

RESEARCH PAPER

Moisture Sorption Isotherms of Tender Cashew Kernel at Varied Temperatures

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ABSTRACT

Adsorption-desorption behaviors of tender cashew kernel were studied at different relative humidity (ERH) ranging from 0 and 100% and temperatures at 30, 40, 50 and 60°C following the static equilibration technique using the saturated solutions of various salts. These data were analysed and fitted Guggenheim-Anderson-de Boer (GAB) sorption model. The temperature dependence of the respective coefficients revealed that the GAB model is acceptable ($r^2 \geq 0.994$; $M_{RES} \leq 904$) in describing the EMC-ERH relationships of the tender cashew kernel. The M_0 , C and K values were in the range of 5.740-5.645, 375.538-111.550 and 0.504-0.490 for adsorption. The corresponding values for desorption are 13.274-12.935, 808.516-342.936 and 0.427-0.421. The net isosteric heats of sorption estimated from the Clausius-Clapeyron equation, decreased exponentially from 1.17 to 0.60 kJ mol⁻¹ with the increase in moisture content of the sample 8 % to 23% (db) for adsorption. The corresponding values were 5.75 to 0.684 kJ mol⁻¹ for desorption.

Keywords: Tender cashew kernel, sorption isotherms, excess heat of sorption, Equilibrium moisture content, GAB Model.

The cashew (*Anacardium occidentale*), native to Brazil was introduced about two centuries ago into the India, which is now one of the major producers of the cashew nut. Botanically, the true fruit is the nut, consisting of a kernel enclosed by a hard shell, while the peduncle develops into fruit like, succulent, carbohydrate rich material, known as the cashew apple (Shobha *et al.* 1992). This crop facilitates running more than 1132 processing unit in the country providing employment for nearly 5 lakh families in the industrial sector. Over 95 per cent of unit workers are women from the low income group belonging to socially and economically backward communities (D'Souza, 2007).

India produces around 5,73,000 MT cashew nuts

and ranks 1st in Cashew production (2009-10). Productivity of cashew nut is 815 kg/ha (Chavan & Gawankar, 2010). Green Cashew fruit is a commonly a tender cashew nut. Its colour varies from dark green to bottle green (fresh fruit). The nut is composed of kernel and pericarp or shell. The kernel is slightly curved back on itself and forms two cotyledons, representing about 20±2% of the nuts weight. It is wrapped in a thin, difficult to remove peel (testa), which in turn weigh approximately to 80±2% of the whole nut.

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The quality of any product on storage is largely depended on the water activity of the product (Wang & Brennan, 1991; Singh & Singh, 1996; McMinn & Magee, 1999), which in turn depends on the moisture content and temperature of storage. Moisture sorption behaviour of tender cashew kernel (green cashew kernel) could be a valuable information on its drying behaviour and storage quality. However, there is very little information available on sorption behaviour of cashew nut (Fig.1(a)) in general and tender cashew kernel (Fig.1(b)) in particular. This study envisaged to collect sorption data of this product at various equilibrium relative humidity and wide range of temperatures.



Fig. 1: (a) Tender cashew nut; (b) Tender cashew kernel

A number of models have been previously suggested to describe the relationship between equilibrium moisture content (EMC) and equilibrium relative humidity (Iglesias & Chirife, 1976; Van den Berg & Bruin, 1981; Madamba Driscoll & Buckle, 1993) and have been adopted as standard equations by American Society of Agricultural Engineers for describing moisture sorption isotherms of biological materials (ASAE, 1996). Some of them take into account the effect of temperature, these are modified Chung-Pfost (Chung & Pfost, 1967), modified Henderson (Henderson, 1952); modified Halsay (Halsay, 1948; Iglesias & Chirife, 1976), modified Oswin (Oswin, 1946; Chen & Morey, 1989), and Guggenheim, Anderson and de Boer (GAB) (Van den Berg, 1984; Maroulis, Tasmis, Kouris & Saravacos, 1988).

The present work is aimed to obtain the moisture

sorption isotherms for tender cashew kernels at 30, 40, 50 and 60°C and fitting them in the GAB model to characteristic parameters involved therein. The net isosteric heats of sorption at different moisture levels have also been evaluated.

MATERIALS AND METHODS

Preparation of the sample

Tender Cashew Kernels were obtained from the local market of Dapoli district Ratnagiri (M.S.). The Tender cashew kernels were tray dried at 60°C for 14.50 h to dry it from 82.33% (db) to 6.73% (db). The dried samples at 6.73% (db) was used for adsorption study. The tender cashew nuts were dried at 60°C for 8.33h to dry it up to 14.03% (db). The dried samples at 14.03% (db) was used for desorption study.

Procedure

The equilibrium moisture contents for adsorption and desorption of the tender green cashew kernel (Green cashew) were determined at 30, 40, 50 and 60°C by static gravimetric technique based on isopiestic transfer of water vapour (Suthar and Das, 1997). Saturated salt solutions of various inorganic salts (LiCl , MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, StCl_2 , $(\text{NH}_4)_2\text{SO}_4$, BaCl_2 and Water) were employed (Greenspan, 1977) to generate controlled humidity environment in a closed chamber ranging between 10-100% (8 levels). The change of equilibrium relative humidity of the salt solutions due to change in temperature were estimated using the relations reported by Labuza, Kannane & Chen (1985).

The dried tender green cashew kernel (triplicate) were weighed in the respective moisture boxes then placed in the vacuum desiccators with a stopcock arrangement. Each desiccator had respective saturated salt solutions to obtain constant relative humidity environment (Greenspan, 1977; Weisser, 1986, McMinn & Magee, 1999). Partial vacuum was created inside each desiccators to accelerate the adsorption or desorption process. All salts were reagent grade. The desiccators were kept in a temperature-controlled cabinet at 30, 40, 50 and 60°C

$\pm 1^\circ\text{C}$. Samples were weighed with an accuracy of 0.001g every 24 h.

Samples were equilibrated for approximately 12 days, as evidenced by constant values (± 0.001 g) of four consecutive weight readings. The moisture content of each sample was determined by the oven method (AOAC, 1990). The equilibrium moisture content was determined as an average of three measurements.

The three-parameter GAB model used for analysis of the moisture sorption isotherm can be written as (Rizvi, 1986).

$$\frac{M}{M_0} = \frac{CKa_w}{(1 - Ka_w)(1 - Ka_w + CKa_w)} \quad \dots(1)$$

where, M - equilibrium moisture content (% db); a_w is the water activity; M_0 , C , K are the GAB parameters related to the monolayer moisture content (% db), heat of sorption of monolayer region, and heat of sorption of multilayer region, respectively.

Non-linear analysis has been followed in the present study to obtain the GAB parameters (Jouppila & Roos, 1997) using SYSTAT 8.0 package (SPSS Inc., Chicago, IL, 1998). The statistical validity of the fit to the model was tested from the mean sum of square of the residuals (residual variance, M_{RES} , directly obtained from the package) and from the plots of residual versus calculated values of M .

M_0 , C , and K were generalized in their temperature (T) dependence form as follows (Suthar & Das, 1997; Das & Das, 2002):

$$M_0 = M'_0 \exp\left(\frac{-\Delta E_a}{RT}\right) \quad \dots(2)$$

$$C = C' \exp\left(\frac{-\Delta H_c}{RT}\right) \quad \dots(3)$$

$$K = K' \exp\left(\frac{-\Delta H_k}{RT}\right) \quad \dots(4)$$

Where ΔE_a = activation energy (kJ mol^{-1}); $\Delta H_c = H_1$ (heat of condensation of pure water)- H_m (total heat of sorption of first layer) (kJ mol^{-1}); $\Delta H_k = H_1 - H_q$ (total

heat of sorption of multilayer) (kJ mol^{-1}); M'_0 , C' and K' are the constants; and R ($8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1}$) is the universal gas constant.

Net isosteric heat of sorption, q_{st} was estimated at constant moisture contents from the slope of the Clausius-Clapeyron equation (5) applicable to sorption process (Rizvi, 1986; Resio, Aguerre & Suarez, 1999).

$$\ln a_w = \frac{q_{st}}{RT} + Z(\text{constant}) \quad \dots(5)$$

RESULTS AND DISCUSSION

Figs. 2, (a) and (b) present the moisture content (% db.) vs. equilibrium relative humidity (%) characteristics for Tender cashew kernel at varied temperatures. The adsorption (Fig. 2(a)) and desorption (Fig. 2(b)) isotherms demonstrate a concurrent increase in equilibrium moisture content with increasing equilibrium relative humidity. This behaviour is manifested in the form of sigmoidal shaped curve thus reflecting the prevalent Type II (according to the BET classification) isotherms characteristics (Brunauer *et al.* 1940).

Quantitative evaluation of experimental adsorption and desorption data were provided on the basis of the GAB model. Table 1 summarizes the estimated constants along with the residual variance (M_{RES}) around the fitted line. The correlation coefficient is also given in the table. The low values of (M_{RES}) and correlation coefficients close to unity indicate that GAB model is good fit to the sorption data, and the estimated parameters were statistically acceptable. Keeping the trends presented in Fig. 2 (a) and (b), the characteristic parameters M_0 , C and K display the concurrent decrease with increasing temperature. In particular, the downward trend M_0 with respect to increasing temperature reflects the anticipated reduction in hygroscopicity, which accompanies temperature elevation. This may be ascribed to a reduction in a total sorption ability of the material, which may in turn reflect temperature induced physical and chemical variations (McMinn & Magee, 1999). The values of the other two GAB parameters

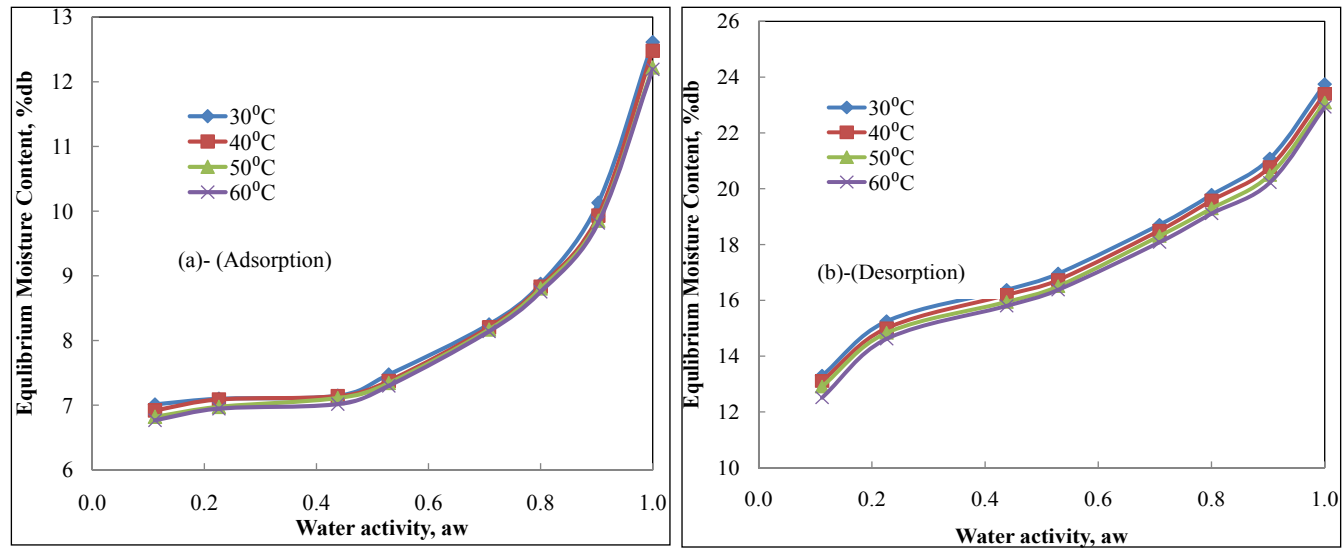


Fig. 2: Equilibrium Moisture Content versus Water activity, a_w for (a) Adsorption, (b) Desorption for Tender cashew kernels at varied temperatures

Table 1: GAB parameters and residual variance (M_{RES}) around the fitted model for adsorption and desorption process of Tender cashew kernels

Process	Temperature (°C)	M_0	C	K	Correlation Coefficient for the fit	M_{RES}
Adsorption	30	5.740	375.538	0.504	0.994	305.510
	40	5.719	200.268	0.499	0.994	299.706
	50	5.695	114.962	0.497	0.995	293.558
	60	5.645	111.550	0.494	0.995	290.795
Desorption	30	13.274	808.516	0.427	0.999	904.585
	40	13.143	661.020	0.425	1.000	880.935
	50	12.984	615.619	0.424	0.999	857.589
	60	12.935	342.936	0.421	0.999	837.736

C and K (Table 1) have been found to decrease with increase in temperature. Such decreasing trends reveal that the binding energies associated with the mono and multilayer sorption of water to the tender cashew kernel decrease with increase in temperature. These trends have been found to be quite common for many foods (Mc Minn & Magee, 1999; Chen & Jayas, 1998).

Table 2 shows the values for the constants of the temperature dependent forms (equations 2-4) of the GAB parameters M_0 , C and K for adsorption and desorption processes. High correlation coefficients

and lower residual variance (M_{RES}) reveals a good fit to all these forms.

In view of the above results it would appear that the sorption characteristics are dependent on the direction of attaining the equilibrium moisture content. Evidence of this hypothesis was provided on comparative analysis of the adsorption and desorption behaviour. It is observed that, irrespective of the temperature, the desorption equilibrium moisture content, at a specific water activity, is higher than the corresponding adsorptive value. This reflects the presence of hysteresis phenomenon. Figs.

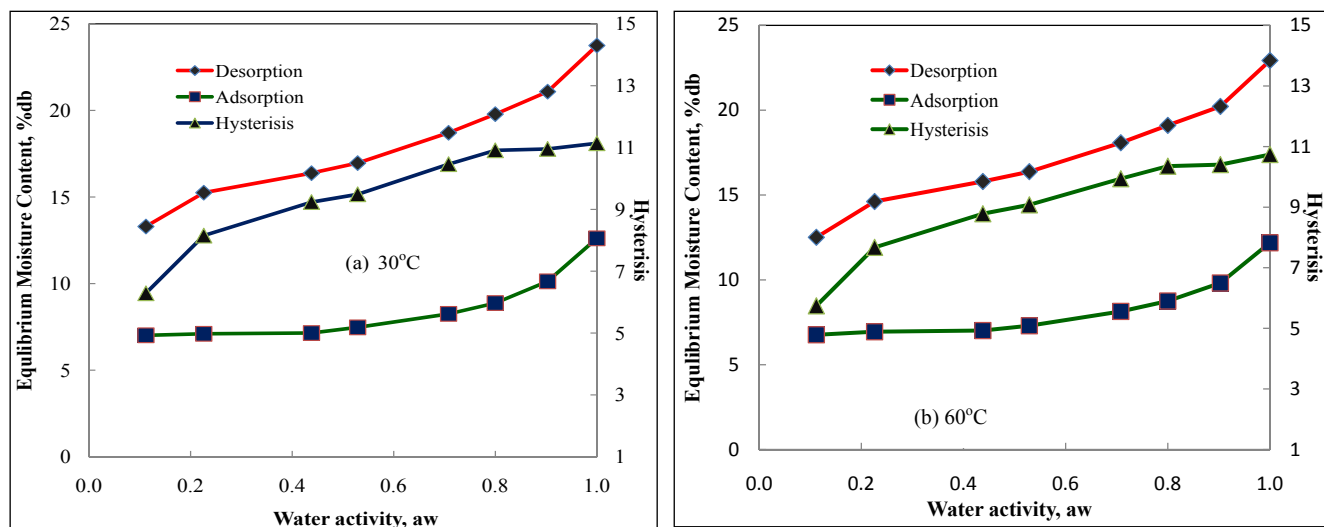


Fig. 3: Hysteresis effect of Desorption and Adsorption of Tender cashew kernels (a) 30°C and (b) 60°C

Table 2: Constants for the temperature dependent forms of the GAB parameters of Tender cashew kernels

Constants	M_0'	C'	K'	ΔE_a (J/mol)	H_c (J/mol)	H_k (J/mol)	M_{RES}			R^2		
							M_0'	C'	K'	M_0'	C'	K'
Adsorption	4.723	0.000155	0.387	0.495	36.917	0.658	80.729	107203.0	0.615	0.963	0.934	0.804
Desorption	9.598	0.363	0.392	0.816	19.492	0.208	423.851	837478.0	0.449	0.980	0.910	0.558

3(a) and 3(b) show typical hysteresis effect for tender cashew kernel at 30°C and 60°C respectively.

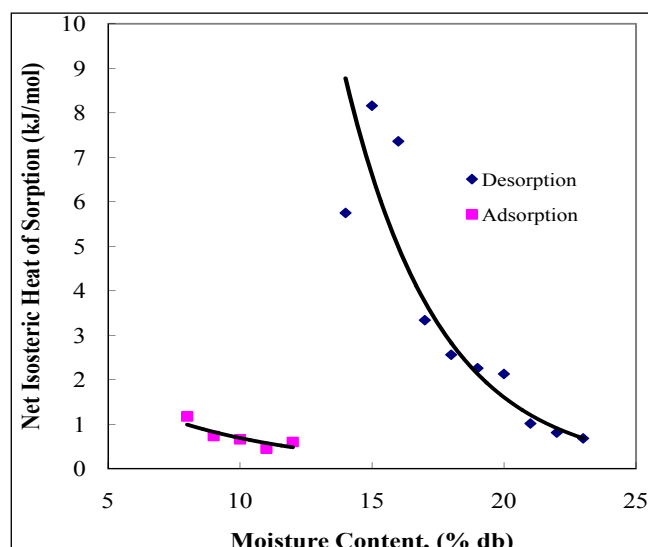


Fig. 4: Net Isothermic Heat of Sorption for Tender Cashew Kernels (a) Adsorption and (b) Desorption

Quantitative evaluation of the hysteresis loop was realized on the basis of the difference in the absorption and desorption equilibrium moisture contents. Accordingly, the amplitude was represented as a function of water activity. The samples present relatively large loop, over almost the entire relative humidity range with the degree of hysteresis becoming more pronounced in the high water activity regions. Such kind of hysteresis effect was well explained by Wolf *et al.* (1972) for protein foods from three categories sugar, protein and starchy foods.

The net isosteric heats of sorption for tender cashew kernel at all the temperatures (30-60°C) for both adsorption and desorption are represented in Fig. 4. The heat for adsorption and desorption was found to decrease exponentially with increase in moisture content. It decreased from 1.176 to 0.604 kJ mol⁻¹ and 5.750 to 0.684 kJ mol⁻¹ for adsorption and desorption, respectively. These trends for adsorption and

Table 3: Characteristic parameters for Eq. (6) (Tsami *et al.* 1990)

Characteristics parameters	q_0	a	M_{RES}	Correlation Coefficient
Adsorption	6.610	0.226	1.441	0.794
Desorption	176.556	0.222	84.092	0.778

desorption are quite similar to many cereal grains, seeds, pulse based foods. (Chung & Pfost 1967, Sopade & Ajisegiri, 1994; Suthar & Das, 1997; Swami *et al.* 2005).

An attempt to evaluate the relationship between the net isosteric heat of sorption (q_{st}) on the equilibrium moisture content, Tsami *et al.* (1990) proposed an empirical exponential correlation. This may be represented in the form:

$$q_{st} = q_0 \exp(-a.M) \quad \dots(6)$$

where q_0 and a are the characteristics parameters.

Table 3 shows the parameters q_0 and a for adsorption and desorption. The isosteric heat of adsorption and desorption become very small at high moisture contents. Lower values of M_{RES} (≤ 1.441) and correlation coefficient ($r^2 \geq 0.794$) for adsorption and M_{RES} (≤ 84.092) and correlation coefficient ($r^2 \geq 0.778$) for desorption suggest a good fit of the data to the equation(6).

CONCLUSION

The trends of moisture sorption isotherms of tender cashew kernel are Type II isotherms. GAB model was found to be suitable for describing the sorption behaviour of tender cashew kernel. The heat of sorption for the tender cashew kernel estimated at different moisture contents showed an exponential relationship. Such equation relating heat of sorption and moisture content would be very helpful in understanding the energetics involved in the process of adsorption and desorption of these nuggets.

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