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DRYING KINETICS OF PRE-OSMOSED FRESH WATER FROG *(Dicroglossus Occipitalis*)

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ABSTRACT

The drying kinetics of frog (Dicroglossus occipitalis) was conducted using convective oven dryer. The results were fitted into three thin-layer models; Lewis, Henderson and Page models. The constants and coefficients of the various models used were evaluated using non-linear regression methods, and the results show that the Henderson model is the best for predicting the drying behaviour of frog and was followed by Lewis model. Furthermore, the drying was discovered to have taken place during the falling rate period and the effective moisture diffusivity was determined using Ficks second law and the values ranged from 8.094x10^{-8}m^2/s to 1.102x10^{-6}m^2/s. The temperature dependence of effective moisture diffusivity obeyed the Arrhenius Law with activation energy of 45.6kJ/mol.

Keywords: *Drying kinetics, moisture diffusivity, frog, moisture ratio*

1. INTRODUCTION

Frog *(Dicroglossus occipitalis*) is a large robustly built amphibian (up to 135mm), possessing incomplete dorsolateral folds on the back with strongly webbed hind-limbs that lives in fresh waters and wetlands. It is used in preparing many African dishes such as soups, stews etc. Frog is a source of protein and is eaten by many people in the world, but is seasonal in harvest and therefore need to be preserved for off-seasons. Since biomaterials are water associated and the rate of deterioration is a function of the moisture content, preservation is therefore needed immediately after harvest in order to lengthen the shelf-life of the products and maintain its quality. Drying is the oldest and most important methods of preserving food materials practiced by man. Drying improves the food stability, since it reduces moisture content and microbial activity of the material and minimizes physical and chemical changes during storage. Another advantage of dried foods is that it takes much less storage space than canned or frozen foods.

Moreover, to increase the storage stability, reduce drying cost and improve the palatability of dried products, certain pre-processing steps are very important. These pre-processing steps include osmotic dehydration, blanching and salting and are used depending on the choice and variety to be dried. Consequently, several works have been done on the drying of biomaterials. They include tomato [1], egg plant [2], apple, [3], Soybean[4],meat, fish and other sea foods[5], cucumber [6], sweet potato [7]. However, there is no available report on the drying behaviour of frog. Thus, the objective of this work is to determine the drying behaviour of freshwater frog and select the most suitable thin-layer model to describe it.

2. MATERIALS AND METHODS

2.1 Sample Preparation and Experimentation

The freshwater frogs were harvested from the freshwater swamps in Bayelsa State, 2015. The samples were taken to the Food Process Engineering Laboratory of the Niger Delta University and were manually sorted and all foreign materials removed and the initial moisture content determined by the oven method as recommended by ASAE standards (S368.41 2000). 100g samples of cut-out specimen were soaked in 5% sodium chloride solution for 10 minutes and dried at temperatures 60, 65, 70, 75, 80, 85, 90, 95, 100, and 105^{0}C using a laboratory-scale

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microwave oven (WMG240EG-Westpoint Microwave Oven) and their weight losses measured with a digital scale at specific intervals until a constant weight was observed on three consecutive measurements. This method was also applied by [8] for Pumpkin seeds and [9] for grape seeds. The drying tests were replicated thrice at each temperature level and averages recorded.

Plate 1: Picture of freshwater frog

2.2 Drying Analysis

Experimental data obtained at each drying temperature were fitted to three thin-layer drying models which include Page model, Henderson-Pabis model and Lewis model. These models are as shown below.

Page model

$$MR = \exp(-kt^n) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots..(1)$$

Henderson-Pab is model

$$MR = A\ \exp(-kt) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(2)$$

Lewis Model

$$MR = exp(-kt) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3)$$

Where

$$MR = \frac{M - M_e}{M_I - M_e} = Moisture\ ratio$$

M is the moisture % (db) at any time, t during drying, M_i is the initial moisture content, % (db)

M_e is the equilibrium moisture content (%db), k is the drying rate constant and A and n are empirical constants.

The drying rate constant, k and other coefficients and constant (A and n) were determined by non-linear regression procedure using XL stat 2010. All other required data (*M*, M_i, drying time and temperature) were measured during experimentation, except the equilibrium moisture content (M_e) which was assumed to be zero as suggested by [10], [9],[11] for thin-layer drying.

2.3 Statistical Analysis

The goodness of fit of all the selected thin-layer models were evaluated using coefficient of determination (R^2), reduced chi-square (χ^2) and the root mean square error (RMSE). The criteria for the best model is the one with highest R^2 value and least RMSE and χ^2 values[3]; The above parameters are mathematically defined as equations (4), (5) and (6). Therefore, the closer R^2 value is to 1 the better the fit.

$$RMSE = \sqrt{\frac{\sum_i^n (MR_{pre} - MR_{exp})^2}{N}} \qquad (5)$$

$$\chi^2 = \sum_{i=1}^{n} \frac{(MR_{pre} - MR_{exp})^2}{N - K} \qquad (6)$$

In (4 - 6), MR_{exp} is the experimental data, MR_{pre} is the predicted data, N is the number of observations and K is the number of constants.

2.4 Moisture Diffusivity and Activation Energy

Moisture transfer during drying of biological materials is known to be controlled by internal diffusion and this process is explained by Fick's second law of diffusion [12] and has been widely used to describe the falling rate drying period of most biological materials [13 , 10]. It is given as follows [12].

$$\frac{\delta M}{\delta t} = D_{eff} \frac{\delta^2 M}{\delta x^2} \qquad (7)$$

In equation (7), M is the moisture content of the product, t is the time; x is the dimension in the direction of transfer, and D_{eff} the coefficient of diffusion. For the determination of moisture diffusivity, the cut-out samples with 13mm thickness were considered as having slab geometries because of their very small relative thickness compared to other dimensions [10]. Thus, the solution of equation (7) for slab-shaped materials with assumptions of moisture transfer by diffusion, constant diffusion coefficients and temperature, and negligible shrinkage is given by equation (8) [12];.

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(Measured\ MR\ value - Predicted\ MR\ values)^2}{\sum_{i=1}^{n}(Measured\ MR\ value - Average\ MR\ values)^2} \qquad (4)$$

$$MR = \left(\frac{8}{\pi^2}\right)\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}e^{\left(\frac{-\pi^2(2n-1)^2D_{eff}t}{4L^2}\right)} \qquad (8)$$

In equation (8), MR is the moisture ratio, D_{eff} is the Coefficient of diffusion (moisture diffusivity), m^2/s, t is the drying time (s), l is the half-thickness of slab, and n is the number of terms in the series

Considering three terms of equation 8 (n = 0, 1 and 2) yields,

When n = 0; $MR = 0.8105\, e^{-2.467\, D_{eff}t/L^2}$

When n = 1; $MR = 0.09006\, e^{-22.21\,\frac{D_{eff}t}{L^2}}$

When n = 2; $MR = 0.0324\, e^{-61.69\,\frac{D_{eff}t}{L^2}}$

Therefore, the solution series for equation (8) is

$$MR = 0.8105\, e^{-2.467\frac{D_{eff}t}{L^2}} + 0.09006\, e^{-22.21\frac{D_{eff}t}{L^2}} + 0.0324\, e^{-61.69\frac{D_{eff}t}{L^2}} \qquad (9)$$

Where $\frac{D_{eff}t}{L^2}$ is the Fourier Number

From equation (9), it is obvious that the first term of the solution series dominates for long drying times as was also observed by other researchers [12; 10]for thin-layer drying of slab-shaped materials. Hence,

$$MR = 0.8105\, e^{-2.467}\,\frac{D_{eff}t}{L^2} \qquad (10)$$

Taking natural log of both sides, we get:

$$\ln(MR) = \ln(0.815) - 2.467\left(\frac{D_{eff}}{L^2}\right)t \qquad (11)$$

Therefore, plotting In *(MR)* against drying time, t yields a slope. The effective diffusivity was then obtained from the slope of the normalized plot as follows.

$$D_{eff} = -\frac{slope(L^2)}{2.467} \qquad (12)$$

More so, to determine the activation energy, the Arrhenius relationship which shows the temperature dependence of effective moisture diffusivity was applied as follows

$$D_{eff} = D_o \exp\left(-\frac{E_a}{RT}\right) \qquad (13)$$

In equation (13), D_o is the pre-exponential factor of the Arrhenius equation (m^2/s), E_a is the activation energy (KJ/mol), R is the universal gas constant (8.314×10^{-3}KJ/molK) and T is the absolute air temperature (^{0}K)

Taking natural log of equation (13) yields,

$$\ln(D_{eff}) = \ln(D_o) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \qquad (14)$$

A plot of In (D_{eff}) versus 1/T gives a straight line and the activation energy, E_a was obtained from the slope method.

3. RESULTS AND FINDINGS

The moisture content data obtained were converted to moisture ratio by fitting into the selected thin-layer models. Figure 1 shows the plots of moisture ratio against drying time at the various drying temperatures. Generally, result shows that moisture ratio decreases with an increase in drying temperature and time. Also, like other biomaterials, the drying rate of freshwater frog falls under the falling rate period, indicating that the drying rate is controlled by internal diffusion. Similar results have been reported on pumpkin seeds [10], and [13] on African nutmeg and ogbono kernels.

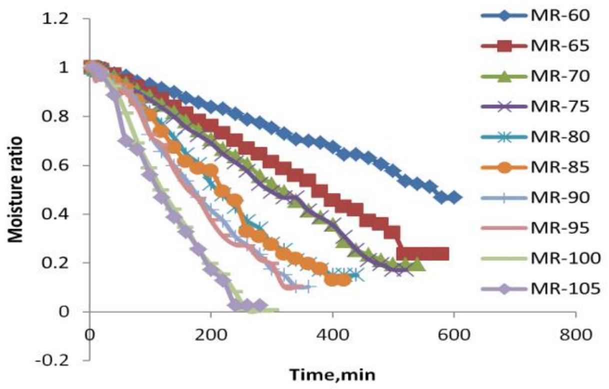

Fig 1: Moisture Ratio for Frog at different temperatures

3.1 Fitting of Drying Models

To evaluate the performance of each thin-layer model selected, the coefficient of determination (R^2), root mean square error (RMSE) and reduced chi-square were (χ^2)values were considered. As shown in Table 1, the R^2 values for Henderson model were in the range of 0.998 - 1.00. For Page and Lewis models the R^2 values were 0.226 - 0.638and 0.993 – 1.00 respectively. For least RMSE values, Henderson model recorded 0.000285 while Page and Lewis models had 0.0483 and 0.0162 respectively. More so, the χ^2 values noted were 0.000000089, 0.00263 and 0.000272 for Henderson, Page and Lewis models respectively. These results show that Henderson-Pabis model with the highest R^2 value and least RMSE and χ^2 values is therefore adjudged the best model for predicting the drying behaviour of freshwater frog and was followed by the Lewis model.

Table 1: Model parameters

Model	Temp,^oC	Constants & Coefficients	R^2	RMSE	χ^2
Henderson	60	K=0.0013,a= 1.068	0.998	0.00197	0.00000415
	65	K=0.0027, a= 1.1874	1.000	0.000808	0.000000798
	70	K=0.0034, a=1.2127	1.000	0.00167	0.000003
	75	K=0.0049, a=1.221	1.000	0.00821	0.0000729
	80	K=0.0049, a=1.2183	0.999	0.000285	0.000000089
	85	K=0.0056, a=1.1660	0.998	0.00162	0.00000289
	90	K=0.0035, a=1.2115	0.999	0.00511	0.0000288
	95	K=0.0071, a=1.3169	1.000	0.007	0.0000668
	100	K=0.0162, a=2.038	1.000	0.0204	0.000471
	105	K=0.0105, a=1.3848	1.000	0.0113	0.000145
Lewis	60	K= 0.0013	0.999	0.00494	0.0000272
	65	K=0.0027	1.000	0.0162	0.000272
	70	K=0.0034	1.000	0.0223	0.000519
	75	K=0.0046	0.998	0.0174	0.000316
	80	K=0.0035	0.999	0.0209	0.00046
	85	K=0.0049	1.000	0.0205	0.00044
	90	K=0.0055	1.000	0.02	0.000419
	95	K=0.0071	1.000	0.0288	0.000874
	100	K=0.018	0.993	0.0501	0.002664
	105	K=0.0105	1.000	0.029	0.000898
Page	60	K=0.025, n=0.1183	0.619	0.0314	0.00105
	65	K=0.0314, n=0.131	0.638	0.0528	0.00455
	70	K=0.0512, n=0.1198	0.512	0.583	0.00305
	75	K=0.072, n=0.1116	0.623	0.0555	0.00333
	80	K=0.082, n=0.1058	0.525	0.0630	0.00433
	85	K=0.0955, n=0.101	0.499	0.0599	0.00393
	90	K=0.1932, n=0.0777	0.469	0.0531	0.0031
	95	K=0.1932, n=0.077	0.415	0.0635	0.00448
	100	K=0.2024, n=0.0723	0.226	0.0483	0.00263
	105	K=0.052, n=0.1183	0.269	0.0676	0.00522

Figure 2, also compares the experimental data with those predicted with Henderson model for frog samples. It shows the concordance between the predicted and measured as the R^2 value of 0.951 is close to 1, which is an indication of the capability of the model in describing the drying characteristics of freshwater frog. Similar observations had been made on grape seeds [9] and fish [5].

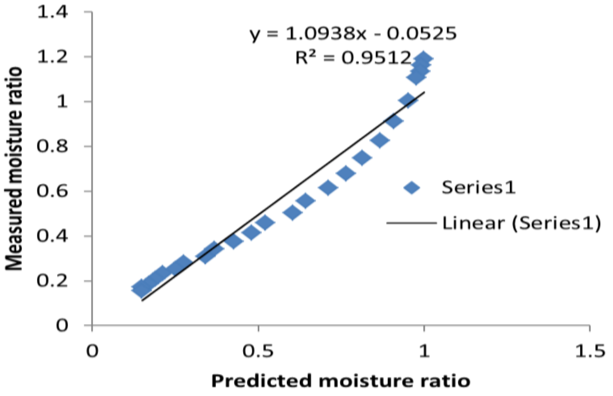

Fig 2: Relationship between experimental and predicted moisture ratio

3.2 Effective Moisture Diffusivity

The effective moisture diffusivity of freshwater frog was calculated using equation (12) and presented in Table 2. Results show that, effective moisture diffusivity values of frog range between 8.904×10^{-8} – $1.102 \times 10^{-6} m^2/s$ at the temperature range of 60^0C to 105^0C.

It was observed that diffusivity values increased steadily from 8.904×10^{-8} to $1.102 \times 10\text{-}6m^2/s$ for corresponding drying temperature increase from 60^oC to 100^oC, but declined to $7.191 \times 10^{-7} m^2/s$ as temperature was further increased to 105^oC. This dipping action of effective moisture diffusivity values at temperatures above 100^oC could be attributed to case hardening effect which was noted on the surface of the sample at that temperature. Similar reports were made by [8-11] and [13-15].

3.3 Activation Energy

The temperature dependence of moisture diffusivity is reported to obey Arrhenius Law, and the activation energy was therefore calculated from the In D_{eff} versus temperature curve using equation (14). The activation energy (E_a) and (D_o) pre-exponential factor values were recorded as 45.6KJ/mol and 1.122x10^{-6}m^2/s respectively with R^2 value of 0.883. The results obtained in this work for activation energy for frog falls under the range of values12.7-110KJ/mol for biomaterials as reported by [16].

Table 2: Average effective diffusivity values of frog at different temperature levels.

Temperature (°C)	Average Effective Diffusivity (m^2/S)
60	8.904×10^{-8}
65	1.849×10^{-7}
70	2.328×10^{-7}
75	2.397×10^{-7}
80	3.356×10^{-7}
85	3.356×10^{-7}
90	3.767×10^{-7}
95	4.863×10^{-7}
100	1.102×10^{-6}
105	7.191×10^{-7}

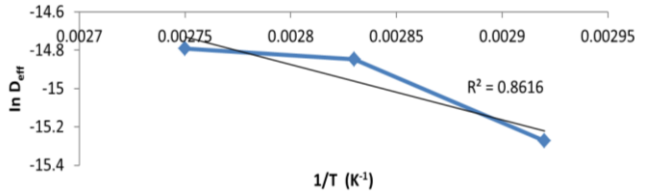

Fig 4: Estimation of Activation Energy for Frog

4. CONCLUSION

The drying behaviour of freshwater frog was investigated, and results show that the drying process of Frog falls under the falling rate period like other biological materials. It was also noted that amongst the three thin layer models considered, the Henderson-Pabis model proved to be the best for predicting the drying kinetics of freshwater frog. For effective moisture diffusivity, values obtained ranged between 1.232x10^{-7}m^2/s and 1.198x10^{-6}m^2/s over the various temperatures considered and activation energy value obtained was 45.6kj/mol.

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