SciencePG
Science Publishing Group

Moisture Desorption Isotherms and Thermodynamic Properties of Sorghum-Based Complementary Foods

Sengev Abraham Iorfa[*], **Ariahu Chukwuma Charles, Abu Joseph Oneh, Gernah Dickson Iorwuese**

Department of Food Science and Technology, University of Agriculture, Makurdi, Nigeria

Email address:
talk2sengev@gmail.com (S. A. Iorfa), ccariahu@yahoo.com (A. C. Charles), joabuza@yahoo.co.uk (A. J. Oneh),
gernah04@yahoo.com (G. D. Iorwuese)

[*]Corresponding author

Abstract: Moisture desorption and thermodynamic properties of sorghum-based complementary foods were investigated. Products were obtained from various ratios of Non-fermented sorghum (NFS), Fermented sorghum (FS), crayfish (C), Mango mesocarp (M) and fluted pumpkin leaf (P) powders. Four products, NFSMC, FSMC, NFSPC and FSPC were formulated based on 16% protein using material balance. Established procedures/methods were used for sample preparation and analyses. The equilibrium moisture contents (EMCs) generated through static gravimetric method was fitted with Guggenheim-Anderson-de Boer (GAB) model by polynomial regression analysis. The moisture desorption isotherms of the samples exhibited sigmoidal shape (Type II). The enthalpy of monolayer ranged from 48.12 - 61.78 kJ/mol, multilayer ranged from 44.53 - 47.98 kJ/mol and bulk water ranged from 42.98 - 44.20kJ/mol. The isosteric heat of sorption decreased with increase in moisture content while the entropy of desorption for all the products increased as their moisture contents increased. The isosteric heat and entropy of desorption exhibited asymptotic behaviour at 14% moisture content. The isokinetic temperature ranged from 376.50 - 814.14 K while the harmonic mean temperature was 297.78 K. The enthalpy-entropy compensation theory indicated that the desorption process was enthalpy controlled.

Keywords: Fermentation, Crayfish, Isosteric Heat, Entropy, Water Activity, Desorption

1. Introduction

Hunger and malnutrition are prevalent in most developing countries. The World Health Organization (WHO) and United Nations Children's Emergency Funds (UNICEF) are concerned about Protein-Energy Malnutrition (PEM) and micronutrient deficiencies (hidden hunger) among infants, pregnant women and the sick people. Recent survey conducted by International Food Policy Research Institute (IFPRI) found that one out of three people is malnourished in one form or another [1]. A survey indicated that only one-third of breastfed babies between the ages of 6 and 23 months received appropriate dietary diversity and proper feeding frequencies [2]. In Nigeria, one of the major causes of malnutrition in recent times is the insurgence in the North-East and other parts of the country which displaced about 1.9

million people [3]. The most urgent priority remains to address the significant food insecurity which is affecting thousands of internally displaced people (IDPs) in accessible and newly accessible areas as well as the alarming under nutrition levels [3]. Therefore, efforts towards addressing these problems at national and international levels include nutritional supplementation of staple foods and modification of traditional diets as well as the use of fermentation technology to meet specific nutrition requirements.

A mathematical model based on the principles of desorption isotherms can be a suitable way to predict the aw of a product during dehydration using the moisture content data. Moisture sorption isotherms are of special importance in many aspects of food processing involving water transport

such as dehydration [4]. The authors also reported that differential and integral properties could be used to determine the interactions of water and food substances and to provide useful information for assessing food processing operations such as mixing, drying and storage. Thermodynamic properties such as net isosteric heat, differential enthalpy and entropy of foods can be calculated from sorption isotherm data [5]. These parameters provide information about the properties of water in the food and also permit the estimation of energy requirement for drying. A recent investigation also reported that the enthalpies of desorption are used for drying operations [6]. The objective of this study was to evaluate the moisture desorption characteristics and thermodynamic properties of food products from blends of sorghum, crayfish, mango mesocarp and fluted pumpkin leaf powders.

2. Materials and Methods

2.1. Sample Procurement

About 10 kg of red sorghum grains [Sorghum bicolor, (L) Moench] and 5 kg of semi ripe mango fruits (a local variety) (Mangifera indica) popularly known as Wua nyian and Chul kpev in Tiv respectively, 1 kg of crayfish (Procambarus clarkii) and fluted pumpkin leaves (Telfairia occidentalis) each were sourced from a local market in Makurdi, Benue State. These materials were transported to the Department of Food Science and Technology, University of Agriculture, Makurdi for processing prior to product formulation and analyses.

2.2. Preparation Sorghum Flour and Fermentation

About 10 kg of sorghum was dehulled using rice huller (Model: Navin, Madras) and washed with tap water, drained and dried for 12 h. in a fan driven electric oven (Model: Genlab Widnes, U.K, model T12 H) maintained at 70°C. The dehulled grains were milled using a disc attrition mill (Model: Asiko AII Asiko, Nigeria). The flour was sieved using a laboratory test sieve of 0.5 mm aperture. The resultant flour was divided into two sub-lots. One sub-lot was non-fermented (NF) while the other was subjected to natural fermentation for 48 h. The natural fermentation was achieved using the method described by Ariahu et al. [7] with modification. In this method, sorghum flour was mixed with tap water at the ratio of 2:1 w/v and subjected to natural fermentation at room conditions (30 ± 2°C) in covered plastic bowls. During this process, pH and titratable acidity (an index of lactic acid bacteria activity) were monitored at 12 h intervals. The fermentation process was continued until the pH of the medium stabilized at 3.80 and remained constant. The fermented concentrates were dried at 70°C for 12 h. in a fan driven electric oven (Genlab Widnes, U.K, model T12 H) to constant weight and milled using a single disc attrition mill (Asiko A11, Addis Nigeria) to a particle size of 0.5 mm to obtain fermented sorghum flour (FS). The control from the

non-fermented sorghum flour was referred to as NFS.

2.3. Mango Mesocarp Powder

The method described by Sengev et al. [5] was adopted. In this method, 5kg of partially ripe local variety of mango fruits (Chul kpev) of pH = 3.80, Brix = 7.0 and Refractive Index = 1.34 were sorted and washed with tap water followed by peeling using stainless steel knives. The mesocarps were manually sliced to an average thickness of 2.5 mm. The slices were spread one layer thick on a tray covered with aluminum foil followed by drying in a fan driven electric oven at 70 ± 1°C for 24 h to a moisture content of about 10%. The dry slices were then milled using a single disc attrition mill (Model: AII Asiko, Nigeria) to pass through a 0.5mm sieve to obtain mango mesocarp flour (M). The mango powder was then packaged in rigid plastic with air tight lid and used promptly for product formulation.

2.4. Crayfish Powder

Crayfish powder was prepared using the method reported by Sengev et al. [5] was adopted with modification. About 1 kg of dry crayfish was washed with tap water to remove extraneous materials followed by drying in an electric oven at 65°C for 12 h. The resulting material (crayfish) was milled using a hammer mill (Model: Brook Crompton Series 2000, England) and sieved through 0.5 mm laboratory test sieve to obtain crayfish powder (C). The crayfish powder was packaged in plastic jars with air tight lid prior to use for products formulation.

2.5. Fluted Pumpkin Leaves Powder

Fluted pumpkin leaf powder was prepared as described by Sengev et al. [5] with modification. The leaves were destalked and washed with tap water, steam blanched for 3 sec. and dried in a single layer using an electric oven maintained at 65°C for 6 h. The dried leaves were then milled using a single disc attrition mill (Model: AII Asiko, Nigeria) and screened through a 0.5 mm sieve to obtain fluted pumpkin leaf powder (P).

2.6. Products Formulation

Four products were formulated as shown in Table 1. The products comprised NFSMC: Non-fermented sorghum flour (NFS) + Mango mesocarp powder (M) + Crayfish powder (C); FSMC: Fermented sorghum flour (FS) + Mango mesocarp powder (M) + Crayfish powder (C); NFSPC: Non-fermented sorghum flour (NFS) + Fluted pumpkin leaf powder (P) + Crayfish powder (C) and FSPC: Fermented sorghum flour (FS) + Fluted pumpkin leaf powder (P) + Crayfish powder (C). Each product was formulated to give 16g protein/100 g as recommended by PAG [8]. The amounts of the materials required to meet the protein target were achieved through material balancing from their respective protein contents using the method described by Chiba [9].

Table 1. *Formulation of Blends.*

Product	Ingredient mix (g/100 g)			
	SorghumFlour	Mango Mesocarp Powder	Fluted Pumpkin Leaf Powder	Crayfish Powder
NFSMF	91.06	0.17		8.77
FSMF	91.06	0.17		8.77
NFSPF	91.04	-	0.19	8.77
FSPF	91.04	-	0.19	8.77

Key: NFSMC= Non-Fermented Sorghum + Mango Mesocarp + Crayfish, NFSPC = Non-Fermented Sorghum + Fluted Pumpkin Leaf + Crayfish, FSMC = Fermented Sorghum + Mango Mesocarp + Crayfish, FSPC =Fermented Sorghum + Fluted Pumpkin Leaf + Crayfish

2.7. Preparation of Water Activity and Measurements Equilibrium Moisture Content

Equilibrium moisture content was determined gravimetrically by exposing the samples to atmospheres of known relative humidities following the method described by Ariahu et al. [10]. Sulphuric acid (H_2SO_4) solutions of 10, 20, 30, 40, 50 and 60% were prepared to provide water activities ranging from 0.15 to 0.96 as described by Ruegg [11]. A thermostatically controlled biochemistry incubator (Model: SPX-80-II, Searchtech Instruments) and 500 mL plastic containers were used for temperature and humidity controls respectively. The solutions made from the acid (200 mL each) were carefully transferred into the plastic containers. A screen made of wire gauze was arranged in the plastic containers above the acid solutions to provide a platform for the samples to rest.

For desorption process, the samples were rewetted with distilled water and held at 30°C and 98% relative humidity until equilibrium was reached. Duplicate samples were weighed (0.5 g each) into crown corks and placed on the wire gauze above the acid solutions. The containers were covered tightly and placed in the incubator at temperatures of 10, 20, 30 and 40°C. Samples at relative humidity above 50% were treated with a solution of 0.25% sodium azide (Sodium trinitrite) to prevent mould growth. The samples were removed and weighed after every 48 h using a 4-decimal electronic balance (Model: AE Adam 160L, USA) until differences between consecutive readings were ≤0.5% (i.e. 0.0025 g) of initial sample weight. The total time for removal and putting back in the air tight containers ranged between 2 - 5 min. as recommended by the Cooperative Project Cost 90 [12].

2.7.1. Calculation of Equilibrium Moisture Content

The equilibrium moisture contents were determined by material balance from the initial moisture content using equation 1.

$$EMC = \frac{MW_1 + 100(W_3 - W_2)}{W_1 + (W_3 - W_2)} \qquad (1)$$

M = Initial moisture content of the sample, W_1 = Weight of sample used during sorption, W_2 = Initial weight of sample and crown cork, W_3 = Final weight of sample and crown cork at equilibrium and EMC = Equilibrium Moisture Content.

2.7.2. Modeling and Analysis of Sorption Isotherm Data

The relationship between the equilibrium moisture contents (% db) and the water activities of the samples was predicted using GAB model. This model was chosen due to its reported simplicity, versatility and physical applications to food systems [10, 13]. The GAB parameters were obtained using Microsoft Excel (2007) through polynomial regression method. The GAB model is presented as shown in equation 2.

$$\frac{M}{M_o} = \frac{CKa_w}{(1 - Ka_w)(1 - Ka_w + CKa_w)} \qquad (2)$$

where C and K are constants related to the energies of interaction between the first and distant sorbed molecules at the individual sorption sites. Theoretically, they are related to sorption enthalpies as shown in equations 3 and 4.

$$C = c_o \exp\left((\overline{H}_o - \overline{H}_m)/RT\right) = c_o \exp\left(\Delta\overline{H}_c\right)\Big/RT \qquad (3)$$

$$K = k_o \exp\left((\overline{H}_m - \overline{H}_l)/RT\right) = k_o \exp\left(\Delta\overline{H}_k\right)\Big/RT \qquad (4)$$

where c_o and k_o are entropic accommodation factors; $\overline{H}_o$, $\overline{H}_m$ and $\overline{H}_l$ are the molar sorption enthalpies of the monolayer, the multiplayer and the bulk liquid, respectively. When K is unity, the GAB equation reduces to BET.

The adequacy of fit of the models was evaluated using percent root mean square of error (% RMSE) between experimental (M_{obs}) and predicted (M_{est}) moisture contents as described by [14].

$$\%RME = \sqrt{\frac{\sum\left[\dfrac{M_{obs} - M_{est}}{M_{obs}}\right]^2}{N}} \; x100 \qquad (5)$$

Where N = Number of experimental data.

2.8. Heat of Sorption

The net isosteric heat of sorption was calculated by applying Clausius-Clapeyron equation to the isosters obtained at constant moisture content following the procedure reported by [10]. By plotting $\ln(a_w)$ versus $1/T$ for a specific moisture content, ΔH_{st} was evaluated from the slope ($-\Delta H_{st}/R$). The differential entropy of sorption (ΔS) was also obtained from the coefficient ($\Delta S/R$) and intercept of the same plot.

$$\ln a_w = \frac{\Delta H_{st}}{RT} - \frac{\Delta S}{R} \qquad (6)$$

Where a_w = Water activity, R = Universal gas constant (0.008314 kJ/mol K)

For enthalpy–entropy compensation, plotting $\ln(a_w)$ versus $1/T$ for a given moisture content (M), ΔH_{st} and ΔS were determined from the slope ($-\Delta H_{st}/R$) and intercept ($-\Delta S/R$) respectively. Applying this at different moisture content allows the dependence of ΔH_{st} and ΔS with moisture to be determined. The isokinetic temperature (T_β) and the Gibbs free energy (ΔG), were obtained from the slope and intercept respectively of the plot of ΔH_{st} versus ΔS.

$$\Delta H_{st} = T_\beta \Delta S + \Delta G \tag{7}$$

Where T_β = Isokinetic temperature (K), ΔG = Gibbs free energy (kJ/mol), ΔS = Net isosteric entropy of sorption (kJ/mol) = $S_s - S_1$ with S_s and S_1 as entropy of sorption of the species and pure water respectively. In order to corroborate the compensation theory a statistical analysis test as proposed by Krug et al. [15] was used. The harmonic mean temperature (T_{hm}) is presented as follows:

$$T_{hm} = \frac{n}{\displaystyle\sum_{i=l}^{n}\left(\frac{1}{T}\right)} \tag{8}$$

3. Results

3.1. Moisture Desorption Isotherms

The moisture desorption isotherms of NFSMC, FSMC, NFSPC and FSPC are presented in Figure 1. The moisture desorption isotherms are sigmoidal, corresponding to the Type II isotherms. It was observed that the equilibrium moisture contents (EMCs) decreased with decrease in water activity (a_w) at constant temperature. In Figure 2, the equilibrium moisture contents of the products decreased as the temperature increased. It was also observed that as the temperature increased to 40°C, there was crossing over behaviour of the isotherms at water activity of 0.55 for NFSMC and 0.74 for NFSPC, FSMC and FSPC.
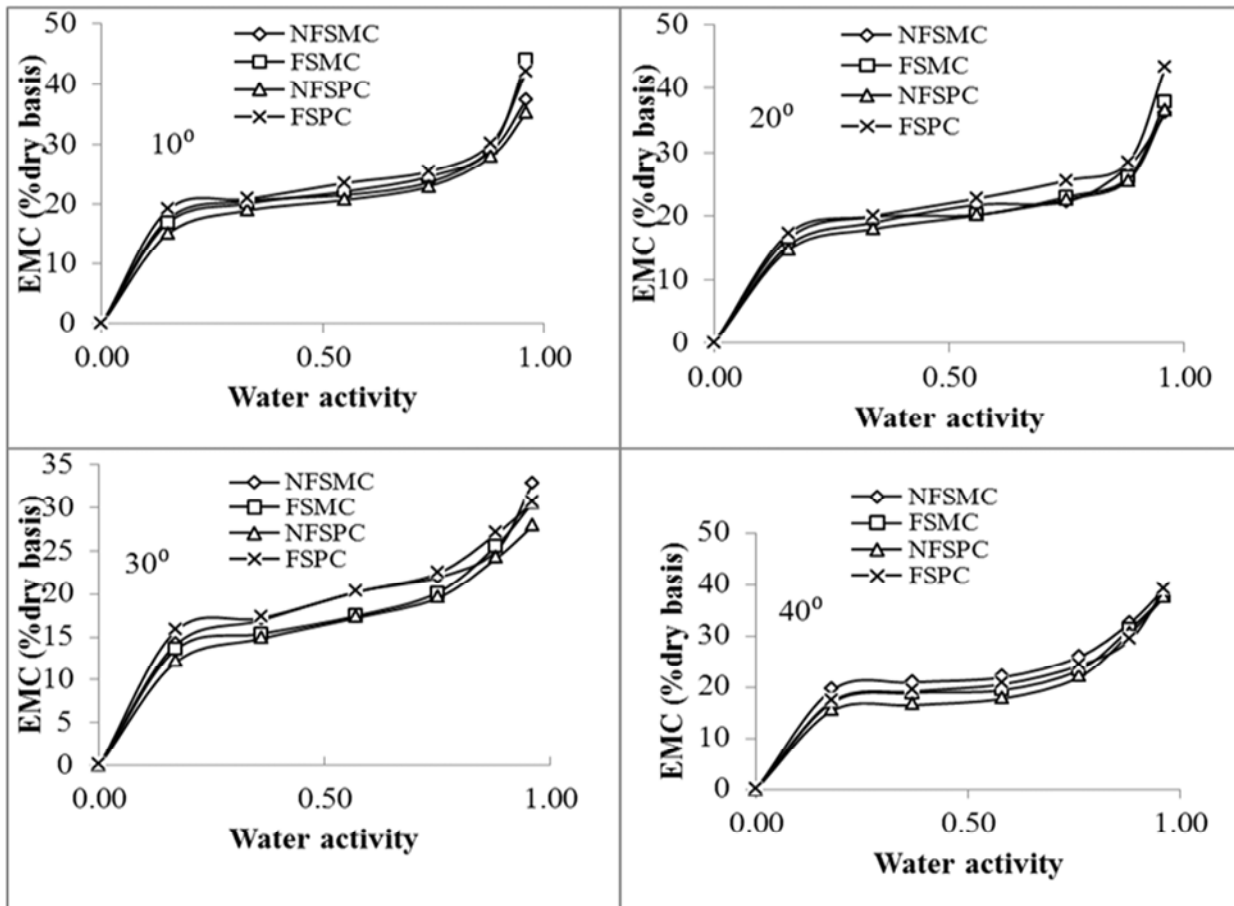

Figure 1. Moisture desorption isotherms of sorghum-based complementary foods.
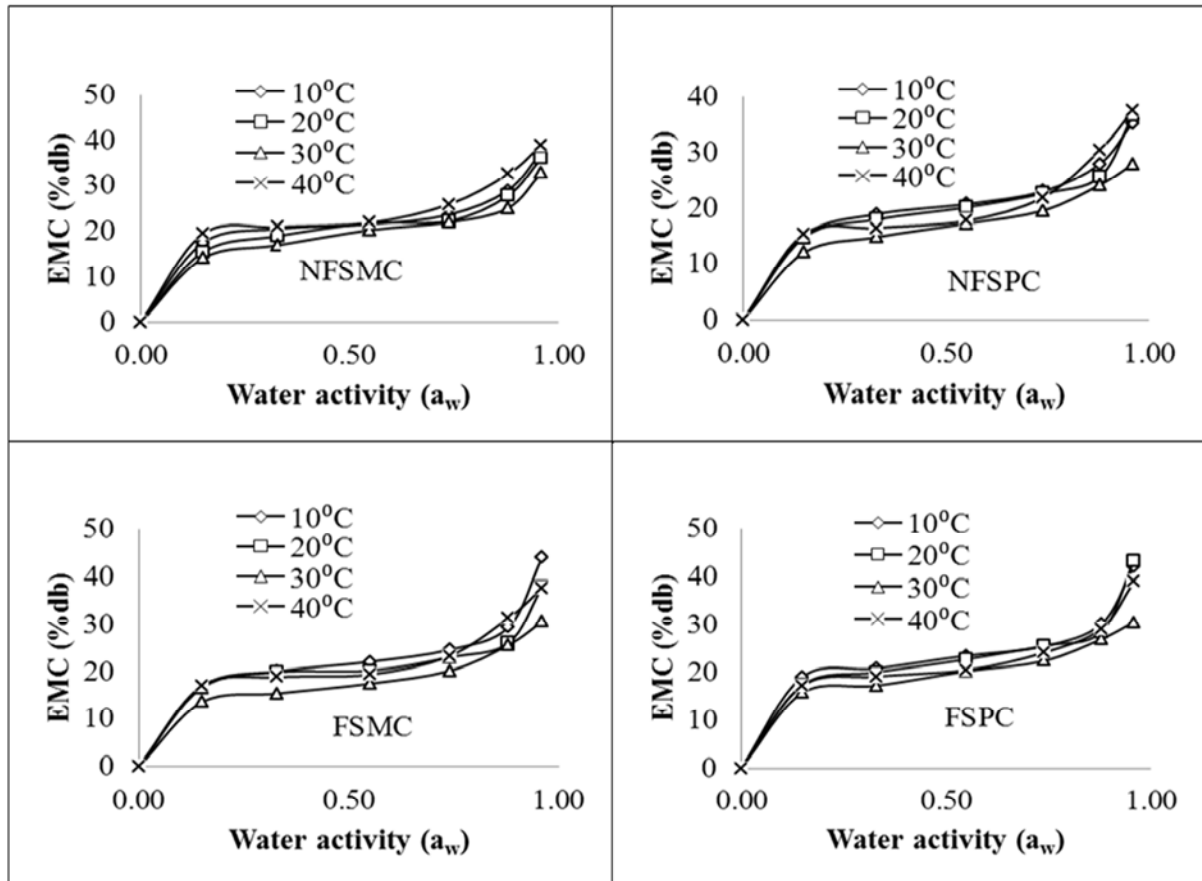
***Figure 2.** Effect of temperature on moisture desorption isotherms of sorghum-based complementary foods.*

3.2. The Fitting Ability of GAB model

The adequacy of fit of GAB model expressed in terms of percent root mean square of error (% RMSE) for moisture desorption is presented in Table 2. The percent root mean square of error (% RMSE) for moisture desorption of NFSMC ranged from 5.60 to 9.42, NFSPC from 4.78 to 9.33, FSMC from 0.5 to 2.70 and FSPC from 1.20 to 2.43. The RMSE values for all the products were less than 10% indicating that the GAB model adequately fits the desorption data.

***Table 2.** Adequacy of Fit (%RMSE) of GAB Model.*

Product	Temperature (°C)				Mean
	10	20	30	40	
NFSMC	5.78	9.42	6.36	5.60	6.79
FSMC	0.50	2.70	1.06	1.59	1.46
NFSPC	9.33	6.04	5.29	4.78	6.36
FSPC	2.43	1.44	1.20	1.25	1.58

3.3. GAB Desorption Enthalpy

The results of GAB desorption enthalpies of the products are presented in Table 3. The molar enthalpy $\overline{H}_o$ (kJ/mol) of monolayer ranged from 60.56 to 61.78 for NFSMC, 61.29 to 62.51 for NFSPC, 54.06 to 55.28 for FSMC and 48.12 to 49.31 for FSPC. The molar enthalpy $\overline{H}_m$ (kJ/mol) of multilayer ranged from 46.76 to 47.98 for NFSMC, 46.84 to 48.06 for NFSPC, 44.64 to 45.86 for FSMC and 44.53 to 45.75 for FSPC, while the molar enthalpy $\overline{H}_l$ (kJ/mol) of vaporization of liquid water ranged from 42.98 to 44.20 for all the products. It was observed that the molar enthalpies of the products decreased with increase in temperature.

***Table 3.** GAB Desorption Enthalpy of Sorghum-based Complementary Foods.*

Product	Temperature (°C)	$\overline{H}_o$ (kJ/mol)	$\overline{H}_m$ (kJ/mol)	$\overline{H}_l$ (kJ/mol)
	10	61.78	47.98	44.20
NFSMC	20	61.41	47.61	43.83
	30	61.00	47.20	43.42

Product	Temperature (°C)	$\overline{H}_o$ (kJ/mol)	$\overline{H}_m$ (kJ/mol)	$\overline{H}_l$ (kJ/mol)
	40	60.56	46.76	42.98
	10	55.28	45.86	44.20
	20	54.91	45.49	43.83
FSMC	30	54.50	45.08	43.42
	40	54.06	44.64	42.98
	10	62.51	48.06	44.20
NFSPC	20	62.14	47.69	43.83
	30	61.73	47.28	43.42
	40	61.29	46.84	42.98
	10	49.31	45.75	44.20
FSPC	20	48.97	45.38	43.83
	30	48.56	44.97	43.42
	40	48.12	44.53	42.98

Key: $\overline{H}_o$, $\overline{H}_m$ and $\overline{H}_l$ are the molar sorption enthalpies of the monolayer, the multiplayer and the bulk liquid, respectively.

3.4. Evaluation of Isosteric Heat and Entropy of Desorption

The net isosteric heat and entropy of desorption produced from the slopes and intercepts of the isosters respectively using the relationship between Clausius-Clapeyron and water activity are presented in Figure 2 and 3. The net isosteric heat (ΔH_{st}) of sorption generally decreased with increase in EMCs. The net isosteric heat for desorption decreased from 3.69 to -0.57 for NFSMC, 10.01 to 1.83 for NFSPC, 8.87 to 3.84 for FSMC and 13.22 to 4.46 for FSPC. The non-fermented products had lower net isosteric heat compared to the fermented ones. The entropy values ranged from 3.8×10^{-3} to 7.2×10^{-3} for NFSMC, -20.0×10^{-3} to -4.1×10^{-3} for NFSPC, -14.8×10^{-3} to -9.3×10^{-3} for FSMC and -27.8×10^{-3} to -11.7×10^{-3} for FSPC. The fermented products were observed to be more orderly than non-fermented blends.
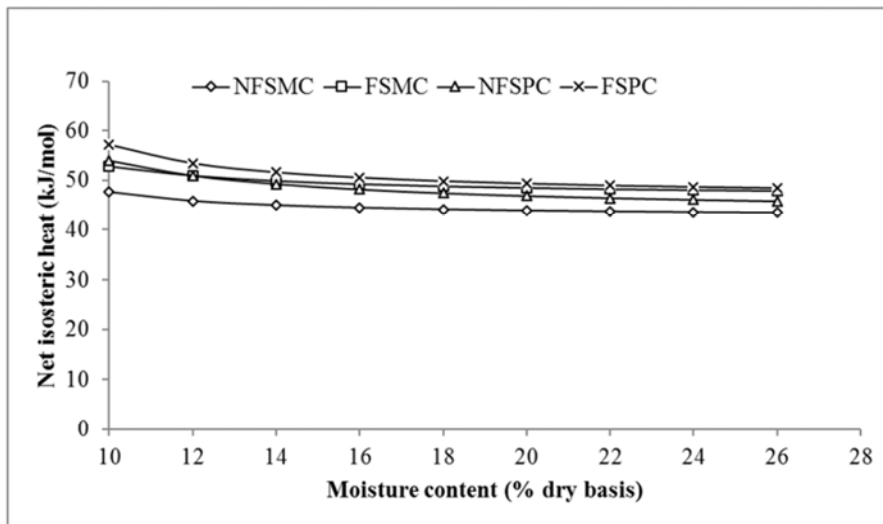

Figure 3. *Variation of net isosteric heat of desorption with moisture content.*
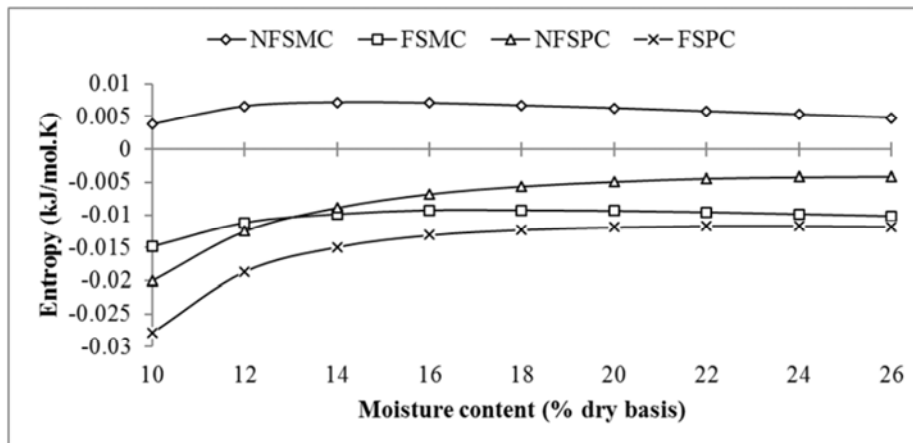

Figure 4. *Variation of entropy of desorption with moisture content.*

3.5. Enthalpy-Entropy Compensation Theory

The enthalpy-entropy compensation parameters of sorghum-based complementary foods are presented in Table 4. The desorption isokinetic temperatures (K) for NFSMC, NFSPC, FSMC and NFSPC are 381.98, 502.77, 814.14 and

522.25 respectively. The r2 values of the products ranged from 0.10 - 0.96. The gibbs free energies (kJ/mol) for desorption are 2.90, 1.72, -3.11 and -0.84 for NFSMC, NFSPC, FSMC and FSPC respectively. The harmonic mean temperature for the sorption process was 297.78K.

***Table 4.** Enthalpy-Entropy Compensation Parameters.*

3	Product	$T_\beta(K)$	$T_{hm}(K)$	$\Delta G(kJ/mol)$	r^2
Desorption	NFSMC	381.98	297.78	2.90	0.10
	FSMC	814.14	297.78	-3.11	0.75
	NFSPC	376.50	297.78	1.72	0.86
	FSPC	522.25	297.78	-0.84	0.96

Key: T_β = Isokinetic temperature (K), ΔG = Gibbs free energy, T_{hm} = Harmonic mean temperature (K), r^2 = Coefficient of determination.

4. Discussion

4.1. Effect of Water Activity and Temperature on the Moisture Desorption Isotherms

As presented in Figure 1, the EMCs for all the products decreased as aw decreased. Higher EMCs were more evident at aw above 0.55. This is a common phenomenon in sorption as higher EMCs are observed at higher aw. Scientific evidences have reported higher EMCs of African arrowroot and bermuda grass at higher aw [16, 17]. Some researchers have also reported that at lower relative humidities, water strongly is adsorbed to the binding sites of the film surface, while by increasing moisture content, owing to the swelling of the hydrophilic network of films, more new sites for water were available to bind, causing higher moisture content (MC) [18]. The desorption isotherms of the products exhibited sigmoidal isotherms translating to the Type II classification. The sigmoidal shape of the sorption isotherms has been reported for starchy food materials in literature [19]. The Type II isotherm observed suggests that sorption occurred according to the multilayer mechanism throughout the equilibrium relative humidity range.

The equilibrium moisture contents (EMCs) of the products decreased as the temperature increased from 10 to 30°C. This trend is very common in sorption studies and may be explained by considering excitation states of water vapour molecules with changes in temperature. As the temperature increases, the kinetic energy of water vapor molecules also increases and discourages their binding on the active sorption sites available on substrate [5]. Conversely, the EMCs of the products increased as the temperature increased to 40°C. This could be due to product composition and also faster dissolution of the food constituents at higher temperatures. Increased water binding at higher temperature has also been reported elsewhere for foods particularly rich in soluble solids that are susceptible to structural orientations [20]. Therefore, removal of water molecules during drying becomes difficult. It was also reported that foods high in protein and sugar contents absorbed more water to overcome the negative effect of temperature at higher hydration levels [21]. The intersection or crossover behavior of edible films of

blends of starch, amylose and methylcellulose has been reported [22]. The EMC shift by temperature was mainly due to the change in water binding, dissociation of water or increase in solubility of solute in water [23]. This implies that at higher temperatures, sorghum-based complementary foods would become more hygroscopic and therefore spoilage becomes eminent.

The higher EMCs observed in FSPC could be attributed to the higher carbohydrate content of fluted pumpkin leaf powder. Previous studies indicated that fluted pumpkin leaves and mango fruit pulp contained 44.56% and 16.25% carbohydrate respectively [24, 25]. Hence, as expected, addition of flute pumpkin leaf powder will increase the carbohydrate content thereby increasing the sorptive sites of FSPC resulting to higher EMCs.

4.2. Adequacy of Fit of GAB Model

The mean values of% RMSE for GAB model were < 10%. The lower the% RMSE values, the better the adequacy of fit of the model. The RMSE values higher than 10% indicates a poor fitting ability. Reports indicated that percent root mean square of error (% RMSE) of ≤ 10% indicates a reasonably good fit for practical purposes [14].

4.3. GAB Desorption Energetics

The enthalpies of desorption of sorghum-based complementary foods revealed higher enthalpy at monolayer than multilayer. This is expected since monolayer moisture is strongly attached to the food matrix and therefore, the energy requirement of monolayer > multilayer > pure water [5]. Reports indicated that at final stages of desorption, there are several active polar sites on the surface of the food material, which are covered with water molecules to form mono-molecular layer [26]. Hence, more energy will be required to remove the water molecules from those sites. The enthalpies also decreased with increase in temperature. This could be due to increase in the kinetics of water molecules at higher temperature. Reports have it that water vapour molecules are discouraged from binding to the active sites at higher temperatures [27].

4.4. Evaluation of Isosteric Heat of Desorption

The net isosteric heat is defined as the heat in excess of the latent heat of vaporization of pure water. The sorption heat was considerably more at lower moisture content, and decreased gradually to approach the latent heat of vaporization of pure water (q_{st} = 0) as the moisture content increased. The net isosteric heat of the products decreased as the moisture content approached 14% and became asymptotic as the moisture content increased. The decrease in the isosteric heat with higher amounts of sorbed water can be quantitatively explained by considering that initially sorption occurs on the most active available sites, giving rise to high interaction energy [14, 28]. As these sites become occupied, sorption occurs on the less active ones, resulting in lower heats of sorption due to formation of multi-layers. At high water content, it tilts towards the heat of condensation of pure water [29]. In addition, the variation in heat of sorption with moisture content provides valuable data for energy consumption calculations and subsequent design of drying equipment, and knowledge of the extent of the water–solid versus water–water interactions [30].

4.5. Evaluation of Desorption Entropy

The relationship between entropy and moisture content of NFSMC, FSMC and FSPC decreased as the moisture content increased, although the products showed very low degree of disorderliness. The low degrees of disorderliness indicate that water molecules are strongly bounded to the adsorbent at this zone, they are more ordered and less available to participate in deteriorative reactions [31]. The entropy of desorption of the products increased up to 14% moisture content and became asymptotic as the moisture content increased. It could be speculated that the increase in moisture content and availability of hydrophilic sites balanced each other, thereby resisting marked increase or decrease in entropy. The asymptotic tendencies of various products have been reported elsewhere in literatures [28, 31]. The negative entropy observed in this study may be ascribed to chemical desorption or structural modification of the desorbent [31].

4.6. Enthalpy-Entropy Compensation Theory

Enthalpy–entropy compensation theory is used to evaluate physical and chemical phenomena such as sorption reactions. The theory states that in order to minimize free energy changes (ΔG) due to these phenomena, compensation arises from the nature of the interaction between the solute and solvent causing the reaction and that the relationship between the enthalpy and entropy for a specific reaction is linear [28]. The plot of net isosteric heat versus entropy of sorghum-based complementary foods showed acceptable linear relationship for FSMC, NFSPC and FSPC. The relationship indicated that r^2 values of FSMC, NFSPC and FSPC are within the acceptable range of 0.5 -1.0. Reports indicated that r^2 ranges from 0 to 1, with higher values indicating less error variance, and typically values greater than 0.5 are considered acceptable [32, 33]. The r^2 value of 0.10 is an indication of poor linearity and high error variance for NFSMC. The low r^2 value of 0.10 also suggests that the assumption of linearity is unrealistic or untrue and as such the regression equation does not represent a reasonable relationship between the dependent and independent variables [34]. Therefore, compensation does not hold for NFSMC.

The enthalpy-entropy compensation parameters revealed that the moisture sorption process was enthalpy driven since the isokinetic temperatures are greater than the harmonic mean temperature ($T_\beta > T_{hm}$). The isokinetic temperature has an important physical meaning as it represents the temperature at which all reactions in the series proceed at the same rate [5]. The isokinetic temperature values reported in this study were higher than that reported for starch materials [30]. The higher values could be attributed to the nature and composition of the food products.

From the concept of thermodynamics, the free energy (ΔG) is an indicative of the affinity of the sorbent water. It also provides a condition as to whether the sorption process will be spontaneous (-ΔG) or non-spontaneous (+ΔG). Therefore, considering the values of ΔG presented in this study, it could be deduced that the desorption process for fermented products was spontaneous while the non-fermented was non spontaneous.

5. Conclusion

Moisture desorption studies carried out on sorghum-based complementary foods indicated that the sorption isotherm were sigmoidal (Type II), equilibrium moisture content decreased with decrease in water activity and decreased with temperature. Enthalpies at monolayer regions were higher followed by multilayer and bulk water. The isosteric heat of desorption of the products decreased with increase in equilibrium moisture content while the entropy of desorption increased with increase in EMCs. The respective decrease and increase for both isosteric heat and entropy reached their troughs and peaks at 14% moisture content and assumed asymptotic behaviour. The enthalpy-entropy compensation revealed that the desorption process was enthalpy controlled.

References

[1] FAO, IFAD and WFP. (2015). The State of Food Insecurity in the World 2015. Meeting the 2015 international hunger targets: taking stock of uneven progress. Rome, FAO.

[2] WHO. (2011) "Essential Nutrition Actions: Improving maternal-newborn-infant and young child health and nutrition", May 2011.

[3] European Commission (2017). European civil protection and humanitarian aid operations. ECHO Factsheet – Nigeria. Pp. 1 – 3. http://ec.europa.eu/echo.

[4] Hua, Z., Yanhong, B., Xuewei, Z. and Ruiquian, D. (2016). Water desorption isotherms and its thermodynamic analysis of gluteneous rice flour. American Journal of Food Technology, 11: 115 – 124.

[5]   Sengev, A. I., Ariahu, C. C., Abu, J. O. Gernah, D. I. (2016). Moisture adsorption and thermodynamic properties of sorghum-based complementary foods. International Journal of Food Engineering and Technology, 2(1): 26 - 33.

[6]   Biswal, S., Mohapatra, M., Panda, M. K. and Dash, S. K. (2017). Moisture desorption isotherms of fresh Jamun (Syzygium cumini) fruit. Indian Journal of Agricultural Research, 51 (3): 267 – 271.

[7]   Ariahu, C. C., Ukpabi, U. and Mbajunwa, K. O. (1999). Producrion of African breadfruit (Treculia africana) and soybean (Glycine max) seed based food formulations, 1: Effect of germination and fermentation on nutritional and organoleptic quality. Plant Foods for Human Nutrition, 54: 193 – 206.

[8]   PAG (1971). Guidelines on protein rich mixtures for use in weaning foods. Protein Advisory Group, United Nations. pp. 45-76.

[9]   Chiba, L. I. (2009). Animal nutrition handbook. Section 18: Diet formulation and common feed ingredients. pp. 481– 531.

[10]   Ariahu, C. C., Kaze, S. A., and Achem, C. D. (2006). Moisture sorption characteristics of tropical fresh water crayfish (Procambarus clarkii). Journal of Food Engineering, 75: 355 - 363.

[11]   Ruegg, M. (1980). Calculation of the activity of water in sulfuric acids solution at various temperatures. Lebensmittel-wiss and Technologie, 13: 22-24.

[12]   Gal, S. (1988). The need for practical application of sorption data. In: Physical properties of food.Jewitt, R., Escher, F., Hallstrem, B., Mefffert, H. F., Spiess, W. E. L. and Vos, G. (eds). London, Applied Science Publishers, pp. 13 – 25.

[13]   Johnson, P. N. T. (1998). Applicability of the BET and GAB models to the moisture adsorption isotherms data of some Ghanaian food flours. Ghanaian Journal of Agricultural Science, 31: 107 – 112.

[14]   Wang, N., and Brennan, J. G. (1991). Moisture sorption isotherms characteristics of potatoes at four temperatures. Journal of Food Engineering, 14: 269 - 282.

[15]   Krug, R. R., Hunter, W. G. and Grieger, R. A. (1976). Enthalpy-entropy compensation .2. Separation of the chemical from the statistical effect. Journal of Physical Chemistry, 80: 2335 - 2342.

[16]   Igbabul, B. D., Ariahu, C. C. and Umeh, E. U. (2013). Moisture adsorption isotherms of African arrowroot lily (Tacca involucrata) tuber mash as influenced by blanching and natural fermentation. Journal of Food Research, 2(3): 79 – 92.

[17]   Al-Mahasneh, M. Alkoaik, F., Khalil, A., Fulleros, R. and El-Waziry, A. (2014). Effect of temperature on moisture sorption isotherms and monolayer moisture content of bermuda grass (Cynodon dactylon). Bulgarian Journal of Agricultural Science, 20(6):1289 - 1294.

[18]   Bahareh, S., Quan, V. V., Suwimol C., John, B. G., Christopher, J. S. and Costas, E. S. (2015). Water sorption isotherm of pea starch edible films and prediction models. Foods, 5(1): 1 – 18.

[19]   Tunc, S. and Duman, O. (2007). Thermodynamic properties and moisture sorption isotherms of cottonseed protein isolate and different forms of cottonseed samples. Journal of Food Engineering, 81: 133 – 143.

[20]   Ramesh, M. N. (2003). Moisture transfer properties of cooked rice during drying. Lebensmittel-wiss and Technologie, 36(2): 245 - 255.

[21]   Zuo, L., Rhim, J. and Lee, J. H. (2015). Moisture sorption and thermodynamic properties of vacuum-dried Capsosiphon fulvescens Powder. Preventive Nutrition Food Science, 20(3):215-220.

[22]   Chowdhury, T. and Das, M. (2012). Moisture sorption isotherm and isosteric heat of sorption of edible films made from blends of starch, amylose and methyl cellulose, International Food Research Journal, 19(4): 1669-1678.

[23]   Rahman, M. S. and Al-Belushi, R. H. (2006). Dynamic isopiestic method (DIM): measuring Moisture sorption isotherm of freeze-dried garlic powder and other potential uses of DIM. International Journal of Food Properties, 9: 421–437.

[24]   Kajihausa, O. E., Sobukola, O. P., Idowu, M. A. and Awonorin, S. O. (2010). Nutrient contents and thermal degradation of vitamins in organically grown fluted pumpkin (Telfairia occidentalis) leaves, International Food Research Journal, 17: 795-807.

[25]   Ubwa, S. T., M. O. Ishu, M. O., Offem, J. O., Tyohemba, R. L. and Igbum, G. O. (2014). Proximate composition and some physical attributes of three mango (Mangifera indica L.) fruit varieties. International Journal of Agronomy and Agricultural Research, 4(2): 21 – 29.

[26]   Kurozawa, L. E., de-Oliveira, R. A. Hubinger, M. D. and Park, K. J. (2015). Water desorption thermodynamic properties of Papaya. Journal of Food Processing and Preservation, 39(6): 2412 -2420.

[27]   Chen, C. (2006). Obtaining the isosteric sorption heat directly by sorption isotherm equations. Journal of Food Engineering, 74: 178–185.

[28]   Oliveira, E. G., Rosa, G. S., Moraes, M. A. and L. Pinto, L. A. A. (2009). Moisture sorption characteristics of microalgae Spirulina platensis. Brazilian Journal of Chemical Engineering, 26(1): 189 – 197.

[29]   Neila, B., Nourhene, B. and Nabil, K. (2008). Moisture desorption-adsorption isotherms and isosteric heats of sorption of Tunisian olive leaves (Olea europaea L.). Industrial Crops and Products, 28: 162–176.

[30]   McMinn, W. A. M. and Magee, T. R. A. (2003). Thermodynamic properties of moisture sorption of potato. Journal of Food Engineering, 60: 157–165.

[31]   Ayala-Aponte, A. A. (2016). Thermodynamic properties of moisture sorption in cassava flour. DYNA., 83(197): 139-145.

[32]   Santhi, C., Arnold, J. G., Williams, J. R., Dugas, W. A., Srinivasan, R. and Hauck. L. M. (2001). Validation of the SWAT model on a large river basin with point and nonpoint sources. Journal ofAmerican Water Resources Association, 37(5): 1169-1188.

[33]   Van-Liew, M. W., Arnold, J. G. and Garbrecht, J. D. (2003). Hydrologic simulation on agricultural watersheds: Choosing between two models. Transactions of the American Society of Agricultural Engineers, 46(6): 1539-1551.

[34]   Oloyo, R. A. (2001) Fundamentals of research methodology for social and applied sciences, Ilaro, Nigeria, ROA Educational Press, 286pp.