

# Mathematical modelling of the drying kinetics of *Clupeaharengus* from Congo

## Abstract

Modeling means finding a mathematical relationship between coordinates. The work we carried out focused on the kinetics of herringfish. Herring fish, known in the Congo vernacular as “makouala”, is available in large quantities in the country. Its consumption and exploitation constitute an important source of nutrients and revenue. The aim of this study was to investigate the behavior of herring (*Clupeaharengus*) flesh during continuous convective oven drying at three different temperatures (50, 60 and 70°C). The methodology adopted was that of following oven-drying kinetics at the three (3) temperatures mentioned above. Five (5) semi-theoretical mathematical models were used to describe the drying kinetics, with the coefficient of determination ( $R^2$ ), the statistical parameter reduced chi-square ( $\chi^2$ ) and the root-mean-square error (RMSE) being used to assess the quality of the smoothing of the curves for mass loss, dry base content and drying speed as a function of time. Effective diffusivity and activation energy were also evaluated and discussed in this work. The results obtained provided plots of the evolution of mass, dry base content and drying rate as a function of time. Among the models examined, the “Midilli et al.” model appeared to best describe the drying behavior of herringfish under the experimental conditions studied, with coefficient of determination ( $R^2$ ) values of 0.99808, 0.99663 and 0.99811 at 50, 60 and 70°C respectively. Effective diffusivity ( $D_{eff}$ ) values calculated in  $m^2/s$  were for the same temperature order  $2.52993 \times 10^{-5} m^2/s$ ;  $2.45657 \times 10^{-6}$  and  $4.21370 \times 10^{-6}$  for an activation energy ( $E_a$ ) equal to 83.80 kJ/mol.

**Key words:** Activation energy, Effective diffusion, Modeling, *Clupeaharengus*, Drying

## 1. Introduction

According to the FAO, fishing activities are an important source of nutrients and job creation for populations in the coastal areas of certain developing countries [1]. The products derived from this activity, which is fishing, are an affordable source of protein because they are cheaper and more accessible than other sources of animal protein. They also provide a diversification of essential omega-3 fatty acids that are indispensable in a diet [1]. Fish in particular is a food rich in essential micronutrients, important fatty acids and high-quality proteins. Among the Congo's fishery resources, the herring *Clupeaharengus*, otherwise known as “Makouala” in the vernacular of the Congo, figures prominently. It is one

of the most prized fish in Congo-Brazzaville, particularly in the southern part from Pointe-noire to southern Brazzaville. This fish is rich in protein (18.45%) [2] and its oil (1.14%) is rich in essential fatty acids (EPA: 11%) [3]. Most of the fish caught in Congo waters is consumed either fresh, smoked or salted and sun-dried by fishermen-processors or by processors-traders. For lack of processing facilities and to combat product loss, drying and smoking have become the ultimate techniques [4] for conservation in Congo. The rest of the fish products that could not be processed are often thrown away. Drying is a very important operation or technology for improving food preservation [5] cited by Brasiello et al., [6]. To achieve this, it is necessary to extract free water or moisture from the product in order to preserve food from deterioration due to the growth of micro-organisms [7] cited by Brasiello et al., [6], enzyme action and oxidation reactions [8] cited by Brasiello et al., [6]. Thermal energy (sun, electricity, natural gas, wood, coal) is required for drying. To improve drying, a number of parameters need to be controlled, such as thermal energy, the characteristics of the fresh product, and the ideal air speed at product level [9]. The mastery of drying techniques would provide alternatives to combat production loss. The aim of the study was therefore to apply a model to describe the behavior of herring flesh during oven-drying kinetics, using three (3) different temperatures set at 50, 60 and 70°C.

## **2. Materials and methods**

### **2.1. Biological material**

The biological material (Fig. 1), consisting of fresh herring fish, known scientifically as *Clupea harengus* and by its vernacular name Makouala in Congo, was purchased in bulk from the ocean city of Pointe-Noire in the Kouilou department in the south of the country. This material was then transported to Brazzaville, specifically to the INRSITT's Laboratoire de Technologie Agro-alimentaire for the study.



Fig. 1. Fresh herring fish (*Clupea harengus*)

## 2.2 Methods

### 2.2.1. Drying kinetics

Before drying, the herring was first prepared. This involved several steps or operations, including weighing, cleaning, washing, scaling, heading, gutting and filleting. Once the fish had been prepared, they were dried in an INDERLAB oven (0 - 250°C) at 50, 60 and 70°C. Weighing was carried out using a Radwag precision balance (0.01 g) at 30-minute intervals until the mass had stabilized.

By monitoring changes in mass over time, we were able to determine the moisture content of the wet base and the drying rate. These parameters were calculated using the formulas below:

$$\text{Moisture content on wet basis: } X = \frac{m - MS}{MS} [10] (1)$$

With :

X: moisture content on wet basis (kg water/kg dry matter)

m: product mass

Ms : dry matter mass (Ms = total starting mass - starting water mass (calculated from wet-base water content)).

The wet-base water content also enabled us to determine the drying rate over time according to the formula :

$$\text{Drying speed : } - \frac{dX}{dt} = \frac{(X(t + \Delta t) - X(t))}{\Delta t} [11] (2)$$

With :

-  $dX/dt$ : drying rate in kg water/kg dry matter/sec

X: water content in dry basis (kg water/kg dry matter)

$\Delta t$ : time difference in seconds.

Three (3) curves were obtained as a function of time and temperature. These are: the mass loss curve, the wet-base water content curve and the drying rate curve.

### 2.2.2. Modeling drying curves

To model the drying kinetics, we used Origin Pro 8 software, which enabled us to determine the  $R^2$  (coefficient for predicting the best equation describing the drying curves), the reduced chi-square ( $\chi^2$ ) and the root mean square error (RMSE). These parameters will be used to assess the fit between experimental and predicted data [12]. Selection of the best model was based on the highest  $R^2$ , lowest  $\chi^2$  and RMSE [13].

$$R^2 = \frac{\sum_{i=1}^n (M_{Ri} - M_{Rpre,i})^2}{\sqrt{[\sum_{i=1}^n (M_{Ri} - M_{Rpre,i})^2] [\sum_{i=1}^n (M_{Ri} - M_{Rexp,i})^2]}} [14] (3)$$

$$\chi^2 = \frac{\sum_{i=1}^N (M_{Rexp(i)} - M_{Rpre(i)})^2}{N-n} [15] (4)$$

$$RMSE = \sqrt{\frac{1}{N} \times \sum_{i=1}^N (M_{Rexp(i)} - M_{Rpre(i)})^2} [16] (5)$$

Where :

$R^2$  Coefficient of determination

$\chi^2$  Reduced chi-square

RMSE Mean square root error

$M_{Rexp(i)}$  the  $i$ th experimental reduced water content,

$M_{Rpre(i)}$  the  $i$ th predicted reduced water content,

N the number of experimental points

$n_p$  the number of constants in the model studied

The data used for modeling with Origin Pro 8 software were obtained from the reduced water content calculated as follows:

$$\text{Reduced water content : } X^* = \frac{X}{X_{initial}} [17] (6)$$

With :

$X^*$  : Reduced content;

$X$  :moisture content in wet basis (kg water/kg wetmatter) at a given time  $t$ ;

$X_{initial}$ : the initial water content of the product.

The equations for the variousmodelsused are presented in Table 1below:

Table 1. Semi-theoretical drying models

Models	Equations
Newton	$X^* = \exp(-kt)$
Page	$X^* = \exp(-kt^n)$
Henderson et al	$X^* = a \times \exp(-kt)$
Midilli et al	$X^* = a \times \exp(-kt^n) + b \times t$
Logarithmique	$X^* = a \times \exp(-kt) + c$

$a, b, c$ , coefficients and  $n$ , specificexponent of each drying equation;  $k$  specific coefficients of each drying equation,  $t$  is the drying time.

### 2.2.3. Water diffusivitymodels

- **Determination of effective diffusivity ( $D_{eff}$ )**

Effective diffusivity and activation energy have been determined in accordance with the proposals of severalauthors. Water diffusivity ( $D_{eff}$ ) is an essential parameter for quantitative characterization of drying [18]. The formula used to determineit isgiven in equation 7 below:

$$X = \frac{8}{\pi} \exp\left(\pi^2 \frac{D_{eff}}{L^2} \times t\right) \text{ or } \ln X = \ln\left(\frac{8}{\pi^2}\right) - \pi^2 \frac{D_{eff}}{L^2} \times t \quad (7)$$

- Ko slope

The slope ( $K_0$ ) wascalculated by plotting  $\ln(X)$  against time according to equation 8 :

$$K_0 = \frac{\pi^2 D_{eff}}{4L^2} \quad (8)$$

- Determination of activation energy

The activation energywascalculatededusing Arrhenius equation 9 [19, 20]:

$$D_{eff} = D_0 \left(-\frac{E_a}{RT}\right) \quad (9)$$

Plotting  $\ln D_{eff}$  as a function of  $1/T$  gives a straight slopedetermined by the following formula 10 :

$$k_1 = \frac{E_a}{R} \quad (10)$$

With:

$E_a$ : Activation energy (kJ/mol)

$R$ : Universal gas constant (8.3143kJ/mol K)

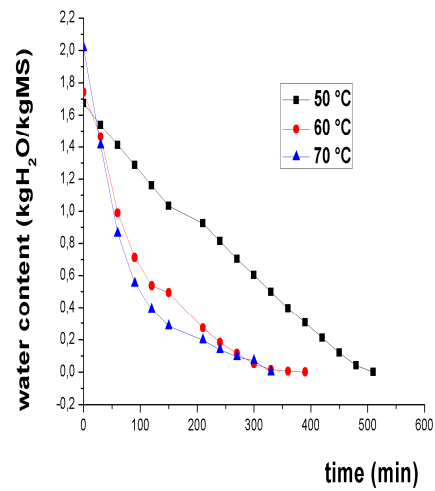
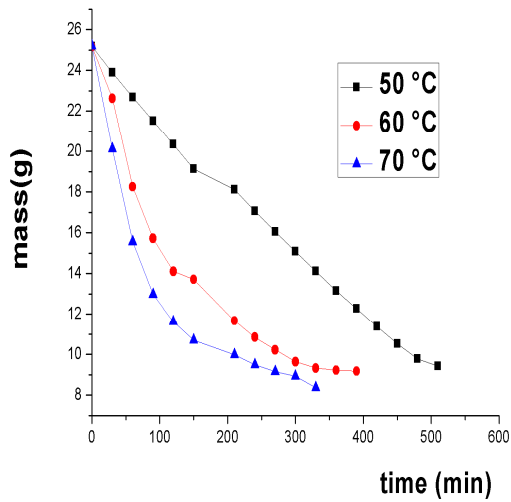
$T$ : Absolute air temperature (k)

$D_0$ : Pre-exponential factor of the d-Arrheniusequation ( $m^2/s$ )

### 3.Results and discussion

#### 3.1. Drying kinetics of oven-dried herring

Figures 2a, 2b and 2c below show variations in mass, moisture content and drying rate as a function of time.



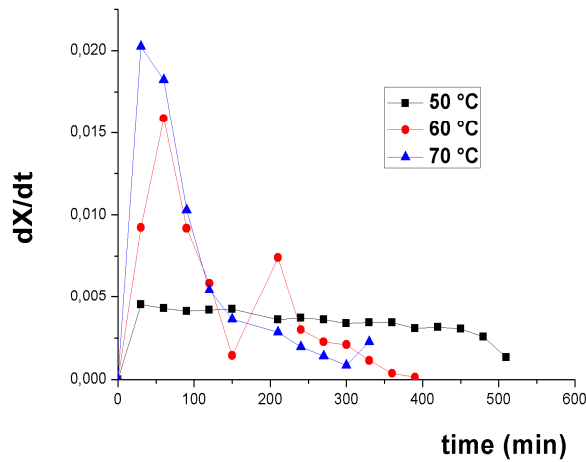


Fig.2. a) Variation in mass as a function of time ; b) Variation in water content as a function of time ; c) Variation in drying speed as a function of time.

Figures 2a, 2b and 2c show changes in mass loss, water content and drying speed as a function of time at three temperatures (50°C, 60°C and 70°C).

Analysis of figure 1 shows a significant loss in mass during the first 150 minutes of drying (19.14g/25g at 50°C, 13.71g/25g at 60°C and 10.71g/25g wetweight at 70°C). A period of deceleration in mass loss from 150 min can be explained by the depletion of free water in the fish. Bound water is strongly adsorbed and therefore difficult to extract. The higher the temperature, the greater the heat and moisture mass transfer [21]. In our case, drying at 70°C is the fastest and shortest, followed by drying at 60°C and finally at 50°C.

The time required to reach a moisture content of 9.42 g/25 g wetweight (wwb); 9.18 g/25 g wetweight (wwb) and 9.33 g/25 g wetweight (wwb) was 510 min (8.5 h), 390 min (6.5 h) and 330 min (5.5 h) respectively for oven drying at 50°C, 60°C and 70°C respectively.

We also noticed that the decreasing trend of the water content variation curves (Figure 2b) is similar to that of the mass variation as a function of time for all tests, whatever the temperature used.

Analysis of the velocity curve (figure 2c) showed that, at the start of drying, velocity was very high for temperatures of 60 (0.0159 kg water/ kg Ms/min) and 70°C (0.0203 kg water/ kg Ms/min). Crusting, the reduction in water diffusivity during drying, and the diffusion of water into the product that occurs during drying, may explain the decrease in drying speed. The speed curve at 50°C tends to be linear and decreasing (0.0045 kg water/ kg Ms/min), that at 60°C fluctuates at first, then decreases after 50 min, and finally the speed curve at 70°C is also decreasing (0.0203 kg water/ kg Ms/min).

From these three figures, we can see that the drying time of a product can be a function of the temperature applied to it. Reducing drying time goes hand in hand with increasing temperature.

### **3.2. Analysis of mathematical models for oven-drying herring**

After application of the five mathematical modeling models selected for the case of fresh herring in our study, the parameters  $R^2$ ,  $\chi^2$ , RMSE as well as the values of the statistical constants obtained under drying conditions at specific temperatures for these same models are presented in Table 2.

Table 2. Parameters of the herringoven drying model

T°	Models	K	K'	K''	a	b	c	n	R <sup>2</sup>	X <sup>2</sup>	RMSE
50 °C	Newton	0,00379	-	-	-	-	-	-	0,97074	0,00634	0,07733
	Page	3,09595E-4	-	-	-	-	-	3,09595E-4	0,98855	0,00252	0,05018
	Henderson et al	0,00407	-	-	0,00407	-	-	-	0,97483	0,0055	0,07415
	Midilli et al	0,07415	-	-	0,00453	0,00137	-	1,00181	0,99808	2,4477E-4	0,01565
	Logarithmic	0,07965	-	-	3,18033	-	-2,19635	-	0,01658	2,74929E-4	0,01658
60 °C	Newton	0,00935	-	-	-	-	-	-	0,99466	0,00117	0,03419
	Page	0,03419	-	-	-	-	-	0,00528	0,99623	9,82773E-4	0,03003
	Henderson et al	0,03003	-	-	0,00968	-	-	-	0,99536	0,00111	0,99536
	Midilli et al	0,0072	-	-	1,01537	1,04872	-	-6,46922E-5	0,99663	9,01654E-4	0,03135
	Logarithmic	0,00867	-	-	1,06009	-	-0,03918	-	0,99650	9,18851E-4	0,03031
70 °C	Newton	0,01332	-	-	-	-	-	-	0,99519	4,99357E-4	0,02336
	Page	0,02207	-	-	-	-	-	0,96885	0,99769	5,20495E-4	0,02281
	Henderson et al	0,01336	-	-	1,00278	-	-	-	0,9976	5,40352E-4	0,02325
	Midilli et al	0,01235	-	-	1,00581	7,11909E-5	-	1,02607	0,99811	4,57703E-4	0,02207
	Logarithmic	0,02235	-	-	0,98979	-	0,02046	-	0,99819	5,45629E-4	0,02235

- **Modeling at 50°C**

For modeling at 50°C, the values obtained for  $R^2$  range from 0.97074 to 0.99808, for  $X^2$  from  $2.4477 \times 10^{-4}$  to 0.00634, and for RMSE from 0.01565 to  $2.4477 \times 10^{-4}$ . The model with the highest  $R^2$ , lowest  $X^2$  and RMSE is that of Midilli et al, whose parameter values are 0.99808,  $2.4477 \times 10^{-4}$ , 0.01565 respectively, followed by Page's model ( $R^2 = 0.98855$ ;  $X^2 = 0.00252$  and  $RMSE = 0.05018$ ). The model best suited to describe the 50°C oven drying of herringfish (*Clupeaharengus*) is that of Midilli et al.

- **Modeling at 60°C**

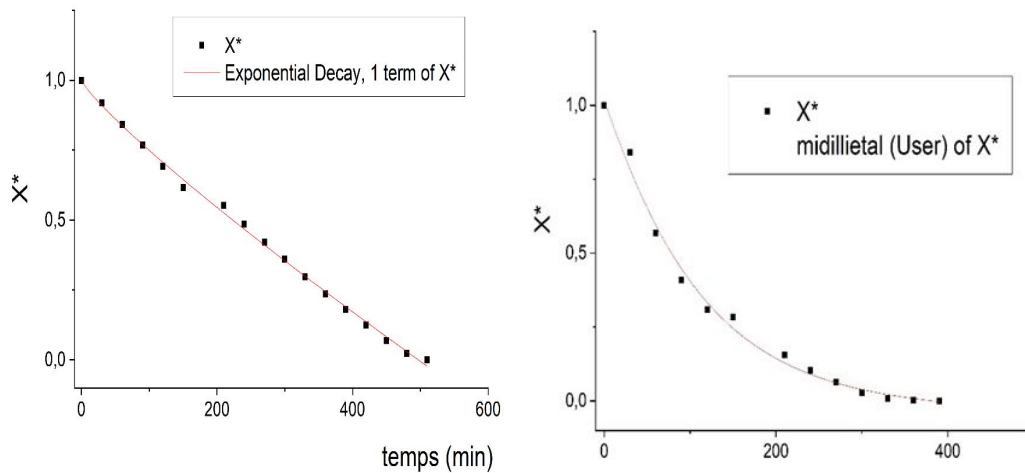
For modeling at 60°C,  $R^2$ ,  $X^2$  and RMSE values range from 0.99466 to 0.99663,  $9.01654 \times 10^{-4}$  to 0.00117 and 0.03135 to 0.99536 respectively. The model with the highest  $R^2$ , lowest  $X^2$  and lowest RMSE is that of Midilli et al, whose parameter values are 0.99663,  $9.01654 \times 10^{-4}$  and 0.03135 respectively. The model best suited to describe the 60°C oven drying of herringfish (*Clupeaharengus*) is that of Midilli et al, followed by the Logarithmic model ( $R^2 = 0.99650$ ;  $X^2 = 0.00252$  and  $RMSE = 0.03031$ ).

- **Modeling at 70°C**

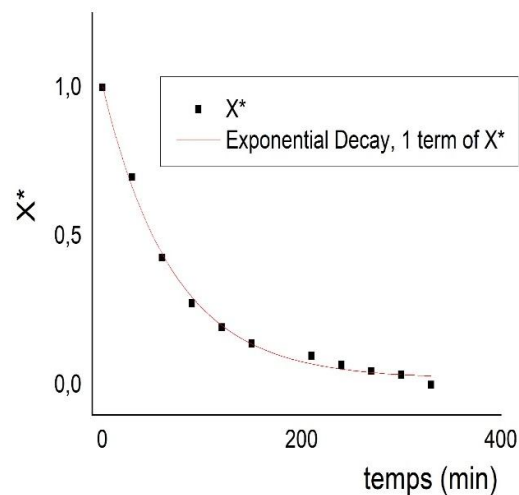
For modeling at 70°C,  $R^2$ ,  $X^2$  and RMSE values range from 0.99519 to 0.99811,  $4.57703 \times 10^{-4}$  to  $5.45629 \times 10^{-4}$  and 0.02207 to 0.02336 respectively. The highest  $R^2$ , as well as the lowest  $X^2$  and RMSE, is that of Midilli et al. with parameter values of 0.99811,  $4.57703 \times 10^{-4}$  and 0.02207 respectively. The model best suited to describe the 70°C oven-drying of herringfish is therefore that of Midilli et al,

From Table 2, the best-suited model for drying fresh herring is that of Midilli et al. Similar results were reported by Gampoula et al., [11] on drying both ends of the pulp of Gambomayam (*Dioscorea cayenensis*).

The best model as proposed by Table 2 over the three temperatures was that of Midilli et al. whose graphical representations are given in Figure 3a, 3b and 3c below:



a) b)



c)

Figure 3. a) Midilli et al. at 50 °C; b) Midilli et al. at 60 °C; c) Midilli et al. at 70 °C

### 3.3. Diffusivity and activation energy

Diffusivity and activation energy as a function of operating conditions are presented in Table 3. The calculated effective diffusivity ( $D_{eff}$ ) values ( $m^2/s$ ) of herringfillets for oven drying at 50°C, 60°C and 70°C were  $2.52993 \times 10^{-5} m^2/s$ ;  $2.45657 \times 10^{-6}$  and  $4.21370 \times 10^{-6} m^2/s$ , respectively. The activation energy found was 83.8 Kj/ mol.

**Table 3.** Diffusivity and activation energy as a function of operating conditions

Temperature (°C)	$D_{eff}$ (m <sup>2</sup> /s)	$Ea$ (kJ/mol)
50	$2,52993 \times 10^{-5}$	
60	$2,45657 \times 10^{-6}$	83,80
70	$4,21370 \times 10^{-6}$	

Analysis of Table 3 shows that at temperatures 60 and 70°C, diffusivity values increase with temperature. If all three temperatures are taken into account, the effective diffusivity decreases with temperature. These values range from  $4.21370 \times 10^{-6}$  m<sup>2</sup>/s to  $2.52993 \times 10^{-5}$  m<sup>2</sup>/s. The highest diffusivity is for drying at 50°C. Al-Harashseh et al.[22] obtained values in the order of  $10^{-6}$  m<sup>2</sup>/s for microwave drying of tomatoes.

### Conclusion

Drying techniques applied to food or non-food matrices have a significant effect on moisture loss rates and duration. The aim of this study was to evaluate the behavior of oven-drying herring using three (3) different temperatures at 50, 60 and 70°C. This work revealed that the higher the drying temperature applied to the product, the shorter the drying time. Oven-drying herring at 70°C resulted in short drying times of 5.5 h. Modeling of the drying data revealed that, for all three temperatures, the models of interest for describing herring oven-drying behavior are those of Midilli et al.

The modeling results have enabled us to optimize product drying, since the quality of the drying process determines the quality of the final products. The modeling also provided the data needed to select the type of oven best suited to drying the products. This work could be completed by studying the impact of different temperature ranges on the nutritional properties of herring.

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