

## Moisture Desorption Isotherms of African Arrowroot Lily (*Tacca involucrata*) Tuber Mash as Influenced by Blanching and Natural Fermentation

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**Abstract:** The moisture desorption isotherms of the African arrowroot lily (*Tacca involucrata* S) tuber mash as influenced by blanching and natural fermentation were investigated using gravimetric method. Equilibrium Moisture Contents (EMCs) of four products comprising Non Blanched Non Fermented Mash (NBNFM), Non Blanched Fermented Mash (NBFM), Blanched Non Fermented Mash (BNFM) and Blanched and Fermented Mash (BFM) were obtained at 10-30°C and water activity ( $a_w$ ) of 0.08-0.95. Percent Root Mean Square of error (RMS%) was used to evaluate goodness of fit of common moisture sorption models to experimental data while isosteric heats of desorption were calculated using the Clausius-Clapeyron equation. The isotherms were sigmoid in shape (type II) with the EMCs being lowest for the blanched and fermented mash. The GAB, Halsey and Oswin equations in that order provided good fit to experimental data (<10% RMS). BET monolayer moisture contents were lower for pretreated samples and ranged from 10.6-16.3 g H<sub>2</sub>O/100 g solids for the Native Mash (NBNFM) and 6.04-8.9 g H<sub>2</sub>O/100 g solids for the BFM, surface areas for monolayer desorption ranged from 370.6-572.9 m<sup>2</sup> g<sup>-1</sup> solid for NBNFM and 212.2-312.9 m<sup>2</sup> g<sup>-1</sup> solid for BFM. Net isosteric heats of desorption significantly ( $p < 0.05$ ) decreased with increase in moisture content with maximum values varying from 6.6 kJ mol<sup>-1</sup> for the native mash to 27.6 kJ mol<sup>-1</sup> for the BFM.

**Key words:** Blanching, desorption isotherms, fermentation, isosteric heats, *Tacca involucrata*

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### INTRODUCTION

The African arrowroot lily (*Tacca involucrata*) is a perennial plant. It belongs to the family Araceae of the order Arales. The plant is native to tropical Africa and is widely distributed in most parts of the forest and savannah regions of Nigeria. The tuber known as gbache and onu-umwah, respectively by the Tiv and Etulo people is one of the unconventional and less exploited sources of food for human and animal nutrition.

In Benue, Nassarawa and Plateau States of Nigeria, the tubers are processed into thick gels which are eaten with soups, stews and benniseeds. The starch is used as a thickening agent for soups and in local textile industries for improving the strength and shine of clothing. There is increasing attention to the cultivation of the plant since it acts as a bridge tuber crop between the planting and harvesting periods of the more conventional roots and tubers such as cassava, potato and yam. Unfortunately, the African arrowroot lily tubers are highly perishable and therefore require prompt and adequate preservation or processing for shelf life extension. Locally, the tubers are mashed, squeezed and the semi solid matter allowed to

undergo bulk natural fermentation in bags or baskets. The fermented mash is then molded into balls which are boiled in water, sliced and sun dried. Such dried products are subsequently milled and utilized for various food applications. Poor drying and storage techniques most often result in great losses of the processed products.

Moisture content of foods influences texture, storage stability and their susceptibility to microbial spoilage (Labuza, 1968). Most microorganisms have specific water activities ( $a_w$ ) below which they will not grow. The relationship between moisture content and water activity in dehydration processes is often expressed in terms of moisture desorption isotherms. In order to better control the quality of dehydrated African arrowroot lily tubers during production and storage, data are needed for determining interactions of water and the food substances following various pretreatments such as cooking and fermentation.

Knowledge of the monolayer moisture contents ( $M_0$ ) of such African arrowroot lily tuber products which is regarded as moisture contents for maximum stability of dehydrated products are essential for estimating appropriate drying times and packaging requirements

(Labuza, 1968). The mean and total net heats of desorption are useful data for predictive drying modeling, calculating energy consumption during drying of agricultural materials, design of drying equipment and describing of the heat and mass transfer related processes (Tsami *et al.*, 1990). Such information which can be obtained from moisture desorption isotherms abound in literature for most other roots and tubers (Gevaudan *et al.*, 1989; Wang and Brennan, 1991; McLaughlin and Magee, 1998; Mcminn and Magee, 1999; Mcminn *et al.*, 2003) but lacking for the African arrowroot lily tuber products.

The objectives were to determine the effects of blanching and natural fermentation on moisture desorption isotherms of the African arrowroot lily tuber mash at 10, 20, 30 and 40°C, determine the goodness of fit of common sorption models to the data and evaluate heats of desorption that characterize the moisture transfers.

## MATERIALS AND METHODS

Matured (4-5 months) African arrowroot lily (*Tacca involucreta*) tubers (5-6 cm diameter) of about 76% moisture content (wet basis) were harvested from the farm lands in the University of Agriculture, Makurdi, Nigeria. The tubers were promptly transported in jute bags to the laboratory, sorted and washed with tap water to remove adhering soil and other foreign matter. The cleaned tubers were stored in a cold room maintained at 8±2°C and utilized within 8 h for experiments. A 500 mL capacity air tight transparent plastic containers (11.8 cm diameter x 12.5 cm height) and stainless wire steel wire gauzes were purchased from a local market.

**Samples preparation:** Four experimental mashes comprising Blanched Non Fermented Mash (BNFM), Blanched and Fermented Mash (BFM), Non Blanched Fermented Mash (NBFM) and Non Blanched Non Fermented Mash (NBNFM) were produced as described below. The cleaned tubers were peeled and sliced to 0.5 cm thickness under chilled tap water (5±1°C) using stainless steel knives. The slices were wet milled into a mash using a disc attrition mill (Asiko All, Addis, Nigeria) with a nip of about 3 mm. The chilled mash was divided into two equal parts. One lot was subjected to steam blanching while the other was not blanched. The samples for heat treatment were wrapped with aluminum foil in 500 g packs and subjected to saturated steam (15 psi; 121.1°C) for 30 min to achieve a 95% gelatinization of the starch. The degree of starch gelatinization was determined using a rapid spectro-photometric method described by

Wootton and Munk (1971). Adequacy of blanching was verified using peroxide test strips (Sigma Company, California, USA).

Each lot was divided into two, a sub lot from each was then subjected to accelerated natural fermentation (30±2°C, 72 h) as described by Ariahu *et al.* (1999). Total 120 g of mash were placed in a covered 500 mL glass beaker at room temperature (30±2°C) for 24 h. At the end of this period, 50% of the fermenting mash was used as starter for a new fermentation cycle. During this process, the pH and titratable acidity which are indices of lactic acid bacteria activities were monitored until they remained fairly constant (pH 4.6, 0.8 g lactic acid/100 g mash) after 72 h. The Non Blanched and Non Fermented (NBNFM) sub lot was designated as native sample and acted as control in the desorption experiments.

**Desorption studies:** Desorption was measured at 10, 20, 30 and 40°C, respectively for each mash type. In order to avoid possible contamination caused by the activity of microorganisms, especially at high water activities, 0.25% of sodium azide was added to each mash (Gevaudan *et al.*, 1989). Sulphuric acid solution were used to provide water activities ranging from 0.08-0.95 as described by Ruegg (1980). About 100 mL of each acid solution were introduced into each of the 500 mL airtight plastic containers. The quantity of acid solution was chosen so that the variation of concentration due to water desorbing from the mash samples was <0.1%. Stainless steel wire gauzes were forced in to place over the sulphuric acid solutions to from support for the samples. Duplicate samples (each 0.5 g) of each mash type were weighed in crown corks and placed on the wire gauze above the solutions. The containers were covered tightly with lids and allowed to equilibrate in thermostatically controlled incubators set at the selected temperatures. The samples were weighed every 2 days with a precision electronic balance (±0.001 g) until differences between consecutive readings were <0.5% of sample weight. Variations in the densities of the acid solutions after each desorption study was <0.2%.

The dry matter content of the samples on equilibration was obtained by weighing after drying to constant weight in a vacuum oven at 70±1°C for 24 h.

**Proximate analysis:** Proximate compositions of the various mash types were determined by the AOAC (1984) standard procedure 14.062 for moisture content, 14.063 for ash and 14.064 for crude fiber, 14.066 for crude fat and 14.067 for crude protein. Carbohydrate was calculated by difference.

**Moisture sorption models:** The Brunauer-Emmett-Teller (BET), Guggenheim-Anderson-de Boer (GAB), Oswin, Halsey and Henderson models as outlined earlier by Ariahu *et al.* (2006) were considered. The BET isotherm equation (Brunauer *et al.*, 1938) is presented in Eq. 1:

$$a_w/(1-a_w) M = 1/M_0 C + (C-1) a_w/M_0 C \quad (1)$$

Where:

M = Equilibrium moisture content  
M<sub>0</sub> = Monolayer moisture content  
C = A constant related to heat of sorption  
a<sub>w</sub> = Water activity

The GAB model (Bizot, 1983) is as shown in Eq. 2:

$$M/M_0 = GK a_w / (1 - K a_w) (1 - K a_w + G K a_w) \quad (2)$$

where, G and K are constants related to the energies of interaction between the first and distant sorbed molecules at the individual sorption sites. Bizot (1983) transformed Eq. 2 into a quadratic Eq. 3:

$$a_w/M = A a_w^2 + B a_w + C \quad (3)$$

With:

$$A = K/M_0 [(1/G)-1] \quad (4)$$

$$B = K/M_0 [1-(2/G)] \quad (5)$$

$$C = 1/M_0 GK \quad (6)$$

Equation 5 is rearranged with respect to the moisture content (M) to give Eq. 7:

$$M = \frac{a_w}{A a_w^2 + B a_w + C} \quad (7)$$

From Eq. 3-7:

$$M_0 = 1/(B^2 - 4AC)^{1/2} \quad (8)$$

One of the earliest models describing the temperature effect was described by Henderson (1952) as provided in Eq. 9:

$$\ln(1-a_w) = -ATM^B \quad (9)$$

Where:

A and B = Constants  
T = Temperature (°C)

The Halsey (1948) equation is as presented in Eq. 10:

$$a_w = \exp(A/RTQ^s) \quad (10)$$

Where:

A and s = Constants  
Q = M/M<sub>0</sub>

The Oswin (1946) equation is shown in Eq. 11:

$$M = A (a_w/1-a_w)^B \quad (11)$$

where, A and B are constants. The Oswin equation has been found as a good fit model for the sorption of various starchy food products (Lomauro *et al.*, 1985).

**Sorption data analysis:** From the data generated, equilibrium moisture contents versus water activities for each temperature were plotted. The acquired sorption data were analyzed using the BET (Eq. 1), GAB (Eq. 2), Henderson (Eq. 9), Halsey (Eq. 10) and Oswin (Eq. 11) models. The parameters of BET, Henderson, Halsey and Oswin models were calculated by linear regression analysis while the GAB quadratic parameters were analyzed on an IBM 308 ID Computer using SPS package. The accuracies of fit of the models were verified by calculating the Root Mean Square of error (RMS%) according to Ariahu *et al.* (2006) as shown in Eq. 12:

$$RMS(\%) = \frac{\sqrt{\sum \left( \frac{M_{obs} - M_{est}}{M_{obs}} \right)^2 \times 100}}{n} \quad (12)$$

Where:

M<sub>obs</sub> = Experimental values  
M<sub>est</sub> = Predicted moisture values  
n = Number of experimental data

The BET monolayer values (Brunauer *et al.*, 1938) were calculated from the regression equation of the BET plot using the moisture sorption data up to 0.46a<sub>w</sub> since the BET equation holds well below 0.5a<sub>w</sub> (Labuza, 1968). The GAB monolayer values were calculated from the data in the a<sub>w</sub> range 0.08-0.95. For each equilibrium moisture content, the corresponding water activity values for desorption were calculated using Clausius-Clapeyron equation as described by Labuza *et al.* (1985).

## RESULTS AND DISCUSSION

**Description of isotherms:** The desorption isotherms of the meshes are shown in Fig. 1. The isotherms gave the characteristic sigmoid shapes which conform to type II classification exhibited by most biological tissues (Iglesias and Chirife, 1976). At water activities >0.5, higher amount of water was desorbed for a small decrease in

water activity indicating that moisture in this region is weakly bound to the solid surface. At  $a_w > 0.5$ , relatively lower moisture was desorbed for a higher decrease in  $a_w$ . This implies that moisture desorption by the mashes is more difficult as more tightly bound water are encountered. As explained by Dural and Hines (1993), the first concave region of the desorption isotherm represents least strongly bound and most mobile water. The second region corresponds to approximately linear curve in which water is held by the material in the matrix. Water removed in this region expose binding sites in the first layer. The last convex region represents the monolayer moisture zone in which water is bound by the hydrophilic water-ion or water-dipoles interactions. Thus, water in this region is most strongly held. Generally, the graphs showed decrease in Equilibrium Moisture Content (EMC) with decreasing  $a_w$  at constant temperature. These changes in EMC are due to inability of the mashes to maintain vapor pressure at unity with decreasing moisture content. According to McLaughlin and Magee (1998) as moisture content decreases, moisture in food tends to show a lower vapour pressure, acting as if in solution, changing with atmospheric humidity and resulting in the characteristic sigmoid shape of water desorption isotherms.

From Fig. 1, it can also be seen that at a constant water activity, EMCs increased with decreasing temperature. Similar trends were reported by earlier researchers such as McLaughlin and Magee (1998), Wang and Brennan (1991) and McMinn *et al.* (2003) for other root and tuber products. This trend may be explained from kinetic molecular theory point of view. At increased temperatures, water molecules are in an increased state of excitation, thereby increasing their distance apart and decreasing the attractive forces between them. This results in relative ease of removed of the water and hence lower EMC.

**Effect of pretreatments:** The proximate composition of the native and processed African arrow root lily tuber mashes are shown in Table 1. The results indicate that the products have total carbohydrates contents of 90-93 g/100 g solids of which starch is  $\geq 82\%$ . The precooking and fermentation processes significantly ( $p < 0.05$ ) reduced the total carbohydrate contents.

From Fig. 1, it can be observed that the native (NBNFM) mash has higher EMC at all the sorption temperatures considered. Also the Blanched and Fermented product (BFM) had the least EMCs. This implies that both precooking and fermentation pretreatment have significant effect on moisture desorption isotherms of the African arrowroot lily tuber.

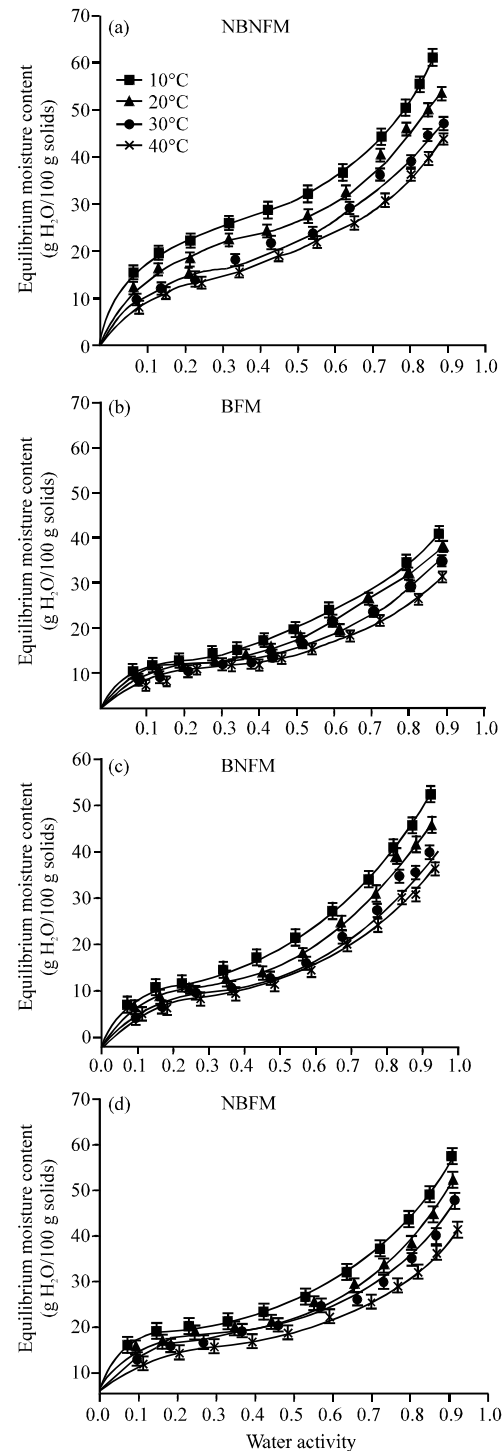


Fig. 1: Moisture desorption isotherms of African arrowroot lily tuber mash; a) NBNFM = Non Blanched non Fermented mash; b) BFM = Blanched Fermented Mash; c) BNFM = Blanched non fermented mash and d) NBFM = Non Blanched Fermented Mash

Table 1: Proximate composition of African arrowroot lily (*Tacca involucreata*) tuber mashes

*Parameters (g/100 g solids)	Mash			
	NBNFM (native)	NBFM	BNFM	BFM
Protein	4.60±0.10 <sup>b</sup>	5.60±0.10 <sup>a</sup>	4.20±0.10 <sup>b</sup>	5.80±0.10 <sup>a</sup>
Fat	1.11±0.08 <sup>b</sup>	1.80±0.06 <sup>a</sup>	1.40±0.05 <sup>ab</sup>	2.23±0.06 <sup>b</sup>
Total fiber	14.80±0.20 <sup>a</sup>	15.20±0.30 <sup>a</sup>	14.60±0.20 <sup>a</sup>	15.60±0.20 <sup>a</sup>
Ash	1.61±0.06 <sup>a</sup>	1.30±0.01 <sup>a</sup>	1.24±0.08 <sup>a</sup>	1.81±0.01 <sup>a</sup>
Carbohydrates	92.75±0.81 <sup>b</sup>	91.30±0.50 <sup>c</sup>	93.22±0.70 <sup>a</sup>	90.20±0.43 <sup>d</sup>
Starch (%)	84.01±0.52 <sup>a</sup>	83.40±0.77 <sup>b</sup>	84.31±0.00 <sup>a</sup>	82.73±0.55 <sup>c</sup>

Values are NBNFM = Non Blanched Non Fermented Mash; NBFM = Non Blanched Fermented Mash; BNFM = Blanched Non Fermented Mash; BFM = Blanched Fermented Mash

When starchy products are heated in an aqueous medium, a transition from an ordered to a disordered state occurs. This process is known as gelatinization (Pravisan *et al.*, 1985). Gelatinization involves loss of crystallinity absorption of heat and swelling of the starch granules. The swelling of the granules implies exposure of more moisture binding sites to the environment for desorption. Again, the heat treatment results in the weakening of bonds and production of damaged starch granules. During fermentation, the starch molecules are further modified and also degraded. According to Ariahu *et al.* (1999), lactic acid bacteria fermentation of starchy foods leads to breakdown of the starch into oligosaccharides, simple sugars and organic acids with structural modifications being higher for damaged starches. These structural modifications result also in higher porosity and hence increased mass transfer rates.

The lower EMCS for the precooked and fermented samples denote the relative ease of drying of the pretreated mashes. The higher EMCs for the native samples could be attributed to the higher crystallinity and content of undamaged starch granules relative to those of the blanched and/or fermented products. Earlier reports by Yadav *et al.* (2006) indicated that native potato starch has greater degree of associative forces in the granules. This could also explain the higher affinity for water molecules by the native mash in the present study. Effects of blanching or precooking and fermentation on the desorption pattern of the mashes are in conformity with reports by Johnson and Brennan (2000) who indicated that the desorption capacity of a product is increased by pre-treatments such as heating, desalting and pH changes. Bizot *et al.* (1985) and Gevaudan *et al.* (1989) had earlier shown that water desorption capacity was higher for gelatinized potato starch and cassava mash respectively than the native samples.

**Goodness of fit of models:** The percentage Root Mean Square of errors (RMS%) for the models considered is shown in Table 2. According to Wang and Brennan

Table 2: Goodness of fit of various sorption models to moisture desorption data of *Tacca involucreata* tuber mashes

Product	Sorption model	Means square of error (RMS %) Temp. (°C)				
		10	20	30	40	Mean
BNFM	<sup>1</sup> GAB	7.13	5.40	5.74	5.78	6.01
	<sup>2</sup> Oswin	7.94	10.94	8.84	11.10	9.71
	<sup>3</sup> Henderson	12.98	15.90	12.53	10.56	12.98
	<sup>4</sup> Halsey	7.17	10.26	10.40	9.29	9.28
NBFM	GAB	5.38	6.75	6.79	7.08	6.50
	Oswin	8.79	9.90	5.12	5.91	7.43
	Henderson	14.14	16.14	14.18	10.72	13.80
	Halsey	5.87	5.52	4.80	4.72	5.23
BFM	GAB	6.82	6.53	8.40	8.61	7.59
	Oswin	3.81	10.34	6.56	5.94	6.66
	Henderson	18.79	17.64	12.74	10.83	15.0
	Halsey	3.57	4.98	5.04	4.70	4.63
NBNFM	GAB	5.12	7.82	4.20	6.05	5.80
	Oswin	9.01	6.08	5.15	6.20	6.61
	Henderson	7.05	7.03	7.91	5.56	6.84
	Halsey	9.01	10.48	9.64	10.40	9.88

<sup>1</sup>GAB equation (Bizot, 1983), <sup>2</sup>Oswin (1946), <sup>3</sup>Henderson (1952), <sup>4</sup>Halsey (1948). \*BNFM = Blanched Non Fermented Mash, NBFM = Non Blanched Fermented Mash, BFM = Blanched Fermented Mash, NBNFM = Non Blanched Non Fermented (native) Mash

(1991), RMS% values of  $\leq 10\%$  for sorption models indicate a reasonably good fit for practical purposes. The RMS% and coefficient regression ( $r^2$ ) were used in literature to evaluate the goodness of fit of different mathematical models as applied to experimental data (Lomauro *et al.*, 1985; Wang and Brennan, 1991). The GAB model predicted the desorption isotherms ( $r^2 \geq 0.982$ ) NBNFM and NBFM with the smallest RMS% of 5.8 and 6.01, respectively. Therefore, this model best described the desorption data of NBNFM and NBFM. The Halsey equation ( $r^2 \geq 0.965$ ) best described the desorption isotherms of BFM and NBFM with mean RMS% of 4.63 and 5.23, respectively. The Oswin model ( $r^2 \geq 0.930$ ) with mean RMS% range of 6.61-9.71 also gave satisfactory fit to the data. The Henderson equation ( $r^2 \leq 0.869$ ) gave the highest mean RMS% values (6.84-15.0). Wang and Brennan (1991) reported a better fit with Oswin model than the Halsey equation. Generally, the GAB, Halsey and Oswin models in that order best fitted the desorption isotherms of the African arrow root lily tuber mash.

**Moisture desorption derivatives:** The BET and GAB models were employed to calculate monolayer Moisture contents ( $M_0$ ) as shown in Table 3. The  $M_0$  value represents the moisture content of the material when the entire surface is covered with a unimolecular moisture content. The  $M_0$  values varied with the pretreatments and desorption temperature ranging within 10-40°C from 13.64-10.61 g H<sub>2</sub>O/100 g solids (BNFM), 11.94-8.22 g H<sub>2</sub>O/100 g solids (NBFM), 9.80-7.29 g H<sub>2</sub>O/100 g solids (BFM) and 19.60-13.32 g H<sub>2</sub>O/100 g solids (NBNFM) from the GAB Model. The BET monolayer moisture contents were lower and ranged within 10-40°C from 11.01-7.71 g H<sub>2</sub>O/100 g

solids (BNFM), 9.79-7.04 g H<sub>2</sub>O/100 g solids (NBFM), 8.91-6.04 g H<sub>2</sub>O/100g solids (BFM) and 16.31-10.55 g H<sub>2</sub>O/100 g solids for the native (NBNFM) mash. These values are comparable to those reported by Lomauro *et al.* (1985), Wang and Brennan (1991) and Fasina (2006) for other starchy foods at 10-45°C. The decrease in monolayer moisture contents with increase in temperature, as observed in this study is consistent with the reports of McMinn *et al.* (2003) for starch gels and McMinn and Magee (1999) for potatoes.

These researchers suggested that with increases in temperature, some water molecules are activated to energy levels that allow them to break away from their sorption sites, thus decreasing the M<sub>0</sub> values. The lower M<sub>0</sub> values for the blanched and/or fermented mashes can be explained by considering the structural changes in starch polymers due to the pretreatments. Such processes tend to reduce the degree of hydrogen bonding in the polymer there by decreasing the availability of active sites for water binding. This coupled with structural modifications such as increase in porosity, as stated earlier could account for the lower M<sub>0</sub> values due to precooking and fermentation.

Studies on the rate of reaction causing deterioration of dehydrated foods have shown that there is a residual moisture content at which the rates are at a minimum (Labuza, 1968). These reactions include enzymic hydrolysis, Maillard browning, non-enzymic changes and microbial growth. All but oxidation reaction are at a minimum as moisture content is further reduced. The critical moisture content corresponds to the M<sub>0</sub> value (Labuza, 1984). Above the M<sub>0</sub> value, the amount of water held is sufficient as a solvent in which chemical species dissolve becoming mobile and active. High residual moisture content results in faster reaction rates due to higher solubility. Thus the monolayer moisture contents correspond to moisture contents at which the various dehydrated African arrow root lily tuber products will be most stable. Knowledge of such data will be necessary in the dehydration and packaging of the products since drying to the M<sub>0</sub> values and maintaining them at those values will maximize their shelf lives. As reported by Ariahu *et al.* (1999), the monolayer moisture values may be used to determine the apparent surface area of the sorbent (S<sub>0</sub>) since:

$$S_0 = (1/M_s) N_0 A M_0 \text{ (m}^2/\text{g solid)} \quad (13)$$

Where:

- M<sub>s</sub> = The relative molecular mass of water
- N<sub>0</sub> = Avogadro's number (6.023×10<sup>23</sup> molecules mol<sup>-1</sup>)
- A = The apparent surface area of one water molecule (1.05×10<sup>-19</sup> m<sup>2</sup>)

Table 3: GAB and BET isotherm derivatives for moisture desorption by African arrowroot lily tuber mashes

Product	Temp. (°C)	GAB	BET	S <sub>0</sub> (m <sup>2</sup> /g solids)
		M <sub>0</sub> (gH <sub>2</sub> O/100 g solids)	M <sub>0</sub> (gH <sub>2</sub> O/100 g solids)	
BNFM	10	13.64	11.01	386.65
	20	10.99	8.78	308.36
	30	10.48	8.33	292.72
	40	10.61	7.71	270.87
NBFM	10	11.94	9.79	344.09
	20	9.52	8.13	285.66
	30	9.21	7.90	277.48
	40	8.22	7.04	242.44
BFM	10	9.80	8.91	312.90
	20	7.97	7.47	262.29
	30	8.32	6.73	236.62
	40	7.29	6.04	212.16
NBNFM	10	19.60	16.31	572.92
	20	11.07	14.11	495.68
	30	14.79	11.92	418.68
	40	13.32	10.55	370.58

M<sub>0</sub> = Monolayer moisture contents, S<sub>0</sub> = Apparent surface area of sorbent.  
 \*BNFM = Blanched Non Fermented Mash; NBFM = Non Blanched Fermented Mash; BFM = Blanched Fermented Mash; NBNFM = Non Blanched Non Fermented (Native) Mash

The S<sub>0</sub> values are shown also in Table 3. As expected from Eq. 13, the data followed the same trend as for M<sub>0</sub> values. Low EMCs and hence low M<sub>0</sub> values imply that quantitatively, moisture desorption was higher and hence less water available. The desorption process causes drying out, shrinkage and general collapse of the capillary porous structure thus reducing surface areas for monolayer sorption (Wang and Brennan, 1991). The S<sub>0</sub> values obtained for the various mashes were higher than the values of 100-250 m<sup>2</sup> g<sup>-1</sup> solid exhibited by most foods as reported by Labuza (1968). The M<sub>0</sub> values used for the derivations of S<sub>0</sub> vary with food composition and processes.

**Isosteric heats of moisture desorption:** The net isosteric heats of desorption of the various African arrowroot lily tuber mash using the Clausius-Clapeyron equation (Labuza *et al.*, 1985) yields Eq. 14:

$$\ln a_w = C_{st} - (\Delta H_{st}/R) (1/T) \quad (14)$$

Where:

- ΔH<sub>st</sub> = H<sub>L</sub> - H<sub>v</sub> = Net isosteric heats of desorption
- H<sub>L</sub> = Isosteric heats of desorption (kJ mol<sup>-1</sup>)
- H<sub>v</sub> = Latent heat of vaporization of pure water (kJ mol<sup>-1</sup>)
- T = Absolute temperature (°K)
- R = Molar gas constant (0.008314 kJ mol<sup>-1</sup> °K)

The net isosteric heats (ΔH<sub>st</sub>) were derived from the slopes of the linear regression analysis of the relationship

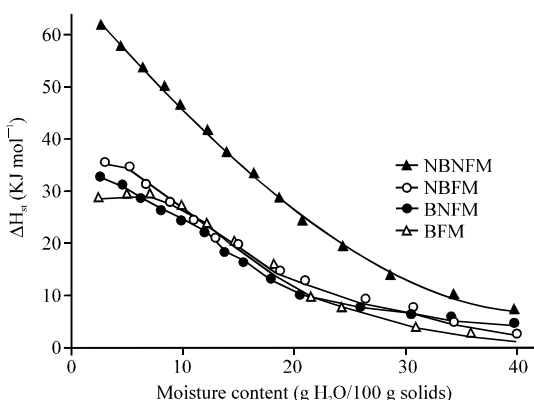


Fig. 2: Variations of net isosteric heats of desorption ( $\Delta H_{st}$ ) with moisture content of African arrow root lily tuber mash; NBNFM = Non Blanched Non Fermented, NBFM = Non Blanched Fermented Mash; BNFM = Blanched Non Fermented Mash and BFM = Blanched and Fermented Mash

between  $\ln a_w$  and inverse absolute temperature at constant moisture contents. Figure 2 is a graphical representation of the net isosteric heats of desorption as a function of moisture contents. The mashes showed marked increase in isosteric heats with decreasing moisture contents with the native samples having the highest and the blanched and fermented mash having the least values at comparable moisture contents. According to McLaughlin and Magee (1998), foodstuffs are complex in structure and the main water sorbing polymers in food (e.g., starch, cellulose etc.) will exhibit water binding sites of varying degrees of activity. From Fig. 2, it can be explained that initially, desorption occurred at the least active sites which require low interactive energies in addition to the latent heat of vaporization of pure water. The variations in heat of desorption with moisture content and magnitude relative to the latent heat of vaporization of pure water provides valuable data for energy consumption calculations and subsequent design of drying equipment and an understanding of the extent of the water-solid versus water-water interactions (McMinn and Magee, 2003). As desorption progresses, sorption took place at active sites requiring higher interactive energies. Different polar groups on the water binding polymers and changes in the dimensions and geometry of the polymers during sorption are thought to give rise to these range of activities at the binding sites (McLaughlin and Magee, 1998). As explained by Dural and Hines (1993), the differences in net isosteric heats may be due to surface heterogeneity elaborated by the blanching and fermentation treatments. Energetically non-uniform surfaces possess sites with different sorption potentials

that lead to variations in the isosteric heats. When considering the application of Clausius-Clapeyron equation, it is obvious that anything that affects desorption isotherms of the mashes would affect the thermodynamic quantities derived from it. These include the prehistory of the sample such as the various pretreatments (blanching and fermentation). These pretreatments may have changed the polar and other groups that bind water along with changes in capillary and other configurations of the food structure. Aviara and Ajibola (2002) observed that the heat of desorption for native cassava was higher than that of gari indicating that gelatinization of starch may have a lowering effect on the binding energy of water sorbed by starchy products. The maximum net isosteric heats obtained in this study (65.5 kJ mol<sup>-1</sup> for the native mash; 32.3 kJ mol<sup>-1</sup> for BNFM, 34.7 kJ mol<sup>-1</sup> for NBFM and 27.6 kJ mol<sup>-1</sup> for BFM) are higher than those reported for tapioca (12.6 kJ mol<sup>-1</sup>) and cassava mash (16.2 kJ mol<sup>-1</sup>) by Iglesias and Chirife (1976) and Gevaudan *et al.* (1989), respectively. The value (40 kJ mol<sup>-1</sup>) reported by McLaughlin and Magee (1998) for potatoes fell within the range obtained for the African arrowroot lily tuber mashes. The differences could be attributed to differences in composition and pretreatments given to the products. Tsami *et al.* (1990) proposed the empirical Eq. 15 to describe the relationship between  $\Delta H_{st}$  and the equilibrium moisture contents:

$$\Delta H_{st} = \Delta H_0 \exp(-M/M_c) \quad (15)$$

Where:

- $M$  = The equilibrium moisture content
- $\Delta H_0$  = The net isosteric heat of desorption of the last molecule of water on the sorbent
- $M_c$  = A characteristic moisture content of the food material

Equation 15 was transformed into a linear form by using the natural logarithm on both sides. The transformed equation was fitted to  $\Delta H_{st}$  data as a function of moisture content by linear regression. The estimated models for the various African arrowroot lily tuber mashes are as expressed in Eq. 16-19:

$$\text{NBNFM: } \Delta H_{st} = 79.5206 \exp(0.0661M) \quad (r^2 = 0.993) \quad (16)$$

$$\text{BFM: } \Delta H_{st} = 40.1737 \exp(0.0752M) \quad (r^2 = 0.983) \quad (17)$$

$$\text{NBFM: } \Delta H_{st} = 49.6571 \exp(0.0727M) \quad (r^2 = 0.986) \quad (18)$$

$$\text{BNFM: } \Delta H_{st} = 43.8429 \exp(0.0641M) \quad (r^2 = 0.985) \quad (19)$$

The models can be useful in the estimation of energy requirements for drying of the products to specified moisture contents.

**Drying energy estimates:** According to Tsami *et al.* (1990), the net heat of sorption of water  $Q$  ( $\text{kJ mol}^{-1}$ ) from moisture content  $M$  to dryness ( $M = 0$ ) is defined by Eq. 20:

$$Q = \int_0^{M_2} \Delta H_{st} dM \quad (20)$$

Substituting  $\Delta H_{st}$  from Eq. 15 into Eq. 20 and integrating yields Eq. 21:

$$Q = \Delta H_0 M_c (1 - \exp(-M/M_c)) \quad (21)$$

For very high moisture contents ( $M \rightarrow \infty$ ), Eq. 21 gives the total net isosteric heat of desorption of water ( $Q_T$ ):

$$Q_T = \Delta H_0 M_c \quad (22)$$

The net heat of desorption of water for a change of moisture content from a change of moisture content from  $M_1$ - $M_2$  ( $Q_{12}$ ) is as expressed in Eq. 23:

$$Q_{12} = \Delta H_0 M_c [\exp(-M_1/M) - (\exp(-M_2/M_c))] \quad (23)$$

The mean net heat of desorption of water ( $q$ ) in the moisture range ( $M_1, M_2$ ) is defined by Eq. 24;

$$q = \int_{M_1}^{M_2} \Delta H_{st} dM \int_{M_1}^{M_2} dM \quad (24)$$

which upon integration becomes Eq. 25:

$$q = \Delta H_0 \left[ \frac{\exp(-M_1/M_c) - (\exp(-M_2/M_c))}{(M_2/M_c) - (M_1/M_c)} \right] \quad (25)$$

Data obtained using Eq. 22, 23 and 25 are shown in Table 4 for the various tuber mashes. The mean and total net heat of desorption ( $q$  and  $Q_T$ ) ranged from 10.44 (BFM) to 23.19 (NBNFM)  $\text{kJ mol}^{-1}$  and 296.86 (BFM) to 668.75  $\text{kJ kg}^{-1}$  dry matter, respectively. The  $q$ -values were estimated in the moisture range  $M_1 = 0.0$ - $M_2 = 0.6$   $\text{kg H}_2\text{O/kg}$  dry matter. These estimates clearly show the advantages of blanching and fermentation of the tubers with respect to energy requirement during further processes such as dehydration. For example, the  $Q_T$  value is about 3 times higher for the native sample (non blanching and non fermented) than for the Blanching and

**Table 4: Energy estimates for drying of African arrowroot lily tuber mashes**

Product	$Q_T$ ( $\text{kJ g}^{-1}$ dry matter)	$Q_{12}$ ( $\text{kJ kg}^{-1}$ dry matter)	$q$ ( $\text{kJ mol}^{-1}$ )
BNFM	379.9 <sup>a</sup>	-200.8 <sup>a</sup>	13.1 <sup>m</sup>
NBFM	379.6 <sup>a</sup>	-183.3 <sup>a</sup>	13.3 <sup>m</sup>
BFM	296.9 <sup>b</sup>	-135.6 <sup>a</sup>	10.4 <sup>L</sup>
NBNFM	668.8 <sup>d</sup>	-338.8 <sup>a</sup>	23.2 <sup>k</sup>
Average	397.9	-214.6	13.9

$Q_T$  = Total heat of desorption;  $q$  = Mean net heat of desorption;  $Q_{12}$  = Energy for drying from 0.6-0.1  $\text{kg H}_2\text{O/kg}$  dry matter. BNFM = Blanching Non Fermented Mash; NBFM = Non Blanching Fermented Mash; BFM = Blanching Fermented Mash; NBNFM = Non Blanching Non Fermented Mash. Values within each column with common superscripts are not significantly ( $p > 0.05$ ) different

Fermented Mash (BFM). Similar variations in the sorption energetic with various pretreatments have been reported for rice, potato and cassava (Aviara and Ajibola, 2002; McMinn and Magee, 2003; Fasina, 2006). The net heat of desorption ( $Q_{12}$ ) in drying from 0.6  $\text{kg H}_2\text{O/kg}$  dry matter to 0.1  $\text{kg H}_2\text{O/kg}$  dry matter range from -338.8  $\text{kJ kg}^{-1}$  dry matter for the native sample (NBNFM) to -135.56  $\text{kJ kg}^{-1}$  dry matter for the blanching and fermented material. The  $Q_{12}$  values become negative, meaning that extra thermal energy is needed in addition to heat of vaporization of water. This extra energy is more for the native than for the pretreated samples.

## CONCLUSION

The moisture desorption isotherms (10-40°C) of African arrowroot lily tuber mash follow the type II isotherm pattern and the magnitudes influenced by blanching and fermentation pretreatments. The GAB, Halsey and Oswin models are satisfactory in describing the isotherms. Blanching and/or fermentation of the mash results in reduced equilibrium moisture contents, monolayer moisture and apparent surface areas of monolayer sorption and net isosteric heats of desorption. The pretreatments would therefore enhance drying of the material.

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