz and Rovedo, 1999). Many other empirical two-parameter isotherm models have also been proposed for different a_w ranges. Although at present there is not a unique model to accurately represent moisture sorption data in the whole range of water activity, due mainly to the complex sorption mechanisms involved, the GAB equation has been recognized as the most versatile sorption model. Quirijns *et al*. (2005) underlined the GAB sorption isotherm ability to deduce the thermodynamic state of the different types of water (bound and free) in a food system, as well as the transition among them. However, it has been claimed that the GAB model does not hold on rough or irregular surfaces such as those of grains and other starchy powders, and that it is more appropriate for homogeneous planer surfaces. An isotherm describing the multilayer adsorption on fractal surfaces, based on BET theory, was presented by Aguerre *et al*. (1996) and successfully applied to amaranth starch by Calzetta-Resio *et al*. (1999). On the other hand, Viollaz and Rovedo (1999) proposed an extension of the GAB model to correlate sorption data for a_w values that include the range above 0.9, not considered in the original GAB model. This model has also been successfully applied to starchy and powdery products in our previous work (Perdomo *et al*., 2009; Brett *et al*., 2009; Barreiro *et al*. 2010).

Rice flour is frequently used as an ingredient in many starchy processed food products. Knowledge of the sorption characteristics of rice flour is important to establish the packaging requirements and stability of products containing this ingredient, but few papers have been found in the reviewed literature. Durakova and Menkov (2004) studied the sorption characteristics of rice flour in a temperature range of 10 to 30°C, in a water activity range of 0.11 to 0.85 that excluded elevated water activities. Sigmoidal type-II isotherms were found. Brett *et al*. (2009) presented

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Aleida J. Sandoval. Agroindustrial Engineer, Universidad de los Llanos "Ezequiel Zamora" (UNELLEZ), Venezuela. M.Sc. in Food Science, USB, Venezuela. Ph.D. in Food Science and Technology, University of Reading, UK. Professor, USB, Venezuela. Address: Departamento de Tecnología de Procesos Biológicos y Bioquímicos, USB. Apartado 89000. Caracas 1080-A, Venezuela. e-mail: asandova@usb.ve

José A. Barreiro. Chemical Engineer, Universidad Central de Venezuela. M.Sc. and Ph.D. in Food Science, Louisiana State University, USA. Retired Professor, USB, Venezuela. Currently with J. A. Barreiro & Assocs., Venezuela.

Alejandro J. Müller. Materials Engineer, USB, Venezuela. M. Sc. in Chemistry, Instituto Venezolano de Investigaciones Científicas, Venezuela. Ph.D. in Physics, Bristol University, UK. Professor, USB, Venezuela.

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DETERMINACIÓN DE ISOTERMAS DE ADSORCIÓN DE HUMEDAD DE LA HARINA DE ARROZ USANDO UNA TÉCNICA DINÁMICA DE SORCIÓN DE VAPOR

Aleida J. Sandoval, José A. Barreiro y Alejandro J. Müller

RESUMEN

Las isotermas de adsorción de humedad en la harina de arroz fueron determinadas en un intervalo de temperatura entre 5 y 45°C usando una técnica de sorción de humedad dinámica. Se estudió un intervalo de actividad de agua entre 0 y 0,945 y se obtuvieron isotermas tipo II. En toda la extensión de actividades de agua estudiada, el contenido de humedad de equilibrio (CHE) disminuyó con incrementos de temperatura. Al contrario de lo reportado en estudios previos para la harina de arroz, usando timol como agente antimicrobiano, el CHE no exhibió cruce de isotermas con la temperatura. Los datos de adsorción obtenidos fueron ajustados a varios modelos de isotermas. Se encontró que los datos de CHE fueron mejor descritos por el modelo modificado de GAB. Los datos de sorción de humedad obtenidos en este trabajo pueden ser considerados más confiables y exactos que los reportados previamente para este producto usando una técnica gravimétrica estática, ya que no se usaron agentes antimicrobianos durante las determinaciones.

DETERMINAÇÃO DE ISOTERMAS DE ADSORÇÃO DE UMIDADE DA FARINHA DE ARROZ USANDO UMA TÉCNICA DINÂMICA DE SORÇÃO DE VAPOR

Aleida J. Sandoval, José A. Barreiro e Alejandro J. Müller

RESUMO

As isotermas de adsorção de umidade na farinha de arroz foram determinadas em um intervalo de temperatura entre 5 e 45°C usando uma técnica de sorção de umidade dinâmica. Estudou-se um intervalo de atividade de água entre 0 e 0.945 e se obtiveram isotermas tipo II. Em toda a extensão de atividades de água estudada, o teor de umidade de equilíbrio (TUE) diminuiu com incrementos de temperatura. Ao contrário do relatado em estudos prévios para a farinha de arroz, usando timol como agente antimicrobiano, o TUE não exibiu cruze de isotermas com a temperatura. Os dados de adsorção obtidos foram ajustados a vários modelos de isotermas. Encontrou-se que os dados de TUE foram mais bem descritos pelo modelo modificado de GAB. Os dados de sorção de umidade obtidos neste trabalho podem ser considerados mais confiáveis e exatos que os relatados previamente para este produto usando uma técnica gravimétrica estática, já que não se usaram agentes antimicrobianos durante as determinações.

sorption isotherms for rice flour at temperatures of 5, 23 and 45°C using the SGT for a water activity range from 0.08 to 0.98; these authors used crystalline thymol as an antimicrobial agent at elevated water activities. Isotherm crossover with temperature was reported at elevated water activities.

In view of the above information, the aim of this work was to determine moisture sorption isotherms for rice flour at different temperatures using a DVS technique not requiring the use of antimicrobial agents that could alter isotherm performance and results reliability.

Materials and Methods

Raw material

Native rice flour with initial moisture content of 14.39% (w.b.), manufactured by Kel Industries (Venezuela), was provided by Alfonzo Rivas y Cia., Caracas, Venezuela. Proximate composition of this lot of rice flour (g per 100g, wet basis ±standard deviation) was determined in a previous study (Sandoval *et al*., 2009) and shown to be: moisture 14.39 ±0.09; protein 8.64 ±0.21; fat 0.31 ±0.00; ash 0.92 ±0.02; carbohydrates (from difference) 75.74 ±0.15.

Adsorption isotherms

Moisture adsorption isotherms of native rice flour were determined in a dynamic vapor sorption (DVS) apparatus. The experiments were carried out using an IGASorp moisture sorption analyzer (Hiden Isochema Ltd., UK), consisting on a controlled atmosphere microbalance, in which the relative humidity and the change in sample weight were continuously monitored. The equipment has a real time processor using IGASorp System Software V6.50.42 (Hiden Analytical Ltd.). Equilibrium relative humidity (ERH) values used to build the isotherm were defined by the user. The software determined the mixing ratio of water vapor and dry ultra high purity nitrogen required to obtain each of the desired ERH values. In this process, sample weight data were analyzed to determine kinetic parameters for the prediction of equilibrium uptake in real-time. In order to determine the whole isotherm, this process was repeated for all ERH values set. The maximum operational water activity that can be obtained in this equipment is 0.95. The equipment is able to regulate sample temperature. Results obtained were exported to an MS Excel file and plotted.

Isotherms were obtained by adsorption by setting thirteen ERH values, covering a range from 0 to 94.5%. An amount of 10 ±1mg of rice flour was placed inside the balance and dried in a zero relative humidity ambient for 3h at 30°C, using ultra high purity nitrogen. A maximum time of 720min for complete data collection at each RH-level set (timeout) was used if the equilibrium criterion was not already reached. The equilibrium criterion for stability was defined by the time the weight had relaxed to within 1% of the equilibrium uptake. The isotherms were obtained in triplicate at temperatures of 5, 23 and 45°C.

Adsorption data analysis

Adsorption data obtained were adjusted to various sorption models used for starchy products: BET, Peleg, GAB and modified GAB (see Table I). The goodness of fit was evaluated by determining the correlation coefficient (R^2) and the root mean square error (RMSE). For this purpose, non linear regression was carried out using Matlab™ version 6.5. The monolayer water content was estimated from the BET and GAB models.

The Clausius-Clapeyron equation (Eq. 5) was used to determine the effect of temperature on the sorption data and to calculate the net isosteric heat of sorption. Its expression is

$$\frac{\partial \ln (a_w)}{\partial (1/T)} = -\frac{q_{st}}{R} \quad (5)$$

where T: absolute temperature (K), q_{st}: net isosteric heat of sorption ($J \cdot mol^{-1}$), and R: universal gas constant ($8.314 J \cdot mol^{-1} \cdot K^{-1}$).

Results and Discussion

The adsorption isotherms for rice flour and the error bars (±one standard deviation) for the EMC values obtained are shown in Figure 1. A sigmoidal shape characteristic of type II isotherms, based on Brunauer's classification (Brunauer *et al*., 1940; Al-Muhtaseb *et al*., 2002) was obtained. The isotherms for rice flour presented similar behavior to those of other starch-rich foods (McMinn and Magee, 1999; Al-Muhtaseb *et al*., 2004; Durakova and Menkov, 2004; Brett *et al*., 2009; Perdomo *et al*., 2009).

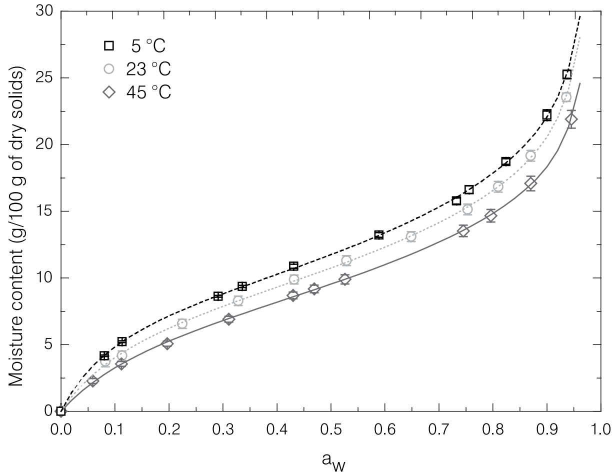

Figure 1. Adsorption isotherms of rice flour for a temperature range of 5 to 45°C. Open squares: 5°C, open circles: 23°C, open diamonds: 45°C. Modified GAB fits are shown on the graph (dashed line: 5°C, dotted line: 23°C, solid line> 45°C).

The effect of temperature on moisture adsorption isotherms can be appreciated in Figure 1. As expected, for a given water activity, the corresponding EMC decreases with increasing temperature. This behavior has been attributed to the higher energy levels and lower stability of water molecules at higher temperatures, favoring their separation from the binding sites present in the food matrix (Palipane and Driscoll, 1992). No cross-over was observed due to the effect of temperature, as reported by Brett *et al.* (2009) for this product using the SGT. These authors used thymol as an antimicrobial agent for water activities >0.80. The presence of isotherm cross-over due to the effect of temperature was attributed to the use of thymol at elevated water activities (Sandoval *et al*., 2011). The moisture sorption data obtained in the present work using a DVS technique can be considered more reliable and accurate than those determined by means of SGT requiring the use of antimicrobial additives at elevated water activities.

Adsorption data obtained using the DVS technique for rice flour at temperatures of 5, 23 and 45°C were fitted to the isotherm models presented in Table I. The results for the constants of the various isotherms tested, as well as the corresponding R^2 and RMSE values, are shown in Table II. Excellent fitting to the experimental data was obtained for all the models tested. However, Peleg and modified GAB models showed the best results. The modified GAB model was selected because it is able to describe the whole isotherm. This model exhibited elevated R^2 values (0.999) and low RMSE values (0.001-0.002). The modified GAB model was used to draw the isotherms shown in Figure 1. The value of constants A, B, C and D presented in Table II for the different temperatures studied were substituted in Eq. 4.

The monolayer water content calculated using the BET and GAB models is represented by constants A in Table II. The rice flour monolayer water content values in a temperature range of 5 to 45°C were lower for the BET model (0.069 to 0.055g

TABLE I
ISOTHERM MODELS FOR EXPERIMENTAL DATA FITTING AND THEIR RANGE OF APPLICABILITY
CONSTANTS RELATED TO THE TEMPERATURE EFFECT

Model	Mathematical expression	a_w range of applicability	Equation
BET (Brunauer, Emmett and Teller, 1938)	$M = A \cdot B \cdot a_w / (1 - a_w) \cdot (1 + (B - 1) \cdot a_w)$	<0.50	(1)
Peleg (Peleg, 1993)	$M = A \cdot a_w^C + B \cdot a_w^D$	<~0.9	(2)
GAB (Van den Berg and Bruin, 1981)	$M = \frac{A \cdot B \cdot C \cdot a_w}{(1 - C \cdot a_w) \cdot (1 - C \cdot a_w + B \cdot C \cdot a_w)}$	<0.95	(3)
Modified GAB (Viollaz and Rovedo, 1999)	$M = \frac{A \cdot B \cdot C \cdot a_w}{(1 - C \cdot a_w) \cdot (1 - C \cdot a_w + B \cdot C \cdot a_w)} + \frac{A \cdot B \cdot C \cdot D \cdot a_w^2}{(1 - C \cdot a_w) \cdot (1 - a_w)}$	<0.98	(4)

a_w: water activity
In Eqs. 1, 3 and 4, A represents the monolayer moisture content of the BET and GAB models, respectively.
B in Eqs. 1, 3 and 4, and C in Eqs. 3 and 4 are energy constants related to the temperature effect.

water/g dry solids) than for the GAB model (0.079 to 0.066g water/g dry solids). Values reported by Rahman (1995) for cereal products ranged from 0.051 to 0.086g water/g dry solids. These values are similar to those determined herein for rice flour. The value of the monolayer water content decreased with increasing temperatures regardless of the model used (Table II).

Values for the monolayer water content of rice flour have been reported by Durakova and Menkov (2004) as 0.0714-0.0680g water/g dry solids in a temperature range of 10-40°C using the BET equation. These values are in agreement with those reported in the present work (Table II). Toğrul and Arslan (2006), working with Baldo type rice, reported abnormally high monolayer water content values using the GAB model, and from 0.0937 to 0.0968kg water/kg dry solids (25-45°C) using the adsorption data with the BET model. These values are higher than those obtained in this study. Brett *et al.* (2009) presented monolayer water contents (5-45°C) ranging from 0.064 to 0.080g water/g dry solids when the BET equations were used. These values are of the same order of magnitude as those obtained in this work.

Monolayer water content values reported by Brett *et al.* (2009) using the GAB model were higher than those obtained in this study. This was probably due to EMC deviations at elevated water activities reported by these authors showing isotherm cross-over with temperature. These abnormal data were taken into account when fitting the GAB model in order to obtain the monolayer water content.

Figure 2 shows the variation of the net isosteric heat of sorption with moisture content. As expected, net isosteric heat of sorption decreased with increasing moisture content; being this relationship described by

$$q_{st} = 23.38e^{-0.137MC} \quad R^2 = 0.996 \tag{6}$$

with the moisture content value (MC in Eq. 6) in g/100g of dry solids.

As shown in Figure 2, the net isosteric heat of sorption varied from 0.5 to 10kJ·mol^{-1} in a moisture content range of 6 to 24% (d.b.). Durakova and Menkov (2004) reported values for rice flour (2.3-22.3kJ·mol^{-1}) in an MC range of 10-22% (d.b.); while Stripatrawan and Jantawat (2006) found values for Jasmine rice crackers of 0.1-24.9kJ·mol^{-1} in a range of moisture content of 1 to 28% (d.b.) for the isosteric heat of sorption.

TABLE II
FITTING PARAMETERS FOR THE MATHEMATICAL EXPRESSIONS APPLIED TO ADSORPTION DATA OF RICE FLOUR AT DIFFERENT TEMPERATURES

Model	Constants	Temperature (°C)		
		5	23	45
BET	A	0.069	0.063	0.055
	B	15.64	12.76	10.97
	R^2 (RMSE)	0.997 (0.002)	0.997 (0.002)	0.998 (0.002)
Peleg	A	0.132	0.165	0.092
	B	0.174	0.118	0.152
	C	7.38	0.616	7.41
	D	0.561	7.81	0.670
	R^2 (RMSE)	0.999 (0.001)	0.999 (0.001)	0.999 (0.001)
GAB	A	0.079	0.073	0.066
	B	18.68	14.92	12.39
	C	0.733	0.738	0.743
	R^2 (RMSE)	0.996 (0.005)	0.996 (0.005)	0.995 (0.005)
Modified GAB	A	0.095	0.091	0.085
	B	14.50	11.46	9.19
	C	0.601	0.587	0.578
	D	0.002	0.003	0.003
	R^2 (RMSE)	0.999 (0.001)	0.999 (0.002)	0.999 (0.001)

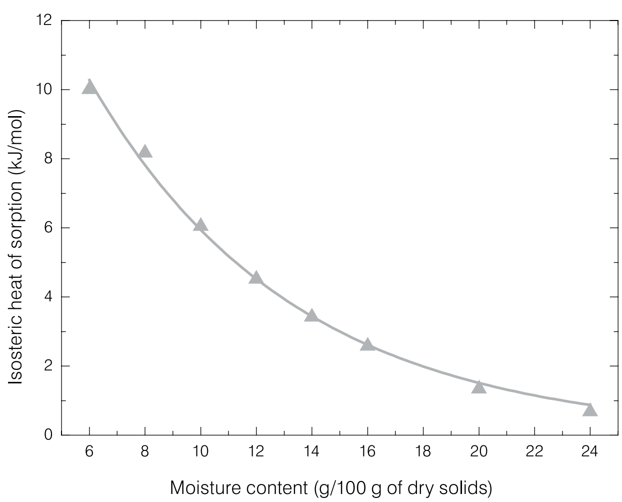

Figure 2. Isosteric heat of sorption of rice flour as a function of equilibrium moisture content.

Conclusions

Adsorption isotherms of rice flour were determined at temperatures of 5, 23 and 45°C using a dynamic sorption vapor technique. Typical type II isotherms were obtained. No isotherm cross-over with temperature was evidenced for these products as reported by other authors using thymol as antimicrobial agent. Adsorption data were better described by the modified GAB model in the whole temperature range studied, evidenced by elevated R^2 values and low RMSE values for both products. The water monolayer contents determined using BET model (a_w<0.5) were similar to previous data obtained with a static technique; while those obtained from the GAB model (a_w<0.95) were different, a fact attributed to the variation of moisture content values obtained when thymol is used as an antimicrobial agent at elevated water activity and particularly high temperatures. In general, moisture adsorption data of rice flour determined by the dynamic technique used in this work can be considered more accurate than those obtained in a previously reported work, where thymol was used at elevated water activities.

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REFERENCES

Aguerre RJ, Viollaz PE, Suárez C (1996) A fractal isotherm for multilayer adsorption in foods. *J. Food Eng. 30*: 227-238.

Al-Muhtaseb AH, McMinn WA, Magee TR (2002) Moisture sorption isotherm characteristics of food products: a review. *Inst. Chem. Eng. Trans IchemE. 80*, Part C: 118-127.

Al-Muhtaseb AH, McMinn WA, Magee TR (2004) Water sorption of starch powders Part 1: mathematical description of experimental data. *J. Food Eng. 61*: 297-307.

Barreiro Jr. JA, Minichini A, Barreiro JA, Sandoval AJ (2010) Water sorption isotherms of NPK 10-20-20/4 MOP fertilizer. *Indust. Eng. Chem. Res. 49*: 887-892.

Brett B, Figueroa M, Sandoval AJ, Barreiro JA, Müller AJ (2009) Moisture sorption characteristics of starchy products. Oat flour and rice flour. *Food Biophys. 4*: 151-157.

Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc. 60*: 309-320.

Brunauer S, Deming LS, Deming WE, Troller E (1940) On the theory of Van der Waals adsorption of gases. *J. Am. Chem. Soc. 62*: 1723-1732.

Calzetta-Resio A, Aguerre RJ, Suárez C (1999) Analysis of the sorptional characteristics of amaranth starch. *J. Food Eng. 42*: 51-57.

Durakova AG, Menkov ND (2004) Moisture sorption characteristics of rice flour. *Nahrung/ Food 48*: 137-140.

McMinn WA, Magee TR (1999) Studies on the effect of temperature on the moisture sorption characteristics of potatoes. *J. Food Proc. Eng. 22*: 113-128.

Palipane KB, Driscoll RH (1992) Moisture sorption characteristics of inshell macadamia nuts. *J. Food Eng. 18*: 63-76.

Peleg M (1993) Assessment of a semi-empirical four parameter general model for sigmoid moisture sorption isotherms. *J. Food Proc. Eng. 16*: 21-37.

Perdomo J, Cova A, Sandoval AJ, García L, Laredo E, Müller AJ (2009) Glass transition temperatures and water sorption isotherms of cassava starch. *Carbohyd. Polym. 76*: 305-313.

Quirijns EJ, van Boxtel AJB, van Loon WKP, van Straten G (2005) Sorption isotherms, GAB parameters and isosteric heat of sorption. *J. Sci. Food Agric. 85*: 1805-1814.

Rahman S (1995) *Food Properties Handbook*. Chapter 1. CRC. Boca Raton, FL, USA. 1-86 pp.

Román-Gutiérrez AD, Mabille F, Guilbert S, Cuq B (2003) Contribution of specific flour components to water vapor adsorption properties of wheat flours. *Cereal Chem. 80*: 558-563.

Sandoval AJ, Núñez M, Müller AJ, Della Valle G, Lourdin D (2009) Glass transition temperatures of a starchy ready to eat breakfast cereal formulation and its main components determined by DSC and DMTA. *Carbohyd. Polym. 76*: 528-534.

Sandoval AJ, Guilarte D, Barreiro JA, Lucci E, Müller AJ (2011) Determination of moisture sorption characteristics of oat flour by static and dynamic techniques with and without thymol as an antimicrobial agent. *Food Biophys. 6*: 424-432.

Stripatrawan U, Jantawat P (2006) Determination of moisture sorption isotherms of *Jasmine* rice crackers using BET and GAB models. *Food Sci. Technol. Int. 12*: 459-465.

Toğrul H, Arslan N (2006) Moisture sorption behaviour and thermodynamic characteristics of rice stored in a chamber under controlled humidity. Biosyst. Eng. 95: 181-195.

Van den Berg C, Bruin S (1981) Water activity and its estimation in food systems. In Rockland LB, Stewart GF (Eds.) *Water Activity: Influences on Food Quality*. Academic Press. New York, USA. pp. 147-177.

Viollaz PE, Rovedo CO (1999) Equilibrium sorption isotherms and thermodynamic properties of starch and gluten. *J. Food Eng. 40*: 287-292.

Yu X, Martin SE, Schimdt SJ (2008) Exploring the problem of mold growth and the efficacy of various mold inhibitor methods during moisture sorption isotherms measurements. *J. Food Sci. 73*: E69-E81.