



DRYING KINETICS OF FROZEN OYSTER MUSHROOMS (*PLEUROTUS OSTREATUS*)

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ABSTRACT

The kinetics of drying of frozen oyster mushrooms (*Pleurotus ostreatus*) was evaluated. Air temperatures of 50 C, 60 C and 70 C, at 2 m/s and 5% relative humidity, were used for drying experiments. In this work, we studied different mathematical models representing mushroom drying kinetics in order to select the best model for drying curves. Statistics used for comparison and selection of models were based on residual standard error and Akaike's information criterion. From all models evaluated, Page was selected as the best model on the basis of its simplicity and good fit of experimental data. The effective diffusivity coefficient (D_{eff}) and the activation energy (E_a) were calculated for working conditions. The D_{eff} ranged from 6.64×10^{-10} to 1.024×10^{-8} m²/s for the temperature range studied. The E_a for the diffusion water was 23.02 kJ/mol.

Key words: Kinetics, frozen mushrooms, modeling, *Pleurotus ostreatus*.

CINÉTICA DE SECADO DE HONGOS CONGELADOS (*PLEUROTUS OSTREATUS*)

RESUMEN

Se evaluó el secado de gírgolas (*Pleurotus ostreatus*) previamente congeladas, bajo las siguientes condiciones experimentales: temperaturas de 50 C, 60 C y 70 C; velocidad

de aire de 2 m/s; y 5% de humedad relativa. El objetivo de este trabajo fue estudiar distintos modelos matemáticos que representen la variación del contenido de humedad de los hongos para seleccionar aquel que mejor se ajuste a los datos experimentales. El error estándar residual y la función de información de Akaike fueron los dos estadísticos utilizados como criterio de bondad de ajuste para la selección y comparación de modelos. De todos los modelos evaluados, Page es el más apropiado por su simplicidad y ajuste a los datos experimentales. El coeficiente de difusividad efectiva (D_{eff}) y la energía de activación (E_a) fueron calculados para las condiciones del trabajo. El D_{eff} varió entre 6.64×10^{-10} y 1.024×10^{-8} m²/s en las temperaturas estudiadas y la E_a obtenida fue de 23.02 kJ/mol.

Palabras clave: Secado, hongos congelados, modelado, *Pleurotus ostreatus*.

INTRODUCTION

The cultivation of edible mushrooms is a biotechnology industry in continuous expansion, becoming increasingly important for the economy of many countries. However, due to a high moisture content and a short shelf life of edible mushrooms, commercial production is a difficult task. The application of suitable post-harvest techniques is fundamental in marketing strategies for extending shelf life and maintaining mushroom quality⁵.

An important factor in processing raw materials is the evaluation of stability during the drying process. Drying can be described as an industrial preservation method, in which water content and activity of fruits, vegetables and mushrooms are decreased by heated air to minimize biochemical, chemical and microbiological deterioration. The major objective of drying food products is the reduction of moisture content to a level that allows safe storage over an extended period⁴. The life of the dried raw material is limited as it is associated with the appearance of fresh products. Frozen products help to extend shelf life, however, the evaluation of their

behavior during dehydration has been poorly studied.

Isothermal drying seems to be the most common model assumption in kinetic studies for solving the variation of the dimensionless moisture as a function of time for different air operating conditions: temperature, velocity and relative humidity. However, in many contributions, only the dry bulb drying air temperature was varied¹⁴. It is evident that the complexity inherent to the analysis of drying processes lies in the diversity of biological materials and their shrinkage, so it is difficult to find a general model. There are several possibilities to model the thin layer drying with many different degrees of complexity. As previously demonstrated by several authors^{14,15}, kinetic parameters vary substantially according to the method used, and even those obtained by the same method are often dependent on the equilibrium moisture content used to express the experimental data in dimensionless form.

Most foods are colloidal-capillary-porous materials, in which the liquid-vapor transport can occur simultaneously. Most dehydration of solids takes place in the

falling-rate period of drying. During this period, the drying rate is normally governed by factors affecting the movement of moisture within the food. To study the phenomenon of drying falling-rate period, several mathematical models have been proposed, some of which are empirical and others are based on the prevailing hypothesis that there is a particular mechanism of moisture movement within the solid. The best known hypothesis is based on the assumption that water migrates into the solid by diffusion due to a concentration difference between the surface and the inside, and that Fick's second law explains the diffusion of this movement. Many of the proposed solutions to this law assume that the value of diffusivity of the liquid is constant throughout the period of decreasing rate^{13,14}.

In this work, we propose drying kinetics of *Pleurotus ostreatus* using mathematical models, selecting those that fit well with the experimental data.

MATERIALS AND METHODS

Raw material. The strain A02 of *Pleurotus ostreatus* (Jacq.) P. Kumm. was used in all experiments, which is deposited at the Centre for Research and Services for the Production of Edible and Medicinal Mushrooms, Neuquén, Argentina. Basidiocarps were cultivated on poplar trunks using standard techniques at the high valley of Río Negro and Neuquén, Argentina. Mature oyster mushrooms were harvested, showing an average water content of $92.7 \pm 1.0\%$ on a fresh weight basis, and they were then kept frozen at -20 C until use.

Drying process. Experiments were carried out in a purpose-built pilot scale

dryer, consisting of a closed system with forced air circulation and appropriate control of drying variables²⁵. Different experiments were conducted at three drying temperatures (50 C , 60 C , 70 C), keeping constant speed (2 m/s) and relative humidity (5%). Rectangles ($2 \times 4\text{ cm}$) of pre-weighed frozen oyster mushrooms were placed and distributed as monolayer in a perforated baskets (22.5 cm diameter by 10 cm height). They were weighed every 15 min during the first 2 h of drying, and from that point every 30 min until constant weight was reached. After cooling at room temperature in a dry atmosphere. Dried mushrooms were placed in sealed glass containers. Labelled containers were stored in a freezer at -20 C until use for experiments.

Measurement of weight loss and dry weight of the samples. The weight loss of partially dehydrated samples was obtained by discontinuous weighing on a digital analytical scale (precision: $\pm 0.001\text{ g}$; Ohaus, Ontario, Canada). The dry weight of each sample was determined by drying to constant weight in a forced air oven at 102 C , using the same scale¹.

Determination of water activity. For estimation of the equilibrium moisture content, a_w was measured experimentally in triplicate at 25 C using a hygrometer (Aqualab, model 3TE, Pullman, U.S.A.). Results were expressed as average.

Determination of the equilibrium moisture content. Was calculated using the five-parameter GAB equation. This equation is often used in studies of foods^{13,17,26} (Equation 1).

$$X_e = \frac{X_m \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w)(1 + (C - 1) \cdot K \cdot a_w)} \quad (1)$$

The three parameters of the model (X_m , C , K)

have physical meanings: X_m represents the moisture content of the monolayer, while C and K are related to the heat of adsorption of water molecules in the monolayer and in the multilayer. The parameters C and K can be correlated with the temperature (Equations 2 and 3), so that the resulting equation will have five parameters (X_m , C_0 , ΔH_C , K_0 , ΔH_K) instead of three, and depend on two variables: temperature and water activity.

$$C = C_0 \cdot e^{\left(\frac{\Delta H_C}{RT}\right)} \quad (2)$$

$$K = K_0 \cdot e^{\left(\frac{\Delta H_K}{RT}\right)} \quad (3)$$

where $\Delta H_C = \Delta H_L - \Delta H_1$ and

$\Delta H_K = \Delta H_L - \Delta H_2$. ΔH_L , ΔH_1 , and ΔH_2 are the heats of water condensation, adsorption of the monolayer and adsorption of the multilayer, respectively. The adjustment was carried out using the method of least squares and the technique of non-linear regression (Systat 12). The quality of the fit of the model was assessed by means of the correlation coefficient (r^2), which must be greater than 0.85 to achieve a good modeling of experimental data⁷.

Modeling of drying kinetics. The dimensionless humidity (X_R) for the different temperatures of drying air was calculated using experimental data from Equation 4:

$$X_R = \frac{x - x_e}{x_0 - x_e} \quad (4)$$

where x is the moisture content at time t (kg water/kg dry solid), x_0 is the initial moisture content, and x_e is the equilibrium moisture content. **Table 1** shows the models used to estimate the dimensionless moisture content (X_R) of dehydrated samples at different drying air temperatures (50 C, 60 C, 70 C).

Table 1. Selected models to analyze the experimental data.

Model	X_R
Lewis ¹²	e^{-kt}
Page ¹⁸	e^{-kt^n}
Henderson and Pabis ⁹	$a \cdot e^{-kt}$
Logarithmic ¹¹	$a \cdot e^{-kt} + c$
Wang and Singh ²⁷	$1 + a \cdot t + b \cdot t^2$
Midilli <i>et al.</i> ¹⁶	$a \cdot e^{-kt^n} + b \cdot t$
Henderson and Henderson ⁸	$C \cdot \left[e^{-kt} + \frac{1}{9} e^{-9kt} \right]$

Determination of the goodness of fit. The fit of data to theoretical models was performed using nonlinear regression in software R. The two statistics used as a goodness of fit criterion for selection and comparison of models were residual standard error (s) and Akaike's information criterion (AIC)⁴.

Residual standard error(s). This is a measure of the distance between experimental data and the curve estimation based on the model used. The relationship between the predictor variable "x" and the answer "y" can be formulated by a nonlinear regression model of Equation 5:

$$y = f(x, \beta) + \varepsilon_i \quad (5)$$

where ε_i is the error term for observation i , and β_1, \dots, β_p the p parameters to be estimated. The residual variance estimated σ^2 for parameters found is obtained by Equation 6 as:

$$\sigma^2 = \frac{RSS}{(n - p)} \quad (6)$$

where:

$$RSS = \sum_{i=1}^n (X_{R_{expi}} - X_{R_{prei}})^2 \quad (7)$$

$X_{R_{expi}}$ is the experimental value, $X_{R_{prei}}$ is the predicted value, $n-p$ are the degrees of freedom, n is the number of data, and p the amount of estimated parameters. The residual standard error (RSE) is then s . The probability function strongly related to:

$$RSS(\beta) = \sum_{i=1}^n (y_i - f(x_i, \beta))^2 \quad (8)$$

is defined as:

$$L(\beta, \sigma^2) = \frac{1}{(2\pi\sigma^2)^{n/2}} \exp\left[-\frac{RSS(\beta)}{2\sigma^2}\right] \quad (9)$$

The estimated parameters ($\hat{\beta}$) are those that maximize L regarding β , equivalent to minimizing RSS as a function of β . The result of the maximum value for the probability function is:

$$L(\hat{\beta}, \hat{\sigma}^2) = \frac{1}{\left[\frac{2\pi RSS(\hat{\beta})}{n}\right]^{n/2}} \exp(-n/2) \quad (10)$$

where the estimator used is:

$$\hat{\sigma}^2 = \frac{(n-p)}{n} s^2 \quad (11)$$

Akaike's information criterion (AIC). This criterion can be considered as an estimate of the distance between the model used and the true but unknown model produced by the data. It is defined as:

$$-2\ln[L(\hat{\beta}, \hat{\sigma}^2)] + 2(p+1) = n\ln(2\pi) + n\ln\left[\frac{RSS(\hat{\beta})}{n}\right] + n + 2(p+1) \quad (12)$$

For nonlinear regression models, AIC is a

function of the residual sum of squares, the number of observations and the number of parameters². By definition, AIC includes a penalty for the number of parameters used [term 2 ($p + 1$)] in Equation 12. It is the Napierian logarithm.

Effective diffusivity coefficient (D_{eff}). This was obtained from the integration of the equation of Fick's second law for an infinite plate without external resistance to mass transfer, assuming that the effective diffusivity is constant, the dehydration is isothermal, and the solid suffers no shrinkage³, Equation 13:

$$X_R = \frac{X - X_e}{X_0 - X_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{D_{eff}(2n+1)^2\pi^2 t}{4l^2}\right] \quad (13)$$

where: X_R is the dimensionless moisture of the sample, X is the moisture content at a given time (kg water/kg dry solid), X_0 is the initial moisture content (kg water/kg dry solid), and X_e is the content of equilibrium moisture content of the sample (kg water/kg dry solid); D_{eff} is the effective diffusion coefficient (m^2/s); t is the time (s) and l (m) is half the thickness of the sample.

Effect of temperature. The Arrhenius equation was used assessing the dependence of effective diffusion coefficients on the drying air temperature (Equation 14):

$$D_{eff} = D_0 e^{\frac{-E_a}{RT}} \quad (14)$$

where: E_a is the activation energy (kJ/mol), D_0 is the pre-exponential factor (m^2/s), R is the universal gas constant, and T is the temperature (K). E_a was obtained from the slope of the Arrhenius plot [$\ln(D_{eff})$ vs. $1/T$].

RESULTS AND DISCUSSION

Estimation of equilibrium moisture

Table 2. Parameters of the GAB equation at 25 C.

Constant	Value
X_m	0.118 kg H ₂ O/kg dry solid
ΔH_c	3.13 kJ/kg
C_0	61.11
ΔH_k	49.78 kJ/kg
K_0	0.98
r^2	0.99
X_{eq}	0.02 kg H ₂ O/kg dry solid

content. **Table 2** shows different parameters of the GAB equation at 25 C with a high correlation coefficient (r^2), which indicates a good fit. The X_m value is an important parameter, since this has a physicochemical meaning representing the water molecule primary layer, which can interact thermodynamically with others components. The satisfactory results obtained when applying the GAB equation to modeling the experimental moisture data as a function of water activity, confirming the applicability of this equation to food products.

Determination of the goodness of fit

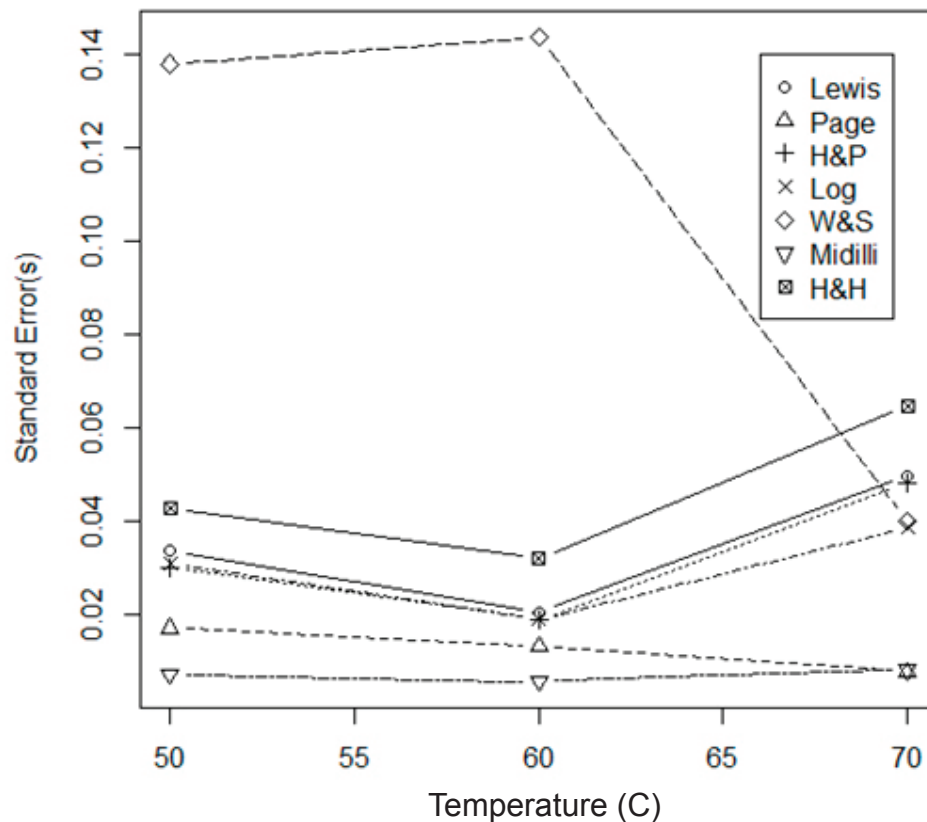


Fig. 1. Standard residual error(s) of models as a function of temperature studied. Models were as follows: Lewis¹², Page¹⁸, Henderson and Pabis (H&P)⁹, Logarithmic (Log)¹¹, Wang and Singh (W&S)²⁷, Midilli *et al.*¹⁶, and Henderson and Henderson (H&H)⁸.

Table 3. Constants and statistics of different models according to each air temperature (C) used for drying oyster mushrooms.

Model	50 C	60 C	70 C
Lewis ¹² e^{-kt}	$k=0.0246275$ $s=0.03352$ $AIC=-64.23283$	$k=0.0269520$ $s=0.02055$ $AIC=-66.079$	$k=0.033639$ $s=0.04969$ $AIC=-25.5543$
Page ¹⁸ e^{-kt^n}	$k=0.009381$ $n=1.255761$ $s=0.01708$ $AIC=-86.2519$	$k=0.01679$ $n=1.12951$ $s=0.01329$ $AIC=-77.4001$	$k=0.0095930$ $n=1.3605531$ $s=0.007735$ $AIC=-58.2379$
Henderson and Pabis ⁹ $a.e^{-kt}$	$a=1.052964$ $k=0.025971$ $s=0.03012$ $AIC=-66.9716$	$a=1.0285070$ $k=0.0278004$ $s=0.01896$ $AIC=-67.4617$	$a=1.051237$ $k=0.035313$ $s=0.04809$ $AIC=-25.3443$
Logarithmic ¹¹ $a.e^{-kt} + c$	$a=1.049731$ $k=0.026322$ $c=0.004886$ $s=0.03099$ $AIC=-65.1798$	$a=1.022781$ $k=0.028413$ $c=0.008200$ $s=0.01894$ $AIC=-66.7$	$a=1.106930$ $k=0.030060$ $c=-0.070465$ $s=0.03882$ $AIC=-28.6646$
Wang and Singh ²⁷ $1 + a.t + b.t^2$	$a=-0.01194$ $b=0.0000311$ $s=0.1378$ $AIC=-15.2608$	$a=-0.01326$ $b=0.00003817$ $s=0.1436$ $AIC=-10.7772$	$a=-0.02280$ $b=0.0001234$ $s=0.03999$ $AIC=-28.6646$
Midilli <i>et al.</i> ¹⁶ $a.e^{-kt^n} + b.t$	$a=1.001$ $k=0.008328$ $n=1.294$ $b=0.0001050$ $s=0.007119$ $AIC=-114.444$	$a=1.004$ $k=0.01587$ $n=1.151$ $b=0.00008777$ $s=0.005693$ $AIC=-99.6992$	$a=0.9958$ $k=0.009575$ $n=1.357$ $b=-0.00005253$ $s=0.008166$ $AIC=-56.2893$
Henderson and Henderson ⁸ $C. \left[e^{-kt} + \frac{1}{9}e^{-9kt} \right]$	$C=0.973169$ $k=0.023968$ $s=0.04268$ $AIC=-55.1221$	$C=0.948409$ $k=0.025457$ $s=0.03213$ $AIC=-52.692$	$C=0.964779$ $k=0.032486$ $s=0.06466$ $AIC=-20.0172$

of the models. **Table 3** shows the results of the evaluation of goodness of fit in seven models studied for each drying air temperature. The standard residual error and Akaike's information criterion for

seven models and for all temperatures of dehydration are compared in **Figures 1-2**, respectively. According to all mathematical models, the standard residual error is less than 0.07 for all temperatures, except for

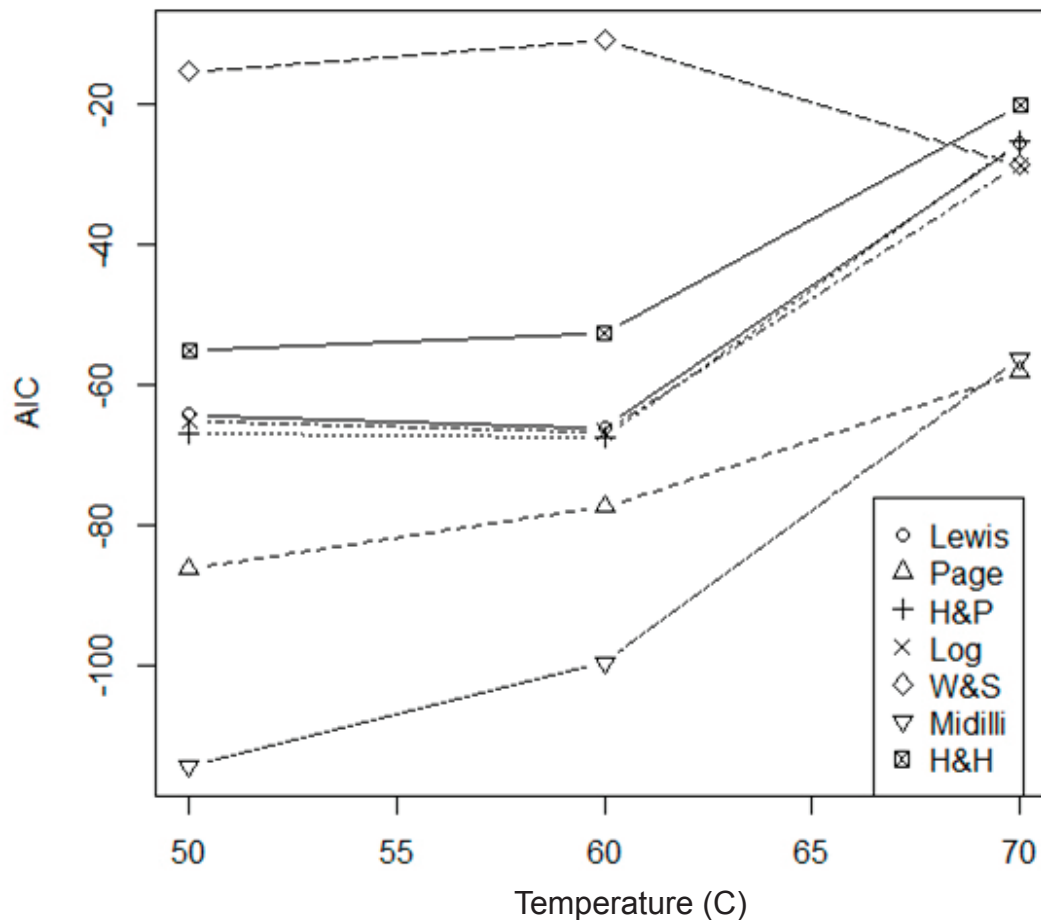
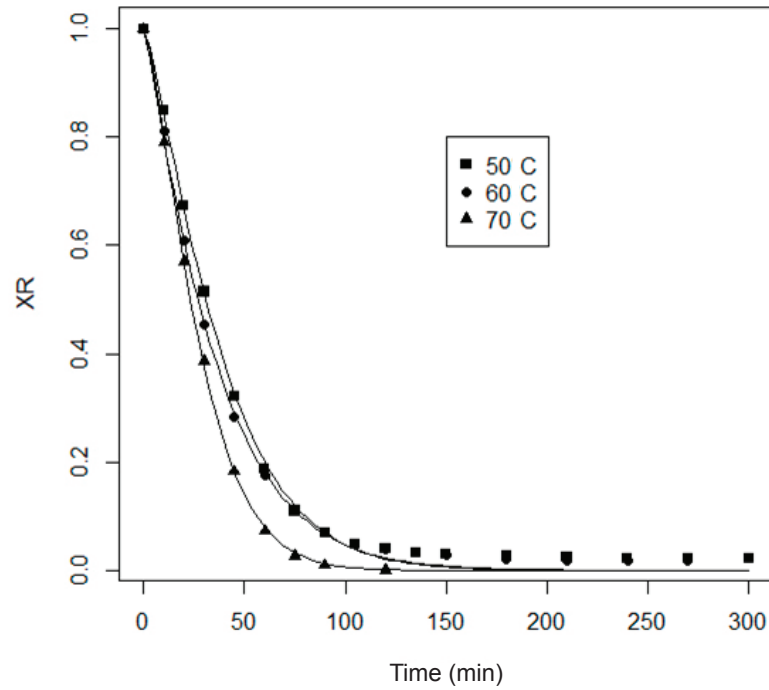


Fig. 2. Akaike's information criterion (AIC) as a function of temperature studied. Models were as follows: Lewis¹², Page¹⁸, Henderson and Pabis (H&P)⁹, Logarithmic (Log)¹¹, Wang and Singh (W&S)²⁷, Midilli *et al.*¹⁶, and Henderson and Henderson (H&H)⁸.

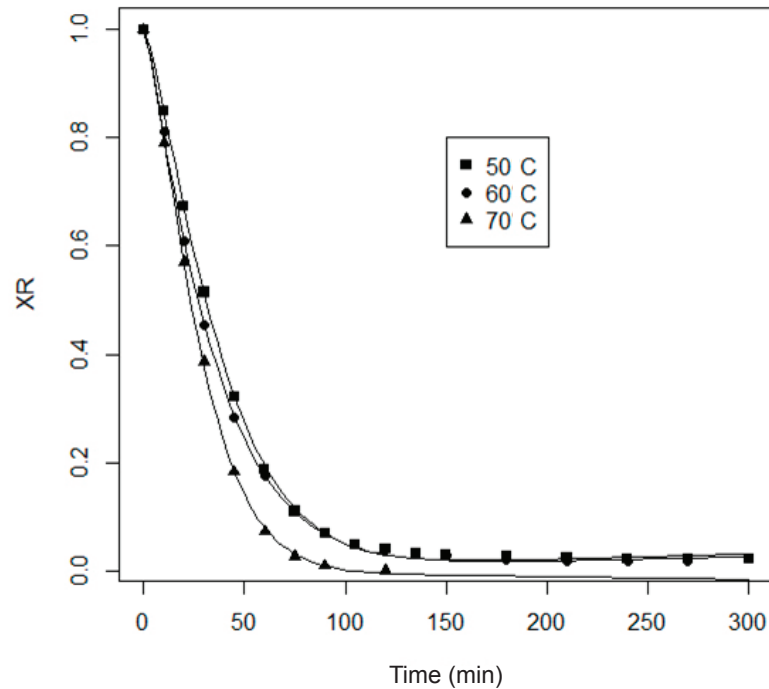
model Wang and Singh²⁷ (W&S: 50 C and 60 C). The best models were Page¹⁸ (2 parameters) and Midilli *et al.*¹⁶ (4 parameters). Both models give similar results over the entire drying process from the beginning to the end. Good modeling was also shown halfway through the drying process, which is a result not given by many models, since the middle of the drying process is the segment, where most of the water is removed from the food, requiring a good simulation prior to the beginning of the water vapor diffusion,

which requires the greatest drying time²¹. **Figures 3-4** show experimental values and the models generated by Page and Midilli *et al.*, respectively. The speed of drying decreased continuously with time and moisture content. The decrease of moisture ratio has a clear exponential tendency, thus recommending the use of the models proposed in this study for the complete drying process. The period of constant drying speed in the experimental curves of *P. ostreatus* was not observed. Only a period of decreasing drying rate was observed,

3



4



Figs. 3-4. 3: Experimental dimensionless humidity (X_R) as a function of time during dehydration (50 C, 60 C, and 70 C) and corresponding predictions by Page model (solid lines). 4: Experimental dimensionless humidity (X_R) as a function of time during dehydration (50 C, 60 C, and 70 C) and corresponding predictions by Midilli *et al.* model (solid lines).

indicating that diffusion is the physical mechanism that governs the movement of water inside oyster mushrooms. These results are consistent with those of previous research studies on foods, such as kiwis²¹, pumpkin seeds²⁰, potatoes and carrots²², and *Pleurotus ostreatus*²⁴. The drying of many foods (fruits and vegetables) is defined only for the period of decreasing drying speed^{19,22,23,26}.

Effective diffusivity coefficient (D_{eff}). **Table 4** shows the D_{eff} obtained from oyster mushrooms dried at different air temperatures for estimating the analytical solution. These values are within ranges previously reported for several fruit products^{13,22,24}. It is noted that the D_{eff} increased with temperature, similarly to what has been found in pumpkin and banana⁶, raisins¹⁹ and cacao¹⁰.

Correlation of the D_{eff} obtained with temperature. The Arrhenius equation was used to evaluate the dependence of the D_{eff} on the temperature^{4,10,19}. Results of the model under study with the logarithmic form of Equation 11 for dehydrated oyster mushrooms are shown in **Figure 5**. There

is a straight line in the temperature range investigated, which confirms the Arrhenius-type relationship proposed between the D_{eff} and temperature. This conclusion has also been reported for other foods, such as corn⁴, cacao¹⁰, and *P. ostreatus*²⁴. The E_a obtained is 23.02 kJ/mol, showing a correlation coefficient (r^2) of 0.98, indicating a good fit of the model to experimental data. This value was consistent with those reported for various foodstuffs, particularly *P. ostreatus*²⁴.

For every temperature used during the drying process of *P. ostreatus*, only a falling rate period could be observed, and no constant drying rate period was recorded. The results obtained (r^2) when applying the GAB equation for modeling the experimental moisture data as a function of water activity confirmed the applicability of such equation to food products. The drying kinetics of *Pleurotus ostreatus* showed a clear exponential tendency. Also, the time required to reach the commercially acceptable moisture value (15% dry basis) was between 150 and 200 min, as the working temperature decreased. From all models evaluated, Page was selected as the best model on the basis of its simplicity and good fit of experimental data. The D_{eff} ranged from 6.64×10^{-10} to 1.024×10^{-8} m²/s, according to air drying temperature, and the E_a obtained was 23.02 kJ/mol.

Table 4. Effective diffusivity coefficients (D_{eff}) of frozen oyster mushrooms dried at differing temperatures.

Temperature (C)	D_{eff} (m ² /s)
50	6.64×10^{-10}
60	3.96×10^{-9}
70	1.024×10^{-8}

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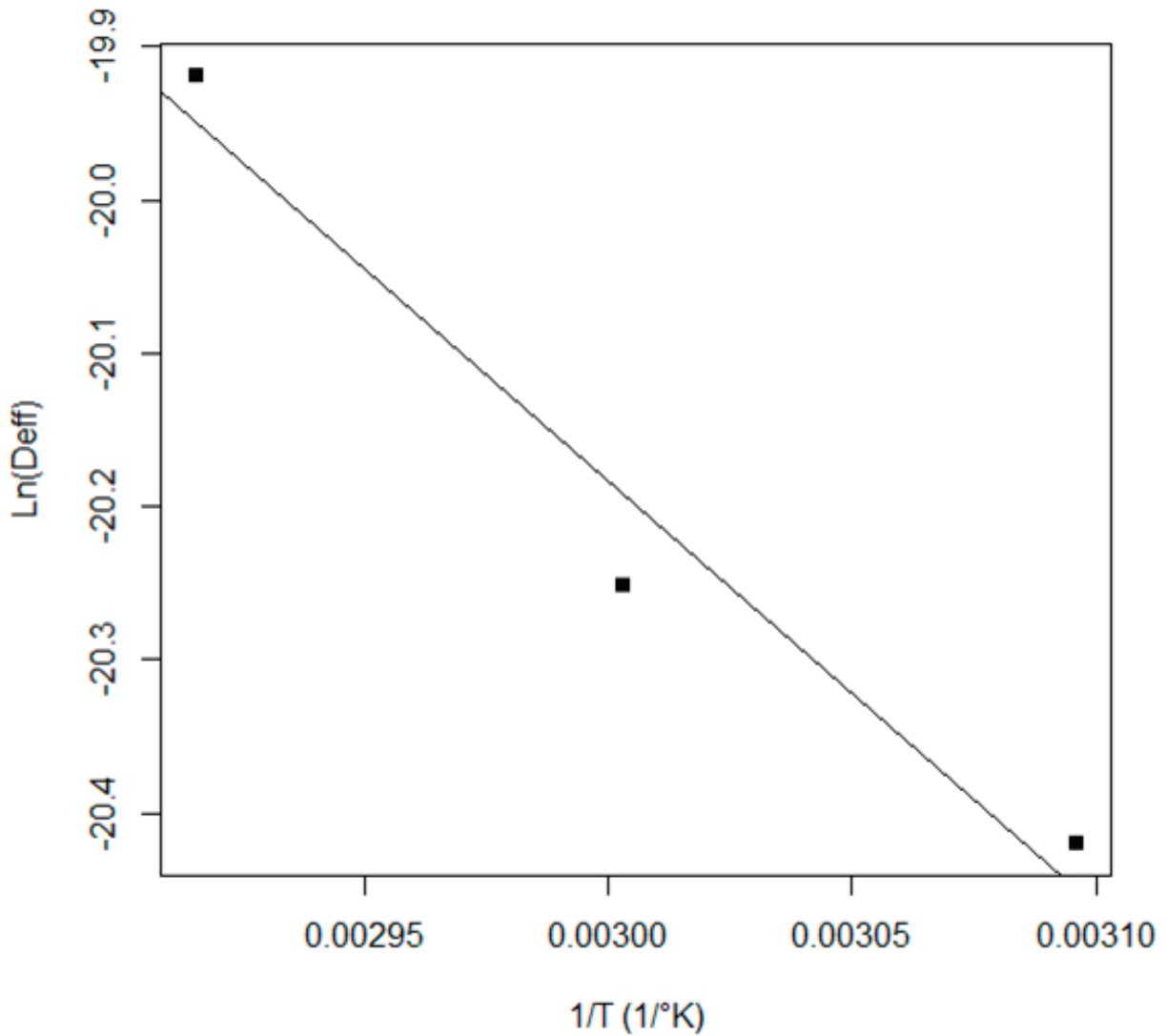


Fig. 5. Dependence of D_{eff} with temperature for dried *Pleurotus ostreatus*.

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