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Chemical Properties and Moisture Sorption Isotherm of Smoke- Dried Catfish *(Clarias gariepinus)* and Mackerel *(Trachurus trachurus)* Produced with a Modified Smoking Kiln: Application of Four Models to Sorption on Data

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Authors' contributions

This work was carried out in collaboration among all authors. Author TOO helped in conceptualization and project administration. Author EEE wrote the original draft, reviewed the manuscript and searched resources for the research, did formal analysis, funding acquisition, performed methodology and also provision of relevant materials done by author EEE. Author TOO wrote, reviewed and edited the manuscript. Author Too supervised the research process and assisted with necessary software prepared, assisted with funding and interpretation of data and also provision of relevant materials. All authors read the previous manuscript and the reviewed manuscript. Author Too wrote, reviewed and edited the manuscript and performed methodology. Author Too reviewed the manuscript and searched resources for the research and did formal analysis. All authors read and approved the final manuscript.

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ABSTRACT

The effectiveness of a modified smoking kiln, the smoking quality, and the moisture sorption characteristics of smoked dried catfish and mackerel were all investigated in this study. Smoked dried catfish protein, ash, fat and moisture ranged between 73.37 and 73.80 %, 5.00 and 5.40% 10.30 and 11.05% and 8.05 and 8.12% respectively and for smoked dried mackerel 70.58 and 70.67%, 5.00 and 5.94%, 12.99 and13.15%, and 6.14 and 6.37% respectively, while the moisture sorption isotherm confirmed type III BET isotherm with marked hysteresis. Smoke dried catfish and mackerel's type III isotherm is as expected given that food items high in protein have been observed to display type III forms. For the Henderson, BET, GAB, and Oswin models, the values of the root means square ranged from 2.6 to 8.7, 4.6 to 9.1, 5.9 to 12.1, and 4.1 to 13.16, respectively. The coefficients of determination for these models ranged from 0.95 to 0.99, 0.93 to 0.96, 0.83 to 0.94, and 0.91 to 0.94. For catfish and mackerel, the isosteric heats of sorption for the adsorption and desorption pathways, respectively, were 4.55 and 1.22 kJ/mol and 4.07 and 1.10 kJ/mol, respectively. With an increase in temperature from 20 to 40 ºC, the apparent sorbate surface area fell for catfish from 99.38 to 85.02 m^2/g solid and for mackerel from 76.01 to 66.25 m^2/g solid. The smoking kiln performed the basic tasks of smoking and drying the fishes very well, with high-quality nutrients.

Keywords: Moisture sorption; isotherm; Africa catfish; smoking kiln; mackerel.

1. INTRODUCTION

Vertebrates that live in freshwater or salt water habitats include fish. Due to its high protein content, fish is a significant food source for people. In comparison to pork or beef, it has the advantages of being affordable, highly acceptable, and having little to no religious bias [1]. According to Strilankshmi [2], fish have a great biological value and include all important amino acids. Catfish play a significant role in Nigeria economy financially. A number of different species of pelagic fish, primarily but not solely those belonging to the family *Scombridae*, go by the common name "mackerel." Once collected, fish is a particularly perishable item that may not reach the intended population in the proper quality and quantity due to the high rate of biochemical changes that occur as a result of subpar processing, packaging, and storage methods [3,4]. There are several preservation techniques that can be used to lengthen the shelf life of caught fish. Fish are preserved through smoking or smoke curing, which combines drying with the buildup of naturally occurring compounds brought on by the thermal decomposition of wood. Fish is smoked not only to preserve it but also to create a flavorful, nutritious product that is well-liked by consumers. Phenols determine how well the fish is smoked, in the traditional technique of smoking to preserve fish, phenolic compounds are of considerable importance for the preservation and organoleptic properties of smoked products [5]. A thermally insulated chamber, or kiln, is a kind of oven that generates temperatures high enough to finish some processes including smoking, drying, hardening, or chemical transformations. As a result, it was necessary to create equipment that was more effective and economical in order to enhance fish processing and lessen the laboriousness of the majority of the methods used today. Studying the moisture sorption isotherm of smoke dried fish is crucial due to the importance of moisture in foods and the fact that the majority of spoiling agents readily rely on moisture [6]. The moisture sorption isotherm (MSI) is a curve that plots the amount of water adsorbed or desorbed by a substance as a function of equilibrium vapour pressure, water activity, or relative humidity at a specific temperature [3]. The main goals of this study was to assess the effectiveness of a modified smoking kiln and identify the chemical composition and moisture absorption properties of smoke-dried catfish as well as mackerel.

2. MATERIALS

Catfish *(Clarias gariepinus)* and Mackerel *(Trachurus trachurus)* were purchased at Nsukka, Main Market in Enugu State, Nigeria. The customized smoking kiln was conceived and built in the Department of Food Science and Technology at the University of Nigeria, Nsukka, while the firewood and sawdust came from a timber shed in Nsukka.

2.1 Smoking kiln Description and Operation

The kiln was constructed of three horizontally stacked chambers, as illustrated in Figs. 1 and 2 with the lid (cover) at the top, a perforated iron slab underneath the chambers (layers), and a brick fire pit below the perforated iron slab. Galvanized wire mesh (2 by 2 mm size), carpet aluminum, plain aluminum, glass fiber for lagging, bricks, and cement were among the materials used in the construction. The chambers are rectangular-shaped containers with a thick cover made of plain aluminum on the inside and carpet aluminum on the outside. Each chamber has two layers of galvanized wire mesh laid out horizontally. Glass fiber is utilized for lagging between the plain and carpet aluminum in the internal and external parts of the cover, respectively. Glass fiber is used to reduce heat loss from the system since plain aluminum, despite its capacity to reflect most heat, acts as a conductor. Additionally, the carpet aluminum reduces heat loss and guards against overheating and handler burns on the equipment's exterior. Given that iron is susceptible to rust, galvanized wire mesh was employed. The lid (cover) was also constructed from the same materials, but it also contains a chimney (a small opening at the top) to let some smoke through. The brick fire pit, complete with an air entrance and wood shavings, was raised from the ground to seven (7) inch in height, 56 inch in length, and 33 inch in width. The built bricks were covered with a perforated iron slab grid with staggered perforations to prevent the contamination of the fish with wood ash and excessive smoke deposit. The kiln chambers and the lid were then placed on the perforated iron slab.

2.2 Sample Preparation

Prior to smoking, the two fish species—catfish and mackerel—were cleaned, decapitated, and sliced into smaller sizes (70 g each), as shown in Fig. 3.

2.3 Smoking Operation

The cooked fish was loaded onto wire mesh in the modified smoking kiln and allowed to smoke while the rate of moisture loss was monitored until the weight remained constant. The smoking kiln's three chambers' temperatures were also measured every hour while the fish was being smoked. The fire woods were first lit and let to burn for a limited period of time before applying the wet sawdust to smolder the flames. By changing the amount of firewood and sawdust in the chambers where the fish were kept, the temperature was kept below 100 ^{o}C to avoid the fish's skin from drying out.

2.4 Proximate Analysis of Smoke Dried Catfish and Mackerel

The hot air oven method outlined by A.O.A.C. [7] was used to evaluate moisture content. The method outlined by A.O.A.C. [7] was used to determine the levels of protein, fat, and ash. The percentage difference was used to calculate the sample's carbohydrate content.

Table 1. Dimension of the modified smoking kiln

Material	Length (inch)	Breath (inch)	Thickness or Height (inch)
wire mesh	38.0	16.0	-
each chamber	44.5	24.5	7.5
perforated iron slab	46.0	25.0	3.5
bricks	56.0	33.0	7.2
lid	10.6	44.7	16.5

2.5 Sorption Experiments

Equilibrium moisture content of the samples was determined.

2.6 Experimental Procedure

Integral gravimetric method [8] was the principle used in the determination of equilibrium moisture content (EMC).

2.7 Fitting of EMC data to Various Isotherm Models

Experimental data were fitted to four moisture sorption isotherm (MSI) models which included

Henderson and Oswin, GAB and Brauneur Emmet Teller as shown in Table 2. Linear regression analysis was used for the linearized form of the equations to calculate the respective constants and coefficient of determinations (R^2).

The percentage root mean square of error (% RMSE) was calculated for each model using:

$$\% \text{ RMS} = \frac{\sqrt{\left(\frac{Mexp - Mcal}{Mexp}\right)^2}}{n} \times 100 \quad (1)$$

Where,

Mexp : Experimental moisture content
Mcalc : Calculated moisture content
N: Number of experimental unit

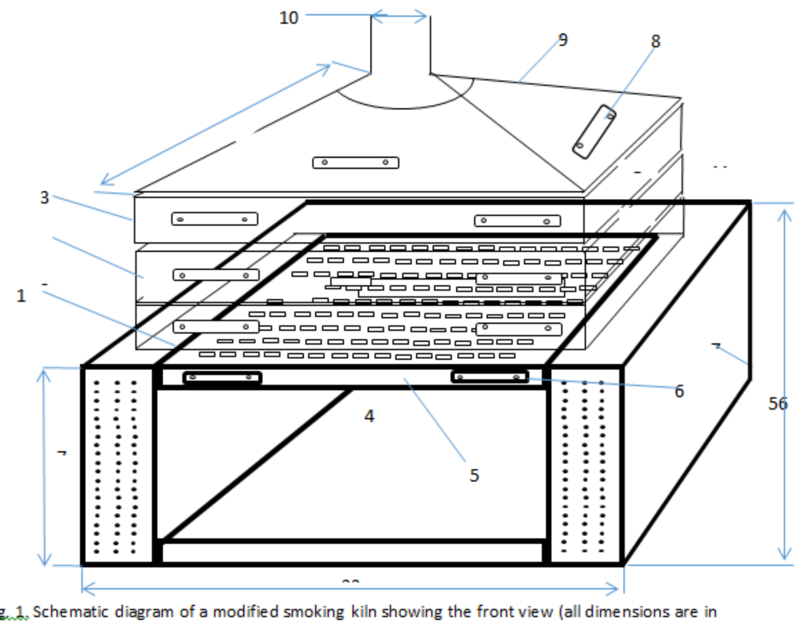

Fig. 1. schematic diagram of a modified smoking showing the front view

Key: 1. = Chamber one; 2. = Chamber two; 3. = Chamber three; 4. = Fire place; 5. = Perforated iron slab; 6. = Perforated iron slab's handle; 7. = Bricks wall; 8. = Lid's handle; 9. = Lid (cover); 10. = Exhaust; 11= Thermometer hole

Fig. 2. Photograph of the modified smoking kiln

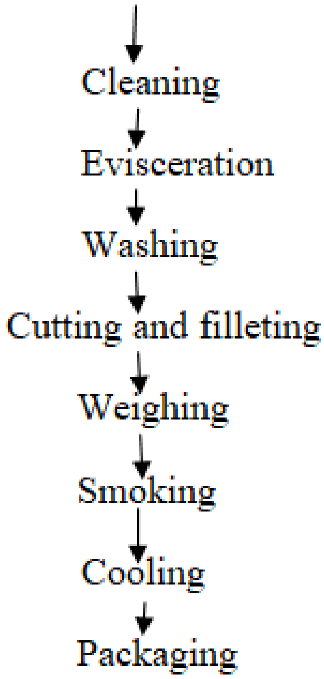

Fig. 3. Production of smoke dried fish (Catfish and Mackerel)

Table 2. Models fitted to the experimental data

Model	Equation	Linearized form of the equation
BET	$\left(\frac{aw}{mcl - aw} = \frac{1}{moc}\right) + \left\lvert\frac{c+1}{moc}\right\rvert aw$	aw/m(1-aw) = Baw + A
Henderson	M = $\frac{-1}{AT}$ In (1 – aw)B^1	In m = In (AT) + B In (1 – aw)
Oswin	M = $\frac{A\,[aw]n}{1-aw}$	In m = In A + B In (aw/1-aw)
GAB	M = MoABaw / (1-Aaw)(1-Aaw +ABaw)	InM = InMoABaw – In ((1-Aaw)(1-Aaw + ABaw))

Where in BET, M = the equilibrium moisture contents, Mo = the monolayer moisture content, c = constant and a_w is the water activity. For Henderson, M is the equilibrium moisture content, T is the absolute temperature of experimentation, a_w is the water activity, A & B are constants. While a_w = water activity, A and n are constants, M is the equilibrium moisture content for Oswin model, A and B are GAB constants

2.8 Net Isosteric Heat of Sorption

The net isosteric heat of sorption for smoke dried catfish and mackerel were determined from isosteres plots of in C against 1/T [9] using the formula:

$$\text{In } C = \text{In } k + Q_s / RT \tag{2}$$

Where, Q_s is the net isosteric heat of sorption estimated from the slope, k is the intercept, R the universal gas constant (0.008314 kg/mole) and T is the absolute temperature of sorption.

2.9 Apparent Sorbate Surface Areas for Sorption

The apparent sorbate surface areas of sorption (m^2/g solid) for the samples were calculated using the [10,11] equation which states that:

$$S_o = 1/ (Ms) (No\ AMo) \tag{3}$$

Where, S_o is the apparent sorbate area for monolayer sorption, M_s is the molecular weight of water (18), N_o is the Avogadro's constant (6.023 × 1023 molecules/mole), Mo is the adsorption and desorption of BET monolayer moisture value (g water/ g solid).

2.10 Statistical Analysis

A completely randomized design (CRD) was used in the investigation. The Statistical Package for Social Statistics (SPSS) was used to perform an analysis of variance on the study's data, and Microsoft Excel was used to perform a linear regression analysis on the moisture sorption data in order to determine the relevant constants and coefficient of determination (R^2). Duncan's Multiple Range Test was used to separate the means, and significance was recognized at p>0.05.

3. RESULTS AND DISCUSSION

3.1 Proximate Composition of Smoke Dried Catfish and Mackerel

The proximate composition of smoke dried catfish and mackerel are presented in Table 3.

3.2 Moisture Content

Mackerel was smoked in chamber one (1) and while catfish smoked in chamber three, respectively, the moisture contents ranged from 6.14% for mackerel to 8.16 %. Between the three chambers of the kiln, there were no appreciable differences in the moisture content of catfish and mackerel ($p > 0.05$). The samples' average moisture content coincided with a previous research by Osibona, Kusemiju. and Akande [12]. Since the majority of fish spoiling agents are moisture dependant [6, 13], the low moisture content obtained is essential for the preservation of the fish. Therefore, it is essential to research the smoke dried fish's moisture sorption properties in order to properly design processing, packaging, and storage systems that can control moisture uptake.

3.3 Fat Content

The fat content of smoke-dried catfish and mackerel varied from 10.303% (w.b) to 13.170% (w.b). However higher fat content was recorded for mackerel samples. Smoked mackerel often included a little more fat than catfish. Large amounts of long-chain polyunsaturated fatty acids with up to six double bonds can be found in fish fat, which is also typically high in vitamin A and D. It offers advantages over eating red meat, which poses health risks but has lower oxidation resistance [3].

3.4 Protein

For catfish and mackerel, the protein content ranged from 70.58% to 73.80%. Between the three chambers of the kiln, there was no discernible difference in the protein content of catfish or mackerel ($p > 0.05$). This can be due to the heating method's minimal impact on protein quantity [14].

Fig. 3A. Smoke dried mackerel

Fig. 3B. Smoke dried catfish

3.5 Ash

Smoked catfish and mackerel ash content ranges from 5.00 to 5.94. This may be due to mackerel's marine habitat, where it comes into touch with numerous minerals and also to his diet. Ash content is a measurement of the mineral contents, which are crucial for the body's healthy operation [1].

3.6 Carbohydrates

The carbohydrate contents of smoked catfish and mackerel ranges from 1.21 to 5.30 % with smoked mackerel samples having higher carbohydrate level.

3.7 Moisture Sorption Characteristics of Smoke Dried Fish

Figs. 4a to 4f display the moisture sorption isotherm (MSI) plots of smoke-dried catfish and mackerel. Figs. 4a to 4c show the smoke-dried catfish isotherms, whereas Figs. 3d to 3f show the smoke-dried mackerel isotherms, both at 20 to 40 ºC. The smoke-dried catfish and mackerel's moisture adsorption and desorption isotherms displayed type III BET isotherm. It was shown that the equilibrium moisture contents (EMC) for both adsorption and desorption increased with an increase in water activity at constant temperature and decreased as the temperature increased. This increase in EMC with higher water activities was anticipated since the water vapour gradient increases when more water is accessible in the environment. hence the higher will be the equilibrium moisture content [15, 16]. Since dietary items high in protein have been reported to exhibit the type III morphologies, the type III isotherm displayed by smoke dried catfish and mackerel is as expected [17, 18]. According to Fennema, Onimawo and Akubor [6, 3], proteins have many sorption sites where each water molecule makes hydrogen bonds with up to four nearby water molecules. This results in a high value of EMC for protein-rich materials. The desorption equilibrium moisture content for all the samples was higher than the adsorption path demonstrating hysteresis effect at all the temperatures taken into consideration, as seen by the moisture sorption isotherm plots. The majority of foods exhibit the hysteresis effect [19,20,21, 22].

Most foods have been found to have a hysteresis effect [19, 22]. This cause hasn't been fully explained. Researchers have made several unsuccessful attempts to determine the true equilibrium moisture content.

According to some, the adsorption path represented actual equilibrium, whereas according to others, the desorption path. According to Sopade and Ajisegri [19], the composition of the food material, the temperature, and the pre-treatments applied to the food items all had a significant impact on the hysteresis effect [19,23]. Observations from the sample plots showed that at low water activities, hysteresis increased with an increase in temperature, but at greater water activities, the effect of temperature on hysteresis was minimal. This was in line with earlier reports [22, 24], which suggested that temperature may have a more significant impact at low water activity levels due to its effects on polar sites than at higher water activity levels. Especially where the majority of food components are free due to the abundance of water, which then interferes with the temperature effects. The higher moisture content in the desorption pathway supported [25] hypotheses that solutes hold more water during desorption because there are more closed pores in dry goods than during adsorption. The capillaries shrink as the meal moves through desorption, trapping water molecules in the process [26].

3.8 Effect of Sorption Temperature

The moisture sorption isotherm (MSI) of smoke-dried fish is clearly affected by temperature, as shown in Figure 4. When the temperature was constant, the EMC increased as water activity increased but decreased as temperature increased. This is because higher temperatures make water molecules more active, which reduces the attractive forces between molecules [25, 27]. The smoke-dried fish becomes less hygroscopic as temperature rises, independent of relative humidity. This data implies that, in an environment with constant relative humidity, smoke-dried fish can absorb moisture more readily at lower temperatures than at higher temperatures. Since the water molecules are free to move at higher temperatures, increasing the temperature lowers isotherm curves and increases water activity at constant moisture content, making the products more vulnerable to moisture-dependent deteriorations [28]. Temperature should be lowered in order to decrease water activity in food while maintaining the same moisture content.

Table 3. Proximate composition of smoke dried fish

	Moisture content %	Fat %	Crude protein	Ash %	Carbohydrates
A_1	$8.050^a \pm 0.100$	$10.303^d \pm 0.103$	$73.79^a \pm 0.021$	$5.16^b \pm 0.020$	$2.7^c \pm 0.21$
A_2	$8.160^a \pm 0.100$	$11.033^c \pm 0.057$	$73.37^a \pm 0.459$	$5.00^b \pm 0.015$	$1.74^d \pm 0.35$
A_3	$8.120^a \pm 0.100$	$11.047^c \pm 0.058$	$73.80^a \pm 0.015$	$5.40^b \pm 0.046$	$1.21^d \pm 0.16$
B_1	$6.140^b \pm 0.200$	$13.153^a \pm 0.016$	$70.67^b \pm 0.020$	$5.94^a \pm 0.010$	$4.08^b \pm 0.12$
B_2	$6.370^b \pm 0.459$	$13.170^a \pm 0.100$	$71.02^b \pm 0.017$	$5.11^a \pm 0.017$	$4.33^b \pm 0.11$
B_3	$6.150^b \pm 0.100$	$12.987^b \pm 0.057$	$70.58^b \pm 0.026$	$5.00^b \pm 0.017$	$5.3^a \pm 0.01$

A1, A2 and A3 are catfishes in lower, middle and upper chamber respectively while B1, B2 and B3 are mackerels in the three chambers respectively. Means within the column with common superscript letters are not significantly different (p < 0.05)

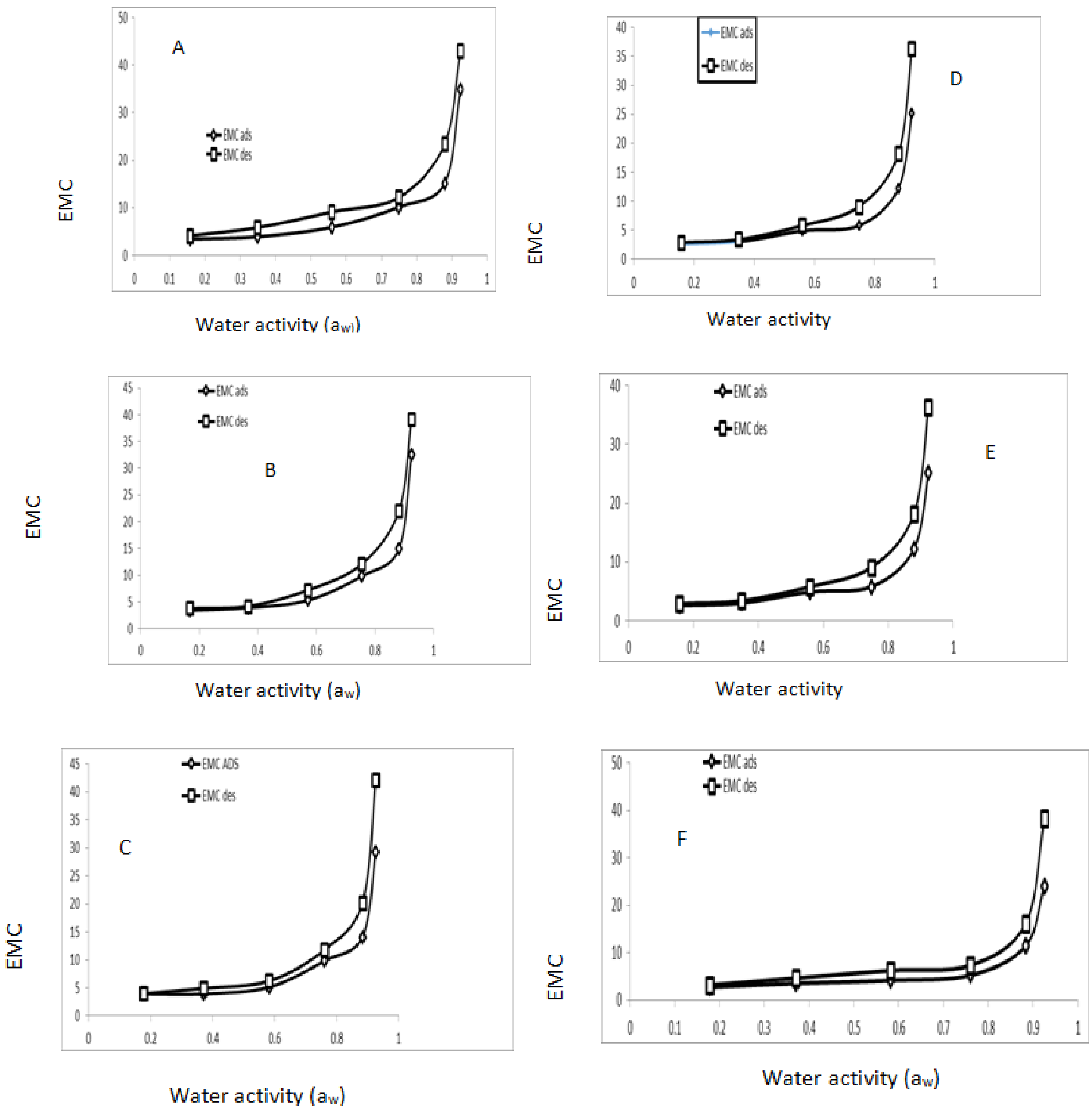

Fig. 4. Moisture sorption isotherms of smoke dried fishes
Legend, EMC = equilibrium moisture content, Des = desorption, Ads = adsorption

3.9 Influence of Nucleated Relative Humidity Environment

The MSI of smoke-dried fish displayed a type III BET isotherm with an increase in EMC that was directly correlated to the environment's nucleated relative humidity at constant temperature. This was caused by the food's sorption sites' strong affinity for environmental moisture. The equilibrium moisture content increases with the amount of water present in the environment when the temperature remains constant [4, 29].

3.10 Application of Henderson Model to Sorption Data

The plot of ln m against ln (1- a_w) of Henderson equation are shown in Figs. 5.1 to 5.6 for catfish and mackerel. For forecasting the equilibrium moisture content at a specific water activity and temperature, the Henderson model provides a flexible tool. This model's inclusion of the temperature influence on MSI makes it extremely important. Table 4 displays the value of the Henderson constants A and B, Table 5 displays the regression parameters and the % root-mean-square of the Henderson model. The Henderson equation gave a good fit for smoke dried fish with correlation coefficient ($R^2 \geq 0.95$) for both adsorption and desorption mode, and the percentage root means square (% RMS) less than 10. The closer the experimental data to the real EMC, the better will be the goodness of fit for such data. Lower the % RMS for a model, the better the fit for predictive purposes in sorption experiments. The determination of the Henderson constants A and B for smoke dried fish was an important accomplishment that opened the door for further research that is anticipated to provide answers to problems that have not yet been thoroughly explored for sorption reasons.

3.11 Application of Branuar Emmet Teller (B.E.T.) model to sorption data

The linearized form of the BET model: aw/m ($1-a_w$) = Baw + A, was derived from the original equation:

$$a_w / M (1-a_w) = 1/ Mo C + C -1 \times a_w / Mo C$$

Where Mo is the monolayer moisture content, aw is the water activity, M is the equilibrium moisture content, B and A are slopes and intercepts respectively. The BET model is known to fit experimental sorption data in the water activity range of up to 0.5 [13,30]. Despite this limitation, the BET model provides values of monolayer moisture content which is an important parameter in food deteriorative mechanism. The monolayer moisture content (Mo) is the amount of first layer of moisture closely bonded to the polar sites, and are not available for any microbial or biochemical deterioration. Regression parameters for sorption data of smoke dried fish using BET model are presented in Table 6.

It was observed that the model fitted all the EMC data of the fish samples as indicated by the correlation coefficients ranging from 0.90 % to 0.96 % ($R^2 \geq 0.90$ %), and the percentage root mean square of error less than 10. The lower the % RMS (generally lower than 10), the better the model's fit for sorption data [31]. The values of BET constant (C) and the monolayer moisture values (Table 7) were estimated from the slopes and intercepts of the BET plot (a_w / M ($1-a_w$) against a_w). It was observed that the value of Mo ranged from 1.4% db (adsorption at 40 ºC) for smoke dried mackerel to 3.1% db (desorption at 20 ºC) for smoke dried catfish. The Mo value of the desorption operations was higher than the adsorption path. According to the observation, some thermodynamically irreversible reactions must take place during desorption, adsorption, or both. The polar sites on which water is sorbed are not completely satisfied in the wet state (the substance being desorption). The water-holding sites are brought together (shrinking) when they dry out in order to satisfy one another. Less water affinity is displayed in the adsorption phase as a result, reducing the water holding capacity during adsorption [4,26]. As earlier observed [25, 27,28], the food materials become less hygroscopic at higher temperature, therefore decreasing the moisture content bound to the polar sites. This was the reason why the value of the EMC and the Mo value decreased inversely with the temperature. The BET constant has been reported [22] to contain a temperature dependent term whose magnitude is derived from the sorptive capacity of the material. By taking into account the value of the universal gas constant and the experiment's absolute temperature, the BET constant can be used to estimate the isosteric heat of sorption of the material. The assessment of apparent sorbate surface area of sorption (So), which takes into account the value of the Avogadros constant and the molecular weight of water [32], further makes use of the BET monolayer moisture content, which is the safest moisture content for storage.

Table 4. Values of henderson constants (A and B) for smoke dried fish

Sample	20 ºC		30 ºC		40 ºC	
	A	B	A	B	A	B
Catfish						
Adsorption	0.0094	-0.9178	0.0086	-0.9184	0.0088	-0.8524
Desorption	0.0120	-0.9399	0.0098	-0.9817	0.0095	-0.9705
Mackerel						
Adsorption	0.0072	-0.8899	0.0062	-0.9093	0.0065	-0.8652
Desorption	0.0079	-1.0222	0.0078	-1.0054	0.0079	-0.9606

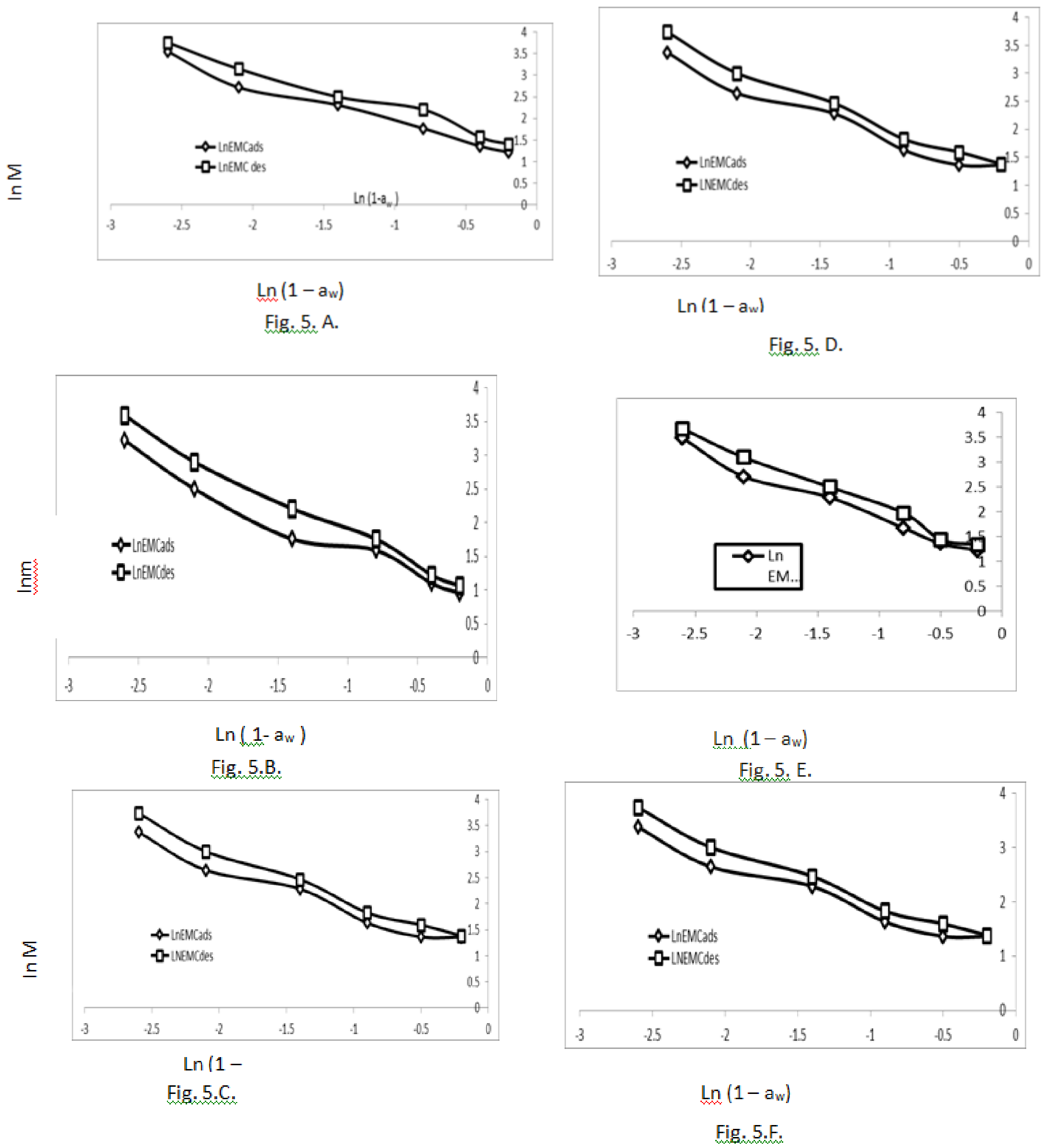

Fig. 5. Henderson plots for smoke dried fishes
Legend, M = Equilibrium moisture content, a_w = water activity

3.12 Application of Oswin model to sorption data

The linearized form of Oswin model: ln m = ln A + B Ln (aw/1-aw) was derived from the original equation: M = A (aw/ 1-aw)^B.

Where ln A and B are intercept and slope respectively, and M is the equilibrium moisture content [33]. The regression parameters, the Oswin constants and the percentage root means square of error are shown in Table 8 and 9 respectively. The Oswin model gave a high correlation coefficient (R^2 ≥ 0.91) and %RMS value less than 10. The predictive equation for desorption gave better fit than the adsorption path. This agreed with the research results of Sopade, Ajisegiri and Abbas [34] that the desorption branch is closer to equilibrium than the adsorption branch of a sorption isotherm. The effect of temperature on the Oswin constants, coefficient of determination and the % RMS were obvious. This agreed with postulation by Sopade, Ajisegri and Abbas [21] that the constant A in Oswin's model was found to be temperature dependent as it decreased with increased temperature at constant water activity [35].

Table 5. The henderson regression parameters for smoked dried fish

SAMPLE	20 ºC			30 ºC			40 ºC		
	Predictive equation	R^2	% RMS	Predictive equation	R^2	%RMS	Predictive equation	R^2	% RMS
Catfish									
Ads	Y= 0.9178x+1.0077	0.98	4.8	Y=0.9184x+0.9569	0.98	3.4	Y=0.8524x+1.018	0.96	4.6
Des	Y=0.9399x+1.2584	0.98	4.4	Y=0.9817x+1.0899	0.99	5.6	Y=0.9705x+1.092	0.98	5.8
Mackerel									
Ads	Y=0.8898x+0.7420	0.97	5.8	Y=0.9093x+0.6368	0.96	6.8	Y=0.8652x+0.708	0.95	6.1
Des	Y=1.02223x+0.849	0.99	2.6	Y=1.0054x+0.8613	0.98	7.7	Y=0.9606x+0.918	0.96	8.7

Table 6. The BET regression parameters for smoked dried fish

20 ºC				30 ºC			40 ºC		
Sample	**predictive equation**	**R^2**	**% RMS**	**Predictive equation**	**R^2**	**% RMS**	**Predictive equation**	**R^2**	**%RMS**
Catfish									
Ads	Y =0.47x – 0.03	0.94	6.6	Y= 0.50x-0.03	0.90	4.8	Y=0.57x-0.0	0.92	4.9
Des	Y=0.34x-0.02	0.96	6.4	Y=0.36x-5.62	0.96	4.2	Y=0.38x-0.013	0.92	4.6
Mackerel									
Ads	Y=0.66x-0.046	0.92	7.8	Y=0.61x-0.04	0.94	9.1	Y=0.76x-0.07	0.94	7.1
Des	Y=0.40x-0.08	0.94	5.7	Y=0.44x-0.007	0.94	5.3	Y=0.49x-0.03	0.90	8.2

Table 7. BET monolayer value and constants for smoked dried fish

Sample	**M_o**	**C**	**M_o**	**C**	**M_o**	**C**
Catfish						
Adsorption	2.3	14.7	2.1	15.7	1.92	10.4
Desorption	3.1	16.0	0.9	0.2	2.70	2.9
Mackerel						
Adsorption	1.6	13.3	1.8	14.3	1.40	9.9
Desorption	2.5	50.9	2.3	59.3	2.20	15.9

Table 8. Oswin regression parameters

	20 ^{0}C			30 ^{0}C			40 ^{0}C		
Sample	**Predictive equation**	**R^2**	**%RMS**	**Predictive equation**	**R^2**	**% RMS**	**Predictive equation**	**R^2**	**% RMS**
Catfish									
Ads	Y=1.8435+0.5354x	0.9574	8.9	Y=1.3809+0.178x.	0.9508	6.7	Y=1.6841+0.35x	0.9396	6.10
Des	Y=2.1078+0.5569x	0.9473	7.4	Y=1.5578+0.187x	0.9609	9.5	Y=1.9626+0.56x	0.9164	9.70
Mackerel									
Ads	Y=1.5513+0.5176x	0.9481	10.0	Y=1.0353+0.181x	0.9612	4.1	Y=1.4927+0.49x	0.9242	13.16
Des	Y=1.7735+0.6000x	0.9683	8.7	Y=1.3142+0.197x	0.9746	5.9	Y=1.7801+0.55x	0.9407	11.92

Table 9. Oswin constants for smoke dried fish

	20°C		30°C		40°C	
Sample	**A**	**B**	**A**	**B**	**A**	**B**
Catfish						
Ads	1.8435	0.5354	1.3809	0.1783	1.6841	0.3568
Des	2.1078	0.5569	1.5578	0.1871	1.9626	0.5665
Mackerel						
Ads	1.5513	1.7735	1.0353	0.1817	1.4927	0.4959
Des	0.5176	0.6000	1.3142	0.1979	1.7801	0.5582

Table 10. GAB regression parameters

S/MODE	TEMP °C	M_o	K	C	R^2	% RMS
(Catfish)						
ADS	20	2.9821	1.0547	6.1735	0.8434	11.4
DES	20	4.3154	1.05183	5.8330	0.9451	12.1
ADS	30	2.6523	22.8035	2.2197	0.8672	12.1
DES	30	3.5989	1.0659	5.0815	0.8269	9.3
ADS	40	2.5287	1.06089	7.7497	0.8381	6.7
DES	40	3.1105	1.08114	6.8046	0.9196	7.4
(Mackerel)						
ADS	20	2.0137	1.0633	7.7965	0.8939	11.5
DES	20	2.8302	1.0792	5.3322	0.8792	5.9
ADS	30	1.6484	1.0843	7.3354	0.9273	11.1
DES	30	2.4785	1.0872	7.4263	0.9917	8.6
ADS	40	1.6616	1.0754	11.4921	0.9866	13.9
DES	40	2.5183	1.0698	8.1044	0.9436	10.7

Table 11. Coeficients of determination (R^2) of the used models

S/mode	Sample	Temp (°C)	Henderson	BET	GAB	Oswin
Adsorption	Catfish	20	0.98	0.94	0.84	0.96
		30	0.98	0.90	0.87	0.95
		40	0.96	0.92	0.84	0.94
Adsorption	Mackerel	20	0.97	0.92	0.90	0.95
		30	0.96	0.92	0.93	0.96
		40	0.93	0.94	0.99	0,92
Desorption	Catfish	20	0.98	0.94	0.95	0.95
		30	0.99	0.96	0.83	0.96
		40	0.98	0.97	0.92	0.92
Desorption	Mackerel	20	0.99	0.92	0.88	0.97
		30	0.98	0.94	0.99	0.97
		40	0.96	0.90	0.94	0.94

Application of Guggenhein-Anderson-DeBoer (GAB) model to sorption data: GAB model was applied to sorption data of smoke dried catfish and mackerel at the selected temperatures (20, 30 and 40 °C) and the entire range of water activity investigated during the experiment. This was because, GAB has advantage over BET, Oswin and Henderson since it has a viable theoretical basis and it is a refinement of Langmuir and BET equation [35]. From Table 10, the GAB monolayer moisture content (Mo) for smoke dried fish which is the safest moisture value for storage ranged between 2.53 and 4.32 for catfish, 2.01 and 2.83 for mackerel. The coefficient of determination (R^2) ranged from 0.83 to 0.95 for catfish and 0.88 to 0.99. The percentage root means square (% RMS) ranged from 6.7 to 12.1 for catfish and 5.9 to 13.1 for mackerel. This values shows that GAB model gave a good fit to the experimental data.

3.13 General Comparison of the Models

Table 11 and 12 show the summary of the comparison of all the models used in this study. The % RMS ranged from 3.4 to 6.8 for the adsorption in Henderson model, 4.8 to 9.1 (for BET model), 5.9 to 13.9 (GAB) and 4.1 to 13.2 (for Oswin model). For desorption mode, the % RMS ranged from 2.6 to 8.7 (Henderson model), 4.6 to 8.2 (BET model) and 5.9 to 11.9 (Oswin model). Based on closeness of coefficients of determination (correlation coefficient) to 100 %, and low % RMS, it can be inferred that the performance of the Henderson model, gave the best fit.

3.14 Net Isosteric Heat of Sorption

The net isosteric heat of sorption (Table 13) for smoke dried catfish and mackerel were determined from isosteresis plots of Ln C against 1/T [32]

According to Kaymark-Ertekin and Sultanoglu [36], the net isosteric heat of sorption, which is depicted in Table 13, can be used to calculate the amount of energy needed for dehydration procedures. It can be described as the sum of the heats of sorption and vaporization of the water from the substance [26].

Table 12. Percentage RMS of smoke dried fish

S/mode	Sample	Temp(^{O}C)	Henderson	BET	GAB	Oswin
Adsorption	Catfish	20	4.8	6.6	11.4	8.9
		30	3.4	4.8	12.1	6.7
		40	4.6	4.9	6.7	6.1
Adsorption	Mackerel	20	5.8	7.8	11.5	10.0
		30	6.8	9.1	11.1	4.1
		40	6.1	7.1	13.9	11.2
Desorption	Catfish	20	4.4	6.4	12.1	7.4
		30	5.6	4.2	9.3	9.5
		40	5.8	4.6	7.4	9.7
Desorption	Mackerel	20	2.6	5.7	5.9	8.7
		30	7.7	5.3	8.6	5.9
		40	8.7	8.2	10.7	10.9

Table 13. Net isosteric heat of sorption for adsorption and desorption of smoke dried fish

Samples	Q_s (ads) KJ/mol water	Q_s (des) KJ/ mol water
Catfish	4.55	4.07
Mackerel	1.22	1.10

Table 14. Apparent sorbate surface areas for sorption (m/g solids) for smoke dried fish

Samples	Temp (^{o}C)	M_o (gH_2O/g solid	S_o (m^2/g solid)
Catfish adsorption	20	2.30	84.6566
	30	2.13	78.3994
	40	1.92	70.6699
Mackerel adsorption	20	1.63	59.9958
	30	1.80	66.2531
	40	1.41	51.5301
Catfish desorption	20	3.10	114.102
	30	1.90	69.9337
	40	2.70	99.3795
Mackerel desorption	20	2.51	92.0181
	30	2.30	84.6566
	40	2.21	80.9759

According to observation, the isosteric heat of sorption for the fish samples fell rapidly as moisture content rose, with the adsorption branch exhibiting greater values than the desorption branch, which had a larger moisture content. This finding is consistent with Benado and Rizvi [37] finding that water adsorbs at the strongest binding sites on the solid's exterior surface at low moisture content. The polymer expands as moisture content rises, creating more high-energy sites for water to bond. Lower temperatures of sorption were produced as sorption happened on the less active site as these sites became occupied [31, 38, 39].

3.13 Apparent Sorbate Surface Areas for Sorption

The apparent sorbate surface areas of sorption (m^2/g solid) for the samples were calculated using the [10] equation which states that S_o = 1/Ms) (No AMo). Where S_o is the apparent sorbate area for monolayer sorption, M_s is the molecular weight of water (18), N_o is the Avogadro's constant (6.023 × 1023 molecules/mol.), Mo is the mean (adsorption and desorption) of BET monolayer moisture value (g water/ g solid) and A is the apparent surface area of one molecules of water (1.10×10^{-19} m^2). Table 14 showed that the apparent surface area (So) (Table 14) decreased with increase in temperature. This implied that at low temperature, the sorbent molecules are exposed to larger areas for sorption. Increasing the temperature can cause molecular shrinkage or thermal denaturation which pose negative effect on the polar sites [25, 27, 40].

The apparent sorbate sorption area serves as a guidance for heat-related pre-treatment operations on food samples by estimating the area over which moisture sorption is anticipated to occur per unit mass of the food [41].

4. CONCLUSIONS

According to the short processing time and high phenolic content of the smoked fish samples, the smoking kiln performed the basic tasks of smoking and drying the fishes very well. Smoke-dried catfish and mackerel's moisture sorption isotherm produced a type III isotherm with noticeable hysteresis at all temperatures. The Henderson model better represented the moisture sorption data for smoke-dried catfish and mackerel than other used models. The best moisture level for storage was found to be the monolayer moisture content (Mo) of smoke-dried catfish and mackerel. Since water is adsorbed at the strongest binding sites on the exterior surface of the solid at low moisture contents, less energy is needed to remove moisture when the moisture content is high compared to low. It would be possible to anticipate the behavior of smoked dried fish during storage, processing, and other activities using the constants produced from all of the sorption models that were utilized.

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DATA AVAILABILITY

Data will be made available upon request

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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