Varietal effect on the moisture adsorption isotherm of yellow-fleshed cassava root starches

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Abstract
The Moisture Adsorption Isotherm of three Yellow-fleshed Cassava Root Starches (YfCRS) were determined by the static gravimetric method at temperatures of 27 °C, 37 °C and 42 °C and water activities level of between 0.10 and 0.80. Data obtained were fitted to four sorption models (Peleg, GAB, Oswin and Langmuir). The model fit was evaluated using the coefficient of determination (R^2), root mean square error (RMSE) and mean percentage deviation (%E). The results showed that Peleg model gave the best fit for predicting the moisture adsorption data of the starches (R^2=0.99, RMSE=0.00, %E=0.00). TMS 06/1630 YfCRS had the highest monolayer moisture (M_o) while that of TMS 01/1368 had the lowest. The high β-carotene content of TMS 01/1368 YfCRS could be responsible for its low M_o (r = -0.96), irrespective of the storage temperatures. However, all the YfCRS might be stored for longer periods at all the temperatures since their M_o fall within acceptable limit for storage stability.

Key words: starch; adsorption isotherm; water activity; monolayer moisture; β-carotene

Introduction
The yellow flesh colour found in some cassava varieties is associated with the density of micronutrients, such as β-carotene (Iglesias *et al.,* 1997; Chávez *et al.,* 2005). Yellow-fleshed cassava root (YfCR) has been at the centre-stage in breeding for enhanced micronutrients, because of the use of cassava as a staple food in most of the poverty-stricken African countries (Ssemakula *et al.,* 2007). Food products such as yellow *gari*, powdered *fufu*, chips and high quality cassava flour have been produced from YfCR (IITA, 2011; Omodamiro *et al.,* 2012), with no information on the starches.

Starch is the commonest form of carbohydrate stored in plant and the largest source of energy in human diet. Its array of functional properties makes it a flexible ingredient with compatible attributes for innumerable edible and non-edible industrial applications (Singh *et al*., 2010). Starch finds primary uses in food products like soups, sauces and gravies, bakery products, dairy, confectionery, snacks, batters, coatings and meat products (Davies, 1995). Non-food applications of starch are in the field of pharmaceuticals, textiles, alcohol-based fuels and adhesives (Kaur *et al*., 2012). Other uses of starch include low-calorie substitutes, biodegradable packaging materials, thin films and thermoplastic materials with improved thermal and mechanical properties (Biliaderis, 1998). The storage stability of YfCR starches for these uses has not been established.

A fundamental property of biological material, which is important for predicting stability and quality changes during packaging and storage of dehydrated foods and formulations, is the water adsorption characteristics (Labuza, 1975). Moisture Adsorption Isotherm (MAI) often represents the water adsorption characteristic of foods. This isotherm, which represent the functional relationship between water activity and equilibrium moisture content of a foodstuff at a given temperature, characterize the state of water in foods and are of primary interest for several food science and technology applications. From a drying standpoint, adsorption isotherm is required to evaluate the driving force and to define the end-point of the process, and as well for modelling and simulation. In addition, the adsorption of water at the surface of a food product may have physical or chemical origin and adsorbed water may occupy one or several layers (Mathlouthi and Roge, 2003). There is dearth of information on the effect of β-carotene on the MAI of YfCR starches. The interactions of this starch with water need to be studied with regard to predicting its stability in order to make it available for food and non-food applications in time of raw material scarcity.

Therefore, this work was conducted to study the effect of YfCR varieties on the MAI of their starches, and as a means of predicting their storage stability for food and non-food applications.

Materials and Methods

All the three yellow-fleshed cassava roots used in this work are of the Tropical Maniot Selection (TMS), obtained from the cassava farm of IITA, Ikenne, Ogun State, Nigeria. These are TMS01/1368, TMS01/1371 and TMS06/1630.

Production of yellow-fleshed cassava root starch

Yellow-fleshed cassava root (YfCR) starch was produced using the traditional method of starch extraction as described by Oyewole and Obieze, (1995) with some modifications. Freshly harvested YfCRs were peeled, washed in water and grated with an electric motor powered mechanical grater. The resultant pulp was immediately sieved through a muslin cloth and suspended in water. This separates the fibrous and other coarse root material from the starch pulp. The starch pulp was allowed to settle for 4-6 h before decanting. The supernatant containing a mixture of yellow carotenoid and starch was decanted into a bowl and the thick sediment is the wet starch. The wet starch was reconstituted in water for washing twice, allowed to settle, decanted and then mixed with the yellow carotenoid/ starch mixture, pressed and dried using a convectional cabinet dryer(model, manufacturer) at 45±5 °C for 18 h. It was then allowed to cool at room temperature, milled, and packed in polythene nylon prior to further investigations (Figure 1).

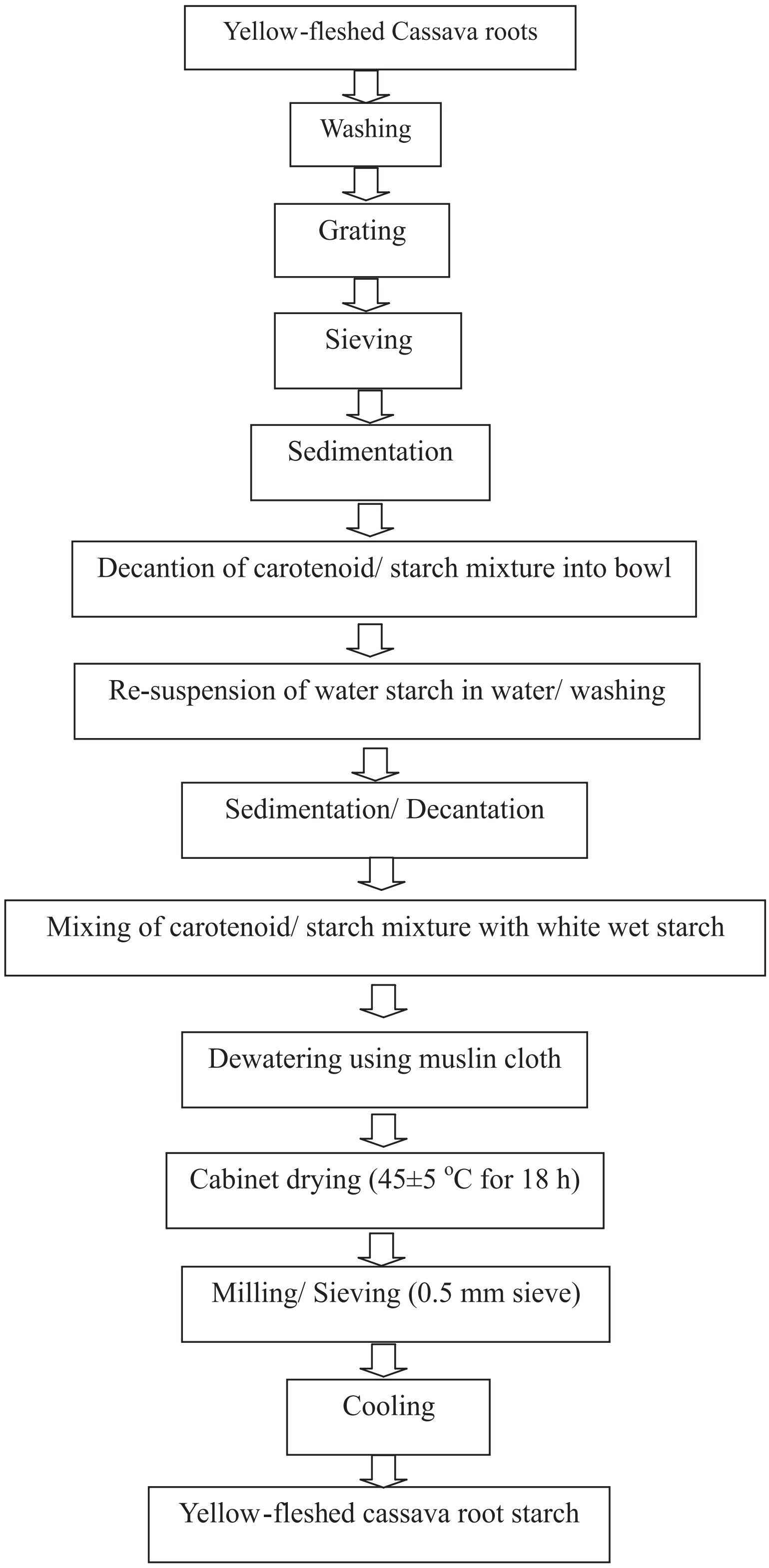

Figure 1: Flow chart of Yellow-fleshed Cassava Root Starch production (Modified from Oyewole and Obieze, 1995)

Determination of the total β-carotene content of Yellow-fleshed Cassava Root Starch

The total β-carotene content of Yellow-fleshed Cassava Root Starches was determined as reported by Rodriguez-Amaya and Kimura (2004).

Determination of equilibrium moisture content and moisture adsorption isotherm

Static gravimetric method according to Oyelade ***et al.*** (2001) and Famurewa ***et al.*** (2012) was used to determine the equilibrium moisture content (EMC) of the starches. For the adsorption process, the samples were dehydrated in a hot air oven for 8 h at 105±5°C (AOAC, 1990). Triplicate samples, 0.50 ± 0.001g each were weighed into moisture pans in the desiccators. The concentrated sulphuric acid quantities used to make up a 250 ml of desiccant with deionised water was prepared at 27 °C, 37 °C and 42 °C, using water activity and temperature tables of Perry and Green (1984). The acid was then dispensed into the desiccators according to their respective water activities (Table 1). The desiccators were maintained at water activity values of between 0.1 and 0.8, and then placed in a Genlab (England) incubator (Model M75CPD) to maintain the required temperature level (27, 37 and 42 °C). Each of the samples was weighed every day using a digital balance until constant weight was obtained in three consecutive recordings, then the sample was assumed to be at equilibrium (±0.001g). The time to reach equilibrium ranged between 10 to 14 days depending on the water activity in each of the desiccators; those at higher water activities reaching equilibrium faster than those at lower water activities. The EMC were calculated from which the MAI were plotted for the starches.

Table 1: Desiccants preparation for 27°C, 37°C and 42 °C

Water activities	Quantity of Conc. H_2SO_4/250ml water for 27°C (ml)	Quantity of Conc. H_2SO_4/250ml water for 37°C (ml)	Quantity of Conc. H_2SO_4/250ml water for 42°C (ml)
0.80	71.29	71.29	71.13
0.70	86.28	86.79	86.92
0.60	99.36	100.71	101.07
0.50	111.65	112.72	113.15
0.40	123.30	124.55	125.11
0.30	135.92	137.30	137.91
0.20	149.08	150.35	150.94
0.10	167.61	168.99	169.63

2.3.1 Data analysis and modelling of adsorption results

The experimental data were fitted to four commonly used models using linear regression analytical procedure. The models were the four parameters such as Peleg, three parameters such as Guggenheim, Anderson and de Boer (GAB), and two parameters such as Oswin and Langmuir equations. These models were chosen because of their suitability for high carbohydrate foods, simplicity and ease of evaluation (Ajisegiri *et al.,* 2007). The linear forms of the models are presented in Table 2. The quality of fitness of the models was evaluated by calculating coefficient of determination (R^2), root mean square error (RMSE) and mean percentage deviation (%E). The RMSE and % E are defined as shown below:

$$\mathrm{RMSE} = \sqrt{\frac{\sum (M_{exp} - M_{pred})^2}{n}}$$

$$\% E = \frac{100}{n}\sum\left|\frac{M_{exp} - M_{pred}}{M_{exp}}\right|$$

Where M_{exp} is the experimental equilibrium moisture content, M_{pred} is the predicted moisture content and n is the number of observations.

In addition, all analyses were carried out in triplicates and subjected to one way analysis of variance (ANOVA) using Statistical Analysis System (SAS) package (version 9.1, SAS Institute, Inc., Cary, NC) (SAS, 2008). Means was separated using fisher's protected least significant difference test.

Table 2: Linear forms of the sorption models used to fit the experimental values

Models	Equations
GAB	$M = \dfrac{M_0 b\, a_w}{1 - ca_w \quad 1 - ca_w \ + b\, a_w}$
Oswin	$M = C\,(a_w/1 - a_w)^n$
Peleg	$M = C_1 a_w\, c^3 + C_2 a_w\, c^4$
Langmuir	$M = \dfrac{Cm_0^2\, a_w}{M_0\,(1 + a_w)}$

GAB = Guggenheim, Anderson and de Boer equation, M = equilibrium moisture content (%, dry basis); a, b, c, n = constant parameters; T = temperature (^{o}C), a_w = water activity, Mo=monolayer moisture content

Results and Discussions

The Moisture Adsorption Isotherm (MAI) of the YfCRS at 42, 37 and 27 ^{o}C is as shown in Figures 2, 3 and 4 respectively. The result reveals that the equilibrium moisture content (EMC) of all the starches increased with increased water activity (a_w), with TMS01/1371 YfCRS having the highest and TMS01/1368 YfCRS the least. The high EMC of TMS01/1371 YfCRS may be attributed to its low total β-carotene content.

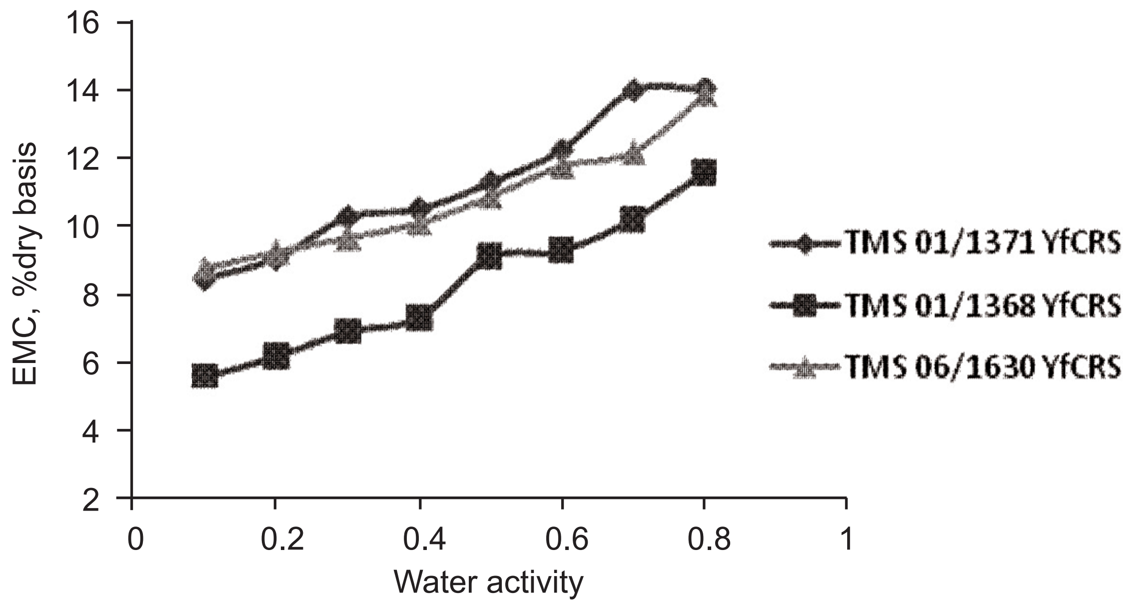

Figure 2: Moisture Adsorption Isotherm of Yellow-fleshed Cassava Root Starches (YfCRS) at 42 ^{o}C

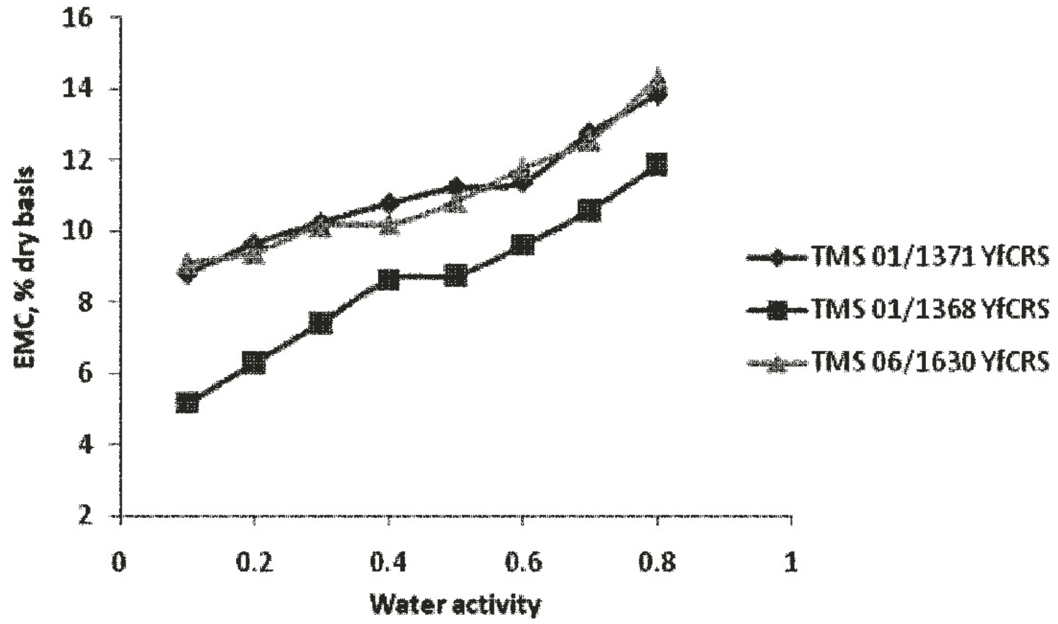

Figure 3: Moisture Adsorption Isotherm of Yellow-fleshed Cassava Root Starches (YfCRS) at 37 °C

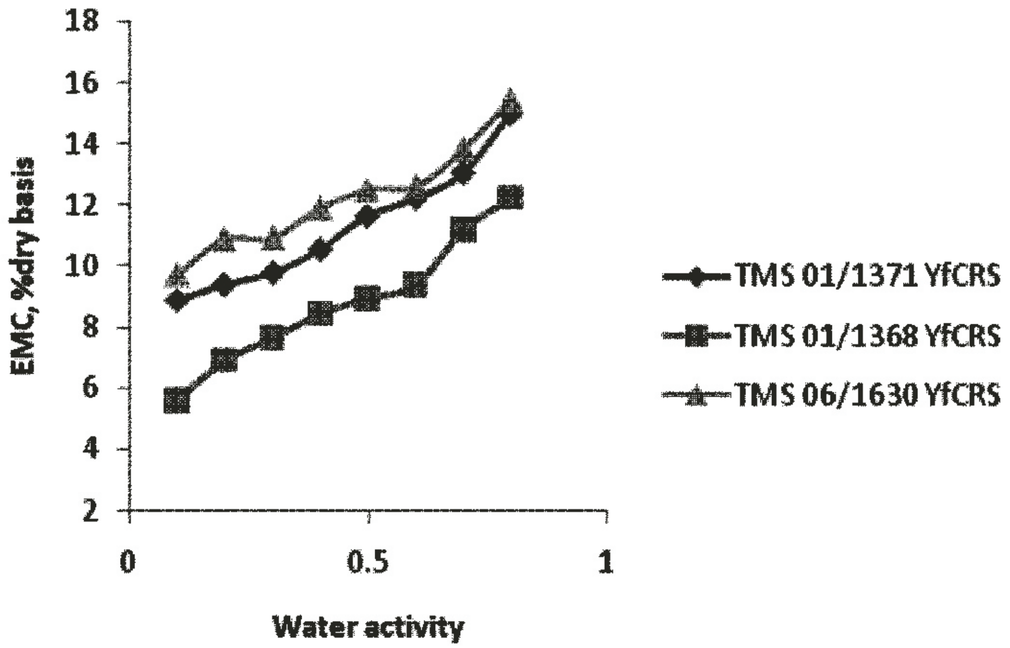

Figure 4: Moisture Adsorption Isotherm of Yellow-fleshed Cassava Root Starches (YfCRS) at 27 °C

Food sorption isotherm describes the thermodynamic relationship between a_w and the EMC of a food product at constant temperature and pressure (Andrade *et al.,* 2011). The knowledge of the sorption isotherm characteristics are needed for shelf-life prediction and determination of critical moisture content for acceptability and storage of food product (Alakali and Satimehin, 2007). The increased EMC of the starches with increased a_w might be due to the fact that the vapour pressure of water present in the samples increased with that of the surroundings. This observation agrees with the work of Inchuen *et al.* (2009) on moisture sorption of Thai curry powder.

In addition, the observed differences in the EMC of the starches may be attributed to the difference in their total β-carotene content (Table 4), and variation in physical adsorption of water on polymeric molecules (Pezzutti and Crapiste, 1997). Hence, the polymeric molecules present in TMS 01/1371 YfCRS may have more tendencies to adsorb moisture than that of TMS 01/1368 YfCRS. Therefore, food products such as custard powder made from TMS 01/1368 YfCRS may keep longer than that of TMS 01/1371 (Johnson, 1998), if properly packed in an hermetically sealed container. It was also observed that the MAI of all the YfCRS had a sigmoid shape, which is typical of type II isotherm curve going by Brunauer *et al.* (1938) classification. This was also in accordance with the work reported by Adebowale *et al.* (2007) on tapioca grits.

Furthermore, the parameters of the various sorption models used for the sorption data are as presented in Table 3. From the results, the Peleg, GAB and Oswin models had coefficient of determination (R^2) > 90 %, and both the mean percentage deviation (% E) and root mean square error (RMSE) < 10 %, signifying good fit, while the Langmuir model had R^2 < 90 %, RMSE < 10 % (except for TMS 01/1368 YfCRS) and % E < 10 % (Tables 3). However, the order of fitness of the models are; Peleg > GAB > Oswin. This implied that Peleg model might be more suitable for fitting the moisture adsorption data of the YfCRS (Kuye and Ariri, 2005). Additionally, the stability of these starches during storage could be predicted using their monolayer moisture content (M_o) (Iglesias *et al.,* 1975).

Table 3: Models for the adsorption isotherm of yellow-fleshed cassava root starches (CSs)

Samples	Models	A	B	C	D	R^2	RMSE	%E	F-Cal	F-Tab(0.05)
TMS01/1371YfCRS	Peleg	10.35	7.85	0.08	3.16	0.99	0.00	0.00	3738.09	6.39
	GAB	8.62	1.33E+08	0.50		0.98	0.01	0.00	3575.16	5.41
	Oswin	11.52	0.15			0.97	0.00	0.00	3890.94	5.14
	Langmuir	11.34	14.25			0.72	0.06	0.02	450.43	5.14
TMS01/1368YfCRS	Peleg	8.69	13.22	2.30	4.51	0.99	0.01	0.00	2549.83	6.39
	GAB	6.64	71.7	0.56		0.99	0.00	0.00	2262.16	5.41
	Oswin	8.81	0.22			0.98	0.01	0.00	3413.60	5.14
	Langmuir	4.53	13.84			0.86	0.14	0.07	472.57	5.14
TMS06/1630YfCRS	Peleg	9.57	10.57	2.38	2.14	0.99	0.00	0.00	2776.45	6.39
	GAB	8.75	6.33E+08	0.48		0.97	0.00	0.00	3392.40	5.41
	Oswin	11.65	0.13			0.95	0.01	0.00	3044.88	5.14
	Langmuir	14.39	13.76			0.65	0.04	0.01	423.00	5.14

GAB-Guggenheim, Anderson and de Boer equation; A, B, C, D- constant parameters; R^2- Coefficient of determination, RMSE- Root mean square error, % E- Mean percentage deviation

The M_o is the minimum amount of water bound to active sites and guaranties the stability of flour/starch during storage (Iglesias *et al.,* 1975). The results of the M_o of the starches showed a higher value in TMS 06/1630 YfCRS and a lower value in that of TMS01/1368 irrespective of the storage temperatures (Table 4). The observed decrease in the M_o of TMS 01/1368 YfCRS as the temperature increased may be due to the fact that the absorbed molecules gained kinetic energy making the attractive forces loosened and this allowed for some water molecules to break away from their sorption sites, hence decreasing the M_o (Arevalo-Pinedo *et al.,* 2004; Labuza *et al.,* 1985). This also agrees with the findings of Geankoplis (1993). In addition, the high total β-carotene content of TMS01/1368 YfCRS may be responsible for its low $M_{o,}$ hence, the negative but not significant (p>0.05) correlation (r = -0.96) that exist between these parameters (Table 5). However, all the M_o of the YfCRS were within the range for storage stability (< 10 % dry basis) (Labuza *et al.,* 1985).

Table 4: GAB monolayer moisture content (Mo) at different temperatures (T) and total β-carotene content of Yellow-fleshed Cassava Root Starches (YfCRS)

Samples	T (^{o}C)	M_o (g H_2O/100g solid)	Mean M_o (gH_2O/100g solid)	F-Cal	Total β-carotene content
TMS01/1371YfCRS	42	8.74		1973.69	0.1700(0.00)[c]
	37	8.84	8.62	3667.64	
	27	8.29		5084.14	
TMS01/1368 YfCRS	42	5.76		1375.45	0.2150(0.01)[a]
	37	6.74	6.64	2497.43	
	27	7.41		2913.60	
TMS06/1630 YfCRS	42	9.60		2725.08	0.1800(0.00)$_b$
	37	8.47	8.75	4621.72	
	27	8.17		2830.39	

Means with different superscript are significantly different at $p \leq 0.05$. Values in bracket represent standard deviation. F-Tabulated at $p<0.05$ = 5.41

Conclusion

This study showed that all the YfCRS had a type II sigmoidal shape, which is typical for most starchy foods, and that the Peleg model gave the best fit for predicting the moisture adsorption data of the starches. It was also observed that the M_o was higher in TMS06/1630 YfCRS and lower in that of TMS01/1368 irrespective of the storage temperatures. There was a negative but not significant correlation between β-carotene and the M_o of the starches. However, all the YfCRS could be stored for longer periods at all the temperatures and used for food and non-food applications, as their $\mathbf{M_o}$ falls within acceptable range for storage.

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References

Adebowale, A.A., Sanni, L., Awonorin, S., Daniel, I., and Kuye, A. 2007. Effect of cassava varieties on the sorption isotherm of tapioca grits. International Journal of Food Science and Technology, 42: 448–452

Ajisegiri, E.S.A., Chukwu, O., Sopade, P.A. 2007. Moisture- sorption study of locally parboiled rice. Australian Journal of Technology, 11(2):86 -90.

Alakali, J. S. and Satimehin,A. A. 2007. Moisture Adsorption Characteristics of Bambara Groundnut (*Vigna subterranea*) powders. Electronic Journal of Agricultural Engineering International, 9:1-15

Andrade, R.D.P., Lemus, R.M., and Pérez C.E.C. 2011. Models of sorption isotherms for food: Uses and limitations. Vitae, Revista De La Facultad De Quõmica Farma. Utica, 18(3): 325-334

AOAC 1990. Official Methods of Analysis of the Association of Official Analytical Chemists (15th ed.). Arlington. Virginia, USA

Arevalo-Pinedo, A., Murr, F.E.X., Giraldo-Zun˜iga, A.D. and Are' Varo, Z.D.S. 2014, Vacuum drying of carrot *(Daucus carota):* effects of pretreatments and parameters process. in proceedings of the 14th International Drying Symposium, Sa˜o Paulo, Brazil Pp. 2021 - 2026.

Biliaderis, C. G. 1998. Structures and phase transitions of starch polymers. In R. H. Walter (Ed.), Polysaccharide association structures in food (pp. 57-168). New York: Marcel-Dekker, Inc.

Brunauer, S., Emmett, P. and Teller, E. 1938. Adsorption of gases in multimolecular layers. Journal of American Chemical Society, 60: 309-319

Cardoso, A.P.; Mirione, E.; Ernesto, M.; Massaza, F.; Cliff, J.; Haque, M.R. and Bradbury, J.H. 2005. Processing of cassava roots to remove cyanogens. *Journal of Food Composition and Analysis*, *18*: 451-460

Chávez, A.L., Sánchez, T., Jaramillo, G., Bedoya, J.M., Echeverry, J., Bolanos, E.A., Ceballos, H., and Iglesias, C.A. 2005. Variation of quality traits in cassava roots evaluated in landraces and improved clones. Euphytica, 143: 125–133.

Davies, L. 1995. Starch-composition, modifications, applications and nutritional value in food stuffs. Food Technology Europe, 6(7), 44-52.

Famurewa, J.A.V., Oluwamukomi, M. O. and Alaba, J. O. 2012. Storage stability of *pupuru* flour (a cassava product) at room temperature. *British Journal of Applied Science and Technology 2(2): 138-145*

Geankoplis, C.J. 1993. Transport Process and Unit Operations, third ed. Prentice-Hall, Inc.

Iglesias, H.A., Chirife, J. and Lombardi, J.L. 1975. Compression of water vapor sorption by sugar beet root components. International Journal of Food Technology, 10 : 385

Iglesias, C., Mayer, J., Chávez, A.L., and Calle, F. 1997. Genetic potential and stability of carotene content in cassava roots. Euphytica 94: 367-373.

IITA. 2011. New vitamin A-fortified cassava released in Nigeria, set to improve health of millions. Bulletin issue No. 2098, 5-9 December. Pp. 1-2

Inchuen, S., Narkrugsa, W. and Pornchaloempong, P. 2009. Moisture sorption of Thai red curry powder. Maejo International Journal of Science and Technology, 3(03):486-497. Johnson, P.N.T. 1998. Application of the BET and GAB models to the moisture adsorption isotherm data of some Ghanaian food flours. Ghanaian Journal of Agricultural Science, 31:107-112

Kaur, B., Ariffin, F., Bhat, R. and Karim, A. A. 2012. Progress in starch modification in the last decade. Food Hydrocolloids, 26, 398-404

Karel, M. 1975. Stability of low and intermediate moisture foods. In: *Freeze Drying and Advanced Food Technology*. (Goldbright, B. A., L. R. Rey and W. W. Rothmayer, Eds). Academic Press. New York, Pp. 643

Kuye, A. and Ariri, I. 2005. Modelling the equilibrium moisture sorption data for some Nigerian foods. International Journal of Food Properties, 8:1–13.

Labuza, T. P., Kaanene, A. and Chen, J. Y. 1985. Effect of temperature on the moisture sorption isotherms and water activity shift of two dehydrated foods. *Journal of Food Science*, 50: 382-391.

Labuza, T.P. (1975). Sorption-phenomenon in foods: Theoretical and practical aspects. In: Chokyum Rha, D. (ed.). Theory, determination and control of physical properties of food materials. D. Reidel Pub. Co., Dordrecht, the Netherlands, pp. 197-219.

Mathlouthi, M. and Rogé, B. 2003. Water vapour sorption isotherms and the caking of food powders. Food Chemistry, 82 (1): 61-71

Omodamiro, R. M., Oti, E., Etudaiye, H. A., Egesi, C., Olasanmi, B. and Ukpabi, U. J. 2012. Production of fufu from yellow cassava roots using the odourless flour technique and the traditional method: Evaluation of carotenoids retention in the fufu. Advances in Applied Science Research, 3 (5):2566-2572.

Oyelade, O.J., Igbeka, J.C. and Aworh, O.C. 2001. Moisture isotherms of cowpea flour at 30°C and 40°C. Journal of Applied Sciences, 4: 1700-1711.

Oyewole, O.B. and Obieze, N. 1995. Processing and characteristics of "Tapioca" meal rom cassava. Tropical Science, 35:19–22

Perry, R.H. and Green, D. 1984. Chemical Engineers Handbook, sixth edition. McGraw Hill, New York

Pezzutti, A. and Crapiste, G.H. 1997. Sorptional Equilibrium and Drying Characteristics of Garlic Content. *Journal of food Engineering,* 31(1):113-123.

Rodriguez-Amaya, D.B. and Kimura, M. 2004. HarvestPlus handbook for carotenoid analysis. HarvestPlus Technical Monograph 2. Washington, DC and Cali, Colombia. International Food Policy Research Institute (IFPRI) and International Center for Tropical Agriculture (CIAT).

SAS 2008. Statistical Analysis Software (SAS) System for Windows, Version 9.1, SAS Institute Inc., Cary, NC, USA.

Singh, A. V., Nath, L. K. and Singh A. 2010. Pharmaceutical, food and non-food applications of Modified starches: a critical review. Electronic Journal of Environmental, Agricultural and Food Chemistry, *EJEAFChe, 9 (7),* 1214-1221.

Ssemakula, G., Dixon, A. G. O. and Maziya-Dixon, B. 2008. Stability of iron and zinc concentrations in selected genotypes of cassava (*Manihot esculenta* Crantz) tuberous roots. *Journal of Food, Agriculture and Environment, 6 (3&4): 362-367.*