# Mathematicalmodelling of the drying kinetics of *Clupeaharengus*from Congo


## Abstract

Modeling meansfinding a mathematicalrelationshipbetweencoordinates. ~~The workwecarried out~~ thisworkfocused on the kinetics of herringfish. Herring fish, known in the Congo vernacular as “makouala”, isavailable in large quantities in the country. Itsconsumption and exploitation constitute an important source of nutrients and revenue.The aim of thisstudy~~was~~isto investigate the behavior of herring (*Clupeaharengus*) fleshduringcontinuous convective oven drying at threedifferenttemperatures (50, 60 and 70°C). The expriment wascarried out by~~The methodologyadoptedwasthat of following~~oven-drying kinetics at the three (3) temperaturesmentionedabove. Five (5) semi-theoreticalmathematicalmodelswereused to describe the drying kinetics, with the coefficient of determination ($R^2$), the statisticalparametersreducedki-square ($\chi2$) and the root-mean-square error (RMSE) beingused 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 energywerealsoevaluated and discussed in thiswork. The resultsobtainedprovided plots of the evolution of mass, dry base content and drying rate as a function of time. Among the modelsexamined, the “Midilli et al.” model appeared to best describe the drying behavior of herringfishunder 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 (Deff) values calculated in $m^2/s$ were for the sametemperatureorder 2.52993 x $10^{-5}$ $m^2/s$; 2.45657 x $10^{-6}$ and 4.21370 x $10^{-6}$ for an activation energy (Ea) equal to 83.80 kj/mol.



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


Comment [u1]: Fish or fresh ?

## 1. Introduction

According to the FAO,fishingactivities are an important source of nutrients and job creation for populations in the coastal areas of certain developing countries [1]. The productsderivedfromthisactivity, whichisfishing, are an affordable source of proteinbecausethey are cheaper and more accessible thanother sources of animal protein. Theyalsoprovide a diversification of essential omega-3 fattyacidsthat are indispensable in a diet[1].Fish in particularis a foodrich in essential micronutrients, important fattyacids and high-qualityproteins. Among the Congo'sfisheryresources, the herringClupeaharengus,

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otherwiseknown as “Makouala” in the vernacular of the Congo, figures prominently. It is one of the mostprizedfish in Congo-Brazzaville, particularly in the southern part fromPointe-noire to southern Brazzaville. This fishisrich in protein (18.45%) [2] and itsoil (1.14%) isrich in essential fattyacids (EPA: 11%) [3].Most of the fishcaught in Congo waters isconsumedeitherfresh, smoked or salted and sun-dried by fishermen-processors or by processors-traders. For lack of processingfacilities and to combat productloss, drying and smoking have become the ultimate techniques [4] for conservation in Congo. The rest of the fishproductsthatcould not beprocessed are oftenthrownaway.Drying is a very important operation or technology for improvingfoodpreservation[5] cited by Brasiello et al., [6]. To achievethis, itisnecessary to extract free water or moisturefrom the product in order to preservefoodfromdeterioration due to the growth of micro-organisms[7]cited by Brasiello et al., [6], enzyme action and oxidationreactions[8]cited by Brasiello et al.,[6]. Thermal energy (sun, electricity, naturalgas, wood, coal) isrequired for drying.To improve drying, a number of parametersneed to becontrolled, such as thermal energy, the characteristics of the freshproduct, and the ideal air speed at productlevel[9]. The mastery of drying techniques wouldprovide alternatives to combat production loss. The aim of the studywastherefore to apply a model to describe the behavior of herringfleshduringoven-drying kinetics, usingthree (3) differenttemperatures set at 50, 60 and 70°C.

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## 2.Materials and methods

### 2.1.Biologicalmaterial

The biologicalmaterial (Fig. 1), consisting of freshherringfish, knownscientifically as Clupeaharengus and by itsvernacularnameMakouala in Congo, waspurchased in bulk from the ocean city of Pointe-Noire in the Kouilou department in the south of the country. This materialwasthentransported to Brazzaville, specifically to the INRSITT's Laboratoire de Technologie Agro-alimentaire for the study.

Fig. 1. Freshherringfish (*Clupeaharengus*)

**2.2 Methods**

**2.2.1. Drying kinetics**

Before drying, the herringwas first prepared. This involvedseveralsteps or operations, includingweighing, cleaning, washing, scaling, heading, gutting and filleting.Once the fishhad been prepared, theyweredried in an INDERLAB oven (0 - 250°C) at 50, 60 and 70°C. Weighingwascarried out using a Radwagprecision balance (0.01 g) at 30-minute intervalsuntil the mass hadstabilized.

By monitoring changes in mass over time, wewere able to determine the moisture content of the wet base and the drying rate. Theseparameterswerecalculatedusing the formulas below:

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

With:

Comment [u4]: where

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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 (calculatedfromwet-base water content).

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

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

With:

Comment [u6]: replacewithwhere

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

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

Δt: time difference in seconds.

Three (3) curveswereobtained as a function of time and temperature. Theseare : the mass losscurve, the wet-base water content curve and the drying rate curve.

### 2.2.2. Modeling drying curves

To model the drying kinetics, weused Origin Pro 8 software, whichenabled us to determine the $R^2$ (coefficient for predicting the best equationdescribing the drying curves), the reducedki-square ($\chi 2$) and the root mean square error (RMSE). Theseparameterswillbeused to assess the fit betweenexperimental and predicted data [12]. Selection of the best model wasbased on the highest $R^2$, lowest $\chi 2$ and RMSE [13].

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

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

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

Where :

$R^2$ Coefficient of determination

$\chi 2$ Reduced chi-square

RMSE Mean square root error

MRexp(i) the ithexperimentalreduced water content,

MRpre(i) the ithpredictedreduced water content,

N the number of experimental points

np the number of constants in the model studied

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

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

With :

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X* : Reduced content;

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

Xinitial: 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 (Deff)**

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

$$\mathbf{X = \frac{8}{\pi} exp\left(\pi^2 \frac{Deff}{L^2} \times t\right) \text{ or } LnX = Ln\left(\frac{8}{\pi^2}\right) - \pi^2 \frac{Deff}{L^2} \times t} \quad \mathbf{(7)}$$

- Ko slope

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

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

- Determination of activation energy

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

$$\boldsymbol{D_{eff} = D0\left(-\frac{Ea}{RT}\right)} \quad \mathbf{(9)}$$

PlottingLnDeff as a function of 1/T gives a straight slopedetermined by the following formula 10 :

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

With:

Ea: Activation energy (kJ/mol)

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

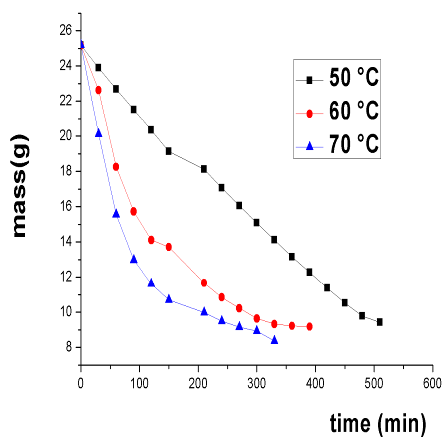
T: Absolute air temperature (k)

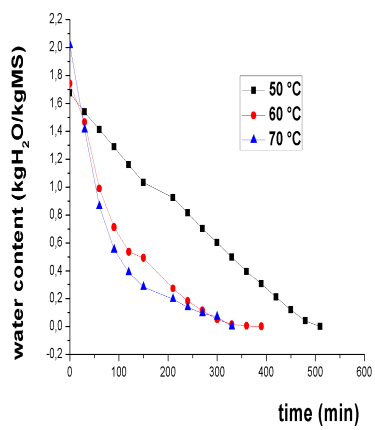
$D_0$: Pre-exponential factor of the d-Arrheniusequation ($m^2/s$)

## 3.Results and discussion

### 3.1. Drying kinetics of oven-driedherring

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



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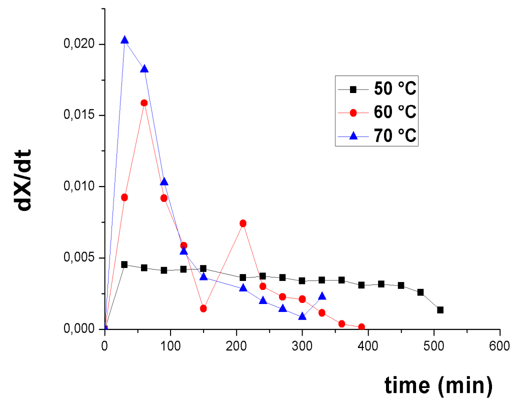


*a)* *b)*

*c)*

*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 threetemperatures (50°C, 60°C and 70°C).

Analysisof figure 1 shows a significantloss 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 lossfrom 150 min can beexplained by the depletion of free water in the fish. Bound water isstronglyadsorbed and thereforedifficult 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.

Wealsonoticedthat the decreasing trend of the water content variation curves (Figure 2b) issimilar to that of the mass variation as a function of time for all tests, whatever the temperatureused.Analysis of the velocitycurve (figure 2c) showedthat, at the start of drying, velocitywasvery high for temperatures of 60 (0.0159 kg water/ kg Ms/min) and 70°C (0.0203

**Comment [u9]:** includethishere ((50°C, 60°C and 70°C).
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**Comment [u14]:** Whatwas the reason for the decreasing trend kg water/ kg Ms/min). Crusting, the reduction in water diffusivityduring drying, and the diffusion of water into the productthatoccursduring drying, mayexplain the decrease in drying speed. The speed curve at 50°C tends to belinear and decreasing (0.0045 kg water/ kg Ms/min), that at 60°C fluctuates at first, thendecreasesafter 50 min, and finally the speed curve at 70°C isalsodecreasing (0.0203 kg water/ kg Ms/min).

Fromthesethree figures, we can seethat the drying time of a product can be a function of the temperatureapplied to it. Reducing drying time goes hand in hand withincreasingtemperature.

**3.2. Analysis of mathematicalmodels for oven-drying herring**

After application of the five mathematical modeling modelsselected for the case of freshherring in ourstudy, the parameters R2, χ2, RMSE as well as the values of the statistical constants obtainedunder drying conditions at specifictemperatures for thesesamemodels are presented in Table 2.

Table 2. Parameters of the herringoven drying model

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| T° | Models | K | K' | K'' | a | b | c | n | $R^2$ | $X^2$ | 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 x 10-4 to 0.00634, and for RMSE from 0.01565 to 2.4477 x $10^{-4}$. The model with the highest $R^2$, lowest $X^2$ and RMSE isthat of Midilli et al, whoseparameter values are 0.99808, 2.4477 x $10^{-4}$, 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*) isthat of Midilli et al.

- **Modeling at 60°C**

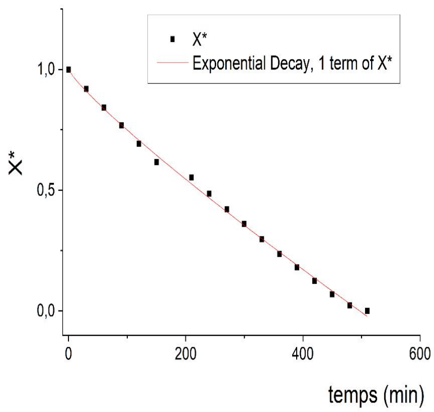
For modeling at 60°C, $R^2$, $X^2$ and RMSE values range from 0.99466 to 0.99663, 9.01654 x $10^{-4}$ to 0.00117 and 0.03135 to 0.99536 respectively. The model with the highest $R^2$, lowest $X^2$ and lowest RMSE isthat of Midilli et al, whoseparameter values are 0.99663, 9.01654 x $10^{-4}$ and 0.03135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

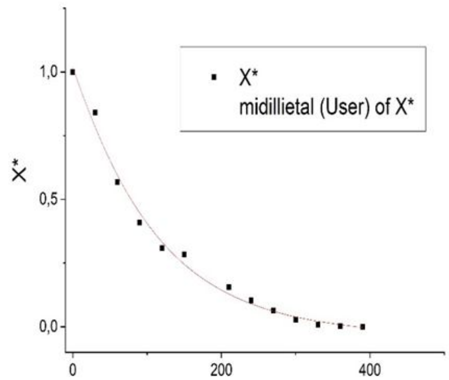
- **Modeling at 70°C**

For modeling at 70°C, $R^2$, $X^2$ and RMSE values range from 0.99519 to 0.99811, 4.57703 x $10^{-4}$ to 5.45629 x $10^{-4}$ and 0.02207 to 0.02336 respectively. The highest $R^2$, as well as the lowest $X^2$ and RMSE, isthat of Midilli et al. withparameter values of 0.99811, 4.57703 x $10^{-4}$ and 0.02207 respectively. The model best suited to describe the 70°C oven-drying of herringfishisthereforethat of Midilli et al,

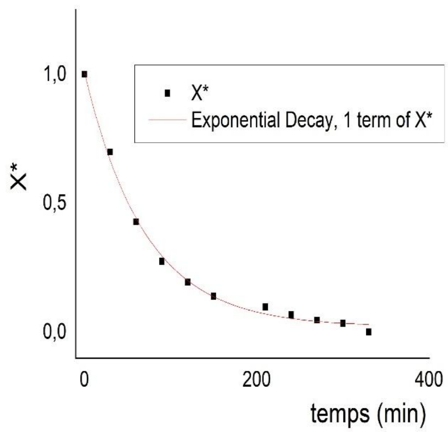
From Table 2, the best-suited model for drying freshherringisthat of Midilli et al. Similarresultswerereported by Gampoula et al., [11] on drying both ends of the pulp of Gambomayam (*Dioscoreacayenensis*).

The best model as proposed by Table 2 over the threetemperatureswasthat of Midilli et al. whosegraphicalrepresentations are given in Figure 3a, 3b and 3cbelow:




*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 (Deff) values ($m^2/s$) of herringfillets for oven drying at 50°C, 60°C and 70°C were 2.52993 x $10^{-5}$ $m^2/s$; 2.45657 x $10^{-6}$ and 4.21370 x $10^{-6}$ $m^2/s$, respectively. The activation energyfoundwas 83.8 Kj/ mol.

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

| Temperature (°C) | $D_{eff}$(m$^2$/s) | *Ea* (kj/mol) |
|---|---|---|
| **50** | 2,52993 x $10^{-5}$ | |
| **60** | 2,45657 x $10^{-6}$ | 83,80 |
| **70** | 4,21370 x $10^{-6}$ | |

Analysis of Table 3 shows that at temperatures 60 and 70°C, diffusivity values increasewithtemperature. If all threetemperatures are takenintoaccount, the effective diffusivitydecreaseswithtemperature. These values range from 4.21370 x $10^{-6}$ m$^2$/s to 2.52993 x $10^{-5}$ m$^2$/s. The highestdiffusivityis for drying at 50°C. Al-Harahsheh et al.[22]obtained values in the order of $10^{-6}$ m$^2$/s for microwave drying of tomatoes.

**Comment [u16]:** Whatis the resaonbehind the decrease in diffusivity as well as temperature ?



## Conclusion

Drying techniques applied to food or non-food matrices have a significanteffect on moistureloss rates and duration. The aim of thisstudywas to evaluate the behavior of oven-drying herringusingthree (3) differenttemperatures at 50, 60 and 70°C. This workrevealedthat the higher the drying temperatureapplied 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 revealedthat, for all threetemperatures, the models of interest for describingherringoven-drying behavior are those of Midilli et al.

The modeling results have enabled us to optimizeproduct drying, since the quality of the drying process determines the quality of the final products. The modeling alsoprovided the data needed to select the type of oven best suited to drying the products. This workcouldbecompleted by studying the impact of differenttemperature ranges on the nutritionalproperties of herring.

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