Thin Layer Drying Kinetics of Freshwater Clawed Lobsters (Astacus astacus)

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Abstract

Fresh-water Clawed Lobsters is seafood consumed in its cooked, dried or semi-dried state. Drying is a veritable technology for its storage beyond immediate consumption. This study thus, investigated the drying behaviour of the lobster on thin-layers. A laboratory convective oven dryer was used as the heating source, on the temperature range of 50 – 100°C applied in a varying manner on multiples of 10°C. The layer thickness was about 20-mm. As with high moisture sea foods, the drying profile showed a typical falling rate period with no distinct constant rate period for all the temperature levels used in this work. Moisture loss (diffusion) data obtained from the experiments were fitted to three popular semi-empirical thin-layer models of Page, Lewis, and Henderson-Pabis, respectively, and their suitability was validated using statistical parameters (of $R^2$, RMSE and $\chi^2$). This was done to select thin-layer model that would suitably describe the drying kinetics of the samples over the range of temperature levels chosen in this work. Consequently, the Page model and that of Henderson-Pabis respectively were taken to have reliably predicted the drying behaviour of the samples at the chosen temperature levels. The effective diffusivity and the temperature-related activation energy values ranged from $2.239 \times 10^{-8}$ m$^2$/min - $4.005 \times 10^{-8}$ m$^2$/min and 28.5kJ/mol, respectively. Drying rates along with characterizing drying constants and curves also showed an exponential increase with temperature.

Keywords: clawed lobsters, thin-layer drying kinetics, drying curves, effective diffusivity, activation energy

1. INTRODUCTION

Clawed lobsters (Astacus astacus, Homaridae) are crayfish in the monophyletic family of marine crustaceans. The fresh water specie (named Imgbede in Iton) is generally dark in color, having relatively long, cylindrical body with muscular tail. They are generally characterized by an enlarged pair of claws (pinchers) on the first pair of legs, one claw (or pincher) of which is much smaller than the other Fig. 1. They are commercially important to humans as a traditional food item, having average meat yield of about 9.93%, and a good meat–to–shell ratio when fresh [1]. It is reported that humans are the principal predators of adult clawed lobsters as they are scaly and highly inimical to most swallowing sea or river creatures [2, 3]. In the fresh-water areas of the Niger Delta of Nigeria they are primarily marketed alive as people eat the heavily muscled abdomen, thorax and claws in the fresh state. They are either eaten whole after cooking or when picked (picking as a processing term refers to the process of removing meat from the shell and claws either by hand or use of a machine) after washing, seasoned and cooked to taste [2]. The Proximate composition shows that it is rich in the proteins 13.7, lipids 3.84, and ash 2.19 all in g/100-g meat. All other nutritional and diet items indicate values that are well balanced in their essential compositions and beneficial to the human diet [1].

At death however, the meat of a fresh-water clawed lobsters goes on to rapid microbial deterioration, making it be placed under the group of highly perishable sea foods (the crabs, cray-fishes, shrimps and other lobsters alike). Thus, harvested quantities beyond immediate consumption would require proper and prompt postharvest handling, preservation and storage [3]. Whereas techniques such as freezing, salting, chilling, cooked-canning and frying are valuable for wet storage [4], dry preservation and storage is a well acclaimed method for prolonged shelf life of most animal muscular bio-materials. Drying does not deplete but would retain required flavour, colour and nutritive value, and also influence physico-chemical and quality characteristic of products [5]. The report of [6] takes drying as an industrial preservation technique in which moisture content and water activity of bio-materials are reduced by motive heated air. This definition thus, excludes drying methods such as sun-drying and freeze-drying where drying is achieved without a significant presence of convective air. Large scale
commercial dry keeping would thus, employ industrial and a better mechanized process of drying. Appropriate technologies designed for such mechanized drying are ripe in technical literature. Shortcomings in such processes sometimes emanate as the lobsters and other counterpart sea foods become rancid even before the drying process is complete. It is especially difficult to dry such animal-muscled visco-elastic bio-material as it presents handling problems due to high constituent water mixed with fats/oil, proteins and certain mucilaginous matter [5]. Many mathematical models have however, been used to describe the thin-layer drying process of several of such food products, and these also serves as tools for process control and in drying simulation studies, and for predicting the suitable drying conditions [6–8]. Therefore, in this work, the drying behaviour of the clawed lobster was investigated on thin-layers and the emanating experimental data were fitted to the selected thin-layer drying models to characterize the drying kinetics of the lobsters. This would also create a good data base for improved equipment design of the drying processes.

1.1. Theoretical Framework

Thin-layer drying as applied to high systemic moisture biomaterials is a complicated process with simultaneous heat and mass transfer. Thin layer as a concept refers to a layer of a product that can be described as sufficiently small in thickness whereon air characteristics everywhere in the layer could be considered identically uniform with no observable variations. Then in thin-layer drying it is expected that all individual particles of the material are fully exposed to the drying air. The conditions of thin layer drying are often divided into two periods of drying which are the constant rate and the falling rate periods [9]. In this work, thin-layer drying was done in batches of single beds or layers split to different small but uniform thickness each. It is usual to place or arrange the different splits in vertical series such that hot air in a forced convective stream could be made to pass over them. The hot air stream can then be seen to absorb moisture from the first split through the others, such that the exhaust from one split becoming input air to the subsequent split, and on through the final or terminal split. Passing through a number of thin splits in this manner, it is evident that the moisture pick-up ability of the air stream declines one over the next layer. For the success of such simulation work therefore, the splits (now to be referred to as thin-layers), be made infinitesimally thin and arranged in such a manner that the inlet hot air stream simply exhausts through the layers undiminished in its moisture carrying capacity. Drying would then become achieved in all the splits, each batch characterized by different drying rates at the different temperature levels applied [10]. Literature reports show that most drying activities of biomaterials generally omit the constant rate period but do so largely in the falling rate period [11–13]. The entire rate period of the drying process is known to be a diffusion (molecular transport) phenomenon through a continuum of interface slits and generally governed by Fick’s second law (moisture flux proportional to the moisture gradient) given as [14, 15]

$$\frac{dM}{dt} = De \left[ \frac{d^2}{dr^2} \right]$$

where $M$ is moisture content at time $t$, $kg_{H_2O}/kg_{solid}$; $t$ is drying time, min., $r$ is radius of an equivalent sphere (distance from the core to the surface), mm. $De$ is effective
diffusivity, mm²/min.

The moisture ratio (MR) prevalent in the drying system can be expressed as [16]

\[ MR = \frac{M - M_e}{M_o - M_e} \tag{2} \]

where \( M_e \) is equilibrium moisture content (emc), kgH₂O/kg solid, \( M_o \) is initial moisture content, kgH₂O/kg solid and \( M \) is as previously defined

1.2. Estimating Effective Diffusivity, \( D_e \)

Effective diffusivity \( (D_e) \) is a temperature and moisture content dependent diffusion parameter that describes and drives the moisture transport process in the condition of any diffusion mechanism during drying of any visco-elastic material. Of the three stages in the drying profile namely, the free stage, the constant rate period and the falling rate period, the effectiveness of moisture transport is observable more in the third - the falling rate period during drying [17, 18]. The mathematical expression for effective diffusivity, \( D_e \) as derived for a material of cylindrical geometry at the falling rate period during drying is [10, 19, 20].

\[ MR = \frac{M - M_e}{M_o - M_e} = \frac{6}{\pi^2} \int_{n=1}^{\infty} \frac{1}{(2n - 1)^2} \exp\left(-\frac{(2n - 1)^2 R^2}{L^2}\right) \tag{3} \]

for \( n = \) number of cylindrical surfaces placed in slits (thin-layers)

Taking \( (2n - 1)^2 = \varepsilon_n \) recognized as the root of a related Bessel function, and for a material of cylindrical geometry, and \( L = R_c = \) radius of cylinder,

Then Eq. (3) will reduce to

\[ MR = \frac{M - M_e}{M_o - M_e} = \frac{6}{\pi^2} \int_{n=1}^{\infty} \varepsilon_n^{-2} \exp\left(-\varepsilon_n \frac{R^2}{L^2}\right) \tag{4} \]

Taking only the first term (\( n=1 \)) rendering others as negligible, Eq. (4) would become [21]

\[ MR = \frac{M - M_e}{M_o - M_e} = \frac{6}{\varepsilon_1} \exp\left(-\varepsilon_1 \frac{R^2}{L^2}\right) \tag{5} \]

where \( MR \) = moisture ratio.

Taking natural log on both sides, equation Eq. (5) will linearize to

\[ \ln(MR) = \frac{6}{\varepsilon_1} \left(1 - \frac{R^2}{L^2}\right) t \tag{6} \]

The effective diffusivity, \( D_e \) in the drying system can then be obtained from the slope of the plot of \( \ln(MR) \) versus drying time, \( t \) with intercept \( \ln(6/\varepsilon_1) \) [19]

\[ D_e = \frac{\text{Slope of plot} \ [R^2]}{\varepsilon_1} \tag{7} \]

And from Eq. (2), if values of \( M_e \) are small in relation to values of \( M \) and \( M_o \) (assumed to be zero) in [22, 23], then the equation would reduce to

\[ MR = \frac{M}{M_o} \tag{8} \]

1.3. Thin-layer Drying Models

The use of mathematical models in estimating the behavior of agricultural and other biomaterials during drying is common in technical literature. Several of such thin-layer drying models are listed in Table 1 [24]. Only three (the Lewis, the Page and the Henderson-Pabis models respectively) are selected for validation in this work on fresh-water clawed lobsters. From Eq. (5), taking \( n = 1 \) and further simplifying would bring about the thin layer drying equation of the Lewis model (see Table 1)

\[ MR = \exp^{-kt} \tag{9} \]

the Henderson-Pabis model (see Table 1)

\[ MR = A \exp^{-kt} \tag{10} \]

and when \( n > 1 \), the Page model (see Table 1)

\[ MR = \exp^{-kt^n} \tag{11} \]

Equation (9) can further simplify as

\[ \ln(MR) = \ln(k) - kt \tag{12} \]

or

\[ \ln\left(\frac{M}{M_o}\right) = \ln(k) - kt \tag{13} \]

Wherein \( k \) is seen as kinetic (drying) rate constant and \( a, b, n \) are model constants. Then the plot of moisture ratio on natural logarithm axis against drying time of Eq. (11), the intercept, \( \ln(k) \) on the moisture ratio axis and slope, \( -kt \), the effective diffusivity, \( D_e \) can now be deduced.

1.4. Activation Energy, \( E_a \)

This is energy required to initiate the diffusion (the phenomenon of moisture transport) during drying of biological materials. Activation energy, \( E_a \) can be estimated from the relationship between Effective diffusivity, \( D_e \) and temperature, \( t \) which is assumed to be an Arrhenius type function given as [36]

\[ D_e = D_o \left(e^{\frac{E_a}{RT}}\right) \tag{14} \]

where \( E_a \) is activation energy, kJ/mol, \( D_e \) is effective diffusivity at \( t^\circ K, \) m²/s, \( D_o \) is pre-exponential factor of the Arrhenius equation at \( 0^\circ K, \) m²/s, \( R \) is universal gas constant \((8.314 \times 10^3, \) kJ/mol.K), \( t \) is air temperature expressed in °K.

Simplification of Eq. (12) gives

\[ \ln D_e = \ln D_o - \frac{E_a}{R} t^{-1} \tag{15} \]
Consideration higher powers of \( t \) as negligible, Eq. (19) can reduce to

\[
\text{Drying rate } \left( \frac{dy}{dt} \right) = -(c_1 + 2c_2t + 3c_3t^2 + 4c_4t^3 + \cdots)
\]  

Equation Eq. (22) is semi-parabolic on a drying rate vs drying time plot, yielding drying curves for the different drying temperatures chosen in this work.

## 2. MATERIALS AND METHOD

### 2.1. Sample Preparation and Experimental Procedure

A large quantity of freshly harvested freshwater clawed lobsters (some 25-kg) was obtained from a local but general market at Odi town in Kolokuma-OpoKumka Local Government Area of Bayelsa state, Nigeria. They were thoroughly washed in fresh water and allowed to stabilize in the ambience of the Laboratory. Using a 0.001-cm precision veneer caliper each of the clawed lobster to be used in the drying tests was measured of the basic dimensions, stratified into groups of different but equal thickness and length (measured from tail fin to the end of the longer claw arm), re-stabilized and stored without any further treatment in refrigerated cabinets in the Food Processing Laboratory, Department of Agricultural and Environmental Engineering of Niger Delta University, Bayelsa State. Identical samples were then drawn from the stratified lot for the drying tests. The samples were then oven dried in a thin-layered form, to a constant final weight using WTC binder oven Model WTCB 1718 at varying temperatures from 50°C- 100°C with increments of 10°C.

### 2.2. Data Collection

Drying is a progressive moisture reduction phenomenon until a final level is reached. Therefore, data collected in the work included initial and final weight of samples, initial and final moisture contents measured in %db. All weight measurements were done using a laboratory-type top digital balance with 0.01-g precision. The initial and all other moisture content values were taken using a 0.001-cm precision veneer caliper each of the clawed lobster to be used in the drying tests was measured of the basic dimensions, stratified into groups of different but equal thickness and length (measured from tail fin to the end of the longer claw arm), re-stabilized and stored without any further treatment in refrigerated cabinets in the Food Processing Laboratory, Department of Agricultural and Environmental Engineering of Niger Delta University, Bayelsa State. Identical samples were then drawn from the stratified lot for the drying tests. The samples were then oven dried in a thin-layered form, to a constant final weight using WTC binder oven Model WTCB 1718 at varying temperatures from 50°C- 100°C with increments of 10°C.

### Table 1: List of Thin-layer Drying Models with References [24].

<table>
<thead>
<tr>
<th>S/No.</th>
<th>Title of Model</th>
<th>Model Expression</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lewis</td>
<td>( MR = \exp(-kt) )</td>
<td>[25]</td>
</tr>
<tr>
<td>2</td>
<td>Wang &amp; Singh</td>
<td>( MR = 1 + at + bt^2 )</td>
<td>[26]</td>
</tr>
<tr>
<td>3</td>
<td>Page</td>
<td>( MR = \exp(-kt) )</td>
<td>[27]</td>
</tr>
<tr>
<td>4</td>
<td>Logarithmic</td>
<td>( MR = a \exp(-kt) + c )</td>
<td>[28]</td>
</tr>
<tr>
<td>5</td>
<td>Henderson &amp; Pabis</td>
<td>( MR = a \exp(-kt) )</td>
<td>[29]</td>
</tr>
<tr>
<td>6</td>
<td>Two Term</td>
<td>( MR = a \exp(-kt) + b \exp(-kt_1) )</td>
<td>[30]</td>
</tr>
<tr>
<td>7</td>
<td>Verma</td>
<td>( MR = a \exp(-kt) + (1-a) \exp(-gt) )</td>
<td>[31]</td>
</tr>
<tr>
<td>8</td>
<td>Hsu, Law &amp; Cloke</td>
<td>( MR = a \exp(-kt_1) + c \exp(-gt_1) )</td>
<td>[32]</td>
</tr>
<tr>
<td>9</td>
<td>Approximation of diffusion</td>
<td>( MR = a \exp(-kt) + (1-a) \exp(-kt_1) )</td>
<td>[33]</td>
</tr>
<tr>
<td>10</td>
<td>Simplified Fick`s</td>
<td>( MR = a \exp(-c(t/L2)) )</td>
<td>[34]</td>
</tr>
<tr>
<td>11</td>
<td>Midilli–Kucuk</td>
<td>( MR = a \exp(-kt_1) + b \exp(-kt) )</td>
<td>[35]</td>
</tr>
<tr>
<td>12</td>
<td>Modified Page - II</td>
<td>( MR = \exp(-c(t/L2)) )</td>
<td>[34]</td>
</tr>
</tbody>
</table>
each temperature level and average values were recorded. The weight differences before and after drying were used to determine the final moisture content for each replicate, all measured on dry-basis as [43]

\[ M = \frac{w_i - w_f}{w_f} \]  \hspace{1cm} (23)

where \( M \) is dry basis moisture content, \( \% \)-db. \( W_i \) is initial weight of the specimen, \( g \) and \( W_f \) is initial weight of the specimen, \( g \).

### 2.3. Statistics Fitting of Experimental Data

Thin-layer drying models can normally be evaluated and the quality of fit compared using certain statistical indicators such as coefficient of determination, \( R^2 \); the non-parametric reduced chi-square, \( \chi^2 \) and the root mean square error, RMSE. The usual criteria is that an acceptable goodness of fit is said to have occurred in describing the drying curve of a given model if \( R^2 \) value is high and the values of other indicators, \( \chi^2 \) and RMSE are low. In this work, the experimental drying data of the samples obtained at different temperatures were used to fit into the three commonly used thin-layer drying models. The goodness of fit of the selected mathematical models to the experimental data was evaluated using the given criteria [44, 45]. The statistical parameters used as the indicators were calculated as follows [22, 46]

\[ R^2 = 1 - \left[ \sum_{i=1}^{n} (MR_{pre,i} - MR_{exp,i})^2 \right] \] \hspace{1cm} (24)

\[ RMSE = \sqrt{\frac{\sum_{i=1}^{n} (MR_{pre,i} - MR_{exp,i})^2}{n}} \] \hspace{1cm} (25)

\[ \chi^2 = \frac{\sum_{i=1}^{n} (MR_{pre,i} - MR_{exp,i})^2}{n - k} \] \hspace{1cm} (26)

where \( MR_{pre} \) is predicted moisture ratio, \( MR_{exp} \) is experimental moisture ratio, \( n \) is number of observations and \( k \) is as previously defined.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterizing Drying Kinetics

It was necessary to transform the drying data obtained from the experiments into dimensionless moisture ratios (MR). These MR values were then plotted as a function of drying time for the freshwater clawed lobsters respectively at the selected temperatures (Fig. 2), while Fig. 3 presents the variations of the moisture ratios given in logarithmic form (\( \ln(MR) \)) plotted as a function of drying time. This is drawn to enable the estimation of activation energy in the drying system. It is known that activation energy promotes the molecular transport phenomenon (diffusion) that drives the drying process. The moisture ratios are all given in dry basis (db). The plots in the Figs are observed to have followed the general trend of drying curves as reported for many bio-materials.

The curves exhibited initial steeper slope, an indication of an initial increased and accelerated moisture loss in drying. This could be due to increased water activity within the samples resulting from a quicker migration of moisture to the surface for evaporation and evacuation, helping to shorten the drying time. The drying process however, became slower (the curves became flattened) at the later stages, even with increasing temperatures (Fig. 3) as lesser and lesser water become available for evaporation at the surface of the samples.

This is rather characteristic of such bio-materials with high constituent moisture mixed with fats/oils and protein which greatly reduce water activity even with increase in drying temperature [10, 47, 48]. The situation is also typical of a falling rate drying period without the feature of case-hardening even on the high temperatures ranges, generally agreeing with reports on
Figure 2: Moisture ratio versus drying time of fresh-water clawed lobsters at different temperatures.

thin layer drying works on fresh water clam [22], salted catfish fillets [42] and fresh fish [49].

3.2. Fitting Experimental Data into Thin-Layer Drying Models

The transformed dimensionless moisture ratios were used to fit to the empirical models of Lewis, Page, and Henderson and Pabis, respectively, and for all the different drying temperatures chosen in this work. The parameters were subjected to statistical analysis for all the drying conditions (Table 2). The fitting results in concurrence with the statistical analysis showed that the coefficient of determination, $R^2$ values were consistently high in the range of 0.953 – 0.998 for all the models. The indication here is that all the used empirical models could satisfactorily describe the drying behavior of the samples. When tuned further with the other statistical parameters, the model expression of Henderson and Pabis followed by that of the Page had the highest $R^2$ values and the lowest $\chi^2$ and RMSE values in the temperature range of the work. This showed the suitability of these models in describing the drying kinetics of the samples. It was therefore, satisfactory to select the Henderson-Pabis model to predict the drying kinetics of the fresh-water clawed lobsters on the drying temperatures applied in this work.

3.3. Estimation of Effective Moisture Diffusivity and Activation Energy

Using data obtained from the drying experiments, the logarithmic moisture ratio values, $\ln(MR)$ were plotted as a function of drying time, $t$ at the various drying temperatures (Fig. 3). Estimation of the effective moisture diffusivity was then done using the method of slopes, derived from the regression line relating the $\ln(MR)$ values and the varying drying times, validated with the corresponding coefficients of determination, $R^2$ (at 0.98). It is clear from Fig. 3 that effective moisture diffusivity, $D_e$ increased fairly greatly as drying temperatures increased. This is expected because, though, the temperature dependency of moisture retention capacity of a visco-elastic material is a function of the body structure and the presence of void fractions and is known to significantly affect moisture diffusivity, it is shown that less energy was required to remove moisture at the higher drying temperatures as the water molecules obviously become more loosely bound to the body matrix of the samples than at lower drying temperatures [50]. In fact, the $D_e$ values ranged from $2.239 \times 10^{-8}$ m$^2$/min or $3.7317 \times 10^{-10}$ m$^2$/s at the lower temperature to $4.005 \times 10^{-8}$ m$^2$/min or $6.675 \times 10^{-10}$ m$^2$/s at the higher temperatures. This observation is similar to that indicated for palm weevil larvae [13] for shrimps [51] and for mud snail meat [47].

Fig. 4 was drawn to linearize Fig. 3 to enable the estimation of the process activation energy, $E_a$ using the slope method. It can be observed in the figure that the plot is only slightly negative meeting with the required orientation for the slope method. The evaluated value of the process activation energy, $E_a$ gave 28.5kJ/mol which is seen to be within the literature range of 12.7 - 110 kJ/mol for high moisture biomaterials [25] and 21.6 - 39.03 kJ/mol for fruits and vegetables [42].

4. CONCLUSION AND RECOMMENDATION

Thin layer drying kinetics of fresh water clawed lobster was investigated. The drying process was observed to have followed the failing rate period model, in line with other related literature. Data from the experiment were fitted into three thin-layer models (Page, Henderson-Pabis and Lewis) to determine the best model that will predict the drying kinetics of the samples. The Page model followed closely by the Henderson-Pabis model were observed to present good estimators of the drying behaviour of the fresh water clawed lobsters over the drying temperature so applied. The activation energy value was deduced to be 28.5KJ/mol and falls within the range as in technical literature over the same temperature range in this work. The effective moisture diffusivity
values increased with increase of drying temperature. The work can be useful in the design and development of drying equipment for the preservation of fresh water clawed lobsters. The work however limited the selection of thin-layer drying models to only three. An attempt could be made to extend the selection base beyond the limit applied in this work to obtain higher degree of freedom on the statistical exactness of the drying data for improved drying system design.

References


Figure 4: Estimation of Activation Energy for specimens of Fresh-water Clawed Lobsters (Astacus astacus).