The sorption isosteric heats of rice grains in China

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Abstract

Equilibrium moisture content (EMC) data for the grains of thirteen rice cultivars were obtained by gravimetric method at 11% to 96% equilibrium relative humidity (ERH) and 10, 20, 25, 30, and 35°C above nine saturated salt solutions. Six commonly used mathematic models, namely, BET, Modified-Guggenheim–Anderson-deBoer (MGAB), Modified-Chung-Pfost (MCPE), Modified-Henderson (MHE), Modified-Oswin (MOE), and Strohman-Yoerger (STYE), were fitted to the data with evaluating the coefficient of determination, residue sum-of-squares, standard error of estimate, mean relative percent error, and residual plots. The best fitted equations to the EMC/ERH data were MCPE and STYE, but MCPE is three-parameter, readily transformed equation and adopted in this study. The isosteric heats for both rice desorption and adsorption, and for both the sorption of Japonica and Indica rice, decreased rapidly with an increase in seed moisture content until the moisture content of 20% d.b. (dry basis) was reached, and thereafter they decreased smoothly with increasing moisture content. The isosteric heats of rice desorption were higher than those of adsorption below 22.5% d.b. EMC, but thereafter there was no difference found between desorption and adsorption. The sorption isosteric heats of Indica rice were slightly higher than those of Japonica rice under all moisture contents at a constant temperature.

Keywords: Equilibrium moisture content, Rice, Adsorption, Desorption, Mathematic model, Ventilation, Drying

1. Introduction

Rice is the major grain in China, with its annual production being around 180 million metric tons in recent years. Due to the large population, a portion of the rice grain is stored for a longer period of time (2 years) in China than in developed countries, with deterioration controlled largely through moisture content and temperature. In order to describe the process of drying, the ambient cooling of grain, and improving physical control in storage, a sound knowledge of the relationship between equilibrium moisture content (EMC) and equilibrium relative humidity (ERH) is essential. The most useful way to define this relationship is fitting the data to a suitable equation (Jayas and Mazza, 1991; Sun, 1999; Li, 2009). Many investigators have developed equations, theoretically, semi-theoretically or empirically to describe the sorption isotherms of rice. Chen and Morey (1989) compared four EMC/ERH equations such as Modified-Chung-Pfost (MCPE), Modified-Halsey (MHAE), Modified-Henderson (MHE), and Modified-Oswin (MOE) for rough and brown rice from three sources, and found except the MHAE, the other three equations could fit some or all of the rice data. In the 1996, version of the ASABE Standard D245.5 “Moisture Relationships of Plant-Based Agricultural Products”, the MCPE, MHAE, MHE, and MOE were recommended. Sun (1999) analyzed 17 source sets of rice EMC/ERH data with four commonly cited models, i.e. MCPE, MHE, MOE, and Strohman-Yoerger (STYE), and considered the STYE as the preferred equation. However, such suitable equation for Chinese rice varieties is rather deficient.

Nomenclature	
C_1, C_2, C_3, C_4	equation coefficients
d.b.	dry basis
EMC	equilibrium moisture content
ERH	equilibrium relative humidity
m.c.	moisture content
M_m	monolayer moisture content (% d.b.)
m_{mi}	the average of experimental value
m_{pi}	the predicated value

Nomenclature	
MRD	mean relative percentage error (%)
n	the number of observations
h_s	the isosteric heat of sorption (KJ/Kg)
h_v	the latent heat of vaporization of free water (KJ/Kg)
h_w	the differential heat of wetting (KJ/Kg)
R^2	coefficient of determination
P_s	saturate vapor pressure (Pa)
r.h.	relative humidity
RSS	residue sum of squares
SE	standard error
T	absolute temperature (^{o}K)
t	temperature (^{o}C)
w.b.	wet basis

Knowledge of the heat of sorption is important in understanding the mechanism of grain sorption. It is a valuable tool in designing the drying process (Iglesias et al., 1976). Design of more efficient drying systems could be achieved by stating the correct mathematical models to estimate the heat and mass transfer mechanisms (Thorpe, 2001; Li, submitted). The purpose of the present work is to determine the most suitable ERH/EMC model corresponding to the sorption isotherms of thirteen rice varieties in China, and calculate the isosteric heat of water sorption from the experimental data.

2. Materials and methods

2.1. Materials and experimental procedures

Thirteen rice varieties in China were used in the sorption isotherm experiments. These rice varieties, including three species of Japonica rice and ten species of Indica rice, were respectively collected from eight provinces of the major rice grain production regions in China during 2007 to 2009. The rough rice grains, paddy, used for this study were intact, clean and plump. For adsorption experiment, the rice grains were dried to the moisture content (m.c.) of 7-8% w.b. at 39.0°C in an oven, and then dehydrated by P_2O_5 solid in a dessicator to below 5% w.b. as being samples. For the samples of desorption experiment, the rice varieties were re-moisturized from below 5% w.b. to the m.c. of 22% w.b., and equilibrated at 4°C for two weeks.

The gravimetric static method, with standard saturated salt solutions in Table 1 to maintain constant vapor pressure (Jayas and Mazza, 1991), was used to obtain nine equilibrium moisture contents at each of five constant temperatures (10, 20, 25, 30, and 35ºC). Twenty-seven glass bottles with a volume of 250 ml each contained 65 ml salt solution, and were kept in one temperature controlled cabinet to maintain nine groups of different relative humidity levels ranging from 11.3 to 96% ERH. Every relative humidity at one temperature was triplicated and a total of 135 bottles was used in the experiment for five sorption isotherms of a rice variety. The temperature of cabinets was often proofed with a standard thermometer ranging from 0 to 50^{o}C, and controlled to an accuracy of ±0.5^{o}C. The sample of rice seeds (about 4-5 g) was put into a small bucket (3 cm diameter × 4 cm length) made from copper wire gauze, and hung into the 250 ml bottle on a copper wire pothook under a rubber plug, just 2-3 cm above saturated salt solutions. The rubber plug was tightly plugged into the bottle mouth. From three weeks after exposing the samples in the saturated vapour at 35^{o}C, the copper wire buckets with samples were weighed every other day until the change in mass between two successive readings was less than 2 mg. When the sample was exposed to a lower temperature, the sample was left several days to equilibrate. However, the rice grains exposed over the saturated potassium nitrate solution for 5 to 7 days at higher temperatures were susceptible to grow molds, and immediately taken out, once one seed had mould. The moisture content of the sample at this constant stage was defined to be the equilibrium moisture content and was determined by the vacuum oven method (AOAC, 1980). The sample was dried to constant weight under 103.0±0.5°C for 22-28 hours.

Table 1 The equilibrium relative humidity (%) produced by nine saturated salt solutions[a].

	Equilibrium Relative Humidity (%)					
	Temperature (°C)					
Saturated salt solution	**10**	**15**	**20**	**25**	**30**	**35**
Lithium chloride	11.29	11.30	11.31	11.30	11.28	11.25
Potassium acetate	23.38	23.40	23.11	22.51	21.61	21.50
Magnesium chloride	33.47	33.3	33.07	32.78	32.44	32.05
Potassium carbonate	43.14	43.15	43.16	43.16	43.17	43.16
Magnesium nitrate	57.36	55.87	54.38	52.89	51.40	49.91
Cupric chloride	68.40	68.40	68.30	67.00	66.50	66.00
Sodium chloride	75.67	75.61	75.47	75.29	75.09	74.87
Potassium chloride	86.77	85.92	85.11	84.34	83.62	82.95
Potassium nitrate	95.96	95.41	94.62	93.58	92.31	90.79

[a]Source: Jayas and Mazza (1991)

2.2. Analysis of the adsorption and desorption data

The adsorption and desorption equilibrium moisture content data of rough rice were fitted to the six moisture sorption isotherm equations given in Table 2, using the non-linear regression procedure in SPSS 13.0 for Windows, which minimizes the sum of squares of deviations between experimental and predicted data in a series of iterative steps. The goodness-of-fit of each equation was evaluated using determination coefficient (R^2), residue sum of squares (RSS), the standard error (SE), mean relative percentage error (MRE). The determination coefficient (R^2) was one of the primary criteria for selecting the best equation to fit the experimental data. In addition to R^2, the other statistical parameters, MRE as a percentage, RSS and SE were used to determine the quality of the fit. The equations (1) - (4) were used for calculating R^2, RSS, SE, and MRE, respectively.

$$R^2 = \sqrt{1 - \frac{\sum_{i=1}^{n} (m_i - m_{pi})^2}{\sum_{i=1}^{n} (m_i - m_{mi})^2}} \quad (1)$$

$$\mathrm{RSS} = \sum_{\mathrm{i=1}}^{\mathrm{n}} (\mathrm{m_i} - \mathrm{m_{pi}})^2 \quad (2)$$

$$\mathrm{SE} = \sqrt{\frac{\sum_{\mathrm{i=1}}^{\mathrm{n}} (\mathrm{m_i} - \mathrm{m_{pi}})^2}{(\mathrm{n}-1)}} \quad (3)$$

$$\mathrm{MRE} = \frac{100 \sum_{\mathrm{i=1}}^{\mathrm{n}} \left| \frac{\mathrm{m_i} - \mathrm{m_{pi}}}{\mathrm{m_i}} \right|}{\mathrm{n}} \quad (4)$$

where m_i is the experimental value m_{pi} the predicated value m_{mi} the average of experimental values, and n the number of observations. The fit of an equation is good enough for practical purposes when MRE is less than 10% (Aguerre et al., 1989).

Table 2 The cited EMC/ERH equations in the study.

Equations	**Formula**[a]
Modified-BET	$M = \frac{(C_1 + C_2 \times t) \times C_3 \times r.h.}{(1 - r.h.) \times (1 - r.h. + C_3 \times r.h.)}$ ($r.h.$ <50%)
Modified-Chung-Pfost (MCPE)	$r.h. = \exp[-\frac{C_1}{t + C_2} \exp(-C_3 \times M)]$ or $M = -\frac{1}{C_3} \times \ln[-\frac{(t + C_2) \times \ln(r.h.)}{C_1}]$
Modified GAB (MGAB)	$r.h. = \frac{2 + \frac{C_3}{t} \times (\frac{C_1}{M} - 1) - \{[2 + \frac{C_3}{t} \times (\frac{C_1}{M} - 1)]^2 - 4 \times (1 - \frac{C_3}{t})\}^{\frac{1}{2}}}{2 \times C_2 \times (1 - \frac{C_3}{t})}$ or $M = \frac{C_1 \times C_2 \times (\frac{C_3}{t}) \times r.h.}{(1 - C_2 \times r.h.) \times (1 - C_2 \times r.h. + \frac{C_3}{t} \times C_2 \times r.h.)}$

Equations	Formula[a]
Modified-Henderson (MHE)	$r.h.=1-\exp[-C_1\times(t+C_2)\times M^{C_3}]$ or $M=[-\frac{\ln(1-r.h.)}{C_1\times(C_2+t)}]^{\frac{1}{C_3}}$
Modified-Oswin (MOE)	$r.h.=\frac{1}{1+(\frac{C_1+C_2\times t}{M})^{C_3}}$ or $M=\frac{C_1+C_2\times t}{(\frac{1}{r.h.}-1)^{\frac{1}{C_3}}}$
STYE	$r.h.=\exp[C_1\times\exp(-C_2\times M)\times\ln(P_s)-C_3\times\exp(-C_4\times M)]$

[a]*r.h.* represents moisture content, *M* is equilibrium moisture content (% dry basis), *t* is temperature (°C), and P_s is saturated vapor pressure. C_1, C_2, C_3, and C_4 are the coefficients of equations.

2.3. Determination of the isosteric heat of sorption

The total energy required to remove a unit mass of water from grain kernels, the differential heat of sorption, h_s, is conveniently partitioned into two components, namely the latent heat of vaporization of free water (h_v) and the differential heat of wetting (h_w). The h_v of adsorption and desorption of rice were respectively calculated by the following six equations according to Thorpe (2001).

$$\frac{h_s}{h_v}=1+\frac{p_s}{r.h.}\times\frac{dT}{dP_s}\times\left.\frac{\partial r.h.}{\partial T}\right|_{m.c.} \quad (5)$$

$$h_v=2501.33-2.363\times t \quad (6)$$

$$P_s=\frac{6\times10^{25}}{(273.15+t)^5}\times\exp(-\frac{6800}{t+273.15}) \quad (7)$$

$$\frac{dP_s}{dT}=\frac{P_s}{(t+273.15)}\times(\frac{6800}{t+273.15}-5) \quad (8)$$

$$\left.\frac{\partial r.h.}{\partial T}\right|_{m.c.}=\frac{C_1\times r.h.}{(t+C_2)^2}\times\exp(-C_3\times m.c.) \quad (9)$$

The equation (5) enables one to calculate

h_s/h_v, provided dP_s/dT and $\left.\partial r.h./\partial T\right|_{m.c.}$

can be evaluated by equations (8) and (9), respectively. The h_v of free water in equation (6) is dependent on temperature. The saturated vapor pressure, P_s, can be calculated by equation (7). The derivative of *r.h.* with respect to t,

$$\left.\partial r.h./\partial T\right|_{m.c.}$$

Depends on the sorption isotherm equation used, and the Modified-Chung-Pfost（MCPE）in equation (9) used in this study.

3. Results

3.1. Fitting of sorption equations to experimental sorption data

The results of nonlinear regression analyses of fitting the sorption equations to the experimental data of desorption and adsorption isotherms were respectively evaluated with the indices such as correlation coefficient (R^2), residue sum of squares (RSS), the standard error (SE), and mean relative percentage error (MRE). Of the six commonly used equations, namely BET, MCPE, MGAB, MHE, MOE, and STYE (Table 2), five equations such as STYE, MCPE, MHE, MOE and MGAB gave the better fit to the experimental data of adsorption and desorption isotherms in a wide range of 11.3 to 96.0% ERH, but the BET equation gave the better fit in the range of 11.3 to 49.9% ERH (data not shown). The further comparisons of the sorption equations with a form of

$$r.h.=f(M,t) \text{ or } M=f(r.h.,t)$$

for twenty-six sets of isotherm data are given in Table 3. The average values of R^2 and error parameters (RSS, SE, and MRE) for the twenty-six sets of isotherm data were calculated. For the form of

$$r.h. = f(M,t),$$

the equations were ranked for accuracy in an order: STYE, MCPE, MHE, MOE, MHE and MGAB, but for that of

$$M = f(r.h.,t),$$

the order was: BET, MCPE, MHE, MOE, and MGAB. However, STYE is four-coefficient, temperature independent equation and can not be explicitly inverted to give EMC as a function of ERH. MCPE, MHE, MOE and MGAB equations all are three-coefficient, temperature dependent and easily invertible equations (Table 2). Thus, the MCPE with a form of

$$r.h. = f(M,t),$$

or with a form of

$$M = f(r.h.,t)$$

was considered to best describe the equilibrium moisture data of thirteen rice varieties in a wide range of 11.3 to 96.0% ERH, and the best fitted coefficients for both adsorption and desorption isotherms of rough rice data were summarized in Table 4. For MCPE model, the three coefficients C_1, C_2 and C_3 of adsorptive isotherm equation were different from those of desorptive isotherm equation, and there were some difference in three coefficients C_1, C_2 and C_3 of between Japonica rice and Indica rice.

Table 3 Summary of the results of fitting equations to the data sets of thirteen pairs of rice desorption and adsorption.

Model function	Equation	Statistical parameters[a]			
		R^2	RSS	SE	MRD %
$r.h. = f(M,t)$	MCPE	0.99570	0.01440	0.00020	3.67480
	MGAB	0.99045	0.03092	0.00074	5.90547
	MHE	0.99192	0.02624	0.00042	5.04545
	MOE	0.99208	0.02421	0.00085	6.30338
	STYE	0.99594	0.01414	0.00044	3.65875
$M = f(r.h.,t)$	BET	0.98096	1.91840	0.10670	2.98630
	MGAB	0.97031	47.73069	1.13642	8.46685
	MCPE	0.99225	12.24169	0.29150	3.02528
	MHE	0.98675	21.32694	0.50775	4.52040
	MOE	0.98031	31.34288	0.74628	6.02336

[a]The statistical parameter is average of the data sets of thirteen pairs of rice desorption and adsorption

Table 4 The best fitted coefficients of MCPE for sorption isotherms of rice.

Model	Data sets[a]	Model coefficients			Statistical parameters			
		C_1	C_2	C_3	R^2	RSS	SE	MRD %
$r.h. = f(M,t)$ (MCPE)	Desorption	412.543	35.300	0.181	0.9986	0.0046	1.094E-04	1.7654
	Adsorption	677.146	110.639	0.184	0.9981	0.0060	1.430E-04	2.1502
	Average	483.486	57.569	0.182	0.9985	0.0048	1.131E-04	1.6690
	Japonica rice	455.064	63.182	0.175	0.9978	0.0071	1.682E-04	2.5580
	Indica rice	504.668	58.354	0.184	0.9985	0.0048	1.136E-04	1.6934

[a]Data sets derivated from the average sorption data of thirty rice varieties. Desorption, desorption isotherm; adsorption, adsorption isotherms; Average, the average values obtained from adsorption and desorption isotherms.

3.2. *Isosteric heat of sorption*

The isosteric heat of sorption (h_s) was calculated from the equations (6) to (9). The coefficients C_1, C_2, and C_3 of MCPE equation in Table 4 were used as the coefficients in equation (9). Figure 1 shows the influence of moisture content on rough rice adsorption and desorption isosteric heats, and on the sorption isosteric heats of Japonica and Indica rice determined from adsorption and desorption isotherms. The isosteric heats for both rice desorption and adsorption (Fig. 1A), and for both the sorption of japonica and India rice (Fig. 1B) decreased rapidly with increase in seed moisture content until the moisture content of 20% d.b. was reached, but above 20% d.b. they decreased smoothly with increasing moisture content. At lower moisture contents below 22.5% d.b., under lower temperatures the isosteric heats of both desorption and adsorption of rough rice, and of both sorption of Japonica and Indica rice were higher than those under higher temperatures. The isosteric heats of rough rice desorption were higher than those of adsorption below 22.5% d.b., but thereafter there was no difference found between desorption and adsorption (Fig. 1A). The sorption isosteric heats of Indica rice were slightly higher than those of Japonica rice at all moisture contents under a constant temperature (Fig. 1B).

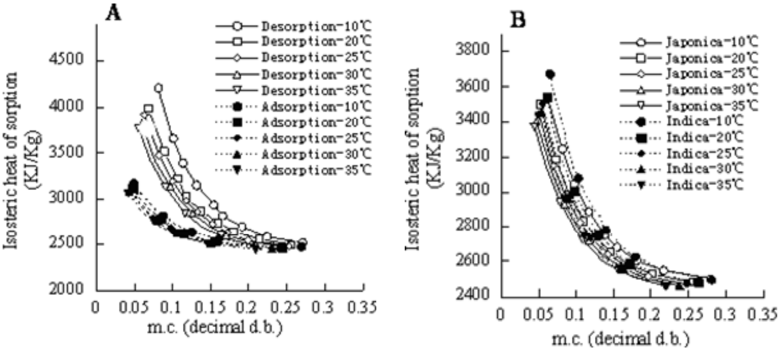

Figure 1 Comparison of adsorption and desorption isosteric heats of rice (A), and of the sorption isosteric heats of Japonica and Indica rice (B) at different temperatures (°C) predicted by the Modified-Chung-Pfost equation.

4. *Discussion*

Sun (1999) analyzed 17 source sets of rice EMC/ERH data with four commonly cited models such as MCPE, MHE, MOE, and STYE, and considered the STYE as the preferred equation. In this study, for the form of

$$r.h. = f(M, t),$$

the equations were ranked for accuracy in an order: STYE, MCPE, MHE, MOE, MHE and MGAB, but for that of

$$M = f(r.h., t),$$

the order was: BET, MCPE, MHE, MOE, and MGAB. We regarded MCPE as the but fitted equation due to it being three coefficients, invertible equations. Thus, MCPE was adopted in this study to calculate the rice isosteric heat of sorption.

The isosteric heats for both rice desorption and adsorption, and for both the sorption of Japonica and Indica rice, decreased rapidly with an increase in seed moisture content until the moisture content of 20% d.b. was reached, and thereafter they decreased smoothly with increasing moisture content (Fig. 1). The isosteric heats of rice desorption were higher than those of adsorption below 22.5% d.b. EMC, but thereafter there was no difference found between desorption and adsorption (Fig. 1A). These results show a little difference from the results reported by Öztekin and Soysal (2000) that the isosteric heats of rice desorption were higher than those of adsorption below 11% d.b. EMC, but above 11% d.b. EMC the isosteric heats of desorption were lower than those of adsorption. The sorption isosteric heats of Indica rice were insignificantly higher than those of Japonica rice under all moisture contents at a constant temperature (Fig. 1B). The rapid increase in the heat of sorption at low moisture content might be due to the existence of highly active polar sites on the surface of rice grains, which were covered with water molecules forming a mono-molecular layer (Tsami, 1991). The decrease in the isosteric heats with higher amounts of sorbed water can be quantitatively explained by considering that sorption initially occurs on the most active available sites giving rise to high interaction energy. As these sites become occupied, sorption occurs on the less active ones, resulting in lower heats of sorption (Wang and Brennan, 1991). In low moisture contents, the values of the isosteric heats were higher than the latent heat of vaporization of water, indicating that the energy of binding between the water molecules and the sorption sites was higher than the energy which holds the molecules of pure water together in the liquid phase (Al-Muhtaseb, et al., 2004). At high moisture contents, there was no significant difference between the sorption isosteric heat and the latent heat of vaporization of water over the broad range of moisture contents. In the present study, the heat of sorption of rice grains might approach that of pure water at the moisture content of about 22.5%d.b.

It has been noted that h_s/h_v was calculated to be dependent on temperature, but the dependence was small (Thorpe, 2001). This temperature dependency of h_s/h_v was rather clear in Figure 1, which might arise from experimental errors in measuring the sorption isotherm, or from the sample properties such as variety, harvest time, pre-treatment, and so on.

In summary, MCPE was the best fitted equation to describe the EMC/ERH data of thirteen Chinese rice varieties, and was adopted to calculate the isosteric heat of sorption. The isosteric heats of rice desorption were higher than those of adsorption below 22.5% d.b. EMC, but thereafter there was no difference found between desorption and adsorption. The sorption isosteric heats of Indica rice were slightly higher than those of Japonica rice under all moisture contents at a constant temperature.

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