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Drying Kinetic Models: Performance Evaluation under Auto-Correlated Observations

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Abstract

The standard drying kinetic models like Lewis and Pages models assume that error terms of fitted models are uncorrelated to each other, which may not hold in reality as the observations are measured on successive time intervals. The best computational solution is to incorporate the correlated error structure into the model fitting process. The present study evaluated the performance of drying kinetic models with auto-correlated errors and compared with the standard drying kinetic models using different goodness of fit statistics obtained from the modified models. Validation study showed that Lewis model with auto-correlated errors was best fitted model for the real time data on moisture ratio of Malabar tongue sole fish than standard Lewis model. The estimated drying constant of the fitted model was 0.09 and auto-correlation coefficient was -0.29. The fitted model had higher R^2 value (0.94) and lower standard error (0.01) for estimated parameters of the model when compared to the standard Lewis model.

Keywords: Drying kinetic models, auto-correlated errors, Malabar tongue sole fish

Introduction

In general, kinetic models used for explaining the drying techniques of food materials are of non-linear form. The basic idea in drying studies is to reduce the moisture content of food material through simultaneous heat and mass transfer. This would improve the stability and quality of food product by minimizing the chemical and physical changes during storage. There are several drying methods by which the moisture content of the food materials can be brought down to an equilibrium condition. The food material undergoes physical and chemical changes during drying process. These changes are being quantified using drying kinetics models (Fyhr & Kemp, 1998; Inyang et al., 2018). The estimated parameters of drying kinetics models would further help to optimize the drying process and also would help in engineering of different drying systems.

Different types of drying techniques were employed in the past for preservation and have tried to explain the moisture dehydration in different species of fish and fishery products (Ankur Nagori et al., 2014; Nambudiri et al., 2013; Alfiya et al., 2018; Prabhu & Kandoran, 1991; Fasludeen et al., 2018; Murali et al., 2019) and it was understood that the drying kinetics varies with species to species and drying techniques. The drying mechanism normally describes drying rate as a function of time. In drying kinetic study, Moisture ratio (MR) is modeled as a function of drying time by keeping all other factors as constant. Statistically, the model can be represented as

$$MR_{t_i} = f(t_i) + e_{t_i}, i = 1,2,3, ...n, ... \quad (1)$$

where MR_{t_i} is the moisture ratio at time 't', e_{t_i} is the error term associated with MR_{t_i}, n is the total number of observations and $f(t_i)$ is any functional form that explains MR_{t_i} as a function of time. Inyang et al. (2018) has given a list of 33 functional forms for $f(t_i)$. The parameters associated with $f(t_i)$ are estimated by employing nonlinear regression procedure via Ordinary Least Square (OLS) method. The adequacy of fitted models was assessed by different statistics like coefficients of determination (R^2), root mean square error (RMSE), reduced chi squared etc.

The Equation (1) assumes that error terms e_{ti} are independently and identically distributed with

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constant variance σ^2. In drying kinetics study, moisture ratio is measured at different successive time intervals; this may lead to observations correlated to each other and violates the independence assumptions. Prajneshu (2005) discussed the advantages and disadvantages of using nonlinear models in fisheries and outlined the problems of violating model fitting assumptions. One way to overcome the correlation among observations measured at different time interval is the incorporation of correlated error structure in the model fitting, which provides an efficient estimate of model parameters and satisfy model fitting assumptions. By keeping this in mind, this study compares the drying kinetic models with auto-correlated error structure with standard drying kinetic models. Drying kinetic models with auto-correlated error structure was applied to a real time data obtained from the drying study of Malabar tongue sole (*Cynoglossus macrostomus*).

Materials and Methods

Fresh Malabar tongue sole having an average size of 110 g was subjected to drying in CIFT mechanical driers of 50 Kg capacity maintained at an average chamber temperature of 55°C. Moisture content (%) was measured by hot air oven drying method (AOAC, 2012) at successive intervals of 0, 2, 4, 6, 8, 10, 12 and 16 h, for studying the drying kinetics.

Moisture ratio in a drying process is defined as

$$MR_{t_i} = \frac{X_{t_i}}{X_{t_o}}, \quad i = 1,2,3, ...n, ... \quad (2),$$

where MR_{t_i} is the moisture ratio at time 't_i', X_{t_i} is the moisture content at time 't_i' and X_{t_o} is the initial moisture content. The moisture ratio defined in the Equation (2) was used for developing drying kinetic models.

Lewis (1921) derived a semi theoretical model to fit MR_{ti} as a function 't_i' based on Newton's law of cooling, later Page modified Lewis model by adding an empirical dimensionless constant (Simal et al., 2005). All the thin layer drying kinetic models developed further are obtained by modifying these two models to overcome one or other short falls of these two models. The functional forms of Lewis and Page models are defined in Equations (3) and (4), respectively.

$$MR_{t_i} = \exp(-kt_i) + e_{t_i}, i = 1,2,3,......n, ... \quad (3)$$

$$MR_{t_i} = \exp(-kt_i^b) + e_{t_i}, i = 1,2,3,......n, ... \quad (4)$$

where k is the drying rate constant and b is the empirical power constant to time 't_i'.

Suppose the elements e_{t_i} of above models are correlated as the moisture ratio MR_{t_i} are measured on successive time intervals during drying. Therefore, for a known variance-covariance matrix **V**, the generalized least square (GLS) estimate of k is $\hat{k}$ and b is $\hat{b}$. These estimates are obtained by minimizing the error sum of squares using the PROC NLIN in SAS 9.3. The independence error terms are assessed by Run test at 5% level of significance.

A first order autoregressive model AR(1) for the errors e_{t_i} in the models (3) and (4) can be represented as $e_{t_i} = \rho\, e_{t_{i-1}} + a_{t_i}$, $|\rho| < 1$, where $\{a_{t_i} : i = 0, \pm 1, \pm 2, ...\}$ are random variables distributed independently and identically with mean zero and constant variance σ_a^2. The restriction $|\rho|<1$ assures the stationarity of $\{e_{t_i}\}$.

Now, the Lewis and Pages models with uncorrelated errors can be written as

$$MR^*_{t_i} = MR_{t_i} - \rho\, MR_{t_{i-1}} = \exp(-kt_i) - \rho^*\exp(-kt_i) + a_{t_i}, i = 1,2,3,......n, ... \quad (5)$$

$$MR^*_{t_i} = MR_{t_i} - \rho\, MR_{t_{i-1}} = \exp(-kt_i^b) - \rho^*\exp(-kt_i^b) + a_{t_i}, i = 1,2,3,......n, ... \quad (6)$$

The predicted value of MR_{ti} is obtained by minimizing residual sum of squares for best chosen values of k, b and ρ. The drying kinetic models with auto-correlated errors can be fitted by conditional least square method as described by Seber & Wild (2003). The above models reduce to normal Lewis and Pages drying kinetic models when ρ = 0. The drying kinetic models with auto-correlated errors were fitted by PROC MODEL in SAS 9.3.

The most commonly used statistics to assess the adequacy of the fitted drying kinetic models are coefficient of determination (R^2), root mean square error (RMSE) and reduced chi-square statistics etc. R^2 is alone not a good statistic to assess the goodness of fit when model is in non-linear nature. Kvalseth (1985) has defined almost 9 different forms of expressions for R^2; suggested most appropriate expression of R^2 for non-linear models and which is defined as

$$R^2 = 1 - \frac{\text{Residual Sum of Squares (RSS)}}{\text{Total Sum of Squares (TSS)}} = 1 - \frac{\sum_{i=1}^{n}(MR^*_{t_i} - \widehat{MR}^*_{t_i})^2}{\sum_{i=1}^{n}(MR^*_{t_i} - \overline{MR}^*_{t_i})^2}$$

The root mean square is obtained by taking the square root of mean square error and it is defined as

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(MR^{*}_{t_i}-\widehat{MR}^{*}_{t_i})^2}{n - p}}$$

The reduced chi-square (X^2) is obtained as

$$X^2_{red} = \frac{X^2}{v}, \text{ where } X^2 = \sum_{i-1}^{n}\left(\frac{MR^{*}_{t_i}-\widehat{MR}^{*}_{t_i}}{\sigma_i}\right)^2, \; v = n\text{-}p$$

In all the above statistics, $MR^{*}_{t_i}$ is the modified observed value, $\widehat{MR}^{*}_{t_i}$ is the predicted value, σ_i is the variance, n is the total number of observations and p is the number of estimated parameters in the model. In this modeling technique, one degree of freedom is spared for estimating auto-correlation coefficient ρ (Joshy et al., 2018). A model with highest R^2 value, lowest RMSE and X^2_{red} close to 1 is considered as best fitted model. The independence of error terms of modified model was also tested by run test. The drying kinetic models with and without auto-correlated errors were fitted to a real time drying data of Malabar tongue sole to evaluate the performance of models. All the models were fitted by using SAS 9.3.

Results and Discussion

Drying kinetics study of Malabar tongue sole indicated a drastic reduction in the moisture content from an initial value of about 78 to 15% up on completing 16 h of drying. Moisture ratio (MR) was computed using the Equation (2). Drying kinetic models given in Equation (1) and (2) were fitted as a function of drying time to the drying data obtained for Malabar tongu soul fish. The parameters of fitted model were obtained by minim izing the residual sum of squares by Levenberg-Marquardt algorithm using SAS 9.3. Lewis model was found to be the best fitted model than Pages model to the drying data as Lewis model had higher R^2 value (0.91) and lower RMSE value (0.055) than Pages model. The estimated drying rate of Lewis model was 0.09 with a standard error of (0.09). The parameters of fitted model along with goodness of fit statistics are given in Table 1. The run test revealed that error terms of Lewis model were not independent (p<0.05), which is non-satisfactory to the assumptions of error terms of fitted model. The model fit diagnostics of usual Lewis model is given in Fig. 1. It is understood from the figure that error terms exhibited some sort of definite pattern, which indicates the violation of independence of error terms.

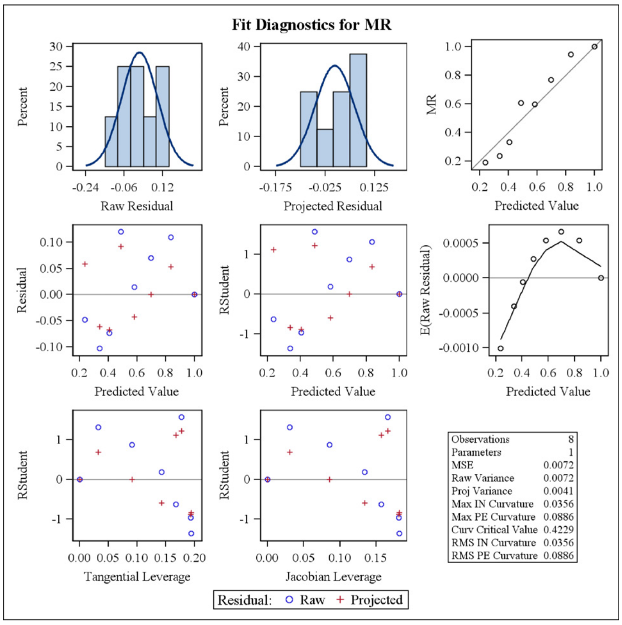

Fig. 1. Model fit diagnostics of usual Lewis model

To overcome this issue, drying kinetics model with auto-correlated errors given in Equation (5) was fitted to the experimental data by conditional least square method using SAS 9.3. The results of fitted model are given in Table 1. The estimated drying rate constant was -0.09 and auto-correlation coefficient was -0.29. Both the estimated coefficients were significant (p<0.05) at 5% level of significance. There was not much difference in the estimated drying rate constant for usual and auto-correlated error models. The R^2 value of auto-correlated model was 0.94 against the value 0.92 of usual Lewis model and both the models had almost similar RMSE values (0.085). The residual sum of square (RSS) of auto-correlated model was less compared to usual model,

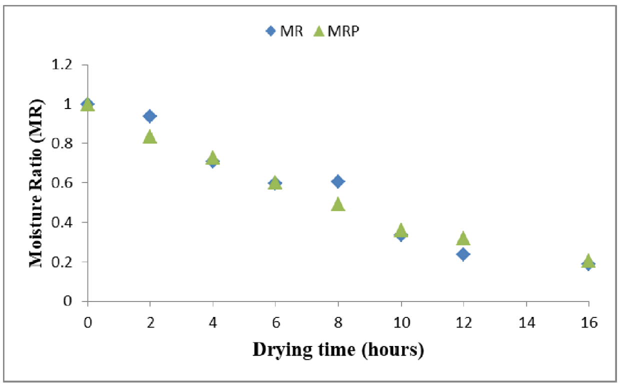

Fig. 2. Observed and predicted values of moisture ratio (MR and MRP) of Malabar tongue sole fish

even though auto-correlated model lost one error degrees of freedom for estimating the auto-correlation coefficient ρ. This could be the reason for increasing the R^2 value of fitted auto-correlated Lewis model. The actual and predicted values of moisture ratio against the drying time in hours are depicted in Fig. 2. The moisture loss of Malabar tongu soul fish during drying was estimated by fitted model. Based on the fitted model, 25% moisture loss happened at 4 h drying, 50% moisture loss happened at 8 h drying and 75% moisture loss happened almost at 14 h drying.

Table 1. Estimated parameters of fitted model

Page model				
Parameters				
k	b	R^2	RSS	RMSE
0.04	1.49	0.91	0.055	0.089
Lewis model				
Parameters				
k	ρ	R^2	RSS	RMSE
Lewis Model with auto-correlated errors				
0.09 (0.09)	NA	0.92	0.051	0.085
0.09 (0.01)	-0.29 (0.41)	0.94	0.045	0.084

*values in the parenthesis indicate the standard error

The run test of error terms of modified model found to be non-significant (p>0.05), which is satisfactory to the assumptions of error terms of fitted model.

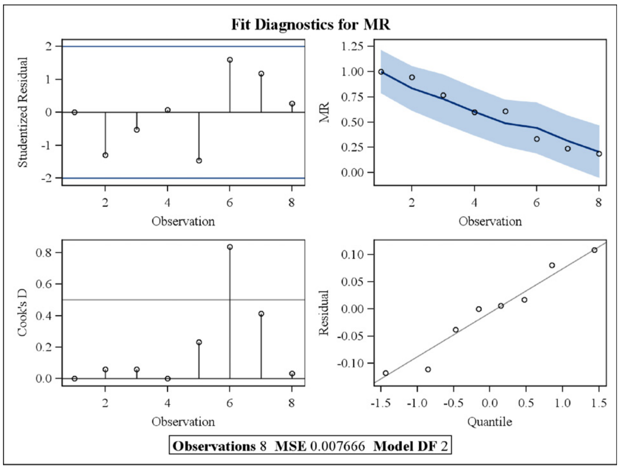

Fig. 3. Model fit diagnostics of auto-correlated Lewis model

The Durbin-Watson statistic of modified model was 1.95, which is close to 2 indicates that resultant error terms of modified model were not auto-correlated and satisfying the stationarity condition of error terms. The model fit diagnostics of auto-correlated Lewis model is given in Fig. 3. The studentized residual falls within the range from -2 to 2, and did not exhibit any definite pattern.

Based on the results it is concluded that Lewis model with auto-correlated errors was found to be best fitted model for the drying data of Malabar tongue sole fish. Drying kinetic models with auto-correlated errors was found to be an efficient alternative modeling technique when the observations obtained from a drying process are auto-correlated.

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References

Alfiya, P. V., Murali, S., Aniesrani Delfiya, D. S. and Manoj P. Samuel (2018) Empirical modelling of drying characteristics of elongate glassy perchlet (*chanda nama*) (hamilton, 1822) in solar hybrid dryer. Fish. Technol. 55: 138-142

Ankur Nagori, Joshi, P. N. and Ravishankar, C. N. (2014) Development of solar dryer with electrical energy backup for hygienic drying of fish and fish products. Fish. Technol. 51: 112-116

AOAC (2012) Official methods of analysis. 19th edn., Association of Official Analytical Chemists, Washington DC, USA

Fasludeen, N. S., Murali, S., Manoj P. Samuel, George Ninan and Joshy, C. G. (2018) Evaluation of Drying Characteristics of Selected Fishes in Dryers developed by ICAR-CIFT. Fish. Technol. 55: 68-73

Fyhr, C. and Kemp, I. C. (1998) Comparison of different drying kinetics models for single particles. Dry. Technol. 16(7): 1339-1369

Inyang, U. V., Oboh, I. O. and Etuk, B. R. (2018) Kinetic models for drying techniques-food Materials. Adv. Chem. Eng. Sci. 8: 27-48

Joshy, C. G., Balakrishna, N., George Ninan and Ravishankar, C. N. (2018) Accelerated Shelf Life Prediction Models with Correlated Errors for Bio Chemical and Sensory Responses of Chill stored Fish. J. Indian Soc. Agricult. Stat. 72(2): 129-140

Kvalseth, T. O. (1985) Cautionary note about R^2. Am. Stat. 1(4): 279-285

Lewis, W. K. (1921) The Rate of Drying of Solid Materials. J. Ind. Eng. Chem. 13: 427-432

Murali, S., Sathish Kumar, K., Alfiya, P. V., Aniesrani Delfiya, D. S. and Manoj P. Samuel (2019) Drying Kinetics and Quality Characteristics of Indian Mackerel (Rastrelliger kanagurta) in Solar–Electrical Hybrid Dryer. J. Aquat. Food Prod. Technol. 28(5): 541-554

Nambudiri, D. D., Pasience Magoha, Mussie Berhane, Tesfay Paulos, Tesfu Berhe, Tesfu G/Medhin, Yemane G/Egziabiher (2013) Preparation of dried anchovies and herrings from eritrean red sea using an indigenously fabricated solar dryer. Fish. Technol. 50: 313-317

Prabhu, P. V. and Kandoran, M. K. (1991) Sun Drying of Anchoviella on Racks. Fish. Technol. 28(2): 134-136

Prajneshu (2005) Statistical modelling in fisheries: A review. Indian J. Anim. Sci. 75(8): 1008-1012

SAS Institute Inc (2011) Base SAS® 9.3 Procedures Guide. Cary, NC: SAS Institute Inc

Seber, G. A. F. and WilD, C. J. (2003). Nonlinear regression. John wiley & sons, Inc., New Jersey

Simal, S., Femenia, A., Garau, M. C. and Rossello, C. (2005) Use of exponential, Page's and diffusional models to simulate the drying kinetics of kiwi fruit. J. Food Eng. 66: 323-328