Modeling of Moisture Desorption Isotherm of Tilapia Fish (Tilapia zilli)

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Abstract: The knowledge of the moisture desorption isotherm of products are necessary for adequate design of drying systems for such food product in order to minimize post-harvest loses. Moisture desorption isotherm of tilapia fish at temperatures ranging between 40 to 70 °Cwith water activity ranging between 0.112 to 0.964 were determined using static gravimetric technique. American Society of Agricultural Engineers (ASAE) recommended a four 3-parameter models as a basic condition for assessing and fitting experimental data to this models usingnonlinear regression program analysis. The recommended models by ASAE are Modified Henderson, Modified GAB, Modified Chung Pfost, Modified Halsevand ModifiedOswinTherecommended ASAE models were compared using Coefficient of Determination (R^2) , Standard Error (SE), Reduced Chi Square (χ^2) and Root Mean Square Error (RMSE). The moisture sorption isotherms of tilapia fish were sigmoid in shape and were found to be temperature dependent.

It is evident from the result that the Modified GAB model was able to predict the equilibrium moisture content of fish samples at temperatures of 40 and 45°C. It was closely followed by Modified Henderson model. At higher temperatures of 50 and 60 °C, Modified Henderson model performed creditably as it could predict the equilibrium moisture content of the fish sample. Modified GAB Modelfollowed Modified Henderson in terms of quality performance. At a temperature of 70° C, the model for predicting the equilibrium moisture content of the fish was Modified GAB and was followed by Modified Oswin Model.

Keywords: *desorption isotherm, equilibrium moisture, water activity, sigmoid, static gravimetric* _____

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I. Introduction

Fisherysubsector of the economy comprise an important sector in the economic development of most developing and developed nations.¹ reported that more than 40million people are engaged either directly or indirectly in the fishery subsector of the economyin the world. However fish is a source of inexpensive high quality protein for human consumption.

Medically fish is endorsed for children, pregnant women and adults because of its high level of protein content, digestibility and lack of cholesterol which prevents heart attack, heart failure and stroke. As with other developing nations, Nigerian coastal areas depend on fish as a source of food and income for its teaming population and provide food security for the citizens.

Nigeria occupies a land area of 923,768 km². It has a continental shelf area of 47,934 km² with the length of littoral zone of 853 kilometers. The country is endowed with an enviablelinkage of internal water bodies such as rivers, flood plains, natural and man-made lakes and reservoirs² as cited by ³.

In 2016, approximately 171 million tonnes of fish were produced globally; of thisquantity, aquaculture and capture fisheries accounted for 47 and 53 percent respectively. Within the same period also, aquaculture production accounted for \$232 billion out of theoverall first saleworth of fisheries production which was projected at \$362 billion. In the same vein, the universalproduction of capture fisheries stood at 90.9 million tonnesof which marine water fisheries supplied 87.2 % and the remaining 12.8 % byinland water.

The total aquaculture production in 2016 comprised 80.0 million tonnes of food fish, 30.1 million tonnes of water plants, in addition to 37 900 tonnes of non-foods. According to ⁴, the production statistics of cultivated food fish(in million tonnes)comprised 54.1,17.1, 7.9 and about 0.94 of finfish, molluscs, crustaceans and other watercreatures respectively. In terms of human participation in the primary sectors of capture fisheries and aquaculture, the report indicated that in 2016, a total of 59.6 million persons were involved- be it on a permanent, part-time or on anintermittent basis. There is a standing-by market for a well-handledtropical fish product in advancednations; thus, the venture is nobleearner of foreign exchange. Though some fishes harvested in the tropics are for direct consumption, a great deal of others is processed into fish meal for livestock production. Harvesting fishes of whatever description is never sufficient to safeguard availability in all seasons

without adequate processing and storage. This is based on the fact that fish is highly perishable. For processing to be done properly knowledge of sorption isotherm is necessary.

Sorption Isotherm: Information onsorption isotherm is important for various foodmaterials processing operations like drying, storage and packaging. Sorption isotherms show the relationship betweenmoisture content atequilibrium and the water activity when temperatures are constant. They provide data on the moisture sorption phenomenonas well as their interrelationship among food constituents and moisture. When modeling drying processes, designing and optimizing drying equipment as well as projecting foods storability, sorption isothermsare very essential. They are also useful in the determination of critical moistureand selection of suitablematerials for packaging.⁵ .⁶ and ⁷ have reported that sorption isotherm studies help to assess quality and water activity of products which deteriorates through moisture increase.

Studying sorption isotherms at different temperaturelevels enable one to evaluate the thermodynamic relationslike net integral enthalpy and isosteric heat, entropy as well as differential entropy. Drying energy can be estimated through the use of net isosteric heat of sorption and also gives basic idea on the state of water in foodstuff.Sorption isotherm of food materials, not onlyis useful in blending processes, but also in new productsdevelopment.Besides itseffectivenessin the determination of critical water activity (alsoknown as moisture content limit) for textural and flow characteristics of foods, it is also helpful in optimizing safe water activity moisture contentformoisture maximizationas well asprevention case of over-drying. From sorption isotherm studies one can rapidly determine moisture content fromanalysis of water activity using isotherm graph.

Drying or dehydration is a term used to describe moisture elimination from fish and otheragricultural productsvia expulsion of the moisture. For good drying systems design, the knowledge of desorption isotherm would be of advantage for a particular agricultural product which will make use of thin layer drying equations as the basic component of the design concept. The thin layer drying equation contain a very important parameter called equilibrium moisture content (Me). Adequate evaluation of the drying equation will depend on the precision of the predictive isotherm equation required to evaluate equilibrium moisture content. Equilibrium moisture content is important in modeling and designing drying and storage systems. Its importance is partly due to the fact that desorption isotherm data are crucial to the proper choice of the end point of a drying process⁸.

From research findings, it has been found that an in-depth understanding of the equilibrium moisture content-water activity (a_w) relationship is of primary importance in order to fully describe the drying process^{10,9}. Some familiar approachesin determining the moisture sorption isotherms of foodstuffs and other agrarian materials have been applied. ¹¹pointed outsome of thoseprocedures, specifically the manometricand the gravimetric methods; gravimetricmethod being the specially recommended as a standard method for use. It should be noted that three parameter models are however generally preferred to two parameter models for describing the equilibrium moisture properties of food substances because they describe changes that result from variations in temperature more accurately. As could be observed from practice, the major constrain associated with traditional method of drying are losses due to infestation with flies, birds and rodent which may be as high as 30-40%. Also the stability of the dried product interms of physical, chemical and microbiological parameters is influenced by water activity. Having seen the importance of sorption isotherm in the processing and storage of agricultural products and having discovered that much work has not been done on sorption isotherm on tilapia fish, this work was undertaken to bridge the existing gap. Hence the objectives of this work areto; (1)obtain desorption equilibrium isotherm for tilapia fish samplesat the prevailing temperatures(2) authenticate the applicability of various moisture sorption isotherm equations in predicting equilibrium data for the fish samples and (3) to choose the model which is appropriate for the experimental data within the range of temperaturesinvestigated.

II. Materials and Method

Materials:The materials needed for this work were fish samples, desiccators, equilibrium relative humidity salt solutions, weighing balance, digital temperature oven, wire gauze and distil water.

Sample Preparation:The salt samples as listed were bought from industrial chemical supply store with high grade and brought to the laboratory. Each of the chemicals were dissolvedseparately in warm distillwater in a conical flask until the salt formed a saturated solution. It was then poured into a petri dish and kept inside glass jar(desiccator) for further work. The fish samples were broughtout from a refrigerated storage and kept at room temperature in the laboratory for ice to thaw before cleaning and cutting it to the sample size of about 3.5g for the experiment.

Experimental Determination of Equilibrium Moisture Content: The method of determination of equilibrium moisture content of fish is the static gravimetric method ⁸. Samples of fish species which were in triplicates each weighing 3.5 g were placed in stainless steel baskets which were in turn placed on a wire mesh held above saturated salt solutions in a petri dish kept in glass jars (desiccators). The saturated solution of the various salts

maintained constant equilibrium relative humidity (ERH). Values for relative humidity of the saturated salt solution were obtained from literature ¹², as shown on Table 1, the jars were then sealed with silicon vacuum grease and placed in a digitally controlled temperature oven (Wise Ven model WoF105,105 litre,Korea.) at temperatures 40,45 50, 60, and 70°C respectively. These temperatures were monitored and controlled within \pm 2°C. The samples were weighed at six hour interval at first day and after at hourly interval on subsequent days until three constant weights (0.01 g) using (Ohaus digital weighing balance) were obtained in quick succession. This took about 4 to 8 days. On completion of the test the sample moisture content was determined by oven drying method at 103°C for 12 hours. This moisture content value represents the equilibrium moisture content at the designated temperature and equilibrium relative humidity (ERH).

experiment									
Temperature°C	40	50	55	63					
	Water Activity	Water Activity(decimal)							
LiCl	0.112	0.111	0.111	0.110					
MgCl ₂ .6H ₂ O	0.318	0.312	0.309	0.306					
Mg(NO ₃).6H ₂ O	0.485	0.456	0.442	0.433					
NaNO ₂	0.616	0.597	0.588	0.578					
NaCl	0.748	0.746	0.745	0.744					
$(NH_2)_2SO_4$	0.806	0.806	0.806	0.806					
K_2CrO_4	0.860	0.860	0.860	0.860					
K_2SO_4	0.960	0.960	0.960	0.960					

Table 1 Equilibrium Relative humidity values (water activity) of the saturated salt solutions used in the

For the enumerated equations in Table 1, T = temperature ($^{\circ}C$), M_{e=} equilibrium moisture content (% db), a_{w=} water activity (in decimal) and A, B, and C are coefficients of equations.

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Model name	Model Equation	References
Modified Henderson	$M_{e} = \left[\frac{-\ln(1-a_{w})}{A(T+B)}\right]^{1/C}$	13,14
Modified Chung-Pfost	$M_{e} = \frac{1}{C} \ln \left[\left(-\frac{T+B}{A} \right) \ln a_{w} \right]$	15
Modified Halsey	$M_{e} = \left[-\frac{\exp\left(A + B \cdot T\right)}{\ln a_{w}} \right]^{\frac{1}{c}}$	16,17
Modified Oswin	$M_e = A + BT \left(\frac{a_w}{1 - a_w}\right)^{1/C}$	18,19
Modified Gab	$M_{e} = \frac{A.B.\frac{C}{T}.a_{w}}{\left(1 - B.a_{w}\right)\left[1 - Ba_{w} + \frac{C}{T}.Ba_{w}\right]}$	20,21,22,23

 Table2: Equations for modeling equilibrium agricultural products' desorption isotherms

Source:²⁴

The equations listed in Table 2 have been found to give best prediction of equilibrium moisture content of food materials over a wide range of temperatures. Non-linear regression was performed using the least square method. It was done with the help of Non Linear Regression Program (NLREG 1991-2010 USA. Coefficient of determination (\mathbb{R}^2), reduced chi-square (χ^2) and standard error (SE),as shown in equations 1-5, were the statistical factors applied as the standards for choosing the finest model.Reduced chi square is given as

$$\chi^{2} = \frac{\sum_{i=1}^{N} [M_{EX} - M_{P}]}{N - z}$$
(2)

Model efficiency or coefficient of multiple determination (R²) is given as

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$$EF = \frac{\sum_{i=1}^{N} \left(M_{EX} - \bar{M}_{EX} \right)^2 - \sum_{i=1}^{N} \left(M_p - M_{EX} \right)^2}{\sum_{i=1}^{N} \left(M_{EX} - \bar{M}_{EX} \right)^2}$$
(3)

Where M_{EX} and M_p are two sets of variables. $M_{EX=}$ observed data or experimental data, $M_{p=}$ predicted data, N = the number of observations; z = the number of constants in each equation.

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N} (M_{P} - M_{EX})^{2}\right]^{\frac{1}{2}}$$
(4)

$$SE = \sqrt{\frac{S^2}{r}}$$
(5)

Where SE = standard error, S^2 = sample variance, r = number of replications

III. Results and Discussion

Equilibrium Moisture content and moisture Desorption characteristics of tilapia fish sample: The experimental result of the desorption equilibrium moisture content of tilapia fish fillets for temperaturesbetween 40 and 70° C as the mean values of three replicateswere as graphically shown in Fig.1.Equilibrium moisture content, as would be anticipated, increased with water activity at a given temperature, butdecreased with temperature at a given water activity. The shape of the curve is sigmoidal which, is a characteristic of most biological tissues^{25,8.}

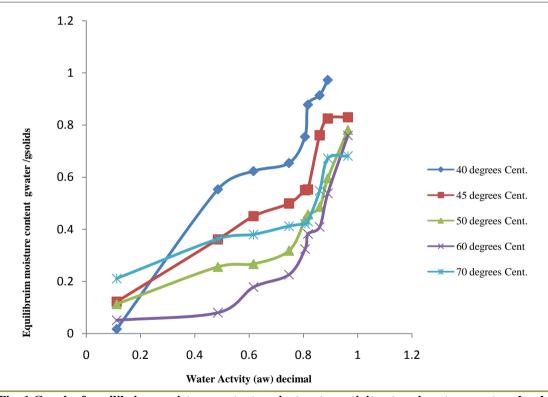


Fig. 1 Graph of equilibrium moisture content against water activity at various temperature levels

For most situations, when water activity exceeds 0.8, a small rise in water activity produces a corresponding rise in equilibrium moisture content. This indicates that above this level of water activity, the storability of the product could be adversely affected as there exist the possibility of mould growth and decay⁸. When water activity lies between 0.11 and 0.8 the gentle slope of the isotherms show that the storage ability of the product generally may not be affected as only little changes in equilibrium moisture content are associated with changes in water activity. When water activity falls below 0.11, the equilibrium moisture content approaches the monolayer moisture content and any further desiccation of the storage environment may lead to the removal of bound moisture from the sample.

Fitting Desorption Isotherm Models to Equilibrium Moisture Content data:The equilibrium moisture isotherm models shown on Table 2, were fitted to the experimental data, and a direct non-linearregression analysis performed by means of Non Linear Regression Program (NLReg1991-2010) in order to estimate the parameters of the equation; and the results of the analysis were as shown on Table 3.

DeterminationCoefficient (\mathbb{R}^2) was one of the primaryconditionsapplied in the choiceof the finest model. Besides \mathbb{R}^2 , the goodness of fit was obtained using number of statistical toolslikeReduced Chi Square (χ^2),Standard Error (SE),and Root-Mean-Square Error (RMSE).For acceptable fit,values \mathbb{R}^2 have to be greateras values of χ^2 , SE and RMSE would be very low^{26,27,2,29}. From the results obtained, at 40°C the water activity varied between 0.112-0.961, by inference, the Modified GAB Model had the lowest values of standard error (SE), reduced chi square (χ^2) and root-mean-square error (RMSE). This relationcorrespondingly gave the peakdetermination coefficient (\mathbb{R}^2). This was followed by the Modified Henderson Model which presented a comparable fitting. Other modified models namely Chung Pfost, Halsey andOswin exhibitedunacceptable fit.

40 Degrees Centigrade				•			
	А	В	С	\mathbb{R}^2	SE	χ^2	RMSE
		-					
Modified Henderson	1.2454565	38.8341752	1.9328	0.8531	0.137597	0.018932	0.10878
Modified Chung-Pfost	41.4906	36.713	2.1452	0.4476	0.266814	0.07109	0.210787
Modified Oswin	0.32808	0.0087	3.64576	0.7316	0.185988	0.034591	0.147036
Modified GAB	5.5449877	0.607	17.3821	0.9471	0.0825454	0.006814	0.065258
45 Degrees Centigrade							
		-					
Modified Henderson	1.61237	44.1913356	1.54768	0.7512	0.149082	0.532573	0.188427
Modified Chung-Pfost	0.939	44.117	1.32737	0	0.432697	0.208003	0.370225
Modified Oswin	0.4087054	0.0004	0.836306	0.4374	0.224213	0.024868	0.128758
Modified GAB	4.743993	0.8696	13.313616	0.9312	0.0783772	0.006142	0.063989
50 Degrees Centigrade							
Modified Henderson	1.1794269	-49.55716	1.4199207	0.8978	0.0740381	0.005482	0.060452
Modified Chung-Pfost	10.962526	40.07	2.1709125	0	0.267382	0.071493	0.218316
Modified Oswin	0.2763929	0.0005	0.9204853	0.749	0.115999	0.013456	0.094713
Modified GAB	7.3641169	0.8688	7.4600532	0.8433	0.0916491	0.0084	0.074831
60 Degrees Centigrade							
Modified Henderson	2.0993261	-59.23761	1.6086724	0.9424	0.0626292	0.003922	0.051136
Modified Chung-Pfost	1.4764577	58.319	1.4764577	0.4677	0.190393	0.036249	0.155455
Modified Oswin	0.171909	0.0011	2.4583314	0.7878	0.120216	0.014452	0.098156
Modified GAB	4.389644	1.1741	8.2956253	0.8839	0.0889017	0.007904	0.072588
70 Degrees Centigrade							
		-					
Modified Henderson	2.0116369	68.8183442	2.2032246	0.4158	0.143608	0.078337	0.228527
Modified Chung-Pfost	2.3944178	67.733	1.3122027	0	0.339601	0.02931	0.442037
Modified Oswin	0.3517135	0.0006	2.3827124	0.5838	0.12122	0.146942	0.098975
Modified GAB	11.861204	0.3339	15.967469	0.7269	0.0981927	0.009642	0.080174

Table 3 Models statistics as used in the drying curve

 30 and 31 reported that in a moisture sorption isotherm model resulting from experimental data, such statistical factors R² or SE could not offersatisfactory indications for the goodness of the fit. However the characteristics of residual graphs would be put into consideration appropriately as shown on Figs2 and 3. Graphs of residuals of the models showed that a haphazard distribution of residuals over the temperature and equilibrium moisture content investigated was presented by Modified GAB and Modified Henderson models, while others exhibited a distribution in a defined pattern. Judgingfrom these results, Modified GAB model was adjudged the best model in the prediction of salted tilapia fish fillets' equilibrium moisture content at 40° C.

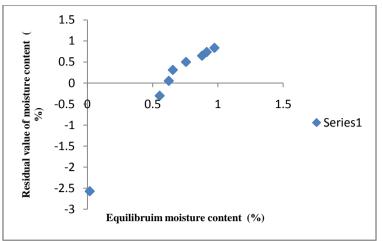


Fig.2 A patterned distribution of residuals by Modified Chung Pfost Model at 40^oC

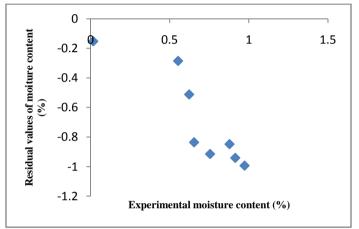


Fig. 3 Random distribution of residuals by Modified GAB Model at 40^oC

In the like manner, the equilibrium moisture content and water activity were considered at $45^{\circ}C$. The result showed that Modified GAB had the highest R² with the least SE,RMSE and χ^2 . Also a residual plot showed a random distribution of residuals in the temperature and water activity values considered hence was regarded as the best at $45^{\circ}C$.

In the same vein, considering the equilibrium moisture contents and water activities at 50 and 60 0 C, some good results were obtained. The result showed that Modified Henderson had the highest R² for these two temperatures and the lowest SE, RMSE and χ^2 . The residual plots showed a haphazard distribution of residuals over the temperature and equilibrium moisture content considered, whereas others displayed a defined distribution. Consistent with these outcomes, Modified Henderson was chosen as the finest for equilibrium moisture content prediction for tilapia fish fillets at those temperature values considered. It was closely followed by GAB model for temperatures of 50 and 60 $^{\circ}$ C. At 70 $^{\circ}$ C, Modified GAB stood out the best with highest R² and lowest SE, RMSE and χ^2 . Modified Oswin was the second best in predicting the equilibrium moisture content of tilapia fish fillets at the second best in predicting the equilibrium moisture content of tilapia fish fillets at the second best in predicting the equilibrium moisture content of tilapia fish fillets at the second best in predicting the equilibrium moisture content of tilapia fish fillets at the second best in predicting the equilibrium moisture content of tilapia fish fillets after considering all the statistical parameters and residual plots associated with a good fit.

IV. Conclusion

Desorption isotherms of tilapia fish for temperature values between 40 and 70° C were studied. In the above-stated temperature regime, the desorption isotherm present an s-shaped graph (sigmoid) and observed to be affected by temperature. It was also noted that at a given moisture content, water activity increased with temperature. Considering the three parameter equations tested: modified versions of Henderson, Chung Pfost, Halsey, Oswin and GAB models, Modified GAB gavesuperlativeindicationfor prediction of equilibrium moisture content of tilapia fish, besides it is temperature-dependent. This was followed by Modified Henderson. Other models results namely Modified ChungPfost, Modified Oswin were found to be unacceptable due to their low coefficients of determination (R²), and high values of standard error (SE), reduced chi square (χ^2),root mean square error (RMSE), and mean relative deviation modulus (P).

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