Comparison of Water Adsorption Characteristics of Plantain and Cocoyam in a Controlled Storage Condition.

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Abstract
This investigation was conducted to study the behaviour of dehydrated products of cocoyam and plantain in a controlled storage environment at temperature range of 25 and 40°C. Salt solutions were used to achieve water activity that ranged from 0.08 to 0.97. Equilibrium moisture content obtained was used to produce sorption isotherms at these temperatures. Sorption models of Halsey, Chung Pfost, and Henderson were evaluated on the experimental data as well as modified versions of Halsey and Henderson. Co-efficient of determination ranged from 0.80 to 0.97 in all the models. Most equilibrium moisture content obtained during the experiment reflected adsorption except for very low water activity. Chung Pfost equation gave the best fit for the absorption characteristics of these crops having the least residual mean square within 0.03 to 0.11%. Plantain exhibited higher affinity for water than cocoyam in all the relative humidity range. Least moisture content derived for storage stability of these crops varied from 6.5 to 8.2 and 6.3 to 8.2 % in cocoyam and plantain respectively. The region of local isotherm II of relative humidity between 23 and 65 % was identified as the region for optimum storage.
Keywords: Equilibrium moisture content, sorption isotherm, storage stability and water activity

1. Introduction

Moisture content of stored agricultural products is usually altered by prevailing temperature and relative humidity of the environment. Equilibrium relative humidity (ERH) or water activity (a_w) supports various biological activities that could result in bio-degradation. (Rockland and Nishi, 1980; Oluwamukomi et al., 2007). The effects of dynamic process of water movement during the storage of crops or crop products require considerable attention for optimum storage qualities.

Plantain (*Musa paradisiacal*), a tropical fruit crop has high starch content when harvested. Matured fruits have average moisture content of 61% and ripen within a short time after harvest thereby rendering long period of storage in natural state difficult (Okunola and Igbeka, 2007). However, unripe plantain are peeled, sun dried and processed into flour for stable storage. Whereas, cocoyam (*Cococasia esculenta*) is a root crop of great potentials widely grown in Nigeria and is an important source of calorie and is rich in starch but low in protein and oil; and is of significant volume in production of root crops within the tropics (F.A.O.1981). It has high moisture content that average 55 % when freshly harvested. In its natural state, the crop does not exhibit durable storage qualities unless it is transformed to stable form by being processed into chips, sun dried and grinded into flour.

The inherent high moisture content of plantain and cocoyam makes biological deterioration by microbial activities inevitable in their natural state. Also the state of adsorbed water, a measure of the physical, chemical and microbial stability of biological materials under storage is essential to increase shelf life and storage stability (Labuza, 1968, Chirife and Buera, 1994). According to Labuza (1980), reduction in moisture content to a safe level results in decrease in metabolic activities of micro-organism and inherent temperature during storage. a_w has been generally accepted to be more closely related to the physical, chemical and biological properties of food than its total moisture content as well as biological growth (Staudt et al., 2013). a_w is the related analogical term which is the fraction of ERH. The relationship between a_w and moisture content of a food-stuff is important in predicting quality stability during drying, shelf life storage and the selection of appropriate packaging materials as well as the main control variables in food preservation technology (Sun, 1999; McMinn and Magee, 1999). According to Labuza (1980), specific changes, in colour, aroma, flavour, texture, stability and acceptability of raw and processed food products have been associated with relatively narrow a_w range. Independent and inter dependent chemical moieties that affect the properties of biological products have been identified to be influenced by affinity for water molecules of its environment and the competing influences of neighbouring hydrophilic or hydrophobic chemical groups. Water sorption characteristics influence inherent shelf life qualities and determine the duration for safe storage (Rockland and Nishi, 1980; Ajisegeri and Sopade, 1990; Okunola and Igbeka 2007; Raji and Ojediran, 2011). Crop losses during storage that are enhanced by moisture have been identified to include biological, bio-chemical enzyme activated reaction, microbiological and physiological types (Labuza, 1968; F.A.O.1981; Moreria et al., 2010).

Moisture Sorption isotherms (MSI) a relationship between a_w and the equilibrium moisture content (EMC) in a material at a constant temperature have been used to understand the behaviour of agricultural products during storage or storage stimulation. (Igbeka et al., 1975; Labuza, 1980; Iglesias and Chirife 1978; Ajisegiri and Sopade, 1990; Okunola and Igbeka 2007; Al-Mahasneh et al., 2011). Many authors have determined experimentally, sorption isotherms for food materials and other biological products. They have found that equilibrium moisture content (EMC) and relative humidity should be over a wide range of temperatures especially when accuracy is desired. (Pixon and Warbuton, 1971; Ajibola 1986; Ajibola et al., 2005; Raji and Ojediran 2011). Labuza (1968) described the behaviour of a loss of hygroscopicity in agricultural products at high temperatures. However, Verma and Maharaji, (1990) in their study of moisture content and ERH of Jaggery (a concentrated sugar product) observed that its hygroscopicity increases with increase in temperature which is in conformity to earlier observations of (Iglesias and Chirife, 1978) on sugar and high sugar containing foods.

Water sorption is one of the most important parameters that contribute to predicting technological performance and product quality in foods during storage (Chirife and Buera, 1994; Vilades et. al., 1995). It is therefore important to know the sorption characteristics of these dried crop products since they are significant in the formulation of foods and in their storage stability. Hence, the comparison of hygroscopic behaviour of cocoyam and plantain at prevailing ambient temperature in south west of Nigeria is of interest. The temperature of the experiment was chosen at 25 and 45^{o}C in order to simulate variation in ambient temperature prevalent during storage in humid climate of south west of Nigeria.

2. Materials and methods

2.1 Sample preparations

Freshly harvested plantain and cocoyam were obtained from an institutional farm in Akure, Nigeria. Thin slices of the materials were sun dried for ten hours and then placed inside a sealed polythene bag and kept inside a refrigerator at 4^{o}C ±1^{o}C until when needed for the experiment. The static gravimetric method was used as described by Henderson and Pixton 1981, saturated salt (analytical grade) solutions of sodium hydroxide, potassium acetate, Magnesium chloride, potassium carbonate, magnesium nitrate, sodium nitrite, sodium chloride, ammonium sulphate, potassium nitrate and potassium sulphate were selected to produce varying a_w between 0.07 to 0.97 % at reasonable intervals. The relative humidity values of these salts are reliable to within 0.005 a_w and experienced minimum changes with temperature at the range of 25 to 40^{o}C. (Rockland, 1960; Rockland and Nishi, 1980).

The saturated salts solutions were placed at the base of glass desiccators and the labeled samples were placed on a wire mesh screen above the salt solutions. The desiccators' lids were then sealed with silica gel and then placed at desired temperatures in GallenKamp DV 300 incubator (Weiss Gallenkamp, UK). At commencement of the experiment, refrigerated materials were brought out to equilibrate with ambient conditions for 6 hours, then 8 – 10 g of sun dried samples were weighed with Mettler PC2200 Delta analytical balance (Mettler-Toledo Inc., USA) having an accuracy of 0.0001 g put in three replicates in the desiccators in all the experiments. Moisture content of cocoyam and plantain at commencement of sample preparation was found to average 54.75 and 60.65 % respectively. Adsorption isotherm is obtained by rehydrating a completely dried material in varying conditions of relative humidity and monitoring the weight gain due to the moisture uptake. A digital Memmert UF 75 air oven (Memmert GmbH +Co KG, Germany) was used for moisture content determination at 105^{o}C ±1^{o}C with sample being weighed at 6 hour interval until constant weight of ± 0.001 g was achieved (AOAC, 1997). Average EMC of three replicates of sample was calculated on dry basis (d.b. %)

2.2. Sorption isotherm

Five sorption equations shown in Table 1 which have been established suitable for predicting EMC for high carbohydrate foods over a wide range of water activity was used to analyze the experimental data in this report. The experimental data (observed EMC) and their respective a_w were imputed into a linear regression programme to predict EMC in the two parameter models using Genstat V statistical procedure. A non linear least grid search was used for the three parameter models using Guass-Newton method having two temperature levels incorporated for its applicability over the varying temperatures. The goodness of fit of these models was evaluated by statistical parameters of determination co – efficient (R^2) and residual mean square (RMS). The model with highest R^2 and least RMS was selected as the best fit.

3. Results and discussion

3.1 Equilibrium moisture content

Figs. 1 and 2 depict the sorption isotherms of experimental data after adsorption was performed on both cocoyam and plantain at 25 and 40^{o}C respectively. The sorption isotherms were type II with a sigmoidal shape profile according to BET classification and the EMC values of the crop products are within the range commonly reported for high starch crops (Brunauer et al., 1940; Igbeka et al., 1975; Sun, 1999; Bell and Labuza, 2000;

Okunola and Igbeka, 2007). It can be seen that adsorption EMCs increased with increase in a_w and were lower at higher temperatures in both crops. This can be explained by the higher active state of water molecules at higher temperature thus the attractive forces between them decreasing (Yan et al., 2008). Similar trends for other tropical crops have been reported in the literatures (Labuza et al., 2006; Yan et al., 2008, Staudt et al., 2013). At low a_w, the equilibrium moisture contents These results were in agreement with the general characteristics of food isotherms, and the theory of physical adsorption which predicts that the quantity of sorbed water at a given water activity increases as the temperature decreases (Yu et al.,1999; Aviara et al., 2006).

Tables 2 summarized the usefulness of the sorption models in predicting adsorptive EMC of the crop product at temperatures of 25 ^oC. Determination co efficient (R^2) for plantain varied from 0.81 to 0.92 and Henderson gave the best fit having the highest R^2 and the least RMS of 0.11 % in the two parameter models while M. Halsey, a three parameter model gave the overall best fit with R^2 of 0.92 and RMS of 4.31 %. For the cocoyam, R^2 ranged from 0.80 to 0.94 with Chung Post giving the best fit for the experimental data with R^2 of 0.90 and R.M.S of 0.11 % in the two parameter models, while M. Halsey with R^2 of 0.94 and R.M.S. of 3.11 % had the overall best of fit among the models. From Table 3, for plantain isotherm at 40 ^oC, R^2 varied from 0.85 to 0.96 with Chung Pfost model had the best fit for all the equations with R^2 of 0.96 and R.M.S of 0.03 % and M. Halsey gave a higher R^2 of 0.94 among the three parameter models. Cocoyam isotherm has high R^2 that varied from 0.86 to 0.97 with which Chung Pfost gave the best fit with R^2 of 0.96 and R.M.S. of 0.03 % in all the models. Generally M. Halsey is most suitable isotherm equation while M. Henderson is least appropriate among all the models; this was in agreement of Sun (1999) observation.

3.2 Water activity and storage stability

The determination of least moisture content is necessary for stable storage of dehydrated food. From, Caurie (1970) model.

$$InC = \frac{1}{0.45Mn} a_w Inr \quad (1)$$

$$C = \frac{100 - \%H_2O}{\%H_2O}$$

Where (2)

In linear regression analysis, the intercept is equivalent to *In A* and M_n is the least moisture content.

$$InA = \frac{1}{0.45 M_n} \quad (3)$$

The significance of Table 4 is the temperature dependence of the monolayer moisture content. This implies that at high temperatures, capacity of stored product to accommodate moisture reduces reflecting less hygroscopicity of starch crops: This may be ascribed to a reduction in total sorption ability of the crop products (McMinn and Magee, 1999). Storage of these crop products below the above M_n values will cause auto oxidation and rancidity development in the crop as earlier found by Rockland, (1960). Optimum storage stability zone therefore exist above this point up to the inflexion point of the isotherm curve between Local Isotherms (L.I.) II and III region, The L.I. II for these crop products existed between 23 and 65 % relative humidity. From Fig. 1 at 25^oC; the point of inflection between L.I. II and III for plantain was found to be at 14.8 % and a_w of 0.66 indicating optimum safe storage ranged within 8.15 and 14.5 %, while the point of inflection between L.I. II and III for cocoyam was 14,5 % and a_w of 0.66, hence optimum safe storage ranged 8.19 and 14.8 %. Looking at Fig. 2; at 40^oC a similar trend occurred with the L.I. II for these crop products existed between 20 and 66 % relative humidity, however, the point of inflection between L.I. II and III for plantain was at 11.6 % and 0.52 a_w. This implies that optimum safe storage existed between 6.08 and 11.6 % while cocoyam had its points of inflection between L.I. II and III at 9.8 % and a_w of 0.45 with optimum safe storage within 6.5 to 9.8 %. From Table 5, all the parameter constant reduces in value as temperature increase from 25 to 40^oC except in parameter B for all Halsey equations in both two parameters model in plantain and cocoyam.

4. Conclusion

Moisture sorption isotherms at two ambient temperatures were obtained for dried products under controlled storage for cocoyam and plantain. The stability of dehydrated food products during storage is affected by environmental conditions apart from inherent chemical and biological factors. The Halsey, Henderson, Chung Pfost, Modified Halsey and Modified Henderson, moisture isotherm equations were used to evaluate goodness of fit to experimental data. All the models showed a high R^2 from 0.80 – 0.97. M. Halsey gave better fit than their original equations at both temperatures. Chung Pfost gave the best fits for the adsorptive characteristics of both crops with the least residual mean square and it can thus be used to predict their EMC with high degree of accuracy.

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Table 1. Sorption Models and their Linearised Forms

Author	Model	Linear form
Halsey (1948)	$M = -\frac{A^{1/B}}{TIna_w}$	$InM = \frac{InA}{BT} + \frac{In(-Ina_w}{B}$
Henderson (1952)	$M = -\frac{In(1-Ina_w)^{1/B}}{AT}$	$InM = \frac{(-In(1-a_w))}{B} + \frac{1}{B} In \frac{1}{AT}$
Chung & Pfost(1967)	$M = \frac{1}{B} In \frac{A}{RT} \frac{-In(-Ina_w)}{AT}$	$M = \frac{1}{B} In \frac{A}{RT} - \frac{1}{B} In(-Ina_w)$
Modified Henderson (Thompson et al, 1968)	$M = \frac{In(1-a_w)^{1/C}}{-A(T+B)}$	$M = \frac{1}{C} In(-In(1-a_w) - InA(T+B)$
Modified Halsey (Iglesias&Chirife,1976)	$M = \frac{e^{(A-BT)^{1/C}}}{-Ina_w}$	$InM = \frac{(A+BT) + In(-Ina_w)}{C}$

M= EMC (decimal, dry basis), a_w = water activity (decimal)
A,B,C, are parameters constant pertinent to each equations.
T= Absolute temperature (Kelvin)
R= Universal gas constant (J/mol)

Table 2. Model Reliability for predicted Water adsorption characteristics of plantain and cocoyam at 25°C

Parameter	Halsey	Henderson	Chung Pfost	M. Hal	M. Hen
Plantain					
R^2	0.81	0.90	0.90	0.92	0.85
RMS (%)	6.99	0.11	8.38	4.31	8.98
Cocoyam					
R^2	0.80	0.90	0.90	0.94	0.86
RMS (%)	7.23	3.37	0.11	3.11	7.15

M.Hal - Modified Halsey
M.Hen - Modified Henderson
R^2 - Co-efficient of determination/percentage variance
RMS Residual Mean Square.

Table 3. Model Reliability for predicted Water adsorption characteristics of plantain and cocoyam at 40°C

Parameter	Halsey	Henderson	Chung Pfost	M. Hal	M. Hen
Plantain					
R^2	0.89	0.96	0.95	0.92	0.85
RMS (%)	7.57	2.4.	0.06	4.31	8.98
Cocoyam					
R^2	0.90	0.97	0.96	0.94	0.86
RMS (%)	5.5	1.89	0.03	3.11	7.15

M.Hal - Modified Halsey
M.Hen - Modified Henderson
R^2 - Co-efficient of determination/percentage variance
RMS Residual Mean Square.

Table 4 Monolayer moisture content (M_n) of plantain and cocoyam at 25 and 40°C

Crop	Temperature. °C	
	25	40
Cocoyam EMC (%)	8.15	6.50
Plantain EMC (%)	8.19	6.28

Table 5 Co - efficient constant of model parameters for plantain and cocoyam

Mode	Temperature °C	A	B	C
Plantain				
Halsey	25	7.998968×10^4	-2.69137	
Henderson	"	0.10882	2.15641	
Chung Pfost	"	2.107945×10^3	14.23114	
M. Halsey	25-40	0.6722036	-269.37958	1.786198
M. Henderson	"	5.090651	0.0331668	2.1508724
Halsey	40	2.69656×10^4	-1.73700	
Chung Pfost	"	1.01727×10^3	12.5027	
Henderson		0.05485	1.52069	
Cocoyam				
Halsey	25	7.998968×10^4	-2.69137	
Henderson	"	0.12148	2.29066	
Chung Pfost	"	2.4364×10^4	15.35381	
M. Halsey	25 – 40	1.2026378	-276.0175	1.92525
M. Henderson	"	7.4137408	0.04219518	2.3188416
Halsey	40	4.7226×10^4	-1.94661	
Henderson	"	0.09089	1.71114	
Chung Pfost	"	1.1951×10^3	15.1192	

M.Halsey - Modified Halsey
M.Henderson - Modified Henderson

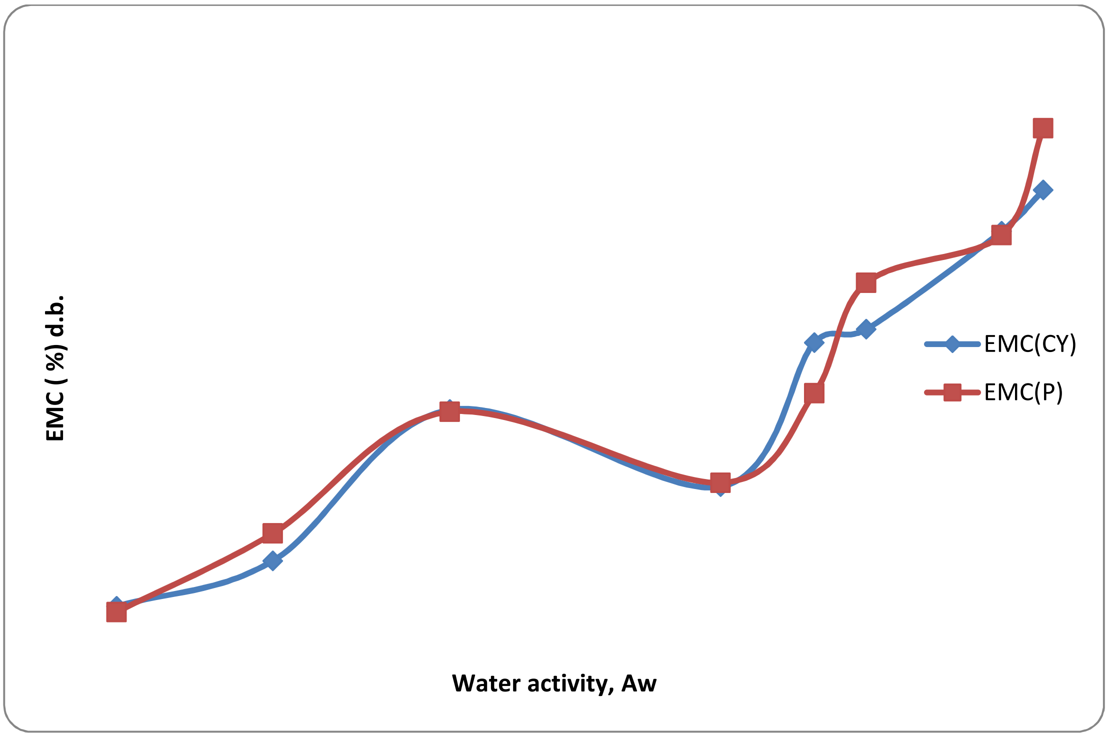

Fig. 1: Moisture Isotherm of Cocoyam and Plantain at 25^{0}C

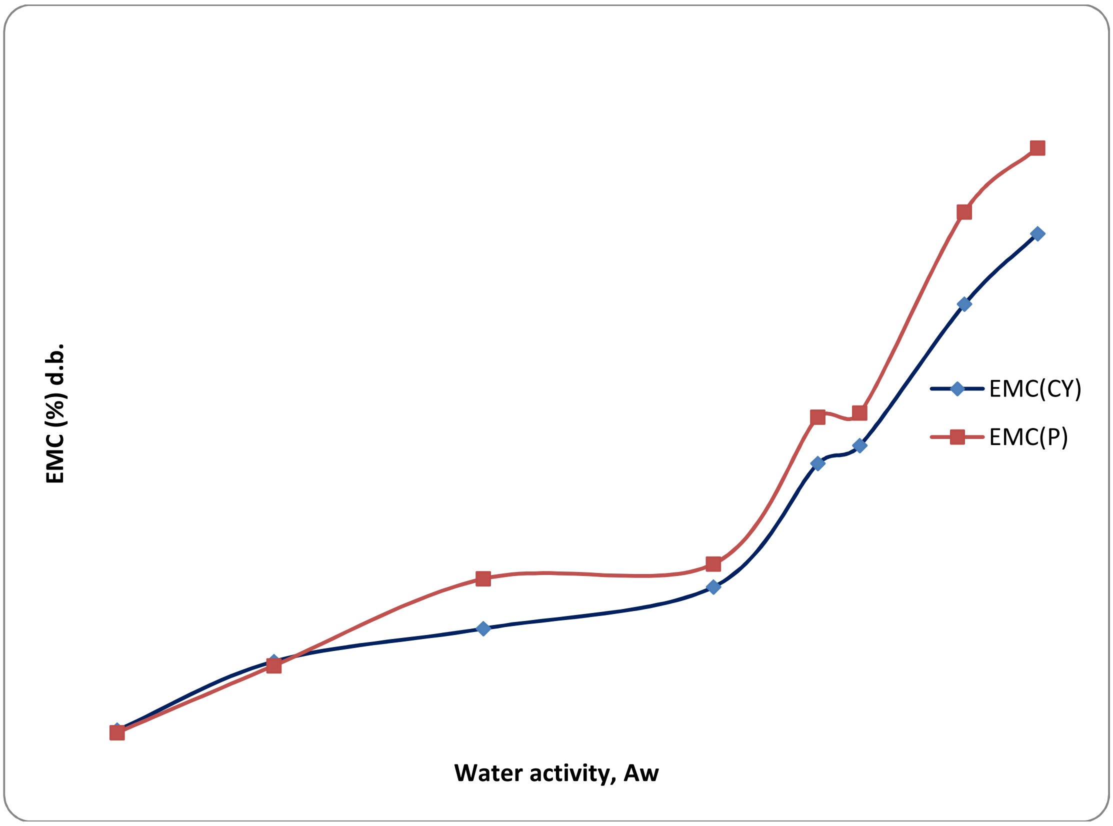

Fig. 2: Moisture Isotherm of Cocoyam and Plantain at 40^{0}C