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Studying the Drying Kinetics of Fresh-water Crayfish (*Austropotamobius pallipes*) on Thin-layers

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ABSTRACT

The drying behaviour of fresh-water crayfish (Austropotamobius pallipes) was investigated using a laboratory convective oven dryer, with the cabinets arranged in thin-layers. Drying air temperatures ranging from 60 – 100 ℃ were applied, varying in multiples of 10 ℃ with unregulated laboratory room air velocities. The initial moisture content of all the samples was 85% db. The investigation showed a drying rate profile that increased with increasing drying temperatures. Drying data from the experiments were fitted to seven empirical thin-layer drying models, and the suitability of individual model was validated using statistical parameters (coefficient of determination, (R^2); root mean square error, (RMSE) and reduced chi-square (χ^2)). The Midilli model was found to perform satisfactorily in describing the drying behaviour of the fresh-water crayfish samples at the chosen temperature levels. The final effective moisture diffusivity of the samples during the drying experiments was 6.675 x 10^{-10} m^2/s, and the temperature related activation energy of diffusion was found to be 28.48 kJ/mol. Drying occurred mainly in the falling rate period, and the characterizing drying curves were exponential with increase in drying temperatures.

1. INTRODUCTION

Fresh-water crayfish [Izon: Opuru] generally, are in the family of crustaceans looking more like mini lobsters and found mostly in fresh water habitat (Plate 1). They are arthropods having tough, smooth exoskeleton that protects them from impacts of water falls and predator attacks. They come in varying sizes, in length and girth. Crayfish are nocturnal, observed to sleep during the day and become active at night, and are omnivorous, eating both plants and animals. The fresh-water crayfish is predominantly greyish-green in colour, but may be of other colours that would blend or camouflage them well with their surroundings and environment (Crandall, 2016).

The fresh-water crayfish makes a tasty meal when consumed in its cooked, grilled, or dried states, with the dried form adapted for long shelf-life table-top marketing. Reports from technical literature show that fresh-water crayfish is rich in nutritional elements, providing 3 to 14% daily values (DVs) of the respective common minerals (Calcium 4% DV, 51 mg; Iron 4% DV, 0.7 mg; Potassium 5% DV, 251.6 mg; Sodium 3% DV, 79.9 mg; Magnesium 7% DV, 28.1 mg; Zinc 14% DV, 1.5 mg) and of the proteins (9% DV, 14.3 mg) (Lovell et al., 2002).

Spoilage is generally undesirable as it results in severe post-harvest losses and withdrawal from human consumption. Well-dried agricultural products are also reported to have long shelf-life in food packaging, lower transportation, handling, and storage costs (Unal and Sacilik, 2011; Yu et al., 2015).

Diffusion is the major phenomena that defines the simultaneous heat and mass transfer concept that consequently results in drying. It is a complicated process causing transfer of moisture from inside the food material to the air-food interface, and from this interface to the surrounds by convection (Menges and Ertekin, 2006; Yi et al., 2012).

Drying time and prediction of suitable drying conditions for a particular product can be deduced using the empirical and semi-empirical thin layer drying models. This would also create a good data base for obtaining generalized drying curves and improve equipment design in the drying processes.

Thin layer drying usually applies to drying of products as a single stratum or several strata arranged in parallels or series such that hot motive air stream could be made to pass over the strata. Each stratum can be made sufficiently small and of uniform thickness such that the air conditions everywhere in it could be of the same ambience and proceed without loss of uniformity. In a series arrangement, the hot air stream from a source would absorb moisture from the first stratum and the exhaust therefrom becoming input air to the subsequent one. Passing through a number of strata in this manner, it is evident that the moisture pick-up ability of the air stream would decline one over the next, inducing an equilibrium moisture content (emc) level for a given water activity in each stratum at different drying times. This results in differential drying rates in each stratum sometimes causing food rancidity as storage defect. Zibokere and Egbe (2019) reported that the occurrence of this defect can be removed if the layers are made thin enough to induce uniformity in the drying kinetics. Drying, whether on thin-layers or otherwise, often proceeds primarily in two rate-periods of drying - the constant-rate and the falling-rate periods. If the strata, now to be referred to as thin-layers, be made infinitesimally thin such that the hot air stream simply exhausts through the layers undiminished in its moisture carrying capacity, then drying would omit the constant rate period (Ikrang, 2014). This condition is reported for visco-elastic biomaterials in technical literature (Brennan *et al.*, 1996; Toledo, 2000; Earle, 2006; Darvishi *et al.*, 2012). The entire rate period of drying process is a molecular transport phenomenon (diffusion) expressible by the Fick's second law given as (Suarez *et al.,* 1980; Bird *et al.,* 2005).

The objectives of this work therefore, are to evaluate the drying kinetics of fresh-water crayfish on thin-layers and to fit experimental data obtained at each of the chosen drying temperatures to seven thin-layer models and to select the suitable drying model for the fresh-water crayfish samples.

Plate 1: A fresh-water Crayfish (*Austropotamobius pallipes*)

2. MATERIALS AND METHODS

2.1. Materials

A large quantity of freshly harvested fresh-water crayfish was obtained from a local market at Zarama in Bayelsa State, Nigeria. The fresh-water crayfish was thoroughly washed to remove debris and stored in a refrigerator in the Processing Laboratory of the Department of Agricultural and Environmental Engineering, Niger Delta University, Bayelsa State, Nigeria. Samples were then taken from the bulk for the drying experiments. Initial moisture content of each set of five replicate samples (45 g each) was determine using the oven-drying method with the temperature of the oven (WTC binder oven Model WTCB 1718) tuned to 105 ^oC based on the process reported in Motevali et al. (2012). All weight measurements were done using a laboratory–type digital balance with 0.01 g precision.

2.2. Methods

An initial moisture content of about 68.8%wb was obtained by averaging the five replications. Thin-layer drying experiments were conducted at five levels of temperature (60, 70, 80, 90 and 100^oC) and on five replications and average values of the final moisture content fixed at about 12% db was reached. Weighing of the samples was continued, monitored at time intervals of 5 minutes until no discernable change of weight was observed between the five replicates as described in Zibokere and Egbe (2019) on red head palm weevil larvae, and Sankat and Mujaffar (2006) on catfish. The drying data obtained at the falling rate period of drying were then worked into dimensionless moisture ratios (MR) (Sahey and Singh, 2005).

$$\text{MR} = \frac{\text{M} - \text{M}_\text{e}}{\text{M}_\text{o} - \text{M}_\text{e}} \tag{1}$$

Where M_e = equilibrium moisture content (emc) (kg_{H_2O}/kg_{solid}) and M_o = initial moisture content (kg_{H_2O}/kg_{solid})

However, for a rather cylindrical geometry of the crayfish samples, it was desired to obtain the equivalent moisture ratios by transformation using the Fick's second law diffusion equation as (Guine et al., 2011; Motevali et al., 2012; Chen et al., 2013).

$$\text{MR} = \frac{\text{M} - \text{M}_\text{e}}{\text{M}_\text{o} - \text{M}_\text{e}} = \frac{8}{\pi^2}\int_{n=1}^{\infty}\frac{1}{n^2}e^{-(n)^2\frac{\pi^2 D_e t}{L^2}} \tag{2}$$

Where: MR is dimensionless

n denotes the number of terms in the series (0, 1, 2, 3,…)
t is drying time
D_e is effective moisture diffusivity ($m^2\ s^{-1}$)
L relates to the geometric diameter (d_c) of the samples (Mohsenin, 1986)
$d_c = (L \times W \times T)^{\frac{1}{3}}$

The factor, d_c is the dimensional estimator for L (length), W (width) and T (thickness) being the major, intermediate and minor diameters of the crayfish sample. Then Equation 2 gives Equation 3 (Guine et al., 2011).

$$\text{MR} = 0.8106\int_{n=1}^{\infty}\varepsilon_n{}^{-2}\,e^{-9.87\varepsilon_n(\frac{D_e t}{r_c{}^2})} \tag{3}$$

Where $\varepsilon_n = n^2$ seen as the root of a related Bessel function in terms of n, r_c = geometric radius of the crayfish, and $(\frac{D_e t}{r_c{}^2})$ can be recognized as a Fourier factor.

For a long period of drying time ($t \approx \infty$), Equation 3 will tend to converge on the integration operation. The term seems dominating for high drying time as required in thin-layer drying of products of cylindrical dimensions; thus rendering other terms in the series small enough to be ignored to give Equation 4 (Zogzas et al., 1996; Babalis and Belessiotis, 2004; Burubai, 2015).

$$\mathrm{MR} = 0.8106e^{-9.87(\frac{Det}{rc^2})} \quad (4)$$

Taking natural log on both sides, equation 4 will linearize to:

$$\mathrm{In(MR)} = -(47\mathrm{D_e}(\frac{1}{R_c})^2\mathrm{t} + 1) \quad (5)$$

2.3. Effective Moisture Diffusivity

The effective moisture diffusivity (D_e) drying parameter can be estimated from the slope of the plot when Equation 5 is plotted on a logarithmic scale (known as the slope method), as follows (Guine et al., 2011).

$$\mathrm{D_e} = -slope\frac{[r_c{}^2]}{47} \quad (6)$$

2.4. Fitting to Thin-layer Drying Models

Data obtained from the drying experiments were fitted to seven thin-layer drying models as detailed in Equations 7- 13.

Midilli model (Midilli et al., 2002)

$$\mathrm{MR} = \mathrm{ae^{-ktn}} + \mathrm{bt} \quad (7)$$

Lewis model (Bruce, 1985)

$$\mathrm{MR} = \mathrm{e^{-kt}} \quad (8)$$

Wang and Singh model (Wang and Sing, 1987)

$$\mathrm{MR} = 1 + \mathrm{bt} + \mathrm{at^2} \quad (9)$$

Henderson-Parbis model (Henderson and Pabis, 1961)

$$\mathrm{MR} = \mathrm{ae^{-kt}} \quad (10)$$

Logarithmic model (Akpinar, 2008)

$$\mathrm{MR} = \mathrm{ae^{-kt}} + \mathrm{b} \quad (11)$$

Page model (Vega-Gálvez, 2010)

$$\mathrm{MR} = \mathrm{e}^{-\mathrm{k}t^n} \quad (12)$$

Parabolic model (Sharma and Prasad, 2001)

$$\mathrm{MR} = \mathrm{c} + \mathrm{bt} + \mathrm{at^2} \quad (13)$$

Where k is the kinetic (drying) rate constant and a, b, n are model constants.

The fitted models were each regressed using the nonlinear least squares regression method (Haydar et al, 2014). The experimental data used in the fitting were processed to statistical indicators such as coefficient of determination, (R^2), the reduced chi-square, (χ^2) and the root mean square error, (RMSE) using SPSS 17.0 and Microsoft Excel software. These were used as indicators in selecting the best drying model. Following the procedure in Ndukwu et al (2010) and Burubai (2015) the statistical indicators were evaluated as follows:

$$\mathrm{R^2} = 1 - \left[\sum_{\mathrm{i=1}}^{\mathrm{n}}(\mathrm{MR_{pre,i}} - \mathrm{MR_{exp,i}})^2\right] \quad (14)$$

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{\mathrm{i=1}}^{\mathrm{n}}(\mathrm{MR_{pre,i}} - \mathrm{MR_{exp,i}})^2}{\mathrm{n}}} \quad (15)$$

$$\chi^2 = \frac{\sum_{i=1}^{n}(MR_{pre,i} - MR_{exp,i})^2}{n - k} \quad (16)$$

Where $MR_{pre.}$ = predicted moisture ratio, $MR_{exp.}$ = experimental moisture ratio, n = number of observations and k = number of constants.

The set decision rule was that the model with the highest R^2 value, and the least χ^2 and RMSE values was selected as the best fit in describing the drying characteristics of the fresh-water crayfish samples. (Wang et al, 2006; Maydeu-Olivares and Garca-Forero, 2010; Darvishi et al, 2012).

2.5. Activation Energy

The energy that is required to initiate molecular diffusion to cause drying in biomaterials is referred to as activation energy. Since in this work temperature, (T) is a measurable parameter, an Arrhenius type function was used to estimate the activation energy as (Saxena and Dash, 2015; Da Silva et al, 2015).

$$D_e = D_o(e^{-E_a/_{RT}}) \quad (17)$$

where E_a = activation energy (kJ/mol), D_e = effective diffusivity (m^2/s), D_o = pre-exponential factor of the Arrhenius equation at 0 K (m^2/s), R = universal gas constant (8.314 x 10^{-3}, kJ/mol.K) and T = air temperature (K).

Simplification of Equation 17 gives:

$$InD_e = InD_o - \frac{E_a}{R}t^{-1} \quad (18)$$

$$-\frac{E_a}{R}t^{-1} = InD_e - InD_o \quad (19)$$

$$\frac{E_a}{Rt} = In(\frac{D_o}{D_e}) \quad (20)$$

$$\frac{E_a}{R}t^{-1} = In(\frac{D_o}{D_e}) \quad (21)$$

Plotting of InD_e as a function of t^{-1} with regression line of slope, (z) that can be given as:

$$z = -\frac{E_a}{R} \quad (22)$$

The activation energy can be estimated as follows (Taheri-Garavanda et al., 2011; Navneet *et al.*, 2012).

$$E_a = -zR \quad (23)$$

3. RESULTS AND DISCUSSION

3.1. Drying Kinetics

Figure 1 presents changes in moisture ratio with drying time of the freshwater crayfish. As with literature report on drying of visco-elastic materials (such as sea foods). The drying environment had significant effect on the moisture migration from the interior to the exterior in the drying of the crayfish samples as expected (Jain and Pathare, 2007; Darvishi et al., 2012; Ikrang, 2014; Burubai, 2015). The figure shows that on the same state of drying indicated by the moisture ratio, increased drying temperature greatly reduced the drying time. When the moisture ratio is at say 0.6, the drying time for the crayfish samples was about 105 minutes at the highest drying temperature, and about 185 minutes at the lowest drying temperature. This indicates that rate of moisture depletion during drying is significantly a function of drying time.

The drying curves in Figure 2 depict the general trend of characteristic drying curves as reported for many bio-materials. The curves present initial steeper slope, and become asymptotic to the axis of drying time even with changing drying temperatures. This form adequately describes a more rapid initial moisture loss. Moisture available for evaporation at the surface of the samples become lesser in drying (Sankat and

Mujalfar, 2006; Jain and Pathare, 2007; Kilic, 2009; Burubai, 2015; Zibokere and Egbe, 2019).

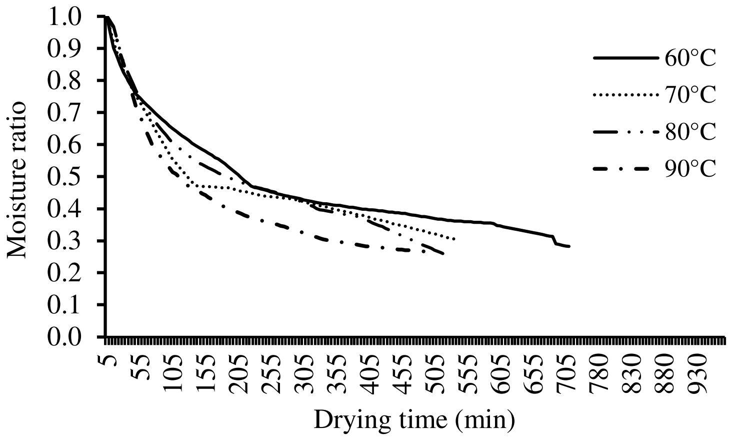

Figure 1: Moisture ratio versus drying time of fresh-water crayfish at different drying temperatures

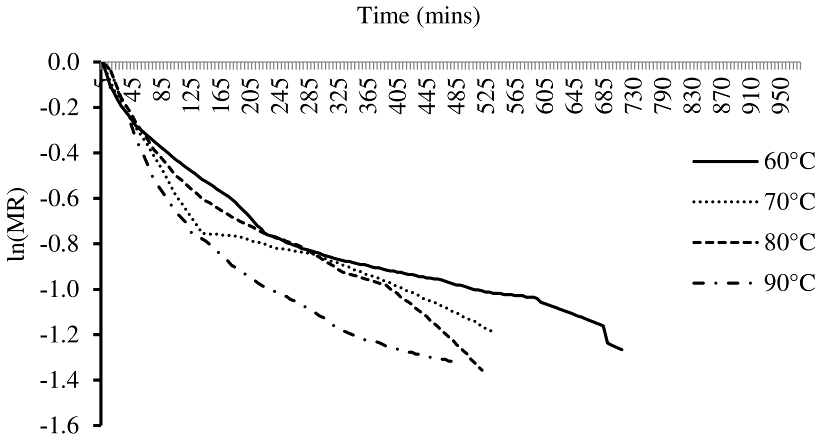

Figure 2: Drying curves of Fresh-water Crayfish

3.2. Fitting Experimental Data into Thin-Layer Drying Models

Table 1 summarizes the statistical results from the thin-layer drying models for the different drying temperatures chosen in this work. The model with the highest R^2 value, and the least $\chi^2$and RMSE values was the criteria applied in selected as the best model describing the thin-layer drying characteristics of fresh water crayfish. The fitting statistical results in the Table showed that the coefficient of determination, R^2 values were consistently high in all the models, all scoring respectively above 0.92 except for Lewis model that is seen to score below this figure yet fairly above 0.83. The simply indicates the suitability of these empirical models in describing drying behavior fresh-water crayfish. However, when further tuned alongside the other statistical parameters, the model expression of Midilli followed by that of the Page gave the highest R^2 values and the lowest χ^2 and RMSE values in the temperature range of the work. It was observed that, though the Page model may describe the drying curve for the experimental data and conditions for the fresh-water crayfish of this work, it hardly gave a clear and accurate overall view of the important processes involved during drying. Fig. 4 compared experimental data with data predicted with the Midilli model at the chosen drying temperatures. It was observed that the value of k (kinetic rate constant with coefficient of determination, R^2 = 0.9996) increased with decrease in the drying temperatures indicating a steady drying rate suitable for good drying stability of the product without case-hardening. And the clustering of the moisture ratio values along the straight line, further indicated the suitability of Midilli model in describing drying characteristics of fresh-water crayfish samples, similar in trend as observed by Darvishi *et al.* (2012) for shrimp.

Table 1: Statistical measures of fresh-water crayfish *on* seven selected thin-layer drying models

Model	Temp. (°C)	Fitting constants & coefficient	χ^2	RMSE	R^2
Wang and Singh	60	a = 0.0018, b = -0.3304	0.0608	0.0042	0.9864
	70	a=0.0088, b = -0.5331	0.0511	0.0029	0.9881
	80	a= 0.0107, b = -0.0982	0.0498	0.0020	0.9867
	90	a= 0.0011, b = -0.0886	0.0412	0.0023	0.9892
	100	a= 0.0021, b = -0.0897	0.0399	0.0028	0.9888
Page	60	k = 0.333, n = 2.242	0.0221	0.0018	0.9977
	70	k = 0.201, n = 1.997	0.0168	0.0016	0.9976
	80	k = 0.159, n = 1.332	0.0135	0.0011	0.9979
	90	k = 0.033, n = 1.544	0.0127	0.0007	0.9991
	100	k = 0.031, n = 1.643	0.0197	0.0005	0.9994
Logarithmic	60	k = 0.221, a = 3.895, b = -2.766	0.0683	0.0032	0.9884
	70	k = 0.094, a = 3.008, b = -1.891	0.0557	0.0030	0.9967
	80	k = 0.099, a = 2.881, b = -1.667	0.0476	0.0018	0.9944
	90	k = 0.065, a = 1.895, b = -1.355	0.0364	0.0012	0.9991
	100	k = 0.063, a = 1.879, b = -1.298	0.0206	0.0011	0.9986
Henderson-Parbis	60	a = 2.876, k = 1.5555	0.4878	0.1771	0.9211
	70	a = 2.067, k = 1.8184	0.3791	0.1421	0.9212
	80	a = 2.006, k = 0.4994	0.3344	0.1451	0.9206
	90	a = 1.998, k = 0.1896	0.2034	0.1008	0.9221
	100	a = 1.899, k = 0.2788	0.2008	0.1055	0.9208
Midilli	60	k = 0.533, a = 1.606, b = - 0.141, n = 2.474	0.0088	0.00018	0.9998
	70	k = 0.449, a = 1.111, b = - 0.774, n = 2.278	0.0075	0.00015	0.9996
	80	k = 0.212, a = 1.061, b = -0.008, n = 1.201	0.0084	0.00013	0.9997
	90	k = 0.0919, a = 1.023, b = -0.0102, n = 1.756	0.0058	0.00012	0.9993
	100	k = 0.0888, a = 1.016, b = -0.0164, n = 1.769	0.0089	0.00010	0.9991
Parabolic	60	a = 0.1216, b = - 0.4477, c = 1.372	0.0528	0.0033	0.9926
	70	a = 0.0978, b = - 0.4121, c= 1.333	0.0423	0.0021	0.9936
	80	a = 0.0267, b = - 0.3394, c= 1.077	0.0334	0.0017	0.9964
	90	a = 0.0199, b = - 0.1764, c = 1.104	0.0312	0.0013	0.9969
	100	a = 0.0192, b = - 0.1799, c = 1.111	0.0301	0.0011	0.9966
Lewis	60	k = 0.8866	0.3413	0.0734	0.8301
	70	k = 0.7898	0.2876	0.0633	0.8529
	80	k = 0.6945	0.2098	0.0771	0.8379
	90	k = 0.4733	0.1999	0.0515	0.8812
	100	k = 0.4701	0.1919	0.0511	0.8865

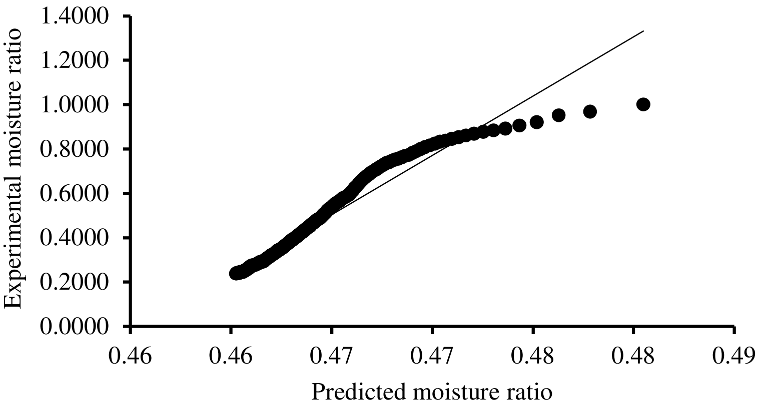

Figure 3: Experimental vs predicted moisture ratio values for drying of fresh-water Crayfish

3.3. Estimation of Effective Moisture Diffusivity and Activation Energy

Activation energy is the minimum amount of energy required for the fresh-water Crayfish to undergo drying**.** All bio-materials have different systemic water capacity, the higher the moisture contained in any of them the higher the activation energy needed to loosen the bond to have effective moisture diffusivity during drying. ln(De) plotted as a function of inverse of drying absolute temperature T^{-1} at the various drying temperatures as shown in Figure 4, was used in the estimation the activation energy. The almost flattened regression line showed that less energy was required to remove moisture at the higher drying temperature as the water molecules within the body matrix tend to become free moisture at the surface of the samples. Effective moisture diffusivity (D_e) thus, increased with drying time and temperature. In this work the D_e values ranged from 2.239 x 10^{-8} m^2/min or 3.732×10^{-10} m^2/s at the lower temperature to 4.005×10^{-8} m^2/min or 6.675×10^{-10} m^2/s with the related activation energy (E_a) value of 24.48 kJ/mol, similar in trend as observed by Xiong et al. (1992) for porous foods and in the work of Zogzas et al. (1996) and Guochen et al. (2009) for shrimp and for fruits and vegetables (Daniel et al., 2016).

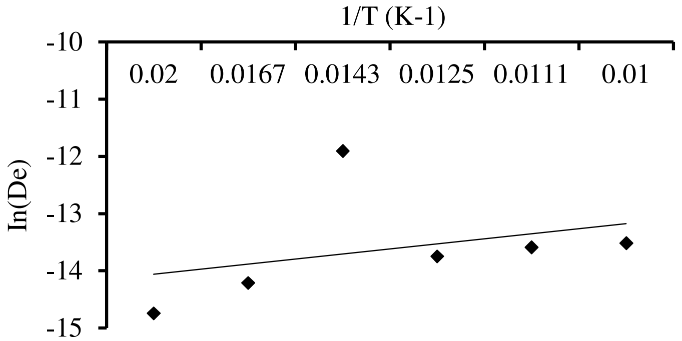

Figure 4: Estimation of activation energy for fresh-water crayfish

4. CONCLUSION

Drying kinetics was investigated for fresh-water crayfish dried on thin layers at drying temperatures of 60, 70, 80, 90 °C and 100 °C. As with other biological materials drying was observed to follow the falling rate period. The Midilli model was considered adequate and was selected as good estimator of the drying behaviour of the fresh-water crayfish at the drying temperatures applied. Following an Arrhenius relationship reduces to the slope method, the activation energy value was deduced to be 28.48 kJ/mol and fall within the values in technical literature over same temperature range of this work. The effective moisture diffusivity also increased in value with increased drying temperatures.

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6. CONFLICT OF INTEREST

There is no potential conflict of interest on this work.

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