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Research Article

Water Desorption Isotherm and its Thermodynamic Analysis of Glutinous Rice Flour

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Abstract

Background: Water sorption isotherm and thermodynamic properties are necessary for food process design. **Methodology:** Moisture desorption isotherms of glutinous rice flour were determined using a static gravimetric method at 10, 20 and 30°C and for water activity ranging from 0.06-0.98. **Results:** Out of the four chosen isotherm models (Chung-Pfrost, Oswin, Dent and Lewicki), the Lewicki model was found to best describe the experimental sorption data. The best-fit model was further used to evaluate the thermodynamic functions of glutinous rice flour on the base of Clausius-Clapeyron equation and Gibbs-Helmholtz relationship. Differential enthalpy and entropy and integral enthalpy for water desorption all were positive in value and decreased with increasing equilibrium moisture content. Integral entropy with reference to pure liquid water was negative in value and increased with increasing equilibrium moisture content. All the four thermodynamic functions were adequately characterized by an exponential model. Spreading pressure decreased with increase in temperature at constant water activity and increased with increase in moisture content at constant temperature. **Conclusion:** The enthalpy-entropy compensation theory was proved to be valid for desorption of glutinous rice flour. Through the entropy-enthalpy theory, it was founded that the water desorption of glutinous rice flour was non-spontaneous and enthalpy-controlled.

Key words: Desorption isotherm, glutinous rice flour, thermodynamics, enthalpy, entropy

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Glutinous rice (*Oryza sativa*) also called waxy rice is the staple food of Asian people. Glutinous rice has almost no amylose content (0~2%)[1]. Glutinous Rice Flour (GRF) is produced from soaked glutinous rice through grinding into powder. Milled GRF is usually used as raw material in various food products such as sweets, desserts, rice cakes and baked rice cracker. The application of GRF in these products mainly takes advantage of the soft and sticky nature of cooked GRF[2]. In China, the main industrial application of GRF in food production is to produce the shell of tangyuan, a traditional Chinese sweet. Rapid freezing is widely used for industrialization of this indigenous food in China.

The relationship between the equilibrium moisture content and water activity of a material, over a range of a_w values, at a constant temperature, yields a moisture sorption isotherm. Moisture sorption isotherms are of special importance in many aspects of food processing involving water transport such as dehydration[3]. Other applications include the analytical determination of control for undesirable physical, chemical and enzymatic reactions[4,5] and control of moisture migration in multi-domain foods[6]. In fact, tangyuan can be treated as a multi-domain food made up of core material with higher water content and shell material (GRF) with relatively lower water content.

Thermodynamic properties are ready to be calculated from sorption isotherm data. The resulted thermodynamic functions, including differential enthalpy and entropy, enthalpy-entropy compensation, integral enthalpy and entropy and spreading pressure etc., provide a more thorough interpretation of the sorption isotherm phenomenon and help to understand better the sorption mechanism[7]. The differential and integral properties could be used to determine interactions of water and food substances and to provide information useful for assessing food processing operations such as drying, mixing and storage. Enthalpy-entropy compensation is a specific example of the compensation effect. The theory states that compensation arises from changes in the nature of the interaction between solute and solvent causing the reaction and that the relationship between enthalpy and entropy for a specific reaction is linear[8]. The concept of spreading pressure, with its dependence on water activity and temperature is a useful tool for interpretation of sorption kinetic data[9].

Although sorption data on starchy products are extensively documented in literature[9-11], there are only limited reports on water sorption of rice flour. Durakova and Menkov[12] presented the adsorption and desorption behaviors of rice flour in a water activity range of 0.11-0.85 at 10, 20 and 30°C. Brett *et al.*[11] determined sorption isotherms for rice flour at temperatures of 5, 23 and 45°C for a water activity range from 0.08-0.98. Sandoval *et al.*[13] determined moisture adsorption isotherms for rice flour in water activity range from 0-0.945 at a temperature range of 5, 23 and 45°C.

Different from rice flour, glutinous rice flour has very limited amylose content. In addition, moisture desorption isotherm data of GRF at very higher a_w levels is necessary for predicting water loss during freezing of Tangyuan and for controlling its quality deterioration such as fissuring. To our knowledge, there are no reports concerning the desorption isotherms and the thermodynamic properties of GRF. The objective of this study was to determine the desorption isotherms of glutinous rice flour in an a_w range of up to 0.98 at 10, 20 and 30°C and to deduce its thermodynamic properties, based on experimental methods and physical laws.

MATERIALS AND METHODS

Materials: Glutinous rice flour was purchased from local market with the composition of 8.08% (dry base) protein, 1.11% (dry base) lipids, 0.92% (dry base) fiber, 0.90% (dry base) ash and 88.99% (dry base) carbohydrate (by difference). The GFR was mixed with water to a final moisture content of 45% (wet base) and conditioned for 3 h before desorption experiment.

Determination of desorption isotherms: The equilibrium moisture content of GRF was determined by a gravimetric technique at ten water activity levels. About 5 g of GRF was placed in desiccators containing different saturated salt solutions (LiBr, LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, NaCl, KCl and K_2SO_3) to maintain the specified water activity inside the desiccators[14]. A test tube containing thymol was placed inside the desiccators with $a_w>0.75$ to prevent mold growth during storage. The desiccators were placed in temperature-controlled cabinets maintained at 10, 20 and 30±1°C and the samples were allowed to equilibrate until there was no discernible weight change (±0.001 g). This involved a period of approximately three weeks. The equilibrium moisture content was determined by drying in an oven at 105°C until constant weight. All measurements were done in triplicate. The moisture content at each water activity represents the mean value of three replications.

A large number of equations have been reported in the literature for sorption isotherms. In the present study, Chung-Pfrost (Eq. 1), Oswin (Eq. 2), Dent (Eq. 3) and Lewick

(Eq. 4) sorption isotherm equations were selected to fit moisture adsorption data for the whole water activity range studied at each temperature:

$$a_w = \exp\,[-a \exp\,(-bM_e)] \tag{1}$$

$$M_e = a\left[\frac{a_w}{1-a_w}\right]^b \tag{2}$$

$$\frac{a_w}{M_e} = Aa_w^2 + Ba_w + C \tag{3}$$

$$M_e = \frac{a}{(1-a_w)^b} - \frac{a}{1+a_w^c} \tag{4}$$

where, M_e is equilibrium moisture content and a_w is water activity and a, b and c are model parameters:

$$A = -\frac{a(b-a)}{bc},\ B = \frac{b-2a}{bc},\ C = \frac{1}{bc}$$

The coefficient of determination (R^2), standard error of estimate (SEE, defined by Eq. 5) and mean relative percentage deviation (MRD, defined by Eq. 6) are commonly used in the literature to evaluate the goodness of fit of sorption models[15,16]. The R^2 indicates how well the variability has been explained by the given model, SEE is a measure of how precisely the parameters have been estimated and MRD gives an idea of the mean departure of the measured data from the predicted data:

$$\text{SEE} = \sqrt{\frac{\sum_{i=1}^{m}(M_e^i - \bar{M}_e)^2}{d_f}} \tag{5}$$

where, d_f is freedom degree of fitting equation and $\bar{M}_e$ is average value of M_e of m number of experiments:

$$\text{MRD} = \frac{100}{m}\sum_{i=1}^{m}\frac{\left|M_e^i - \bar{M}_e\right|}{M_e} \tag{6}$$

Calculation of thermodynamic properties

Differential enthalpy and entropy of desorption: The differential enthalpy of desorption (with reference to sorbed water) was determined using the Clapeyron-Clausius[17] Eq. 7:

$$\left[\frac{d\ln a_w}{d\,(1/T)}\right]_{M_e} = -\frac{\Delta H_{diff}}{R} \tag{7}$$

where, ΔH_{diff} is the differential enthalpy of sorption (J mol^{-1}), T is the absolute temperature (K) and R is the universal gas constant (8.314 J mol^{-1}·K).

The value of water activity a_w could be calculated using the moisture sorption isotherm model which has the best fitness on the experimental data of sorption. Equation 7 is based on the assumption that ΔH_{diff} is independent of temperature. By plotting $\ln(a_w)$ against 1/T at constant moisture content, the ΔH_{diff} can be easily determined from the slope ($-\Delta H_{diff}/R$).

The differential entropy (ΔS_{diff}) can be calculated from the Gibbs-Helmholtz Eq. 8:

$$\Delta S_{diff} = \frac{\Delta H_{diff} - G}{T} \tag{8}$$

Substituting the free Gibbs energy $G = RT\ln(a_w)$ of desorption in Eq. 8, then Eq. 9 is obtained:

$$\ln(a_w)\big|_{M_e} = -\frac{\Delta H_{diff}}{RT} + \frac{\Delta S_{diff}}{R} \tag{9}$$

After plotting $\ln(a_w)$ versus 1/T, differential entropy can be obtained form the y-intercept.

Compensation theory: The enthalpy-entropy compensation theory proposes a linear relationship between the entropy and enthalpy of adsorption or desorption of water as shown in Eq. 10[18]:

$$(\Delta H_{diff})_T = T_B\,(\Delta S_{diff})_T + \Delta G_B \tag{10}$$

where, T_B is the isokinetic temperature (K) at which all sorption reactions will take place at the same rate and ΔG_B is the value of free energy at the isokinetic temperature (J mol^{-1}).

The verification of the compensation theory can be performed by comparing T_B with the harmonic mean temperature (T_{hm})[19], calculated by Eq. 11:

$$T_{hm} = \frac{n}{\sum_{i=1}^{n}\frac{1}{T_i}} \tag{11}$$

where, n is the number of isotherms used. An approximate [(1-α) 100%] confidence interval for T_B may be calculated from Eq. 12:

$$T_B = \hat{T}_B \pm t_{m-2,\alpha/2}\sqrt{\mathrm{Var}(T_B)} \quad (12)$$

where, $\hat{T}_B$ is the slope of the enthalpy-entropy plot with a 95% confidence interval calculated for all data sets, $t_{m-2,\alpha/2}$ is the student's t-distribution value at (m-2) degrees of freedom and m is the number of data pairs (ΔH_{diff}, Δs_{diff}) as in Eq. 13:

$$\hat{T}_B = \frac{\sum\left[(\Delta H_{diff})_T - (\Delta \bar{H}_{diff})_T\right]\left[(\Delta S_{diff})_T - (\Delta \bar{S}_{diff})_T\right]}{\sum\left[(\Delta S_{diff})_T - (\Delta \bar{S}_{diff})_T\right]^2} \quad (13)$$

and Var(T_B), the standard error of the isokinetic temperature will be as Eq. 14:

$$\mathrm{Var}(T_B) = \frac{\sum\left[(\Delta H_{diff} - \Delta G_B - \hat{T}_B \Delta S_{diff})_T\right]^2}{(m-2)\sum\left[(\Delta S_{diff} - \Delta \bar{S}_{diff})_T\right]^2} \quad (14)$$

where, $\Delta \bar{H}_{diff}$ is the average differential enthalpy and $\Delta \bar{S}_{diff}$ is the average differential entropy.

The enthalpy-entropy compensation theory can be further used to model the temperature influence on the sorption isotherm behavior by rearranging Eq. 9 and 10 to get Eq. 15. Parameter ΔG_B in Eq. 8 is neglected for its small contribution in the enthalpy change[17]:

$$-\ln(a_w) = \frac{\Delta S_{diff}}{R}\left(\frac{1}{T} - \frac{1}{T_B}\right) \quad (15)$$

Equation 15 can be further rewritten in the following Eq. 16:

$$\psi_T \ln(a_w) = K\phi(M_e) \quad (16)$$

where, $\psi_T = 1/(1/T_B - 1/T)$ is the temperature correction factor in the isotherm and $\phi(M_e)$ is an empirical function of the equilibrium moisture content.

Aguerre *et al.*[17] proposed an exponential function that represents the water sorption equilibrium of foods and it adequately describes the temperature dependence with the following Eq. 17:

$$\psi_T \ln(a_w) = K_1 M_e^{k2} \quad (17)$$

where, K_1 and K_2 are constants. The equilibrium data can be represented by plotting $\ln(\psi_T \ln(a_w))$ as a function of the equilibrium moisture content.

Spreading pressure: The surface pressure (π) can be calculated using an analytical procedure similar to the one described by Fasina *et al.*[20] from the following relationship given in Eq. 18:

$$\pi = \frac{K_B T}{A_m}\int_0^{a_w} \frac{\theta}{a_w} da_w \quad (18)$$

where, K_B is the Boltzmann's constant (1.38×10^{-23} J/K), A_m is the area of a water molecule (1.06×10^{-19} m^2) and θ is water ratio which is equal to M_e/M_m, where, M_m is the monolayer moisture contents at different temperatures, estimated through applying the BET model (Eq. 19) to the equilibrium moisture content data in the water activity range of <0.5:

$$\frac{a_w}{(1-a_w)M} = \frac{1}{M_m C_2} + \frac{(C_2 - 1)a_w}{M_m C_2} \quad (19)$$

where, C_2 is a constant.

A value of $a_w \to 0$ will make the integral of Eq. 18 indeterminate ($\ln(a_w) \to \infty$). Therefore, the lower limit of water activity employed was 0.05. The computed values of surface potential were adjusted by adding the value corresponding to the water activity interval between 0 and 0.05, which was calculated by assuming a linear relationship (Henry's law) between a_w and θ within the water activity interval[20]. For the above water activity interval, Eq. 18 becomes Eq. 20:

$$\pi = \frac{K_B T \theta}{A_m} \quad (20)$$

In the present study, the spreading pressure corresponding to $a_w \geq 0.05$ was computed by integrating Eq. 18 after substituting the best-fit isotherm model.

Net integral enthalpy and entropy: The net integral enthalpy (ΔH_{int}) was determined in a similar manner as the differential enthalpy but at a constant spreading pressure[20] using Eq. 21:

$$\left[\frac{d\ln(a_w)}{d(1/T)}\right]_\pi = -\frac{\Delta H_{int}}{R} \quad (21)$$

A plot of $\ln(a_w)$ versus 1/T at constant spreading pressure gives the net integral enthalpy from the slope.

Net integral entropy with reference to pure liquid water, ΔS_{int} was given by Benado and Rizvi[21] as Eq. 22:

$$\Delta S_{int} = \frac{-\Delta H_{int}}{T} - R\ln(a_w^*) \quad (22)$$

where, a_w^* is the geometric mean water activity obtained at constant spreading pressure at different temperatures. The temperature term T of Eq. 22 was interpolated linearly for a_w^* from the T and a_w data for a given π[22].

RESULTS AND DISCUSSION

Water desorption isotherm: The equilibrium moisture contents of GRF after desorption at 10, 20 and 30°C are shown in Fig. 1. The solid curves are the prediction of the best-fit model. According to the classification of Brunauer *et al.*[23], GRF had the type II isotherm, which is typical for foods made of biopolymers. It can be seen that the equilibrium moisture contents increased with decreasing temperature at constant water activity. This behavior is generally ascribed to a reduction in the number of active sites due to chemical and physical changes induced by temperature and the extent of decrease depends on the nature or constitution of the food[24].

Experimental data of equilibrium water content and their corresponding water activity at each temperature were fitted to four isotherm models (Chung-Pfrost, Oswin, Dent and Lewicki models). The best-fit model parameters and the statistical criterions are collected in Table 1. The Lewicki model presented the best fitting performance throughout the entire experimental domain (having the highest R^2 and lowest SEE and MRD values), followed by the Chung-Pfrost model. The Dent model, which is often used while calculating spreading pressure in order to circum the mathematical difficulty as mentioned above, gave the worst predicting performance. The most suitable model for rice flour reported by Brett *et al.*[11] is the four-parameter Peleg equation, by Durakova and Menkov[12] the modified Chung-Pfost and modified Oswin equations, by Sandoval *et al.*[13] the modified GAB equation.

Differential enthalpy and entropy: The plot of differential enthalpy of desorption versus moisture content is shown in Fig. 2. The differential enthalpy rapidly decreased from 42.26-7.87 kJ mol^{-1} with increasing equilibrium moisture content from 0.05-0.15 kg water per kilogram dry matter, then slowly decreased with further increasing moisture content.

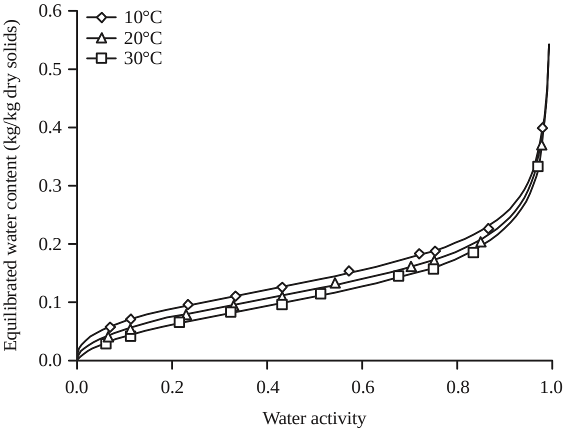

Fig. 1: Equilibrated water content of glutinous rice flour with ten water activity levels at 10, 20 and 30°C

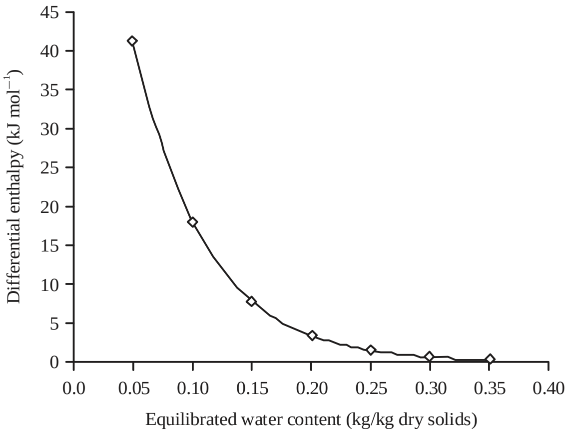

Fig. 2: Differential enthalpy of desorption of glutinous rice flour as a function of equilibrium water content

Table 1: Statistical criterions and best-fit parameters of the four models after fitting to the isotherm data of glutinous rice flour at 10, 20 and 30°C

Model	Temperature (°C)	a	b	c	R^2	SEE	MRD
	10	7.4125	17.1378		0.9996	0.0539	2.5041
Chung-Pfrost	20	5.7923	17.2324		0.9994	0.0467	2.3365
	30	4.7753	17.4817		0.9991	0.0386	2.7322
	10	0.1359	0.2721		0.9978	0.0158	3.9932
Oswin	20	0.1203	0.2971		0.9958	0.0201	6.6982
	30	0.1067	0.3224		0.9931	0.0171	10.6061
	10	0.8238	66.4969	0.0744	0.9830	0.0309	7.7067
Dent	20	0.8332	31.3677	0.0675	0.9881	0.0245	7.6408
	30	0.8321	17.2730	0.0631	0.9916	0.0189	7.5142
	10	0.2457	0.1877	0.4640	0.9995	0.0053	0.8868
Lewick	20	0.2197	0.2032	0.5489	0.9995	0.0047	1.0487
	30	0.1992	0.2150	0.6463	0.9995	0.0046	1.6548

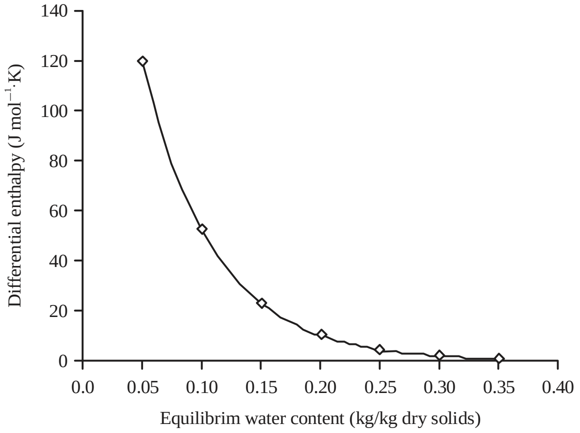

Fig. 3: Differential entropy of desorption of glutinous rice flour as a function of equilibrium water content

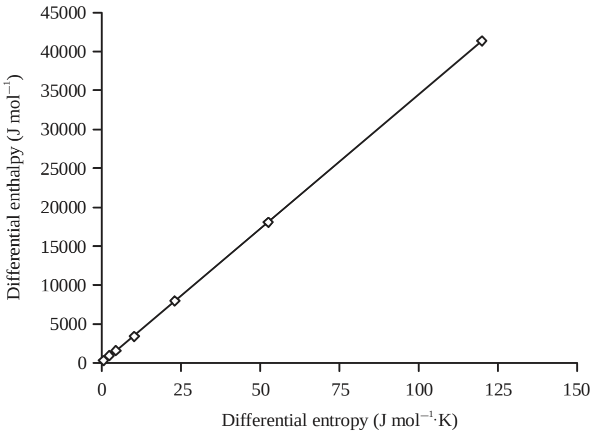

Fig. 4: Relationship between the different enthalpy and entropy of desoption of glutinous rice flour

At higher moisture content level the differential enthalpy approached to zero, meaning that the value of the heat of desorption is the same as the heat of vaporization of pure liquid water. Similar effects of moisture content on differential enthalpy of sorption were reported by Al-Muhtaseb *et al.*[9] for starch powders[16].

The differential enthalpy also called net isosteric heat of sorption, is considered as indicative of the intermolecular attractive forces between the sorption sites and the water vapor[25]. The elevated net isosteric heat of sorption at lower moisture contents is an indication of strong water-solid substance interactions in GRF. As the product moisture content increased, the available sites for sorption of water were reduced, resulting in lower values of differential enthalpy.

Figure 3 presents the ΔS_{diff} of desorption as a function of M_e. Differential entropy also followed a similar trend as the differential enthalpy. Similar evolution of differential entropy with moisture content was observed by Al-Muhtaseb *et al.*[9] for starch powders and by Goneli *et al.*[26] for pearl millet grain. The differential entropy of glutinous rice flour decreased from the value of 0.12 kJ mol^{-1}·K at 5% moisture content to 0.023 kJ mol^{-1}·K at 15% moisture content. At high moisture contents, the entropy approached that of free water. Based on the second law of thermodynamics, a process is reversible when the sum of all entropy changes for all subsystems in a process is constant. The process of water desorption in GRF was clearly irreversible because entropy was produced during the process. An almost constant entropy can be observed at the higher moisture contents suggesting that the desorption of GRF is reversible until a critical moisture content is reached. The differential entropy should be related with the transient variation of the total entropy of water when new molecules are sorbed on the food at a specific moisture level[27]. This parameter represents the algebraic sum of the integral entropy at a given hydration level, plus the change in order or disorder after new water molecules are adsorbed by the system at the same hydration level[28]. Nevertheless, the differential entropy does not mean order or disorder of the total system. According to Al-Muhtaseb *et al.*[9] the differential entropy of a food is proportional to the number of sorption sites available at a determined energy level. As desorption occured throughout glutinous rice flour, free specific sites became more and more, so that the entropies associated with the still vacant sites became larger and larger.

It can be observed from Fig. 2 and 3 the strong dependence of both differential enthalpy and differential entropy on moisture content with an exponential trend. An exponential model (Eq. 23) was fitted to the data:

$$y = a \exp(bM_e) \tag{23}$$

where, y is the a thermodynamic property and a and b are model parameters. The estimated values of a and b from non-linear regression were 95.00 kJ mol^{-1} and -16.62 for differential enthalpy, respectively, 274.07 J mol^{-1} and -16.50 for differential entropy, respectively. Figure 2 and 3 also show the representation of the Eq. 23 with its corresponding parameters for differential enthalpy and entropy, respectively.

Enthalpy-entropy compensation: The plot of ΔH_{diff} versus ΔS_{diff} for GRF is shown in Fig. 4. Linear relationship was exhibited with coefficient of determination (R^2) close to 1. The isokinetic temperature (T_B) and free energy (ΔG_B) determined by linear regression (Eq. 10) for all data were 344.43 K and 50.45 J mol^{-1}, respectively. McMinn *et al.*[10] found T_B values between 366.8 and 466.8 K for adsorption isotherms of starch materials. Tolaba *et al.*[29] found a value of 361.0 K for quinoa grains.

To test the validity of the compensation theory, the isokinetic temperature was compared with the harmonic mean temperature (T_{hm}). The harmonic mean temperature was calculated and a value of 292.92$\pm$0.17 K was found. This value is significantly different from T_B, confirming the suitability of the isokinetic theory for the desorption phenomena of GRF. The compensation theory fulfillment implies that only one mechanism is evident in the entire temperature and moisture content range studied[30], which suggests that the microstructure of the GRF was stable and did not suffer any changes during moisture desorption[10].

According to Leffler[18], if $T_B > T_{hm}$ the process is enthalpy driven, while if $T_b < T_{hm}$, the process is entropy controlled. Since the former condition is satisfied in present study, desorption mechanism of GRF can be considered to be enthalpy-driven. Cladera-Olivera *et al.*[31] also reported an enthalpy-controlled mechanism in desorption of raw pinhao. McMinn *et al.*[10], Aguerre *et al.*[17] and Beristain *et al.*[32] reported an enthalpy-controlled mechanism in the sorption of starch materials as well as Cladera-Olivera *et al.*[33] for adsorption of pinhao flour and Thys *et al.*[16] for adsorption of pinhao starch. From a thermodynamic viewpoint, the free energy change (ΔG) can be viewed as indicative of the affinity of the sorbent for water and further provides a criterion as to whether water sorption is a spontaneous (ΔG) or non-spontaneous (+ΔG) process, depending on the sign of the ΔG value[34]. In this study, the value of ΔG_B was found to be negative (-50.45 J mol^{-1}), indicating a spontaneous desorption process. McMinn *et al.*[10] also reported a spontaneous desorption isotherm for starch materials (potato, potato starch powder and corn starch powder) as well as Koua *et al.*[35] for cassava and McMinn *et al.*[36] for potato. On the other hand, absorption of water from environment is a non-spontaneous process for potato and sweet potato[37] and pinhao flour[33].

The enthalpy-entropy compensation theory was further used for modeling the effect of temperature on moisture desorption according to Eq. 17. Figure 5 shows a typical evolution of $\ln[(1/T_\beta\text{-}1/T)\ln(a_w)]$ with moisture content. A straight line was obtained. This confirms that the effect of temperature on moisture desorption of GRF followed a power law. The values of parameters K_1 and K_2, calculated using linear regression were found to be 9300.28 K and 2.60×10^{-7}, respectively. Reported values for K_1 and K_2 are 4453 K and 0.877 for desorption of potato[36], 8957 K and 0.842 for the sorption behavior of rough rice[17], 5478.95 K and 5.42×10^{-5} for desorption of prickly pear seeds[38], respectively.

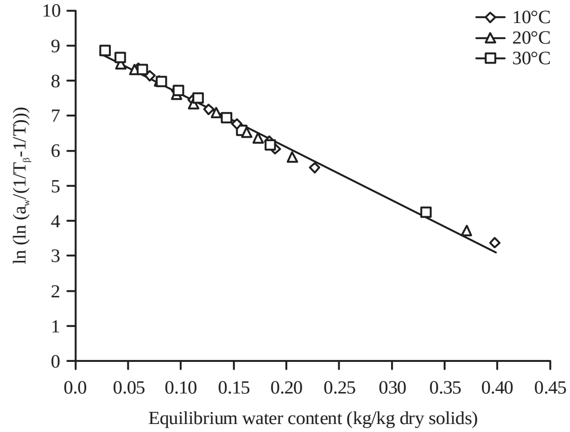

Fig. 5: Equilibrium moisture data of glutinous rice flour plotted according to Eq. 17

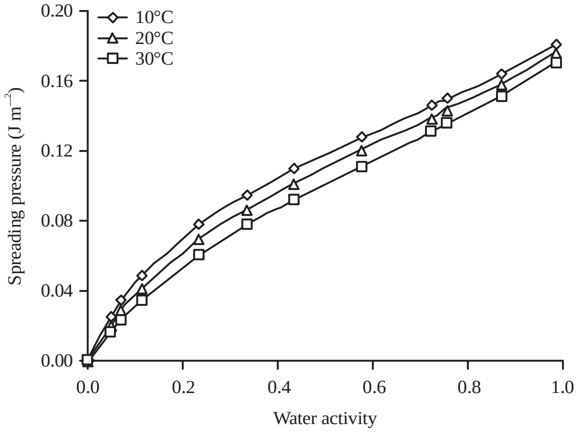

Fig. 6: Spreading pressure of desorption of glutinous rice flour as a function of water activity

Spreading pressure: The spreading pressure can be viewed as the force in the plane of the surface that must be exerted perpendicular to each unit length of edge to keep the surface from spreading[39]. According to Torres *et al.*[40] high spreading pressure values indicate a high affinity of water molecules for active sites and the more hygroscopic the product is, the higher the value π will be.

Figure 6 shows the spreading pressure of GRF as a function of water activity at 10, 20 and 30°C. The spreading pressure decreased with increasing temperature and increased with increasing in water activity. This trend with respect to temperature and water activity is comparable to those reported by Fasina *et al.*[20] for winged bean and gari, Al-Muhtaseb *et al.*[9] for starch powders and McMinn *et al.*[36] for potato.

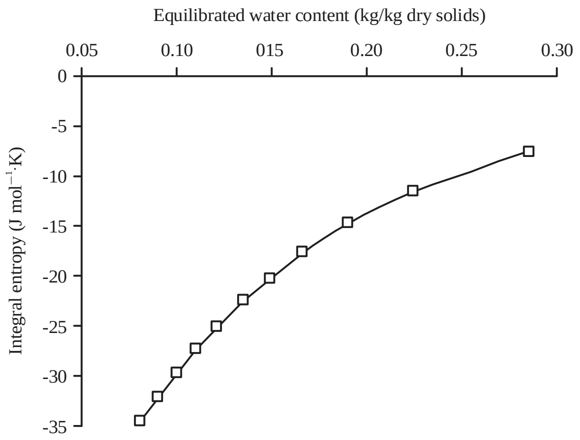

Fig. 7: Integral enthalpy of desorption of glutinous rice flour as a function of equilibrium water content

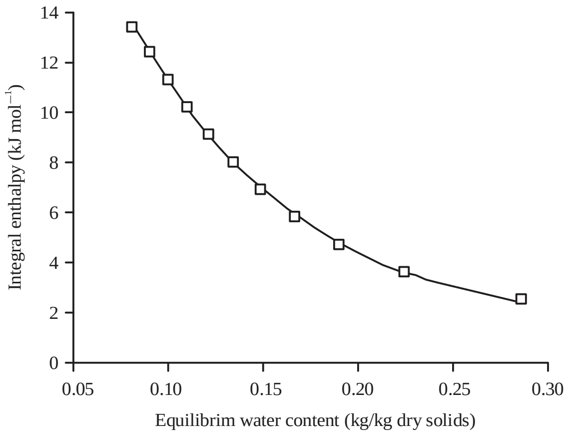

Fig. 8: Integral entropy (with reference to pure liquid water) of desorption of glutinous rice flour as a function of equilibrium water content

Integral enthalpy and entropy: Even though differential properties are easy to evaluate, they are not subject to a simple thermodynamic interpretation. By contrast, integral properties are subject to simple thermodynamic interpretation[41]. The variation of net integral enthalpy with moisture content is shown in Fig. 7.

The ΔH_{int} decreased fast then gradually with increasing moisture content until it approached an asymptote beyond the moisture content of 30% dry base, approximately. Similar trend was observed for sweet potato[42]. This thermodynamic behavior can be attributed to the monolayer covering of the materials[20]. At low moisture contents, water is adsorbed on the most accessible locations on the exterior surface of the solid. The net integral enthalpy then starts to decline as less favorable locations are covered and multiple layers of sorbed water form[9].

The integral entropies plotted as a function of water content are presented in Fig. 8. As can be seen, for the moisture range studied the integral entropy was negative in value and increased with increasing in moisture content. Negative integral entropy values have been reported in the literature for the sorption isotherms of sweet potato[42]. Rizvi and Benado[28] explained that in foods there are two opposing entropic contributions upon moisture adsorption, a loss of entropy from localization of water and an increase in entropy due to structural transformation arising from solubilization and swelling. Iglesias *et al.*[43] attributed the negative entropy values to the existence of chemical adsorption and/or structural modifications of the adsorbent.

The form of the net integral entropy versus moisture content curve is similar to that observed for grain sorghum[28], starch powders[9] and yacon bagasse[44]. As the moisture content reached saturation, the integral entropy tended to reach the entropy of free water (0 J mol^{-1}·K). Similar observation was reported by Al-Muhtaseb *et al.*[9] for potato and corn starches and by Lago and Norena[44] for yacon bagasse.

The net integral properties were also described well with the exponential model (Eq. 23) with the following parameters: for integral entropy, a = -64.44 J mol^{-1}, b = -7.74, for integral entropy, a = 28.80 J mol^{-1}, b = -9.39. The solid curves in Fig. 7 and 8 are the representation of the fitting models.

CONCLUSION

The desorption isotherms of glutinous rice flour took a type II sigmoid form according to the BET classification. Among the four selected sorption models, the Lewicki model was the best model describing the equilibrium moisture data. The differential enthalpy and entropy and integral enthalpy of desorption of GRF were found to decrease as the moisture content increase. The net integral entropy increased with moisture content, but was negative in value with respect to the entropy of pure liquid water. All the four thermodynamic functions can be adequately characterized by an exponential model.

Spreading pressure decreased with an increase in temperature at constant water activity and increased with increasing moisture content at constant temperature.

Enthalpy-entropy compensation theory could be successfully applied to the moisture desorption behaviour of GRF. The desorption processes was enthalpy-controlled and spontaneous.

The thermodynamic information obtained from this study would be valuable for optimizing processing and storage of GRF-based foods in order to guarantee final product quality.

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